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## PAPER

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## Introduction

Ionic liquids (ILs) have drawn considerable attention due to their favourable properties such as negligible vapour pressure, wide electrochemical window, and high thermal stability.<sup>1</sup> Additionally, ILs have been introduced into diverse scientific and technological areas due to the many possible combinations when modifying the structures of both the anion and cation, and consequently the IL properties. To date, ILs have found applications in catalysis,<sup>2,3</sup> materials synthesis,<sup>4</sup> and green chemistry.<sup>5</sup> Among all classes of ILs, those having an imidazolium cation comprise the largest class of compounds examined so far. While these imidazolium-based ILs offer a wide range of modularity, other heterocyclic compounds capable of forming ILs, such as thiazolium,<sup>6</sup> 1,2,3-triazolium,<sup>7</sup> or 1,2,4-triazolium,<sup>8</sup> have been less investigated. Among those, triazolium-based ILs have been explored for biological applications,<sup>9</sup> catalysis,<sup>10</sup> and in the development of energetic materials.<sup>11–13</sup> In addition to these uses, there has been an

## Effect of alkyl and aryl substitutions on 1,2,4-triazoliumbased ionic liquids for carbon dioxide separation and capture<sup>†</sup>

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A series of 1,2,4-triazolium-based ionic liquids have been synthesized and evaluated for their use in supported ionic liquid membrane based CO<sub>2</sub> separations. The properties of these triazolium-based compounds have proven sensitive to isomeric substitutions, such as isopropyl and propyl groups, as well as *ortho* and *para* substitutions in the aryl derivative compounds. While physical properties such as viscosity did not vary significantly between structural isomers, the CO<sub>2</sub> permeability, selectivity, and solubility exhibited significant changes allowing for development of task-specific triazolium-based ionic liquids for separation applications. COSMOtherm studies were also completed to gain a better understanding of the ionic liquids which demonstrated a strong correlation between experimental and computational values for the alkyl bearing ionic liquids. Hence, 1,2,4-triazolium-based liquids comprise a class of compounds offering unique opportunities to examine how structural changes affect the physicochemical properties which are necessary for the continuous development of ionic liquids with enhanced adsorption capacity and selectivity in separations.

increased interest in the application of ILs for post-combustion  $CO_2$  capture.<sup>14–23</sup>

There are numerous physicochemical properties governing both the solubility and permeability of gases within ILs, including free volume, viscosity, and cation-anion interactions.<sup>24</sup> These properties can readily be adapted as needed given the ease of modulation for both the cation and anion within ILs. For instance, in imidazolium-based systems, it has been demonstrated that by adjusting the length of alkyl substituting groups, the CO<sub>2</sub> adsorption capacity can be modified.5 While there exist theoretical studies examining structure-property relationships in various ILs,25 studies examining the direct effect of isomeric substitutions on physicochemical properties of ILs are limited. The latter limitations thus restrain the ability to design novel compounds with enhanced adsorption capabilities, limiting our understanding of anion-cation interactions, and their segregation into 3-dimensional networks that affect CO<sub>2</sub> permeability, among other physicochemical properties.

The interaction of gases with ILs are complex, with numerous physical properties affecting the overall solubility and permeability of the gases within the liquids.<sup>22</sup> The structure of both the anionic and cationic species has been shown to affect the separations properties of ILs, as modulation of the intermolecular interactions, *i.e.* cation–cation and cation–anion interactions, significantly affect both the solubility and permeability of gases.<sup>4,5,22,24,26</sup> Steric or electronic

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<sup>†</sup> Electronic supplementary information (ESI) available: Full synthetic details, TGA plots under ambient conditions, and complete DSC graphs are included in the supplementary information. See DOI: 10.1039/c2ra22646d



Fig. 1 Ionic liquids synthesized and examined in this work.

changes in the ion-pair interactions should then have an influence on the gas separations properties of ILs. As such, 1,2,4-triazolium-based ILs provide a unique opportunity to examine the separation properties imparted by the addition of a nitrogenous lone-pair located in the cationic core of the IL as directly compared with the more commonly examined imidazolium ILs. Given the limited publications currently available for 1,2,4-triazole based ILs, the data acquired from the present studies are necessary to help expand the general knowledge base of ILs,<sup>27</sup> increase the data available for accurate computational studies,<sup>28</sup> and to add candidates useful in the search for superior materials for separation applications.<sup>29</sup>

Herein we report the synthesis and characterization of a series of twelve 1,2,4-triazolium-based ILs with alkyl (compounds 1a-1g), and N-benzyl groups (compounds 2a-2e), which are summarized in Fig. 1. The effects of systematic ancillary nitrogen substitutions on the overall properties of the ILs and their use in supported ionic liquid membrane (SILM) based gas separation was investigated. Of the twelve compounds, seven bear N-alkyl substitutions to examine the effects of increasing chain length and of isomers on physicochemical properties. The remaining five ILs bear N-benzyl substituents to examine the effect of aryl substitutions in addition to examining the effects of ortho, meta, and para aryl substitutions. Our results demonstrate that optimization of the separations properties of triazolium ILs can be achieved through the simple tailoring of isomeric and locational substitutions of ancillary groups. Additional studies using COSMOtherm were completed for the triazolium-based ILs which show a strong correlation between the experimental and computational values for CO<sub>2</sub> solubility of the alkyl-bearing ILs. Hence, these new class of triazolium-based cations are important model systems for the understanding of shifts in the anion-cation interactions and the resulting effects on gas-IL interfaces.

### **Experimental section**

#### General

1-methyl-1,2,4-triazole, 4-methoxytetrafluorobenzyl bromide, 4-(trifluoromethoxy)benzyl bromide, 2-(trifluoromethoxy)benzyl bromide were purchased from Matrix Scientific. Lithium bis(trifluoromethanesulfonimide) was purchased from 3M. All other chemicals were purchased from Sigma-Aldrich in the highest available purity and used as received. <sup>1</sup>H, <sup>13</sup>C NMR, <sup>31</sup>P spectra were recorded on a Bruker Avance 400, at 400 MHz, 100 MHz, and 162 MHz respectively. A JEOL (Peabody, MA) JMS-T100LC (AccuTOFTM) orthogonal time-of-flight (TOF) mass spectrometer was used to characterize the compound. 3-butyl-1-methyl-1H-imidazol-3-ium bis((trifluoromethyl)sulfonyl)amide) [Bmim][TF<sub>2</sub>N],<sup>30</sup> 3-benzyl-1-methyl-1*H*-imidazol-3ium bis((trifluoromethyl)sulfonyl)amide [BzMim][TF<sub>2</sub>N],<sup>31</sup> and 3-hexyl-1-methyl-1H-imidazol-3-ium bis((trifluoromethyl)sulfonyl)amide) [Hmim][TF<sub>2</sub>N]<sup>32</sup> were synthesized according to established literature procedures.

#### **Physical properties**

Thermal stabilities were measured using a Thermal Advantage 2950 Analyzer with platinum crucibles under a nitrogen atmosphere (10 °C min<sup>-1</sup> heating to 750 °C). The instrument was calibrated prior to measurement using a calcium carbonate standard. Melting points were obtained by dynamic scanning calorimetry (DSC) on a Thermal Advantage Q50 instrument using hermetically sealed aluminum pans. The ILs were subjected to three consecutive cycles from -90 °C to 200 °C (5 °C min<sup>-1</sup> rate).

Gas solubility measurements were obtained using a gravimetric microbalance (Hiden Isochema, IGA). A known mass of the ionic liquid (generally of the order of 70 mg) was loaded into a quartz sample boat and sealed in the stainless steel chamber. To remove any residual water, the ionic liquid was then dried under vacuum at a temperature of approximately 60 °C until the mass no longer decreased (minimum of four hours) and the dry mass was recorded. The ionic liquid mass was then measured for various  $CO_2$  pressures up to 10 atm at a constant temperature of 25 °C, which was maintained using a constant-temperature recirculating water bath. Volume-based solubility values were then calculated using the slope of the best fit line.

Gas permeabilities through the ionic liquids were measured by loading the ionic liquid onto a porous polyethersulfone support with a pore diameter of 100 nm and measuring gas flux through the ionic liquid membrane. The permeability measurement system which has been previously described in detail<sup>33</sup> consisted of two chambers separated by the supported ionic liquid membrane. After initially evacuating both chambers, one chamber was filled to a pressure of 35 kPa with either CO<sub>2</sub> or N<sub>2</sub> and the gas flux through the membrane was obtained by recording the pressure rise in the second chamber as a function of time. The permeability was then calculated using eqn (1):

$$P = \frac{\tau}{\phi} \frac{V}{RTA\Delta P_0} \frac{\mathrm{d}P'}{\mathrm{d}t} \tag{1}$$

where  $\tau$  is the tortuosity,  $\phi$  is the membrane porosity, *V* is the permeate volume, *R* is the ideal gas constant, *T* is the absolute temperature, *A* is the membrane area,  $\Delta P_0$  is the pressure difference, and dP''/dt is the rate of pressure increase on the permeate side of the membrane. The tortuosity and porosity were obtained using a standard ionic liquid, [Emim][Tf<sub>2</sub>N]. Ideal CO<sub>2</sub>/N<sub>2</sub> selectivity values were obtained by separately measuring the CO<sub>2</sub> and N<sub>2</sub> permeability and calculating the ratio of these values to obtain the selectivity. Mixed gas measurements were not acquired.

Temperature dependent viscosity measurements were acquired using a cone/plate viscometer (Brookfield, DVII+ Pro), which allowed the use of small sample volumes of approximately 1 mL. The sample was maintained at the desired temperature with a recirculating water bath (VWR) for at least 15 min prior to measurement and five separate measurements at each temperature were obtained and averaged. Viscosity standards (Cannon) were used to calibrate the instrument before ionic liquid viscosities were measured.

#### Calculations

The COSMOtherm program was used to predict gas solubility in the ionic liquids. The COSMOtherm program<sup>34</sup> is based on the COSMO-RS (COnductor-like Screening MOdel for Real Solvents)<sup>35</sup> theory which links the quantum mechanically calculated, solvated molecular surfaces from the COSMO method to interacting molecular surfaces and macroscopic properties such as solubility *via* a statistical thermodynamics model. Full COSMO optimization of the molecular structure was obtained with Turbomole V6.0 at the level of density functional theory (DFT) with the B-P86 functional for electron correlation and exchange<sup>36</sup> and using the resolution-ofidentity (RI) technique and the large TZVP basis set.

#### Synthesis of ionic liquids, ESI<sup>†</sup>

Synthesis of 1,2,4-triazolium ionic liquids were carried out using standard literature procedures for imidazolium based ILs.<sup>29</sup> Full synthetic details are presented in the ESI<sup>†</sup> section.

Briefly, the appropriate bromo alkane was added dropwise to 1-methyl-1,2,4-triazole, and the mixture stirred for a minimum of 24 h. The resultant solid was washed, dissolved in water and decolorized with carbon. The aqueous solution was filtered and lithium bis(trifluoromethanesulfonimide) was added, resulting in the formation of two phases. The formed IL was separated from the aqueous phase and purified.

### Discussion

#### Thermal properties

Thermogravimetric (TG) and calculated derivative curves (DTG) for compounds **1a–g** and **2a–e** recorded in flowing nitrogen atmosphere are shown in Fig. 2, and a summary of the measured physicochemical properties is given in Table 1.

Compounds **1a–g** displayed similar decomposition profiles characterized by a single decomposition step under both air (see ESI† Fig. S1 and S2) and nitrogen, whereas compound **1d** shows two overlapping decomposition steps. The peak maxima of the DTG curve for compound **1d** shows a main decomposition at 343 °C, with the second step happening at 354 °C. All compounds, except **1e** and **1g**, exhibit similar initial decomposition temperatures under both ambient and inert atmospheres.

To better understand the thermal stabilities of the latter compounds, the imidazolium based congener of compound 1e, namely  $[Hmim][TF_2N]$ , was subjected to the same tests in order to provide a direct comparison of properties between the two compounds. Unlike compound 1e, [Hmim][TF<sub>2</sub>N] displayed the same onset temperature for decomposition under either air (377 °C) or N<sub>2</sub> (378 °C). However, compound 1f displayed a higher stability under inert atmosphere (333 °C) as compared to the values reported within the literature for [Omim][Tf<sub>2</sub>N] (325 °C).<sup>41</sup> Similarly, compound **1g** displayed lower decomposition temperatures in air than in N2, and significantly lower thermal stability compared to its imidazolium analog [Bmim][PF<sub>6</sub>] ( $\sim$  360 °C).<sup>42</sup> In general, these results indicate a decreased thermal stability of triazolium-based ILs as compared to imidazolium ILs. This observation was further examined by the isothermal thermogravimetric measurements for compounds 1d and [Bmim][TF<sub>2</sub>N] within 150 °C to 250 °C for 6 h at each selected temperature (see Table 2). After 30 h, compound 1d exhibited a weight loss of ~23 wt%, nearly 2.5 times that of  $[Bmim][TF_2N]$ . It is possible that this decrease in stability arises from the unique reactivity and stability associated with certain triazolium-based cations.43-47 For example, in previous studies the methylene groups of alkyl chains directly bound to triazolium cations were found to be particularly reactive.43 It is plausible that this increased reactivity would lead to additional decomposition pathways under high temperature, accounting for the observed decrease in stability.

Furthermore, the five benzyl-bearing ILs exhibited much lower thermal stabilities than the alkyl-substituted compounds, with almost 100 °C difference in the onset of the decomposition curves. Among the benzyl-containing ILs, the lowest  $T_{dec}$  was observed for 2d (253 °C) while the highest was recorded for 2c (294 °C). In general, those compounds with fluorine in the substituting groups were more thermally stable than the methylated compounds 2d and 2e. In addition, an ortho-substitution in the benzyl ring resulted in slightly higher decomposition temperature than the two other fluorinated para-substituted compounds. Finally, as with the compound 1 series, benzyl-substituted triazolium ILs show lower thermal stability than imidazolium congeners. For instance, compound 3-benzyl-1-methyl-1H-imidazol-3-ium bis((trifluoromethyl)sulfonyl)amide, [BzMim][TF2N], was synthesized and found to decompose at 367 °C, which is nearly 100 °C above the decomposition temperature found for compound 2a. Also, the isothermal thermogravimetric tests for compound 2a and [BzMim][TF<sub>2</sub>N] showed a total weight loss of 82.2 wt% for the triazolium compound, compared to only 4.09 wt% for its imidazolium congener (see Table 2).

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Fig. 2 TG and DTG curves in nitrogen for the alkyl substituted triazolium ILs (A) and (B), and benzyl substituted triazoliums (C) and (D), respectively.

Table 1 Physicochemical parameters for the triazolium based ionic liquids and calculated gas absorption data

Compound	<sup><i>a</i></sup> <i>D</i> (g cm <sup>-3</sup> )	$^{b}T_{\mathrm{g}}$ (°C)	$T_{\rm mp}$ (°C)	$\Delta H_{\rm mp}$ (J g <sup>-1</sup> )	$^{c} T_{dec}$ N <sub>2</sub> (°C)	<sup>c</sup> $T_{\text{dec}}$ Air (°C)	<sup>d</sup> η (cP)	<sup>e</sup> Perm <sub>CO2</sub> (barrer)	$^{f}$ Sel <sub>CO2/N2</sub>	$\int_{co2}^{g} \operatorname{Sol}_{CO2} (\operatorname{mol} L^{-1} \operatorname{atm}^{-1})$	<sup>h</sup> K <sub>H,px</sub> (atm)
1a	_	-69.4	50.0	59.8	358	359	_	_	_	_	_
1b	1.484	-68.1	_	_	290	287	107 $\pm$ 1	$641 \pm 11$	$24 \pm 2$	0.0778	45.0
1c	1.485	-71.1	31.7	58.9	351	348	$102 \pm 1$	786 $\pm$ 14	$28 \pm 1$	0.0813	41.9
1 <b>d</b>	1.489	-65.2	_	_	343	347	$246~\pm~3$	$483~\pm~15$	$22 \pm 1$	0.0713	45.4
1e	1.372	-70.6	_	_	344	327	130 $\pm$ 3	$804~\pm~18$	$22 \pm 1$	0.0766	37.8
1f	1.314	-71.2	17.4	41.6	338	333	$154 \pm 5$	$859 \pm 9$	$17 \pm 1$	0.0755	35.5
1g	_	_	55.3	32.3	308	303	—	_	_	—	_
2a	1.488	-46.0	_	_	271	270	$317~\pm~10$	$304 \pm 10$	$21 \pm 3$	0.0679	44.4
2b	1.590	-44.6	_	_	288	285	530 $\pm$ 33	$407~\pm~10$	$22 \pm 1$	0.0819	34.1
2c	1.598	-45.7	_	_	294	293	573 $\pm$ 23	$277 \pm 11$	$19 \pm 3$	0.0689	38.8
2 <b>d</b>	1.420	-37.3	_	_	253	252	$839~\pm~34$	$223~\pm~19$	$19 \pm 2$	0.0647	43.4
2e	_	-34.4	_	_	290	289	$2048~\pm~51$	$108 \pm 7$	$12 \pm 3$	0.0492	52.8
Bmim[TF <sub>2</sub> N] <sup>i</sup>	1.436	-87	-3	_	423	_	52	1344	19.7	0.090	_
$BzMim[TF_2N]^i$	1.42	_		_	367	_	61	528	31.4	0.080	_

<sup>*a*</sup> Measured density. <sup>*b*</sup> Glass transition temperature from DSC. <sup>*c*</sup> Decomposition temperature taken from the maximum of the first peak on the DTG curves. <sup>*d*</sup> Viscosity. <sup>*e*</sup> Carbon dioxide permeability. <sup>*f*</sup> CO<sub>2</sub> selectivity calculated from the permeability ratios of CO<sub>2</sub> to N<sub>2</sub>. <sup>*g*</sup> CO<sub>2</sub> solubility. <sup>*h*</sup> Henry's Law constant calculated according to  $K_{H,XP} = p/x$ , where *p* is the pressure and *x* the mol fraction of CO<sub>2</sub> in a given IL. <sup>*i*</sup> Data taken from ref. 37–40

Table 2 Results from long-term thermal stability test<sup>a</sup> on compounds 1d and 2a as compared with imidazole based ionic liquids

	150 °C	180 °C	200 °C	220 °C	$250$ $^{\circ}\mathrm{C}$	Total weight loss <sup>b</sup>
1 <b>d</b>	0.015	0.051	0.20	0.65	2.9	23.6
2a	0.074	0.20	1.6	6.8	4.9	82.2
Bmim[TF <sub>2</sub> N]	$2.2 \times 10^{-3}$	0.022	0.084	0.26	1.2	9.36
$BzMim[TF_2N]$	$1.2~ imes~10^{-3}$	$1.6 \times 10^{-3}$	0.019	0.085	0.58	4.09
<sup><i>a</i></sup> (Units given in wt	t% $h^{-1}$ ). <sup><i>b</i></sup> Total weight	lost for entirety of test	: (wt%).			

The DSC results for the observed melting transitions and glass transition temperatures are summarized in Table 1. While only compounds **1a**, **1c**, **1f** and **1g** exhibited melting transitions (see Fig. 3), glass transitions were observed for all ILs (see ESI† Fig. S3–S13). The melting points for the investigated triazolium compounds were higher than those for their corresponding imidazolium based congeners. For instance, compound **1a** displayed an average melting point of 50.0 °C, well above the previously reported melting point of approximately -16 °C for [Emim][Tf<sub>2</sub>N].<sup>48</sup>

The melting point for compound **1c** was 31.7 °C, whereas [Prmim][TF<sub>2</sub>N] exists as a free flowing liquid at room temperature.<sup>48</sup> The melting point for compound **1f** was as low as -17.4 °C,  $\sim 4$  °C above that reported for [Omim][TF<sub>2</sub>N] (-23.3 °C).<sup>49</sup> Compound **1g** was a solid at room temperature and had an observed melting point of 55.3 °C, which is also significantly higher than [Bmim][PF<sub>6</sub>] (11 °C).<sup>50</sup> Interestingly, the increasing length of the substituting alkyl chain did not dramatically change the glass transition temperatures for this series of compounds, being observed within the range of -71 °C to -65 °C. Those were far lower than the glass transition temperatures observed for the benzyl containing ILs, for which the lowest  $T_g$  was observed in compound **2a** at -46.0 °C and



Fig. 3 DSC curves for selected compounds 1a, 1c, 1f, and 1g, with the first three exhibiting cold crystallization (exothermic peaks), and all four showing well-defined melting transitions (endothermic peaks).

the highest for 2e at -34.4 °C. For the latter series of compounds, the lowest glass transition temperatures were comparable to the unsubstituted benzyl ring, with or without the addition of an  $-OCF_3$  in either the *ortho* or *para* positions. Shifts towards higher  $T_{o}$  values were found for fluorinated and protonated rings with methoxy and methyl moieties in para positions, respectively. For instance, compounds 2b and 2c, showed minimal shift in  $T_{g}$  despite the change in position of the perfluoromethoxy group. Similarly, compounds 1b and 1c, differing by the substitution of a propyl chain, displayed very small differences in the  $T_{\rm g}$ , despite the significant decrease in thermal stability associated with steric changes in alkyl chains discussed previously, *i.e.* isopropyl (1b) to propyl (1c). In addition to glass transitions, compounds 1a, 1c, and 1f displayed cold crystallization transitions attributed to molecular rearrangements.51

#### Viscosity

Temperature dependent viscosities for the RTILs within 25 °C to 60 °C are shown in Fig. 4. Compound 1c had the lowest viscosity at 25 °C (102 cP), while 2e displayed the highest at the same temperature (2047 cP). In general, the alkyl bearing ILs displayed lower viscosity than those containing aryl groups, whereas this parameter increased within the alkyl containing ILs with increasing chain length, with a maximum value for the butyl substituted compound 1d. Compounds 2b and 2c varying only by the location of the perfluoromethoxy group, displayed nearly identical viscosities, thus indicating that an ortho or para substitution on the aryl ring did not affect this property. In addition, the viscosity of compound 2d, varying by addition of methyl groups, was more than twice that of compound 2a. Similarly, the fluorinated methoxy derivative, compound 2e, exhibited more than six times the viscosity of compound 2a.

When compared to imidazolium-based ILs, triazolium ILs display significantly higher viscosities. With the exception of **1d**, viscosity values of the alkyl triazolium ILs are approximately double that of their reported imidazolium congeners (see Table 1 for a comparison).<sup>48,52,53</sup> Given the small increase in molecular mass from the substitution of one nitrogen for a carbon in these heterocycles, it is likely that the increases in viscosity arises from an increase in the intra- and intermolecular interactions.

#### **Gas separations**

 $CO_2$  solubility curves for the ionic liquids are displayed in Fig. 5, and calculated parameters are summarized in Table 1. Permeability for the entire series of ILs ranged from 108



Fig. 4 Temperature dependent viscosity for compounds 1b-1f (A) and compounds 2a-e (B)

barrer, for 2e, to 859 barrer for 1f. In general, the alkyl-bearing ILs, compounds 1b-f, showed significantly higher permeabilities as compared to the aryl-bearing ILs, which likely results from the lower viscosities of the former compounds. Within both sets of compounds, the CO<sub>2</sub> permeability decreased with increasing viscosity. In general, for imidazole-based ILs with the same anion, increasing the substituting alkyl chain length leads to increases in viscosity, and consequently lower CO2 permeability.<sup>37</sup> Such a trend within compound 1 series is less obvious, with a sudden increase in viscosity for the butyl derivative. Interestingly, despite the similar viscosity values measured for compounds 1b and 1c, with isopropyl and n-propyl chains, respectively, the latter exhibited 23% higher permeability than the former. Similarly, compounds 2b and **2c**, which vary only by locational substitution of an  $O-CF_3$ group and having similar viscosity values, reveal that the orthosubstituted IL (2b) has ~1.5 times higher  $CO_2$  permeability than the *para*-derivative (2c).



Fig. 5 High pressure  $CO_2$  solubility isotherms at 25 °C for the alkyl-bearing (A) and the aryl-bearing (B) ionic liquid.

Selectivity of the ILs ranged from a low of 12 for compound **2e** to 28 for **1c**, placing the selectivity of triazolium-based ILs in the range typically observed for the standard imidazolium based compounds.<sup>54</sup> The two compounds with the lowest viscosity, namely **1b** and **1c**, display the highest selectivity. Between those compounds, the *n*-propyl substitution not only resulted in higher selectivity, but also increased CO<sub>2</sub> solubility compared to the isopropyl substituted compound. Similarly, the *para*-substituted  $-\text{OCF}_3$  aryl compound, **2b**, displayed higher selectivity, and solubility than the *ortho*-substituted  $-\text{OCF}_3$  compound **2c**. Among the aryl-bearing ILs, compounds **2b** and **2c** have the highest solubility values as compared with the others. This increase in solubility can be attributed to the presence of perfluoromethyl groups which have been shown to have increased affinity to CO<sub>2</sub>.<sup>55</sup>

For the case of these triazolium ILs, solubilities of the alkylbearing ILs display a correlation with viscosity, where the highest viscosity compound, **1d**, had a lower solubility (0.0713 mol  $L^{-1}$  atm<sup>-1</sup>) than the less viscous samples. Furthermore, a ~6% increase in solubility was achieved by replacing the butyl chain with an octyl chain (compound **1f**), which in turn is nearly 37% less viscous than compound **1d**. Finally, the viscosity of compound **2e**, which is too high to readily facilitate

Compound	Mol. weight (g $mol^{-1}$ )	$^{a}$ D (g cm <sup>-3</sup> )	Molar volume (Å <sup>3</sup> )	$^{b}$ $V_{\rm cosmo}$ (Å <sup>3</sup> )	<sup>c</sup> Fractional free volume	<sup>d</sup> Sol <sub>CO2</sub> (mol $L^{-1}$ atm <sup>-1</sup> )
1a	392.20	1.571	414.6	369.5	0.109	0.073
1b	406.33	1.520	443.9	392.8	0.115	0.080
1c	406.33	1.516	445.0	393.8	0.115	0.080
1d	420.35	1.481	471.4	413.6	0.123	0.081
1e	448.41	1.416	525.9	456.8	0.131	0.083
1f	476.46	1.357	583.2	500.9	0.141	0.081
1g	285.17	1.387	341.3	296.8	0.130	0.072
2a	454.37	1.522	491	445	0.103	0.082
2b	538.37	1.594	561	501	0.107	0.071
2 <b>c</b>	538.37	1.588	563	504	0.105	0.077
2d	482.42	1.454	551	489	0.113	0.086
2e	556.36	1.624	569	509	0.105	0.068

 $CO_2$  diffusion, displayed the lowest selectivity and the lowest  $CO_2$  solubility among all the compounds investigated. Of course, viscosity is not the only property that affects permeability and solubility. It has been observed that molar free volume has an influence on gas permeability in ionic liquids.<sup>54</sup> Hence, the  $CO_2$  separations properties of the triazolium ILs are likely influenced by a combination of many physical properties, such as changes in cation–anion interactions and the segregation of the charged species forming porous networks.<sup>24</sup>

#### **COSMOtherm calculations**

In an effort to better understand the changes in CO<sub>2</sub> solubility associated with the triazolium-based ILs, the compounds were examined via computational methods using COSMO-RS, which has been widely employed in previous studies to examine solubility and selectivity of gases in ILs.<sup>25,56,57</sup> The calculated parameters for all compounds are summarized in Table 3. Several structural aspects are known to affect CO<sub>2</sub> solubility in ionic liquids, such as increasing alkyl chain length as well as addition of electronegative atoms.<sup>25,56,57</sup> As can be seen from the values in Tables 1 and 3, the experimental solubility values of the alkyl bearing ILs show good correlation with the calculated values. There is a good correlation between the calculated and experimental values for the alkyl bearing ILs, with calculated CO<sub>2</sub> solubility values being slightly higher than the experimental ones. Such differences are acceptable, given the existence of errors associated to experimental measurements. Compounds 1g and 1d exist as solids at room temperature, precluding the possibility of obtaining experimental solubility data. COSMO-RS calculations, however, predict a solubility of 0.072 mol  $L^{-1}$  $atm^{-1}$  for 1g and 0.081 mol  $L^{-1}$   $atm^{-1}$  for 1d. Based on these data we can conclude that the  $PF_6$  anion in compound 1g lowers CO<sub>2</sub> solubility as compared with the TF<sub>2</sub>N based ionic liquids. This is in agreement with previous literature reports which demonstrate that PF<sub>6</sub> containing ionic liquids have lower CO<sub>2</sub> solubility as compared to their TF<sub>2</sub>N congeners.<sup>40</sup>

The calculated values for  $CO_2$  solubility of the aryl-containing ILs show the expected trends,<sup>25</sup> with the alkyl substituted benzene rings having higher  $CO_2$  solubility (**2a** and **2d**) than the fluorine-bearing benzene rings (**2b**, **2c**, **2e**). In general, the calculated values for the aryl-bearing ILs show larger discrepancies between the experimental values as compared to the values found for the alkyl-bearing compounds. Interestingly, the calculated solubility values decrease when comparing the structurally related compounds **2b** and **2c**, which is the opposite of experimental results, leading to the conclusion that further refinement of computational methods is required.

As has been previously described in the literature, predicting the solubility of gases in ILs poses significant challenges as there are multiple inter- and intra-molecular interactions which effect the solubility. As reported by Bara et al.,58 fractional free volume (FFV) of ILs has been shown to correlate inversely to the solubility and selectivity of gases within imidazolium based IL systems. In an effort to further examine the solubility changes imparted by the locational substitutions within the triazolium ILs, fractional free volumes for all the triazolium compounds were calculated using COSMOtherm, with a summary of relevant values shown in Table 3. With respect to the alkyl-bearing ILs, calculated CO<sub>2</sub> solubility remained approximately the same despite seeing increases in the FFV. Correlation between the calculated and experimental values for the aryl-containing ILs proves to be difficult as no exact trends are readily observed. The constitutional isomers, namely compounds 2b and 2c, were predicted to have nearly identical FFV values of 0.107 and 0.105 respectively, yet as discussed previously show significantly different solubility values. The two methyl substituted aryl ring systems, namely 2a and 2d, were calculated to have the lowest and highest FFV values at 0.103 and 0.113 respectively, a change of approximately 10%. As expected, the experimental solubility values are inversely proportional to the FFV values, with compound 2d having the lower solubility values than 2a.

Overall, the use of COSMOtherm as a method for predicting the solubility of  $CO_2$  within triazolium-based ILs is a viable method, with calculated values showing reasonable agreement with experimental ones in respect to alkyl containing ILs. The aryl-containing ILs show some correlation between experimental and calculated results, with the simpler aliphatic bearing arene systems appearing to show higher correlation than the more complex fluorinated systems. It is likely that further enhancements to current computational methods are required in order to more accurately predict solubility selectivity values for these systems.

## Conclusions

A series of twelve novel 1,2,4-triazolium-based ionic liquids have been synthesized and their physicochemical properties studied. Ten of the compounds remained as free flowing liquids at room temperature, effectively expanding the available library of room-temperature ILs. The ILs displayed high thermal stability under both ambient and inert atmospheres. Overall, while triazolium ILs showed higher viscosities, these displayed CO<sub>2</sub> solubility and selectivity values comparable to imidazolium-based ILs. Previous reports on imidazoliumbased IL showed a direct correlation between increasing CO<sub>2</sub> selectivity and solubility properties with viscosity and length of substituting alkyl groups. In the present study, the triazolium compounds displayed more complex correlations. For instance, the CO<sub>2</sub> adsorption properties greatly changed for isomeric compounds having similar viscosity values. This effect was clearly seen for isopropyl and n-propyl substituted triazolium compounds, as well as for ortho and para-substitutions of the -OCF3 group in aryl-derivatives. Also, addition of perfluoro groups appears to have a beneficial effect on the solubility of CO2, as compared to fully protonated, and to fluorinated benzyl groups. COSMOtherm calculations showed significant agreement between calculated and experimental values for the alkyl-bearing ILs. Triazolium-bearing aryl substitutions proved to be a challenge to model properly using the currently established parameters in COSMOtherm. The latter results demonstrate that further refinement is needed for accurately modeling more complex systems. We are currently using the experimental values acquired for the ILs in this study to develop new methods to increase the validity of computational parameters for 1,2,4-triazolium ILs. Therefore, triazolium-based cations are important model systems for developing a more complete understanding of small changes in the ionic volume of cations, as well as shifts in the anioncation interactions which are crucial for the development of ILs with enhanced separation properties.

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