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

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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.

## 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][$Tf_2$N] 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.

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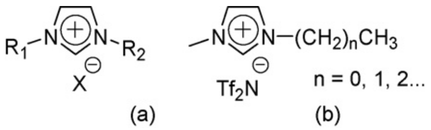


**Fig. 1.** Generalized structure of imidazolium-based RTILs (a) and representative structure of 1-*n*-alkyl-3-methylimidazolium bis(trifluoromethane)sulfonimide [$C_n$mim][$Tf_2N$] RTILs (b).

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 ($\delta$) 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 $\delta$ 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].

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

Widely accepted values of $\delta$ 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 $\delta = 21.8 \pm 0.2$ $MPa^{1/2}$ [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 $\delta$ are not available for the large majority of even the more common of these ionic solvents. Furthermore, $\delta$ 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 $\delta$ 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].

**Table 1**
Solubility parameters ($\delta$) at 298 K for gases of interest to this work.

| Gas | $\delta$ ($MPa^{1/2}$) |
|---|---|
| $CO_2$ | 21.8 |
| $N_2$ | 5.3 |
| $O_2$ | 8.2 |
| $CH_4$ | 11.6 |

**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 |

$$\delta_i = \frac{\sum_j F_j}{V_m} \qquad (2)$$

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 $\delta$ for several RTILs of the family [$C_n$mim][$Tf_2N$], 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 ($-C{\equiv}N$, $F = 725$ $MPa^{1/2}$ $cm^3$ $mol^{-1}$) [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].

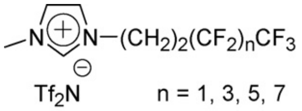


**Fig. 2.** Structure of RTILs containing fluoroalkyl substituents.

However, the trends in $CO_2/N_2$ and $CO_2/CH_4$ solubility selectivity in the ether- and nitrile-functionalized RTILs can be well-rationalized by accounting for the influence of chemical contributions to the solubility parameters of RTILs with similar molar volumes.

While fluoroalkyl chains attached to RTILs have been synthesized and/or studied in other works [7,8,40,41], those studies have focused only on the solubility of $CO_2$ with little attention given to the effects of fluorination of the behavior of other gases or gas pair selectivity [7,40,41]. As shown in Table 2, fluorocarbon groups have smaller contributions to solubility parameters than hydrocarbon groups, thus the solubility parameter of RTILs with fluoroalkyl substituents would expected to be lowered, especially if the density of those RTILs increased. As fluoroalkyl-functionalized RTILs are of much greater molecular weight and expected to be denser than their alkyl-functionalized counterparts, smaller values of $\delta$ would be expected (Eq. (2)). Based on this trend, these RTILs should have lowered $CO_2/N_2$ selectivity relative to the other RTILs that we have studied [2,16,17,19,20]. The direction of $CO_2/CH_4$ selectivity in fluoroalkyl-functionalized RTILs is not as predictable, as hydrocarbons (i.e. $CH_4$) often exhibit anomalous behavior in fluorinated solvents, and their miscibility can differ significantly from the predictions of RST models [31,42–44].

Fig. 2 illustrates the structure of imidazolium salts with fluoroalkyl groups synthesized and used in this work.

Fluoroalkyl groups, when present in polymers (e.g. polytetrafluoroethylene), are known to exhibit enhanced solubility of gases relative to their hydrocarbon counterparts (e.g. polyethylene) [45–48]. However, as these fluorinated materials improve the solubility of all gases, the solubility selectivity of the polymers can be diminished relative to analogous hydrocarbon-based polymers [39,45–47].

As fluoroalkyl groups can be readily tethered to imidazolium cations, the inclusion of these groups in RTILs for the potential enhancement of $CO_2$ solubility is of great interest [7,8,40,41]. Two reports regarding the solubility of $CO_2$ in compounds described by Fig. 2 ($n = 3, 5$) have already been published [7,41]. The more recent paper [7] presents data suggesting that inclusion of fluorinated groups on the imidazolium cation serves to improve $CO_2$ solubility relative to RTILs with alkyl substituents, as a lower Henry's constant was obtained for the fluoroalkyl-functionalized RTILs. However, $CO_2$ solubility alone is not the only factor that must be considered when designing RTILs. Many industrial processes require that $CO_2$ be separated from other gases, and as such, the selectivity of an RTIL in $CO_2/N_2$ and $CO_2/CH_4$ separations should also be examined. The prior works involving RTILs with fluorinated groups did not address the separation performance of this class of materials [7,41]. The affinity of these RTILs for $CO_2$ relative to $N_2$ and $CH_4$ has remained unknown. Furthermore, the behavior of $O_2$ in these RTILs is also of interest, as fluorocarbons are known to show an affinity for $O_2$, and have even been suggested as blood substitutes [49,50]. Additionally, little focus has been devoted to the behavior of $O_2$ in RTILs, with only a small data set existing in the current literature [21,51–54].

In the past, we have employed a pressure-decay technique to measure gas solubility in RTILs of interest [2,16,17,19,20,27]. As we are most interested in gas separation performance, and the solubility of $CO_2$ has already been reported in these fluids [7], we have instead chosen to employ a supported ionic liquid membrane (SILM) configuration [24–26,29]. The SILM configuration has been used to determine low-pressure gas permeability and gas pair selectivity in RTILs [24,29]. It is also a useful tool for the evaluation of gas behavior in viscous RTILs, as only a very thin, supported film is needed to obtain information on gas transport properties [25,26]. The timescales of SILM experiments are governed by the time lag of the membrane, which is typically on the order of seconds or minutes for supported liquid films with thicknesses of 1–1000 μm. The time lag ($\theta_i$) is related to the diffusivity of the gas ($D_i$) and membrane thickness ($l$) (Eq. (3)).

$$D_i = \frac{l^2}{6\theta_i} \quad (3)$$

Data on the steady-state permeability of the SILM is obtained beyond 3× the time lag [24–26]. The SILM technique can be rapid and powerful for determining permeability, solubility, diffusion and gas pair selectivity in RTILs [24–26,29].

In this work, we present a thorough synthetic method for imidazolium-based salts with fluorinated groups tethered to the cation. We have used this method to synthesize four materials, three of which exist as molten salts at ambient conditions. These three RTILs were used in an SILM configuration and tested for their ideal (single gas) permeability to $CO_2$, $N_2$, $O_2$, and $CH_4$ at driving forces near 1 atm. Fluoroalkyl-functionalized RTILs were found to exhibit ideal separation selectivities significantly lower than their alkyl-functionalized analogues. This behavior can be explained in the context of fluorocarbon deviation from "regular" solution behavior and solubility parameters. Furthermore, the solubility of $CO_2$ in fluoroalkyl-functionalized, imidazolium-based RTILs is found to be only slightly greater (<10%) than in analogous alkyl-functionalized RTILs.

## 2. Experimental

### 2.1. Materials

All chemicals were used as received. All fluorinated compounds were obtained from SynQuest Labs (Alachua, FL USA). All other chemicals were obtained from Sigma–Aldrich (Milwaukee, WI USA). All gases were obtained from Air Gas (Radnor, PA USA) and were of at least 99.99% purity.

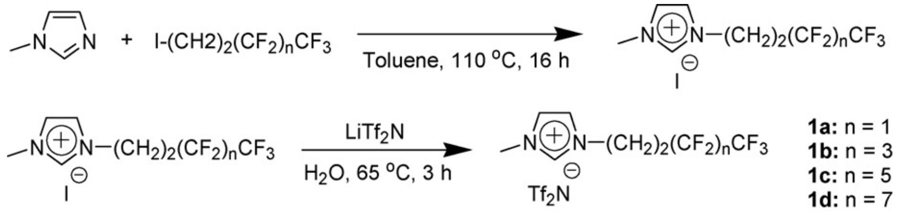
### 2.2. Synthesis of imidazolium salts containing fluorinated substituents (**1a–d**)

Our method for the synthesis (Scheme 1) and purification of imidazolium salts containing fluoroalkyl substituents has been modified from literature methods [7,8].

#### 2.2.1. Typical reaction procedures

1-Iodo-1H,1H,2H,2H-perfluorooctane (25.00 g, 43.6 mmol) was dissolved in toluene (40 mL). 1-methylimidzole (3.93 g, 48.0 mmol) added and the reaction heated at reflux (110 °C) under argon for 16 h. After this time, a separate liquid phase had formed on the bottom of the flask. Upon cooling to room temperature, the lower phase had solidified. Toluene was carefully decanted and the remaining solid broken up and stirred in $Et_2O$ (250 mL) until a powder was obtained. The solid product was filtered and washed with $Et_2O$ (500 mL). It was then dried under vacuum (<500 mtorr) overnight.

The solid, crude product was dissolved in deionized $H_2O$ (100 mL) at 65 °C. Lithium bis(trifluoromethane)sulfonimide [$LiTf_2N$], (12.52 g, 43.6 mmol) was added and the reaction stirred for 3 h. After this time, the product was taken up in EtOAc (250 mL) and washed with deionized $H_2O$ (4 × 150 mL). $AgNO_3$ was added to the separated $H_2O$ phase after the fourth washing to confirm iodide anions were no longer present. The organic phase was dried over $MgSO_4$, and activated carbon was added to remove



**Scheme 1.** Synthesis of imidazolium salts containing perfluoroalkyl substituents.

colored impurities. The mixture then was filtered through a plug of basic alumina. The filtrate was reduced by rotary evaporation and furthered dried under vacuum at 65 °C overnight to produce a clear, colorless oil.

There are two exceptions to this synthetic method. In the case of compound **1a**, the crude iodide salt did not crystallize, and it was added directly to deionized $H_2O$. Compound **1d** is a solid at room temperature, with a melting point of 30.8–31.1 °C.

*1-Methyl-3-(3,3,4,4,4-pentafluorohexyl)-imidazolium bis(trifluoromethane)sulfonimide **1a***: Yield = 18.78 g, 40.4% $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 2.93 (m, 2H), 3.87 (s, 3H), 4.55 (t, 2H), 7.68 (t, 1H), 7.85 (t, 1H), 9.21 (s, 1H); $^{19}$F NMR (376 MHz, DMSO-$d_6$) $\delta$ −118.11 (t, 2F), −86.07 (s, 3F), −79.66 (s, 6F). FT-IR: 3162 cm$^{-1}$, 3125, 3106, 1580, 1568, 1467, 1433, 1352, 1281. HRMS: calculated as $[A]^+[A]^+[B]^-$ = 738.0695, found = 738.0706

*1-Methyl-3-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-imidazolium bis(trifluoromethane)sulfonimide **1b***: Yield = 14.55 g, 35.5% $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 2.99 (m, 2H), 3.86 (s, 3H), 4.56 (t, 2H), 7.71 (t, 1H), 7.87 (t, 1H), 9.19 (s, 1H); $^{19}$F NMR (376 MHz, DMSO-$d_6$) $\delta$ −126.21 (t, 2F), −124.60 (d, 2F), −114.01 (s, 2F), −81.07 (s, 3F), −79.24 (s, 6F). FT-IR: 3161 cm$^{-1}$, 3125, 3103, 1579, 1568, 1468, 1433, 1405, 1352, 1333. HRMS: calculated as $[A]^+[A]^+[B]^-$ = 938.0568, found = 938.0626.

*1-Methyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorohexyl)-imidazolium bis(trifluoromethane)sulfonimide **1c***: Yield = 20.05 g, 44.7% $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 2.99 (m, 2H), 3.86 (s, 3H), 4.56 (t, 2H), 7.71 (t, 1H), 7.87 (t, 1H), 9.19 (s, 1H); $^{19}$F NMR (376 MHz, DMSO-d$_6$) $\delta$ −126.21 (t, 2F), −124.60 (d, 2F), −114.01 (s, 2F), −81.07 (s, 3F), −79.24 (s, 6F). FT-IR: 3161 cm$^{-1}$, 3125, 3104, 1579, 1568, 1468, 1433, 1352, 1333. HRMS: calculated as $[A]^+[A]^+[B]^-$ = 1138.0440, found = 1138.0469.

*1-Methyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorohexyl)-imidazolium bis(trifluoromethane)sulfonimide **1d***: Yield = 15.40 g, 54.6% $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 2.98 (m, 2H), 3.86 (s, 3H), 4.55 (t, 2H), 7.71 (t, 1H), 7.86 (t, 1H), 9.19 (s, 1H); $^{19}$F NMR (376 MHz, DMSO-$d_6$) $\delta$ −126.55 (t, 2F), −123.85 (s, 2F), −123.23 (s, 2F), −122.43 (s, 4F), −122.17 (s, 2F), −113.90 (t, 2F), −81.07 (t, 3F), −79.40 (s, 6F). FT-IR: 3160 cm$^{-1}$, 3122, 3105, 1578, 1568, 1351, 1332, 1291, 1207. HRMS: calculated as $[A]^+[A]^+[B]^-$ = 1338.0312, found = 1338.0393.

### *2.3. Determination of RTIL density and calculation of relevant physical properties*

Densities for the three ambient temperature liquids synthesized were determined by filling a 2.000 cm$^3$ (±0.015 cm$^3$) class-A volumetric flask of pre-determined mass to the calibration line. The quotient of RTIL mass and flask volume was taken as the density of the liquid. The density measurements and values of molecular weight, molar volume and the liquid molarity of each compound are presented below (Table 3).

### *2.4. SILM preparation and gas permeability experiments*

SILMs were prepared by drop-casting RTILs onto a 47 mm diameter circle of porous polyethersulfone (Supor 200, Pall, Ann Arbor, MI USA). The pore size of this membrane is 0.2 μm, the porosity is ~80% and the thickness is 145 μm. The RTIL was allowed to saturate the support, and excess was wiped off with clean, absorbent paper.

The SILM was then transferred to a "time-lag" membrane apparatus, details on which have been outlined in previous works from our group [18,55]. Experiments were performed at ambient temperature, 296 ± 1 K. Membranes were degassed for at least 2 h between runs (50–100× the time lag from the previous experiment) to ensure the SILM was free from dissolved gases. While no membranes failed during the course of these experiments, the membrane support within the apparatus was thoroughly cleaned with MeOH before changing membranes, so that if any RTIL did leak from the SILM, it was removed from the membrane apparatus.

The ideal permeability ($P_i$) of each gas in each SILM was calculated from the steady-state flux through the membrane ($J_i$), membrane thickness ($l$) and pressure drop across the membrane ($\Delta p_i$) (Eq. (4)).

$$P_i = J_i \frac{l}{\Delta p_i} \tag{4}$$

In a dense liquid or solid film, it is assumed that solution-diffusion is the mode of solute (i.e. gas) transport (Eq. (5))

$$P_i = S_i D_i \tag{5}$$

The ideal selectivity for a given gas pair ($\alpha_{i/j}$) is calculated as the ratio of the ideal permeabilities of the gases of interest (e.g. $CO_2/N_2$) and can be separated into both solubility and diffusion contributions (Eq. (6)).

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{S_i}{S_j}\frac{D_i}{D_j} \tag{6}$$

## 3. Results and discussion

### *3.1. Gas permeability and gas pair selectivity in SILMs containing RTILs with fluoroalkyl substituents*

The ideal permeabilities of $CO_2$, $O_2$, $N_2$ and $CH_4$ and gas pair selectivities for $CO_2/N_2$, $CO_2/CH_4$ and $O_2/N_2$ in each of the three RTILs tested in the SILM configuration are presented in Table 4.

$[C_2mim][Tf_2N]$ (Fig. 1b) was used as a standard for comparison with the fluoroalkyl-functionalized RTILs, as it is one of the most widely-studied RTILs in gas separations [17,19,20,23–25,27]. The permeability of $CO_2$ in SILMs of $[C_2mim][Tf_2N]$ is reported as ~1000 Barrers at a trans-membrane pressure differential of 19 kPa [24]. These SILMs exhibited a trend of decreasing permeability with increasing pressure [24]. At a driving force of ~85 kPa,

**Table 3**
Physical properties (296 ± 1 K) of imidazolium salts containing perfluoroalkyl substituents.

| Compound | MW (g/mol) | Density (g/cm$^3$) | $V_m$ (cm$^3$/mol) | mol/L |
|---|---|---|---|---|
| **1a** | 509.32 | 1.70 | 299.6 | 3.34 |
| **1b** | 609.33 | 1.76 | 346.2 | 2.89 |
| **1c** | 709.35 | 1.77 | 400.8 | 2.50 |
| **1d** | 809.36 | Solid | N/A | N/A |

**Table 4**
Ideal gas permeability (296 ± 1 K) in SILMs made from RTILs containing fluoroalkyl substituents.

| RTIL | Permeability (Barrers) | | | |
|---|---|---|---|---|
| | $CO_2$ | $O_2$ | $N_2$ | $CH_4$ |
| **1a** | 320 ± 10 | 27 ± 1 | 12 ± 1 | 17 ± 1 |
| **1b** | 280 ± 10 | 31 ± 3 | 14 ± 1 | 17 ± 1 |
| **1c** | 210 ± 10 | 29 ± 1 | 13 ± 1 | 16 ± 1 |

1 Barrer = $10^{-10}$ $cm^3$ (STP) cm/$cm^2$ s cm Hg.
Uncertainty represents one standard deviation obtained from at least three replicate experiments.

we measured the permeability of $CO_2$ in an SILM composed of $[C_2mim][Tf_2N]$ to be 680 ± 30, with ideal permeability selectivities for $CO_2/N_2 = 31$ and $CO_2/CH_4 = 14$. These selectivity values are consistent with the ideal solubility selectivities for $[C_2mim][Tf_2N]$ reported by our group for this temperature range (296 ± 1 K) in previous works [17,19,20]. This validation with previously reported ideal solubility selectivity values obtained by a pressure-decay method indicates the permselectivity values obtained here by through an SILM method are a good estimations (±10%) of the ideal solubility selectivities of an RTIL for $CO_2/N_2$, $CO_2/CH_4$ and $O_2/N_2$ at a given temperature. The ideal solubility selectivity of $CO_2/N_2$ is perhaps slightly underestimated by the permselectivity, as trends indicate that the diffusion coefficients for these gases in RTILs correlate with molecular size or “liquid” molar volumes ($v^L$) [25,26,31,56]. In RTILs, the diffusivities of the gases of interest are expected to follow the general trend: $O_2 \approx N_2 > CH_4 \approx CO_2$, which correlate with their respective values of $v^L$ at 298 K: 32.4, 33.0, 52 and 55 $cm^3$/mol [31].

As the length of fluoroalkyl substituent increased, the ideal permeability of $CO_2$ decreased. This is most likely due to increasing viscosities as the fluoroalkyl appendage becomes longer. Gas diffusivity and permeability in RTILs strongly correlate with the viscosity of the fluid [25,26]. The ∼33% decrease between SILMS of **1a** and **1c** would be expected as the solubility of $CO_2$ in a family of $[C_2mim][Tf_2N]$ anions that vary only in the length of the substituent group would be fairly constant at a given temperature [20]. However, those with longer length substituents would also become more viscous. Increased viscosity in imidazolium-based RTILs correlates with slower $CO_2$ diffusion, and in turn, decreasing permeability [20,24–26,56]. Interestingly, the ideal permeabilities of $O_2$, $N_2$ and $CH_4$ are relatively the same in each of these SILMs. While the argument for decreasing gas diffusivity with increasing viscosity also holds true for $O_2$, $N_2$ and $CH_4$, the solubilities of these gases have been observed increase across a family of RTILs with increasingly longer alkyl substituents [16,17,19,20]. This behavior has been modeled using solubility parameters and as a function of molar volume [16,17,19,20]. Here, the product of increasing solubility and decreasing diffusivity for $O_2$, $N_2$ and $CH_4$ results in near constant permeability. This behavior negatively impacts $CO_2/N_2$ and $CO_2/CH_4$ ideal separation selectivity. The ideal permselectivity, or the ratio of ideal permeabilities for a given gas pair is defined by Eq. (6). The ideal permselectivity values for RTILs **1a**–**c** with fluoroalkyl substituents are presented in Table 5.

**Table 5**
Ideal separation selectivity (296 ± 1 K) in SILMs with RTILs containing fluoroalkyl substituents.

| RTIL | Ideal permselectivity | | | |
|---|---|---|---|---|
| | $CO_2/N_2$ | $CO_2/CH_4$ | $O_2/N_2$ | $CH_4/N_2$ |
| **1a** | 27 | 19 | 2.3 | 1.4 |
| **1b** | 21 | 17 | 2.2 | 1.2 |
| **1c** | 16 | 13 | 2.2 | 1.2 |

For $CO_2$-based separations, the ideal permselectivity was observed to decrease as the length of the fluoroalkyl substituent became longer. As these permselectivity values are approximations of the ideal solubility selectivity in these RTILs, the data imply that as the length of fluoroalkyl substituent increases, the RTILs are less selective for $CO_2$ relative to $N_2$ and $CH_4$. This trend is similar to the solubility selectivity performances of alkyl-functionalized RTILs (Fig. 1b), where $CO_2/N_2$ and $CO_2/CH_4$ separations have been shown to be less selective with increasing molar volume (increasing alkyl chain length) [20].

In the case of $O_2/N_2$ (and for comparison purposes, $CH_4/N_2$) no significant changes in separation selectivity are observed as the length of the fluoroalkyl chain increases. These constant separation selectivities for gas pairs not including $CO_2$ are also observed in analogous, alkyl-functionalized RTILs [17,19,20]. In imidazolium-based RTILs, $O_2$, $N_2$ and $CH_4$ tend to behave similarly, and relative to $CO_2$, undergo much weaker (or no) interactions with the ionic components [53]. The affinity of these gases for the substituent groups, as well as their ability to fill void volume dictates their relative solubilities, which increase in a proportional manner, resulting in nearly constant separation selectivity.

As the lengths of the substituents on the imidazolium ring become longer, the concentrations of ions are diminished within the RTIL solvent. Thus, the selectivity of the RTIL for any gas pair is dictated by the relative ability of the gases of interest to dissolve in an RTIL composed primarily of the substituent chain. As the molar volume of the RTIL becomes sufficiently large, the selectivities in $CO_2$-based separations reach a nearly constant minimum [17,19,20].

### 3.2. *Interpretation of gas pair selectivity in fluoroalkyl-functionalized RTILs using group contribution theory*

As we have shown for similar imidazolium-based RTILs with $Tf_2N$ anions and alkyl, nitrile-terminated alkyl or oligo(ethylene glycol) substituents, trends in $CO_2/N_2$ and $CO_2/CH_4$ ideal solubility selectivity correlate well with the calculated solubility parameters of each RTIL [2,16]. Values of $\delta$ for imidazolium-based (and other) RTILs can be obtained by accounting for the contribution of functional groups within the ion pairs, and using tabulated values for each of the constituent groups [16,31–36]. Using Eq. (2) and Table 2, we have calculated solubility parameters for fluoroalkyl-functionalized RTILs **1a–c** and their alkyl-functionalized analogues. These values are presented in Table 6.

While the fluoroalkyl-functionalized RTILs have similar values of $\delta$, their ideal solubility selectivities are quite different from their alkyl-functionalized counterparts [19]. For both classes of imidazolium-based RTILs, the ideal selectivity of the solvent diminishes with decreasing value of $\delta$ (increasing length of substituent). However, RTILs with fluoroalkyl appendages have diminished $CO_2/N_2$ separating power relative to those with alkyl units, yet exhibit a significant increase in selectivity for $CO_2/CH_4$. Decreasing

**Table 6**
Solubility parameters (calculated using group contributions) and gas pair selectivities of RTILs containing fluoroalkyl groups (296 ± 1 K) and RTILs containing analogous alkyl groups (298 K).

| RTIL | $V_m$ ($cm^3$/mol) | $\delta$ ($MPA^{1/2}$) | $CO_2/N_2$ | $CO_2/CH_4$ |
|---|---|---|---|---|
| **1a** | 300 | 27.3 | 27 | 19 |
| **1b** | 346 | 25.4 | 20 | 16 |
| **1c** | 401 | 23.5 | 16 | 13 |
| $[C_4mim][Tf_2N]^{19-C}$ | 290 | 27.7 | 31 | 12 |
| $[C_6mim][Tf_2N]^{19-E}$ | 325 | 26.4 | 29 | 10 |
| $[C_8mim][Tf_2N]^{19-C}$ | 355 | 25.7 | 27 | 9 |

Values for $[C_nmim][Tf_2N]$ RTILs taken from reference [19]; *C* = calculated; *E* = experimentally determined.

**Table 7**
Volumetric solubility at 298 K of $CO_2$ in RTILs with fluoroalkyl appendages and structurally analogous RTILs with alkyl groups.

| Compound | $V_m$ (cm$^3$/mol) | mol RTIL/L RTIL | $H$ (atm) (298 K) | $x$ (1 atm) | mol $CO_2$/L RTIL | cc $CO_2$ (STP)/cc RTIL/atm |
|---|---|---|---|---|---|---|
| **1b** [7] | 346.2 | 2.89 | 28.4 | 0.035 | 0.105 | 2.36 |
| **1c** [7] | 400.8 | 2.50 | 27.3 | 0.037 | 0.095 | 2.13 |
| [$C_6$mim][$Tf_2N$] [7] | 328.8 | 3.04 | 31.6 | 0.032 | 0.099 | 2.23 |
| [$C_8$mim][$Tf_2N$] [41] | 365.3 | 2.74 | 30 | 0.033 | 0.094 | 2.12 |

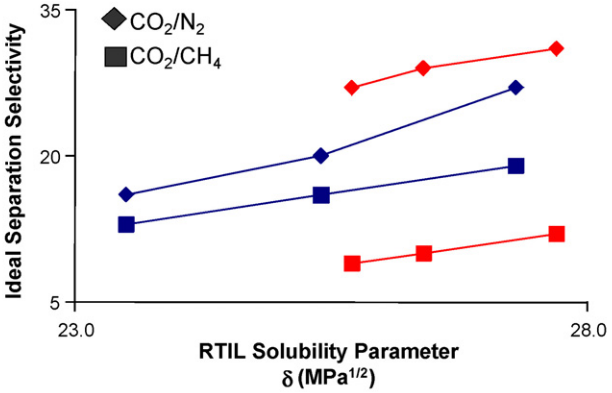


**Fig. 3.** Ideal separation selectivity for $CO_2/N_2$ and $CO_2/CH_4$ in alkyl- and fluoroalkyl-functionalized RTILs.

selectivity in both separations of interest correlate with decreasing solubility parameter, illustrated in Fig. 3

The behavior of fluorocarbon–hydrocarbon solutions has long been observed to deviate from "regular" solution behavior [31,42–44]. These deviations are greater than can be accounted for by the difference in solubility parameters of fluorocarbons and hydrocarbons [42]. While the mechanisms behind this behavior remain somewhat ambiguous, many works have attributed unusually weak interactions between fluorocarbons and hydrocarbons as the reason that fluorocarbons and hydrocarbons do not form "regular" solutions [43,44]. This behavior also manifests itself in greater solubility selectivity for $CO_2/CH_4$ in fluorinated polymers (e.g. PTFE) than in analogous alkyl polymers (e.g. PE) [39,45,48]. The reverse case is true for $CO_2/N_2$. The solubility selectivity between these gases is diminished in fluorinated polymers relative to hydrocarbon-based polymers [39,45,48].

The trends associated with $CO_2$, $N_2$ and $CH_4$ separations in fluorocarbon-containing solutions and polymers also appear to extend themselves to fluoroalkyl-functionalized RTILs. Relative to their alkyl analogues, fluoroalkyl-functionalized RTILs exhibit increased separation selectivity for $CO_2/CH_4$ and a decrease for $CO_2/N_2$, even though the two classes of RTILs lie within the same range of solubility parameters. As shown in Table 6 and Fig. 3, even the lowest ideal separation factor achieved for $CO_2/CH_4$ in fluoroalkyl-functionalized RTILs was greater than the highest observed in analogous, alkyl-functionalized RTILs. On the contrary, the greatest $CO_2/N_2$ separation achieved in fluoroalkyl-functionalized RTILs was only equal to the lowest value found in the alkyl analogues. While we have previously reported on other functionalized RTILs containing nitrile or oligo(ethylene glycol) substituents that have been shown to increase separation of both $CO_2/N_2$ and $CO_2/CH_4$ relative to alkyl analogues [2,16], these fluoroalkyl-functionalized RTILs are the first case where each separation was impacted in a different manner. As our use of group contributions with gas separations in tailored RTILs expands, we find that the solubility parameters calculated in this way are not absolute predictors of gas separation behavior, but rather serve quite well to predict and explain trends in $CO_2$-based separations.

### 3.3. $CO_2$ solubility in imidazolium-based RTILs with fluoroalkyl or alkyl groups

As mentioned earlier in this work, the solubility of $CO_2$ in fluoroalkyl-functionalized RTILs has been examined by other research groups [7,41]. The most recent data suggest that $CO_2$ solubility in RTILs **1b** and **1c** is improved when compared to analogous RTILs with alkyl substituents, but not to the levels initially reported [7,41]. However, the apparent improvements in $CO_2$ uptake are reported only as smaller values of the Henry's Law constants, or the mole fraction of $CO_2$ in each RTIL at a given pressure [7]. When the solubility of $CO_2$ in these RTILs is recalculated using a volume basis with Henry's constants published by other groups in the literature and the physical properties obtained in this study (Table 1), it becomes obvious that RTILs with fluoroalkyl groups attached to the cation exhibit only slight improvements in $CO_2$ solubility relative to their counterparts with alkyl groups. Table 7 presents in both the solubility of $CO_2$ in RTILs **1b** and **1c**, as well as in [$C_6$mim][$Tf_2N$] and [$C_8$mim][$Tf_2N$].

From this and other literature data, it appears that the solubility of $CO_2$ (at ambient temperature and low pressures) in imidazolium-based RTILs (with a variety of functional groups) is limited to a range of approximately 2.00 cc $CO_2$ (STP)/cc RTIL/atm, spanning a range of perhaps ±20% [2,7,16,17,19,20–23,40,41,53,56]. This performance falls short of other organic solvents, such as acetone and acetonitrile, which can dissolve $CO_2$ to levels of 7.1 and 6.6 cc $CO_2$ (STP)/cc/atm, respectively [34]. While there are certainly many other functional groups that can be added to imidazolium (or other) cations in attempts to enhance $CO_2$ solubility in RTILs, these tailored, imidazolium-based systems do not appear to be able to match the performance of molecular solvents in the amounts of $CO_2$ they can dissolve. However, it is the unique properties of RTILs that molecular solvents do not possess, such as non-volatility and inflammability, that may ultimately differentiate RTILs as solvents of choice for use in industrial gas, vapor and liquid separations.

## 4. Conclusions and outlook

A series of four imidazolium salts containing fluoroalkyl substituents were synthesized. The three of these that exist as molten salts at ambient temperature were tested for their gas separation properties relating to $CO_2$, $O_2$, $N_2$ and $CH_4$ in an SILM configuration. The ideal separation selectivities for $CO_2/N_2$ and $CO_2/CH_4$ were observed to decrease as the fluoroalkyl substituent increased in length, while $O_2/N_2$ remained constant. Relative to analogous, alkyl-functionalized RTILs, the fluoroalkyl-containing systems exhibited an enhancement in $CO_2/CH_4$ selectivity, but a diminishment in $CO_2/N_2$ separation. Solubility parameters were calculated for both classes of RTILs using a group contribution approach. As the pendant group increased in length, the solubility parameter also decreased, correlating with the trends in $CO_2/N_2$ and $CO_2/CH_4$ separation in these RTILs. The "anomalous" behavior of $CH_4$ in fluorinated solvents and polymers appears to translate to fluoroalkyl-functionalized RTILs as well. The densities of the fluoroalkyl-functionalized RTILs were obtained and used to calculate the volumetric solubility of $CO_2$-based on literature data in two of the fluoroalkyl-functionalized

RTILs. Fluoroalkyl-functionalized RTILs possess a modest (∼10%) increase in $CO_2$ uptake over their alkyl-functionalized analogues.

Currently, the lack of a wide variety of readily available (and inexpensive) fluorinated starting materials currently hinders the synthesis of a large library of RTILs containing other fluorinated functional groups for testing in gas separations or other applications. Other drawbacks of imidazolium-based RTILs with fluorinated groups are increased viscosity and higher melting points [7,8,41]. However, we have shown that the presence of a fluorinated group on an imidazolium-based RTIL can have significant effects on how RTILs can behave in a given application. The ability to enhance $CO_2/CH_4$ selectivity through the use of a fluorinated substituent may open applications for RTILs in natural gas processing, as well as new ways of thinking about RTIL design. We believe the inclusion of fluorinated groups within RTILs presents very interesting opportunities for expanding the capabilities of these solvents and the number of applications where fluoroalkyl-containing RTILs might find use in the future.

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