ARTICLES

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# Properties of alkylbenzimidazoles for CO<sub>2</sub> and SO<sub>2</sub> capture and comparisons to ionic liquids

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To date, few reports have been concerned with the physical properties of the liquid phases of imidazoles and benzimidazolespotential starting materials for a great number of ionic liquids. Prior research has indicated that alkylimidazole solvents exhibit different, and potentially advantageous physical properties, when compared to corresponding imidazolium-based ionic liquids. Given that even the most fundamental physical properties of alkylimidazole solvents have only recently been reported, there is still a lack of data for other relevant imidazole derivatives, including benzimidazoles. In this work, we have synthesized a series of eight 1-n-alkylbenzimidazoles, with chain lengths ranging from ethyl to dodecyl, all of which exist as neat liquids at ambient temperature. Their densities and viscosities have been determined as functions of both temperature and molecular weight. Alkylbenzimidazoles have been found to exhibit viscosities that are more similar to imidazolium-based ILs than alkylimidazoles, owed to a large contribution to viscosity from the presence of a fused ring system. Solubilities of  $CO_2$  and  $SO_2$ , two species of concern in the emission of coal-fired power generation, were determined for selected alkylbenzimidazoles to understand what effects a fused ring system might have on gas solubility. For both gases, alkylbenzimidazoles were determined to experience physical, non-chemically reactive, interactions. The solubility of CO2 in alkylbenzimidazoles is 10%-30% less than observed for corresponding ILs and alkylimidazoles. 1-butylbenzimidazole was found to readily absorb at least 0.333 gram  $SO_2$  per gram at low pressure and ambient temperature, which could be readily desorbed under an  $N_2$  flush, a behavior more similar to imidazolium-based ILs than alkylimidazoles. Thus, we find that as solvents for gas separations, benzimidazoles share characteristics with both ILs and alkylimidazoles.

benzimidazole, imidazole, ionic liquids, carbon dioxide (CO2) capture, sulfur dioxide (SO2)

### 1 Introduction

Imidazolium salts (Figure 1(a)) have been the dominant motif for the development of ionic liquids (ILs) and have been explored in a diverse and ever-growing number of applications, including  $CO_2$  capture [1, 2], electrochemistry

[3–5], energetic materials [6–8], cellulose processing [9] and polymer science [10–16], to name but a few. Benzimidazolium salts (Figure 1(b)), while possessing the same modularity as their imidazolium counterparts, have rarely been explored for the same applications that have been proposed for imidazolium-based ILs. This might be attributable to the much higher melting points of benzimidazolium salts than imidazolium salts [17]. However, benzimidazolium salts have found great utility as frameworks for

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N-heterocyclic carbenes (NHCs) for catalysis [18–20], as liquid crystals (LCs) [21] and antimicrobials [22]. Benzobis(imidazolium) or "Janus" benzimidazolium salts (Figure 1(c)) have also been of interest for their unique fluorescence and as sensors [23, 24]. Poly(benzimidazolium) salts can be formed form the alkylation of poly(benzimidazole) and used as anion conductors [25]. However, to our knowledge, there are no reports on the use of benzimidazolium ILs (e.g. 1-ethyl-3-methylbenzimidazolium tetrafluoroborate) as bulk liquids, even as related to characterizations of physical properties such as density or viscosity. Thus, although an important building block in many applications [26], the impact of the versatile and readily available benzimidazole moiety on physical and thermodynamic properties has not been quantified.

Although the characterization of physical properties for imidazolium-based ILs has now been a priority of many research efforts for more than a decade [27], there has only recently been an interest in developing a similar understanding of the physical properties of the starting materials for imidazolium-based ionic liquids (ILs), such as alkylimidazoles (Figure 2(a)) [28–32]. Fundamentally, alkylimidazoles can be functionalized in similar manners to ILs to control their physical [28–30, 32, 33] and/or chemical [34] and/or biological [35] properties. As there are likely quadrillions  $(10^{15})$  if not quintillions  $(10^{18})$  of possible ILs [36], encompassing a number of different species, it may be assumed that the number of possible imidazole derivatives (and mixtures) could easily exceed  $10^6$  (if not orders of magnitudegreater).

Imidazoles and benzimidazoles (Figure 2(b)) are known for their antimicrobial, antifungal, and medicinal properties and thus have numerous applications in the pharmaceutical industry [26, 35, 37, 38]. In addition to these vital uses, imidazoles are an important class of building blocks for synthetic organic chemistry [10, 39]. Furthermore, virtually all imidazolium salts originate from imidazoles, and the properties of ILs are better understood via comparisons to imidazoles [30, 40]. Imidazoles have also found industrial utility in separations, as the BASIL<sup>TM</sup> (biphasic acid scavenging using ionic liquids) process directly used 1-methylimidazole as an acid (H<sup>+</sup>) scavenger to form 1-methylimidazolium chloride and enabled significant improvements in the manufacture of alkoxyphenylphosphines [41, 42].

Developing understandings of neutral, imidazole-based molecules can be keys to advancing IL-based technologies.



Figure 1 General structures of (a) imidazolium salts, (b) benzimidazolium salts and (c) benzobis(imidazolium) salts.



Figure 2 Structures of (a) imidazoles and (b) benzimidazoles.

To further this area of research, we have explored the properties of some relatively simple benzimidazole derivatives. Herein, we report on density, viscosity and solubilities of carbon dioxide (CO<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>) in 1-n-alkylbenzimidazoles (Figure 2(b)) and provide comparisons to alkylimidazoles and imidazolium-based ILs. Density and viscosity were found to be strongly related to the length of the alkyl chain and temperature, and highly correlated functions were developed as a means of modeling these properties. Solubility of CO<sub>2</sub> was also found to be correlated to alkyl chain length and temperature, although the 1-n-alkylbenzimidazole solvents appear to have somewhat less of an affinity for CO<sub>2</sub> than alkylimidazoles or ILs. Interestingly, although 0.33 grams of SO<sub>2</sub> could be absorbed per gram of 1-butylbenzimidazole, this was not attributable to a chemical reaction that was previously observed for alkylimidazoles [28]. The properties and behaviors of 1-nalkylbenzimidazoles thus appear to have commonalities with both alkylimidazoles and imidazolium-based ILs.

#### 2 Materials and Method

#### 2.1 Materials

All chemicals were purchased from Sigma-Aldrich (Milwaukee, WI USA) and were used as received without further purification.  $CO_2$  and anhydrous  $SO_2$  were purchased from AirGas (Radnor, PA USA) at a minimum of 99.98% purity.

#### 2.2 Synthesis of 1-*n*-alkylbenzimidazoles

Sodium benzimidazolate (NaBenz) was first produced via the neutralization of benzimidazole with NaOH in THF (Scheme 1(a)) and subsequent drying. NaBenz was then used to produce a series of 1-n-alkylbenzimidazoles (1-8) via reaction with a corresponding 1-bromoalkane (Scheme 1(b)). This synthetic method is based on our prior work with a variety of *N*-functionalized imidazoles [43].

## 2.2.1 Procedure for preparing sodium benzimidazolate (NaBenz)

Benzimidazole (200.00 g, 1.693 mol) was dissolved in refluxing THF (500 mL). NaOH (74.49 g, 1.862 mol) was added and observed to gradually disappear as the reaction was stirred for 16 hours at 65 °C. The reaction was stopped, and while warm (~40 °C), filtered through a thin layer of



Scheme 1 Synthesis of (a) NaBenz precursor and (b) subsequent formation of 1-n-alkylimidazoles (1–8).

basic Al<sub>2</sub>O<sub>3</sub> to remove the small amount of insoluble material present. The solvent was removed via rotary evaporation until a viscous oil remained, which was then spread onto a large area Pyrex® glass tray and placed in a vacuum oven set to 80 °C. After several minutes, the viscous oil underwent a transition to an off-white solid. At this time, the product was briefly removed from the oven and the solid crushed to produce a fine powder. The powdered product was returned to the vacuum oven for 16 hours at 120 °C. 207.633 g of the product containing NaBenz and residual THF and NaOH were collected. By <sup>1</sup>H NMR analysis, about 4 mol% THF remained in the NaBenz product based on the expected chemical shifts of THF in DMSO-d6 (multiplets at  $\delta$  3.60 and 1.76) [44]. The NaBenz product was used without further purification. An image of this <sup>1</sup>H NMR spectra is provided as Supporting Information.<sup>1</sup>H NMR (500 MHz, DMSO-d6)  $\delta$  7.93–7.69 (m, 1H), 7.38 (ddt, J = 6.1, 3.2, 1.7Hz, 2H), 6.80 (ddt, J = 5.9, 3.0, 1.4 Hz, 2H), 2.54–2.47 (m, 1H).

#### 2.2.2 Synthesis of 1-n-alkylbenzimidazoles (1–8)

#### 2.2.2.1 Synthesis of 1-ethylbenzimidazole (1)

NaBenz (50.00 g, 357 mmol) was dissolved in 500 mL THF in a 1000 mL round bottom flask. Bromoethane (35.01 g, 23.98 mL, 321 mmol) was added and a solid precipitate was observed soon thereafter. A reflux condenser was attached and the reaction allowed to proceed overnight at 65 °C while stirring. After this time, the reaction was cooled, the solids filtered and the THF removed via rotary evaporation. The product was extracted into 400 mL of a 50:50 (V:V) mixture of EtOAc and hexanes. The solution was then dried over MgSO<sub>4</sub>, mixed with activated carbon and filtered through a plug of basic Al<sub>2</sub>O<sub>3</sub>, which was then washed with an additional 200 mL of a the EtOAc/hexanes mixture. The filtrate was reduced via rotary evaporation and the product dried under vacuum lines to produce 1 as a pale yellow oil. Yield = 25.885 g (55.1%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.24 (s, 1H), 7.62 (dd, J = 28.1, 7.9 Hz, 2H), 7.22 (dt, J = 27.7, 7.4 Hz, 2H), 4.27 (q, J = 7.3 Hz, 2H), 1.41 (t, J)= 7.3 Hz, 3H). <sup>1</sup>H NMR consistent with published data [45].

#### 2.2.2.2 Synthesis of 1-n-propylbenzimidazole (2)

Compound 2 was produced from NaBenz (30.00 g, 214

mmol) and 1-bromopropane (23.79 g, 17.60 mL, 193 mmol) in a manner similar to that employed for **1**. Yield = 21.81 g (79.4%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.22 (s, 1H), 7.62 (dd, *J* = 24.2, 7.9 Hz, 2H), 7.36–7.09 (m, 2H), 4.20 (t, *J* = 7.0 Hz, 2H), 1.91–1.66 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). <sup>1</sup>H NMR consistent with published data [46, 47].

#### 2.2.2.3 Synthesis of 1-butylbenzimidazole (3)

Compound **3** was produced from NaBenz (50.00 g, 357 mmol) and 1-bromobutane (44.01 g, 34.57 mL, 321 mmol) in a manner similar to that employed for **1**. <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.22 (s, 1H), 7.62 (dd, J = 28.1, 7.9 Hz, 2H), 7.36–7.02 (m, 2H), 4.23 (t, J = 7.1 Hz, 2H), 1.91–1.62 (m, 2H), 1.40–1.08 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H).<sup>1</sup>H NMR consistent with published data [48, 49].

#### 2.2.2.4 Synthesis of 1-pentylbenzimidazole (4)

Compound **4** was produced from NaBenz (30.00 g, 214 mmol) and 1-bromopentane (29.22 g, 23.93 mL, 193 mmol) in a manner similar to that employed for **1**. Yield = 24.72 g (76.6%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.22 (s, 1H), 7.61 (dd, *J* = 27.0, 7.9 Hz, 2H), 7.22 (dt, *J* = 28.0, 7.4 Hz, 2H), 4.23 (t, *J* = 7.1 Hz, 2H), 1.91–1.62 (m, 2H), 1.47–1.03 (m, 4H), 0.83 (t, *J* = 7.2 Hz, 3H). <sup>1</sup>H NMR consistent with published data [50].

#### 2.2.2.5 Synthesis of 1-hexylbenzimidazole (5)

Compound **5** was produced from NaBenz (50.00 g, 357 mmol) and 1-bromohexane (53.06 g, 45.12 mL, 321 mmol) in a manner similar to that employed for **1**. Yield = 51.33 g (78.9%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.22 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.28–7.12 (m, 2H), 4.23 (t, *J* = 7.1 Hz, 2H), 1.83–1.69 (m, 2H), 1.41–1.08 (m, 6H), 0.82 (t, *J* = 6.9 Hz, 3H). <sup>1</sup>H NMR consistent with published data [51].

#### 2.2.2.6 Synthesis of 1-octylbenzimidazole (6)

Compound **6** was produced from NaBenz (50.00 g, 357 mmol) and 1-bromooctane (62.05 g, 55.9 mL, 321 mmol) in a manner similar to that employed for **1**. Yield = 53.44 g (72.2%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.21 (s, 1H), 7.61 (dd, J = 31.0, 7.9 Hz, 2H), 7.32–7.15 (m, 2H), 4.22 (t, J = 7.1 Hz, 2H), 1.85–1.70 (m, 2H), 1.51–1.01 (m, 10H), 0.82 (t, J = 6.9 Hz, 3H).

#### 2.2.2.7 Synthesis of 1-decylbenzimidazole (7)

Compound 7 was produced from NaBenz (50.00 g, 357 mmol) and 1-bromodecane (71.07 g, 66.48 mL, 321 mmol) in a manner similar to that employed for **1**. Yield = 56.64 g (68.2%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.21 (s, 1H), 7.61 (dd, *J* = 28.9, 7.9 Hz, 2H), 7.36–7.09 (m, 2H), 4.22 (t, *J* = 7.1 Hz, 2H), 1.87–1.66 (m, 2H), 1.42–1.03 (m, 14H), 0.84 (t, *J* = 6.9 Hz, 3H). <sup>1</sup>H NMR consistent with published data [50, 52].

#### 2.2.2.8 Synthesis of 1-dodecylbenzimidazole (8)

Compound **8** was produced from NaBenz (50.00 g, 357 mmol) and 1-bromododecane (77.86 g, 74.87 mL, 321 mmol) in a manner similar to that employed for **1**. Yield = 64.52 g (70.1%). <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.21 (s, 1H), 7.61 (dd, J = 33.0, 7.9 Hz, 2H), 7.36–7.07 (m, 2H), 4.22 (t, J = 7.1 Hz, 2H), 1.87–1.64 (m, 2H), 1.46–0.99 (m, 18H), 0.84 (t, J = 6.9 Hz, 3H). <sup>1</sup>H NMR consistent with published data [49].

#### 2.3 Density measurements

Density values for each 1-*n*-alkylbenzimidazole were obtained over the range of 20.00–80.00 °C at 10.00 °C increments using a Mettler Toledo DM45 DeltaRange density meter, using the same methodology as in our previous work [30]. The uncertainty associated with this measurement is  $\pm$ 0.00005 g cm<sup>-3</sup>.

#### 2.4 Viscosity measurements

Viscosity data were obtained for each 1-*n*-alkylbenzimidazole using a Brookfield DV-II+ Pro viscometer, under the same methodology as in our previous work, with the appropriate sized spindle (i.e. ULA) for relatively low viscosity liquids [28, 30]. Measurements were taken over the range of 20.00–80.00 °C, with 5.00 °C increments from 20.00– 50.00 °C and 10.00 °C increments from 50.00–80.00 °C. The temperature of the jacketed sample chamber was controlled via the Brook field TC-602P circulating bath. The viscometer accuracy is  $\pm 1\%$  of the reading for torque measurement with a repeatability of  $\pm 0.2\%$  of the reading.

#### 2.5 CO<sub>2</sub> Solubility measurements

Solubilities of  $CO_2$  in each 1-*n*-alkylbenzimidazole were measured gravimetrically using equipment and methodologies described in our previous works [28–30]. Experiments were conducted at temperatures of 30, 45, 60, and 75 °C (as controlled by an oil bath). An initial charge of gas was fed at 30 °C until the pressure equilibrated at ~5 atm. The respective errors associated with H and S were calculated based upon propagation of error of the experimental parameters (i.e. pressure, temperature, volumes, mass, etc.), in which all errors associated with our instrumentation are known. In this method, both the solubility and molecular weight of the gas are factors that influence the overall error. Measurements for CO<sub>2</sub> solubility exhibit typical experimental errors of less than ~4%, similar to our previous results for 1-n-alkylimidazoles. Based on published vapor pressure data and our previous measurements for 1-n-alkylimidazoles [28-32], the vapor pressure of the 1-n-alkylbenzimidazole compounds can be assumed as negligible under the experimental temperature and pressure conditions, as it is low (~5 mm Hg maximum and typically < 1 torr) and very small (~0.1%) compared to the partial pressure of the gas.

#### 2.6 SO<sub>2</sub> Solubility measurements

Solubility of SO<sub>2</sub> in 1-butylbenzimidazole was measured in a different manner than that of CO<sub>2</sub>. 1-Butylbenzimidazole (5.00 g, 28.7 mmol) was added to a 50 mL round bottom flask with a stir bar. The flask was secured with a clamp, suspended over a stir-plate, and stirring initiated. SO<sub>2</sub> gas at ~1 psig was bubbled via a 1/16" outside diameter stainless steel tube into the stirring mixture. The mass of the flask and its contents, as well as the color of the liquid were recorded at several time intervals over a period of 20 minutes. After this time,  $SO_2$  was desorbed from the liquid via a flush with N<sub>2</sub> for 40 minutes, and the mass of the flask contents and color of the liquid were observed to return to their original value/state. The error associated with the measurement of the mass of the flask and its contents is  $\pm 0.0005$  g, which is the uncertainty associated with the resolution of the balance used.

### 3 Results and discussion

#### 3.1 Densities of 1-n-alkylbenzimidazoles

The measured density values for 1-n-alkylbenzmidazoles over the temperature range of 20-80 °C are presented in Table 1. For each compound, density was observed to decrease linearly with increasing temperature. Also, across the entire group of 1-n-alkylbenzimidazoles, density decreased as the *n*-alkyl substituent length increased, which is similar to observations across families of  $[C_n mim][X]$  ILs as the length of the " $C_n$ " chain increases. Decreased density can be rationalized as the dilution of the polar imidazole ring (or ions in the case of ILs) within the bulk by increasing the volume fraction of the less dense hydrocarbon chains. A surface plot of density against temperature and the contribution of the alkyl chain for the 1-n-alkylbenzimidazoles is shown in Figure 1. As in our previous work, the "molecular weight parameter" (R'), a dimensionless value relating the molecular weight of the side chain to the molecular weight of the entire molecule, was used as means ofquantifying the impact of then-alkyl substituent. R' is calculated according to eq. (1) and values for each compound are presented in Table 1.

$$R' = \frac{M_{\rm w}(\text{alkylchain})}{M_{\rm w}(\text{molecule})} \tag{1}$$

Similar to the results obtained for our characterizations of 1-*n*-alkylimidazoles [30], a surface plot of density is approximately planar with respect to temperature and R' (Figure 3). However, a 7%–10% increase in density is observed when comparing 1-*n*-alkylbenzimidazoles to 1-*n*-alkylimidazoles over the same temperature range. 1-*n*-Alkylbenzimi

Compound	Density (g cm $^{-3}$ ) at given temperature								
Compound	$M_{\rm W} ({\rm g \ mol}^{-1})$	R'	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C
1, ethyl	146.19	0.199	1.09399	1.08626	1.07859	1.07093	1.06327	1.0556	1.04792
2, propyl	160.22	0.269	1.06565	1.05799	1.05039	1.04282	1.03525	1.02769	1.02009
3, butyl	174.24	0.328	1.04381	1.03630	1.02884	1.02141	1.01401	1.00660	0.99918
4, pentyl	188.27	0.378	1.02438	1.01694	1.00936	1.00221	0.99485	0.98750	0.98012
5, hexyl	202.30	0.421	1.00943	1.00210	0.99484	0.98760	0.98037	0.97315	0.96589
6, octyl	230.35	0.492	0.98502	0.97794	0.97092	0.96391	0.95693	0.94996	0.94300
7, decyl	258.40	0.547	0.96606	0.95911	0.95221	0.94534	0.93849	0.93163	0.92477
8, dodecyl	286.45	0.591	0.95587	0.94913	0.94243	0.93569	0.92885	0.92183	0.91483

Table 1 Densities of 1-n-alkylbenzimidazoles (1-8)

dazoles are less dense than many ILs, although this is likely due to the absence of elements other than C, H and N and/or fluorinated groups [27, 53-56].

The data presented in Table 1 and Figure 3 could be fit with a high degree of accuracy to the same form of equation we applied to our density measurements of 1-n-alkylimidazoles (eq. (2)). A surface regression of the data in Figure 3 performed with Matlab provides an excellent fit ( $R^2$  = 0.9968) to eq. (2), with constants  $A = -7.253 \times 10^{-4} \text{ g cm}^{-3}$  $K^{-1}$ , B = -0.3479 g cm<sup>-3</sup>, and C = 1.3710 g cm<sup>-3</sup>, where T is temperature in Kelvin and R' is the dimensionless molecular weight parameter for a given molecule (Table 1). Thus, this relatively simple model provides the ability to accurately describe density at a given temperature for 1-nalkylbenzimidazoles with side chains as large as dodecyl.

$$\rho(T, R') = AT + BR' + C \tag{2}$$

80

60<sub>°</sub>O

40

20

0.591 Les Les

0.547

#### Viscosities of 1-*n*-alkylbenzimidazoles 3.2

1.10

1.05

1.00

0.95

0.90

0.85

Density (g cm<sup>-3</sup>)

The measured viscosity values for 1-n-alkylbenzimidazoles over the temperature range of 20-80 °C are presented in Table 2. Viscosities of the eight 1-n-benzalkylimidazole compounds examined were <100 cP. For each compound, the viscosity was observed to decrease in a nonlinear fashion with increasing temperature. Viscosity was strongly correlated to the length of the *n*-alkyl substituent, with 1-dodecylbenzimidazole observed to be ~3.5× more viscous between than 1-ethylbenzimidazole at 20 °C, although the magnitude of this difference reduced to  $\sim 2 \times$  at 80 °C.

The temperature dependence of viscosity for each compound can be shown to follow the Litovitz Model (eq. (3)), which we have shown provides a very accurate model of the viscosities of 1-n-alkylimidazoles, and has also been successfully applied to imidazolium-based ILs [53]. Using the data in Table 3, we obtained A and B coefficients for compounds 1-8 via regression using Matlab, which are presented along with goodness of fit values  $(R^2)$  in Table 4.

$$\mu(T) = A \exp\left(\frac{B}{T^3}\right) \tag{3}$$

Figure 4 presents a surface plot of the viscosity data in Table 2 with respect to temperature and R'. As can be seen in Figure 4 a relatively smooth surface exists between R'values of 0.269-0.547, which corresponds to the range encompassed by 1-propylbenzimidazole and 1-decylbenzimidazole. Sharper changes in viscosity occur at the edges of the plot, corresponding to 1-ethylbenzimidazole and 1-dodecylbenzimidazole. Attempts to fit the entire surface to a 2-parameter (T, R') Litovitz Model, although successfully applied in our previous work with 1-n-alkylimidazoles, were unsuccessful for 1-n-alkylbenzimidazoles. Thus, a



Figure 3 Three-dimensional plot of 1-n-alkylbenzimidazole densities as related to temperature and R'.

Molecular weight parameter (R')

0.80 0.199 0.269 0.328 0.378 0.421 0.492

Figure 4 Three-dimensional plot of 1-n-alkylbenzimidazole viscosities as related to temperature and R'.

 Table 3
 Viscosities of 1-n-alkylbenzimidazoles (1-8)

	Viscosity (cP) at given temperature									
Compound	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	60 °C	70 °C	80 °C
1 ethyl	27.09	20.67	16.03	12.73	10.32	8.50	7.18	5.31	4.13	3.29
2, propyl	49.01	35.82	26.51	20.06	15.62	12.37	10.05	7.01	5.15	3.99
3, butyl	49.49	38.34	28.19	21.50	16.71	13.23	10.77	7.47	5.45	4.15
4, pentyl	52.79	40.91	30.35	23.25	18.00	14.36	11.60	8.05	5.91	4.54
5, hexyl	60.44	45.37	33.89	25.72	19.98	15.86	13.87	8.85	6.64	4.91
<b>6</b> , octyl	68.10	50.51	38.04	29.25	23.00	18.20	14.83	10.26	7.46	5.67
7, decyl	71.13	54.12	41.02	31.71	24.97	19.95	16.24	11.22	8.17	6.20
8, dodecyl	96.34	70.19	52.55	40.07	31.06	24.54	19.75	13.36	9.54	7.14

Table 4Empirical constants and quality of fit for eq. (3) as applied toviscosities of 1-*n*-alkylbenzimidazoles (1-8)

Compound	A (cP)	$B \times 10^{-8}  (\mathrm{K}^3)$	$R^2$
1, ethyl	0.188	1.24	0.9977
2, propyl	0.129	1.48	0.9979
3, butyl	0.139	1.48	0.9989
4, pentyl	0.155	1.47	0.9989
5, hexyl	0.168	1.48	0.9988
6, octyl	0.195	1.47	0.9994
7, decyl	0.227	1.45	0.9997
8, dodecyl	0.212	1.54	0.9996

single equation for viscosity cannot be applied across the entire series.

However, in examination of Table 4, it appears that for the range of compounds that fall between 1-propylbenzimidazole (2) and 1-decylbenzimidazole (7), a single model can be developed, as the constant 'A' is correlated R' and B is virtually independent of R', as its value is  $1.47 \times 10^8$  K<sup>3</sup> for each of the compounds. We have found that the relationship between A and R' is well-described ( $R^2 = 0.9896$ ) by eq. (4), with coefficients of 0.722 cP and 2.0445 (dimensionless).

$$A = 0.0722 \cdot \exp(2.0445 \cdot R') \tag{4}$$

The substitution of eq. (4) into eq. (3) yields eq. (5), which can be used to describe the viscosity (cP) of 1-*n*-alkylbenzimidazoles ranging from 1-propylbenzimidazole to 1decyl-benzimidazole, with an  $R^2 = 0.9934$ .

$$\mu(T,R) = 0.0722 \cdot \exp\left(2.0445 \cdot R' + \frac{1.47 \times 10^8}{T^3}\right)$$
(5)

Eq. (5) thus presents a useful and accurate model for estimating the viscosity of a range of 1-*n*-alkylbenzimidazoles as a function of temperature and the contribution of the alkyl chain. This model is somewhat more simplistic than that found for describing the viscosity of 1-*n*-alkylimidazoles, although the 1-*n*-alkylimidazoles were much less viscous. This may be due to the fact that viscosities of the 1-*n*-alkylbenzimidazoles span a relatively smaller range of magnitudes than 1-*n*-alkylimidazoles, where the large fused ring system in the former plays a much more influential role in governing molecular motion, while the viscosities of the latter are much more sensitive to the influence of alkyl chain length. This effect of increasing viscosity with increasing chain length is also observed for homologous series of ILs that vary only in the length of the alkyl chain [27, 53, 57–60].

Figure 5 presents a graphical illustration of the relative viscosity ranges exhibited by ILs, 1-*n*-alkylimidazoles and 1-*n*-alkylbenzimidazoles. As is apparent, 1-*n*-alkylbenzimidazoles possess viscosities that mostly exceed those exhibited by 1-*n*-alkylimidazoles, yet fall near the lower range of those exhibited by 1-*n*-alkyl-3-methylimidazolium ILs. As a point of reference, 1-*n*-alkylbenzimidazoles tend to overlap the region occupied by 1-ethyl-3-methylimidazolium salts (e.g.  $[C_2mim][Tf_2N]$ ,  $[C_2mim][dca]$ , etc.). The underlying data points used to form this graph can be viewed in the Supporting Information from our prior work [30].

#### 3.3 Solubility of CO<sub>2</sub>

Henry's constants (H) and volumetric solubilities (S) of CO<sub>2</sub>



**Figure 5** Graphical comparison of reported viscosity ranges of 1-*n*-alkylimidazoles (lower, blue); 1-*n*-alkylbenzimidazoles (this work)(middle, grey); and 1-*n*-alkyl-3-methylimidazolium ILs (upper, red). Modified with permission from Shannon MS, Bara JE. Properties of alkylimidazoles as solvents for  $CO_2$  capture and comparisons to imidazolium-based ionic liquids. *Ind Eng Chem Res*, 2011, 50(14): 8665–8677. Copyright 2011 American Chemical Society.

in 1-*n*-alkylbenzimidazoles at temperatures between 30-75 °C are presented in Table 3.

The data presented are largely indicative of physical solubility behavior, rather than any type of chemical reaction between  $CO_2$  and the benzimidazole molecules. This behavior is consistent with what has been observed for alkylimidazoles and most ILs, indicating that each of these classes of compounds would be most useful under high pressures or high concentrations of  $CO_2$ , rather than in low pressure applications (i.e. post-combustion  $CO_2$  capture).

At any given temperature, 1-ethylbenzimidazole showed the highest CO<sub>2</sub> solubility per volume, as extension of the alkyl chain serves to diminish CO<sub>2</sub> solubility, as has been observed for alkylimidazoles and imidazolium-based ILs [2, 29, 30, 61]. The values reported are lower than those reported for alkylimidazoles and imidazolium-based ILs [2, 29, 30], indicating that the six-membered aromatic ring present within benzimidazoles has a negative effect on CO<sub>2</sub> affinity. A similar effect has been observed for benzyl-functionalized imidazolium-based ILs [2, 62], although interactions between CO<sub>2</sub> and the electrons were expected to increase CO<sub>2</sub> solubility. One possible explanation is that the benzimidazole solvent (and by extension, ILs with benzyl groups) possess less free volume in which CO<sub>2</sub> can dissolve. This is supported by the fact that improved separation of CO<sub>2</sub>/N<sub>2</sub> has been observed in ionic liquid-based membranes where these groups are present [1, 62, 63]. We have not measured comparative data for CO<sub>2</sub> solubility in 1-benzylimidazole due to the fact it is a crystalline solid with a melting point of  $\sim 70 \,^{\circ}$ C [43, 47, 64].

Also shown in Table 3, for the convenience of the reader, are Henry's constants, which describe the solubility of  $CO_2$ in terms of mole fraction at a given temperature. However, as with the same discussion in our previous work, this observation and assessment of using Henry's constants (i.e. mole basis) for gas solubility comparisons among varying substituent chain lengths is not appropriate. It can be seen that although the Henry's constants (i.e. mole fraction of  $CO_2$ ) are similar for each molecule at a given temperature, this is primarily due to an increase in solvent molecular weight (i.e. fewer moles of solvent) rather than increased affinity of  $CO_2$  for the solvent.

#### 3.5 Solubility of SO<sub>2</sub>

Experimental results for SO<sub>2</sub> absorption in 1-butylbenzimidazole are presented below in Table 6, with Figure 6 also provided as visual evidence to support our observations of the color change associated with SO<sub>2</sub> absorption. A larger version of Figure 6 is provided as Supporting Information. The choice of 1-butylbenzimidazole was based on its relatively low viscosity amongst this group of compounds and the expectation that its vapor pressure is lower than that of 1-ethylbenzimidazole. It is likely that any of the 1-*n*alkylbenzimidazole compounds would produce similar results. It should be noted that the small difference in mass recorded between the initial and final readings is slightly less than zero. This is almost certainly due to the loss of small quantities of 1-butylbenzimidazole on the stainless steel tubing that was submerged into the liquid to introduce

**Table 5**Solubility of  $CO_2$  in several 1-n-alkylbenzimidazoles at partial pressures of ~5 atm and temperatures between 30 and 75 °C expressed as bothHenry's constants (H(atm)) and volumetric solubilities (S)

Compound	Temperature (°C)	H (atm)	+/-	$S^{a)}$	+/
1, ethyl	30	96	2	1.80	0.05
	45	126	4	1.36	0.04
	60	160	5	1.03	0.03
	75	202	7	0.82	0.03
<b>3</b> , butyl	30	88	2	1.60	0.04
-	45	123	4	1.14	0.04
	60	160	6	0.83	0.03
	75	200	8	0.70	0.03
5, hexyl	30	89	3	1.30	0.05
-	45	133	6	0.86	0.04
	60	203	12	0.55	0.03
	75	298	22	0.38	0.03

a)  $S = (cm^3 gas (STP)) (cm^3 solvent)^{-1} atm^{-1}$ ; uncertainty represents +/- one standard deviation.

Table 6 Experimental data for absorption of SO<sub>2</sub> in 5.00 g (28.7 mmol) 1-butylbenzimidazole at 25 °C (3)

Time (min)	Flask mass (g)	m (g SO <sub>2</sub> absorbed)	mol SO <sub>2</sub> absorbed	mol SO <sub>2</sub> (mol 1-butylbenzimidazole) <sup><math>-1</math></sup>	Observation
0 (start SO <sub>2</sub> )	98.865	0.000	0.00000	0.00000	pale yellow
5	99.208	0.343	0.00536	0.18676	bright yellow
10	99.851	0.986	0.01541	0.53688	yellow-orange
20 (stop SO <sub>2</sub> , start N <sub>2</sub> flush)	100.641	1.776	0.02775	0.96703	dark orange, more viscous
60 (stop N2 flush)	98.847	-0.018	-0.00028	-0.009801	pale yellow



Figure 6 Progressive darkening from essentially colorless to pale yellow to orange in 1-butylbenzimidazole (3) upon exposure to  $SO_2$  and subsequent return to an essentially colorless liquid upon flushing with  $N_2$  (bottom right).

#### SO<sub>2</sub>.

The data in Table 6 indicate that SO<sub>2</sub> can be readily and rapidly absorbed at room temperature and low pressure (~1 psig) to at least a 1:1 (mol:mol) ratio with 1-butylbenzimidazole. Furthermore, SO<sub>2</sub> can be easily desorbed at room temperature using only an N2 flush. While we previously observed that 1-hexylimidazole was also capable of absorbing at least 1 mole of SO<sub>2</sub> per mole 1-hexylimidazole under similar conditions, a portion of that SO<sub>2</sub> was not readily desorbed from 1-hexylimidazole. SO<sub>2</sub> and 1-hexylimidazole formed a relatively stable 1:2 adduct, and higher temperatures (> 80 °C) and vacuum were required to remove SO<sub>2</sub>. However, while SO<sub>2</sub> has been shown to undergo reversible chemical reaction with alkylimidazoles, alkylbenzimidazoles do not undergo a similar chemical reaction as the reactive nitrogen is likely de-activated by the fused ring system. This behavior is similar to that observed for many imidazolium-based ILs where there is no nucleophilic or basic site to react with  $SO_2[65]$  with exceptions observed when the anion is chemically reactive [66, 67]. Although the interactions between SO<sub>2</sub> and the 1-butylbenzimidazole molecule are weak, the fact that a significant color change is observed at relatively low concentrations could make these molecules useful as visual indicators of the presence of SO<sub>2</sub>.

#### 4 Conclusions

A series of eight 1-*n*-alkylbenzimidazoles was synthesized and their densities and viscosities characterized as functions of temperature and alkyl chain length. Each property was found to be strongly dependent on both variables. A highly-correlated model for density was developed that encompassed all of the compounds of interest, while a similarly accurate viscosity model could be applied from 1-propylbenzimidazole through 1-decylbenzimidazole. Density and viscosity profiles for 1-*n*-alkylbenzimidazoles were noted to possess similar characteristics to 1-*n*-alkylimidazoles and imidazolium-based ILs.  $CO_2$  solubility, however, is somewhat negatively impacted by the presence of the benzimidazole moiety, as measured values were less than those obtained for 1-*n*-alkylimidazoles and many imidazolium-based ILs. Further research is needed as to why the presence of benzene rings in both neutral and charged (i.e. ILs) molecules hinders  $CO_2$  dissolution. Finally, 1-butylbenzimi dazole was demonstrated to exhibit physical, rather than chemical interactions with  $SO_2$ , a property more in line with imidazolium-based ILs than alkylimidazoles.

1-*n*-Alkylbenzimidazoles can be viewed to have hybrid properties of ILs and alkylimidazoles. It is our hope that this initial study on the properties of benzimidazoles in the liquid state will bring greater attention to this versatile class of molecules in identifying applications and gain a more thorough understanding of imidazolium/benzimidazolium ILs.

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- Bara JE, Camper DE, Gin DL, Noble RD. Room-temperature ionic liquids and composite materials: Platform technologies for CO<sub>2</sub> capture. Acc Chem Res, 2010, 43: 152–159
- 2 Bara JE, Carlisle TK, Gabriel CJ, Camper D, Finotello A, Gin DL, Noble RD. Guide to CO<sub>2</sub> separations in imidazolium-based roomtemperature ionic liquids. *Ind Eng Chem Res*, 2009, 48: 2739–2751
- 3 Armand M, Endres F, Macfarlane DR, Ohno H, Scrosati B. Ionic-liquid materials for the electrochemical challenges of the future. *Nat Mater*, 2009, 8: 621–629
- 4 Kato T. From nanostructured liquid crystals to polymer-based electrolytes. *Angew Chem Int Ed*, 2010, 49: 7847–7848
- 5 Ichikawa T, Yoshio M, Hamasaki A, Kagimoto J, Ohno H, Kato T. 3D Interconnected ionic nano-channels formed in polymer films: Self-organization and polymerization of thermotropic bicontinuous cubic liquid crystals. J Am Chem Soc, 2011, 133: 2163–2169
- 6 Gutowski KE, Holbrey JD, Rogers RD, Dixon DA. Prediction of the formation and stabilities of energetic salts and ionic liquids based on ab initio electronic structure calculations. *J Phys Chem B*, 2005, 109: 23196–23208
- 7 Drab DM, Smiglak M, Shamshina JL, Kelley SP, Schneider S, Hawkins TW, Rogers RD. Synthesis of N-cyanoalkyl-functionalized imidazolium nitrate and dicyanamide ionic liquids with a comparison of their thermal properties for energetic applications. *New J Chem*, 2011, 35: 1701–1717
- 8 Pogodina NV, Metwalli E, Muller-Buschbaum P, Wendler K, Lungwitz R, Spange S, Shamshina JL, Rogers RD, Friedrich Ch. Peculiar behavior of azolium azolate energetic ionic liquids. J Phys Chem Lett, 2011, 2: 2571–2576
- 9 Wang H, Gurau G, Rogers RD. Ionic liquid processing of cellulose. Chem Soc Rev, 2012, 41: 1519–1537
- 10 Anderson EB, Long TE. Imidazole- and imidazolium-containing polymers for biology and material science applications. *Polymer*, 2010, 51: 2447–2454
- Ohno H, Yoshizawa M, Ogihara W. Development of new class of ion conductive polymers based on ionic liquids. *Electrochim Acta*, 2004, 50: 255–261
- 12 Gu YY, Lodge TP. Synthesis and gas separation performance of

triblock copolymer ion gels with a polymerized ionic liquid mid-block. *Macromolecules*, 2011, 44: 1732–1736

- 13 Lodge TP. Materials science—A unique platform for materials design. *Science*, 2008, 321: 50–51
- 14 Bara JE, Gin DL, Noble RD. Effect of anion on gas separation performance of polymer-room-temperature ionic liquid composite membranes. *Ind Eng Chem Res*, 2008, 47: 9919–9924
- 15 Bara JE, Hatakeyama ES, Gin DL, Noble RD. Improving CO<sub>2</sub> permeability in polymerized room-temperature ionic liquid gas separation membranes through the formation of a solid composite with a room-temperature ionic liquid. *Polym Advan Technol*, 2008, 19: 1415–1420
- 16 Mecerreyes D. Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes. *Prog Polym Sci*, 2011, 36: 1629–1648
- 17 Katritzky AR, Jain R, Lomaka A, Petrukhin R, Karelson M, Visser AE, Rogers RD. Correlation of the melting points of potential ionic liquids (imidazolium bromides and benzimidazolium bromides) using the CODESSA program. J Chem Inf Comp Sci, 2002, 42: 225–231
- 18 Lin IJB, Vasam CS. Preparation and application of N-heterocyclic carbene complexes of Ag(I). *Coord Chem Rev*, 2007, 251: 642–670
- 19 Amyes TL, Diver ST, Richard JP, River FM, Toth K. Formation and stability of N-heterocyclic carbenes in water: The carbon acid pka of imidazolium cations in aqueous solution. J Am Chem Soc, 2004, 126: 4366–4374
- 20 Chan A, Scheidt KA. Conversion of α,β-unsaturated aldehydes into saturated esters: An umpolung reaction catalyzed by nucleophilic carbenes. Org Lett, 2005, 7: 905–908
- 21 Binnemans K. Ionic liquid crystals. Chem Rev, 2005, 105: 4148-4204
- 22 Pernak J, Rogoża J, Mirska I. Synthesis and antimicrobial activities of new pyridinium and benzimidazolium chlorides. *Eur J Med Chem*, 2001, 36: 313–320
- 23 Boydston AJ, Vu PD, Dykhno OL, Chang V, Wyatt AR, Stockett AS, Ritschdorff ET, Shear JB, Bielawski CW. Modular fluorescent benzobis(imidazolium) salts: Syntheses, photophysical analyses, and applications. J Am Chem Soc, 2008, 130: 3143–3156
- 24 Boydston AJ, Pecinovsky CS, Chao ST, Bielawski CW. Phase-tunable fluorophores based upon benzobis(imidazolium) salts. J Am Chem Soc, 2007, 129: 14550–14551
- 25 Thomas OD, Soo KJWY, Peckham TJ, Kulkami MP, Holdcroft S. Anion conducting poly(dialkyl benzimidazolium) salts. *Polym Chem*, 2011, 2: 1641–1643
- 26 Preston PN. Synthesis, reactions, and spectroscopic properties of benzimidazoles. *Chem Rev*, 1974, 74: 279–314
- 27 Seddon KR, Stark A, Torres MJ. Viscosity and density of 1-alkyl-3-methylimidazolium ionic liquids; in Abraham MA, Moens L. Clean Solvents - Alternative Media For Chemical Reactions And Processing. ACS Symposisum Series, 2002: 34–49
- 28 Shannon MS, Bara JE. Reactive and reversible ionic liquids for CO<sub>2</sub> capture and acid gas removal. *Sep Sci Technol*, 2012, 47: 178–188
- 29 Shannon MS, Tedstone JM, Danielsen SPO, Bara JE. Evaluation of alkylimidazoles as physical solvents for CO<sub>2</sub>/CH<sub>4</sub> separation. *Ind Eng Chem Res*, 2011, 51: 515–522
- 30 Shannon MS, Bara JE. Properties of alkylimidazoles as solvents for CO<sub>2</sub> capture and comparisons to imidazolium-based ionic liquids. *Ind Eng Chem Res*, 2011, 50: 8665–8677
- 31 Emel'yanenko VN, Portnova SV, Verevkin SP, Skrzypczak A, Schubert T. Building blocks for ionic liquids: Vapor pressures and vaporization enthalpies of 1-(n-alkyl)-imidazoles. J Chem Thermodyn, 2011, 43: 1500–1505
- 32 Verevkin SP, Zaitsau DH, Emel'yanenko VN, Paulechka YU, Blokhin AV, Bazyleva AB, Kabo GJ. Thermodynamics of ionic liquids precursors: 1-methylimidazole. *J Phys Chem B*, 2011, 115: 4404–4411
- 33 Emel'yanenko VN, Zaitsau DH, Verevkin SP, Heintz A, Voss K, Schulz A. Vaporization and formation enthalpies of 1-alkyl-3-methylimidazolium tricyanomethanides. *J Phys Chem B*, 2011, 115: 11712–11717

- 34 Lenarcik B, Ojczenasz P. The influence of the size and position of the alkyl groups in alkylimidazole molecules on their acid-base properties. *J Heterocyclic Chem*, 2002, 39: 287–90
- 35 de Luca L. Naturally occurring and synthetic imidazoles: Their chemistry and their biological activities. *Curr Med Chem*, 2006, 13: 1–23
- 36 Rogers RD, Seddon KR. Ionic liquids—solvents of the future? Science, 2003, 302: 792–793
- 37 Bonazzi D, Cavrini V, Gatti R, Boselli E, Caboni M. Determination of imidazole antimycotics in creams by supercritical fluid extraction and derivative UV spectroscop. *J Pharm Biomed Anal*, 1998, 18: 235–240
- 38 Boiani M, Gonzalez M. Imidazole and benzimidazole derivatives as chemotherapeutic agents. *Mini-Rev Med Chem*, 2005, 5: 409–424
- 39 Green MD, Allen MH, Dennis JM, la Cruz DS, Gato R, Winey KI, Long TE. Tailoring macromolecular architecture with imidazole functionality: A perspective for controlled polymerization processes. *Eur Polym J*, 2011, 47: 486–496
- 40 Sturlaugson AL, Fruchey KS, Fayer MD. Orientational dynamics of room temperature ionic liquid/water mixtures: Water-induced structure. J Phys Chem B, 2012, in press. DOI: 10.1021/jp209942r
- 41 Plechkova NV, Seddon KR. Applications of ionic liquids in the chemical industry. *Chem Soc Rev*, 2008, 37: 123–150
- 42 Seddon KR. Ionic liquids: A taste of the future. *Nat Mater*, 2003, 2: 363–365
- 43 Bara JE. Versatile and scalable method for producing nfunctionalized imidazoles. *Ind En Chem Res*, 2011, 50: 13614–13619
- 44 Gottlieb HE, Kotlyar V, Nudelman A. NMR chemical shifts of common laboratory solvents as trace impurities. *J Org Chem*, 1997, 62: 7512–7515
- 45 Hanan EJ, Chan BK, Estrada AA, Shore DG, Lyssikatos JP. Mild and general one-pot reduction and cyclization of aromatic and heteroaromatic 2-nitroamines to bicyclic 2h-imidazoles. *Syn Lett*, 2010, 2759–2764
- 46 Lygin AV, de Meijere A. Synthesis of 1-substituted benzimidazoles from o-bromophenyl isocyanide and amines. *Eur J Org Chem*, 2009, 30: 5138–5141
- 47 Milen M, Grun A, Balint E, Dancso A, Keglevich G. Solid-liquid phase alkylation of N-heterocycles: Microwave-assisted synthesis as an environmentally friendly alternative. *Synthetic Commun*, 2010, 40: 2291–2301
- 48 Kuang DB, Klein C, Ito S, Moser JE, Humphry-Baker R, Evans N, Duriaux F, Cratzel C, Zakeeruddin SM, Gratzel M. High-efficiency and stable mesoscopic dye-sensitized solar cells based on a high molar extinction coefficient ruthenium sensitizer and nonvolatile electrolyte. Adv Mater, 2007, 19(8): 1133–1137
- 49 Kose O, Saito S. Cross-coupling reaction of alcohols for carbon-carbon bond formation using pincer-type NHC/palladium catalysts. Org Biomol Chem, 2010, 8: 896–900
- 50 Bogdal D, Pielichowski J, Jaskot K. Remarkable fast N-alkylation of azaheterocycles under microwave irradiation in dry media. *Heterocycles*, 1997, 45: 715–722
- 51 Wannalerse B, Tuntulani T, Tomapatanaget B. Synthesis, optical and electrochemical properties of new receptors and sensors containing anthraquinone and benzimidazole units. *Tetrahedron*, 2008, 64: 10619–10624
- 52 du Preez JGH, Mattheus C, Sumter N, Ravindran S, Potogieter C, van Brecht BJ. Nitrogen reagents in metal ion separation. Part VIII. Substituted imidazoles as extractants for Cu<sup>2+</sup>. Solvent Extr Ion Exc, 1998, 16: 565–586
- 53 Ghatee MH, Zare M, Moosavi F, Zolghadr AR. Temperature-dependent density and viscosity of the ionic liquids 1-alkyl-3-methylimidazolium Iodides: Experiment and molecular dynamics simulation. J Chem Eng Dat, 2010, 55: 3084–3088
- 54 Smith GD, Borodin O, Magda JJ, Boyd RH, Wang Y, Bara JE, Miller S, Gin DL, Noble RD. A comparison of fluoroalkyl-derivatized imidazolium:TFSI and alkyl-derivatized imidazolium:TFSI ionic liquids: A molecular dynamics simulation study. *Phys Chem Chem Phys*, 2010, 12: 7064–7076

- 55 Gardas RL, Coutinho JAP. Extension of the Ye and Shreeve group contribution method for density estimation of ionic liquids in a wide range of temperatures and pressures. *Fluid Phase Equilibr*, 2008, 263: 26–32
- 56 Ye CF, Shreeve JM. Rapid and accurate estimation of densities of room-temperature ionic liquids and salts. J Phys Chem A, 2007, 111: 1456–1461
- 57 Gardas RL, Coutinho JAP. A group contribution method for viscosity estimation of ionic liquids. *Fluid Phase Equilibr*, 2008, 266: 195–201
- 58 Smith GD, Borodin O, Li LY, Kim H, Liu Q, Bara JE, Gin DL, Noble R. A comparison of ether- and alkyl-derivatized imidazolium-based room-temperature ionic liquids: A molecular dynamics simulation study. *Phys Chem Chem Phys*, 2008, 10: 6301–6312
- 59 Aparicio S, Atilhan M, Karadas F. Thermophysical properties of pure ionic liquids: Review of present situation. *Ind Eng Chem Res*, 2010, 49: 9580–9595
- 60 Rooney D, Jacquemin J, Gardas R. Thermophysical Properties of Ionic Liquids in KIRCHNER B. Ionic Liquids. Berlin/Heidelberg: Springer, 2010: 185–212
- 61 Carlisle TK, Bara JE, Gabriel CJ, Noble RD, Gin DL. Interpretation of CO<sub>2</sub> solubility and selectivity in nitrile-functionalized

room-temperature ionic liquids using a group contribution approach. *Ind Eng Chem Res*, 2008, 47: 7005–7012

- 62 Mahurin SM, Dai T, Yeary JS, Luo H, Dai S. Benzyl-functionalized room temperature ionic liquids for CO<sub>2</sub>/N<sub>2</sub> separation. *Ind Eng Chem Res*, 2011, 50: 14061–14069
- 63 Bara JE, Lessmann S, Gabriel CJ, Hatakeyama ES, Noble RD, Gin DL. Synthesis and performance of polymerizable room-temperature ionic liquids as gas separation membranes. *Ind Eng Chem Res*, 2007, 46: 5397–5404
- 64 Begg CG, Grimmett MR, Wethey PD. The thermally induced rearrangement of 1-substituted imidazoles. *Aust J Chem*, 1973, 26: 2435–2446
- 65 Anderson JL, Dixon JK, Maginn EJ, Brennecke JF. Measurement of SO<sub>2</sub> solubility in ionic liquids. J Phys Chem B, 2006, 110: 15059–15062
- 66 Wang C, Cui G, Luo X, Xu YJ, Li HR, Dai S. Highly efficient and reversible SO<sub>2</sub> capture by tunable azole-based ionic liquids through multiple-site chemical absorption. *J Am Chem Soc*, 2011, 133: 11916–11919
- 67 Shiflett MB, Yokozeki A. Chemical absorption of sulfur dioxide in room-temperature ionic liquids. *Ind Eng Chem Res*, 2010, 49: 1370–1377