

# Reversible physical absorption of SO<sub>2</sub> by ionic liquids†

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Ionic liquids can reversibly absorb large amounts of molecular SO<sub>2</sub> gas under ambient conditions with the gas captured in a restricted configuration, possibly allowing SO<sub>2</sub> to probe the internal cavity structures in ionic liquids besides being useful for SO<sub>2</sub> removal in pollution control.

Room-temperature ionic liquids (ILs) are low-melting salts with extremely low vapour pressures, high thermal and chemical stability, and tuneable solvent power for many organic and inorganic compounds. Due to these characteristics they can be used as environmentally benign solvents for a number of chemical applications, such as separations and catalytic reactions.<sup>1</sup>

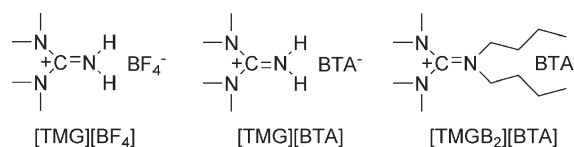
Imidazolium-based ILs, which constitute a representative class of ILs, have been found to display dynamic, locally heterogeneous environments,<sup>2</sup> which allow their use as media for preparation of noble metal nanoparticles useful for different catalytic applications and for synthesis of other nanostructured materials.<sup>3</sup> Moreover, absorption studies of CO<sub>2</sub> gas in 1-*n*-propylamine-3-butylimidazolium tetrafluoroborate by Bates *et al.*<sup>4</sup> indicated that the IL can absorb CO<sub>2</sub> from gas mixtures effectively at ambient pressure. Previous studies have mainly reported that ILs can dissolve many gases, such as CO<sub>2</sub>, ethylene and ethane, especially at high pressure.<sup>5</sup>

SO<sub>2</sub> emission is a significant source of atmospheric pollution when fossil fuels are combusted, causing both environmental and human health concerns due to formation of, *e.g.* acid rain and smog. In contrast, SO<sub>2</sub> is also an important and useful source for many intermediates in chemical production. At present, flue-gas desulfurization (FGD) is one of the most effective techniques to control emission of SO<sub>2</sub> from combustion of fossil fuels, such as coal and petrol. A variety of processes for SO<sub>2</sub> control (*e.g.* wet FGD, dry FGD, and semidry FGD processes) have been adopted widely in commercial units.<sup>6</sup> Usually, however, the most attractive approaches for SO<sub>2</sub> gas separation are pressure swing absorption (PSA) or temperature swing absorption (TSA) technologies, which are energy saving compared to FGD processes and avoid by-products while allowing the SO<sub>2</sub> to be used as a direct source for sulfuric acid production.<sup>7</sup> For practical use it is nevertheless difficult to find a material for reversible and selective absorption of SO<sub>2</sub>. Generally aqueous liquid amines can be applied for

chemically confining acidic gases, like CO<sub>2</sub> and SO<sub>2</sub>, by formation of ammonium carbonate or sulfite. But in the case of large-scale SO<sub>2</sub> capture, amines can evaporate into the gas stream due to their volatility, and the SO<sub>2</sub> proves difficult to desorb from ammonium sulfite. Similarly, water has been found to be a good solvent for SO<sub>2</sub> gas, but when SO<sub>2</sub> gas dissolves in water most of the SO<sub>2</sub> gas reacts with water and converts it into sulfurous acid, which only liberates SO<sub>2</sub> gas on heating.<sup>8</sup> Recently, Han *et al.*<sup>9</sup> described a suitable methodology using an IL (TMGL: 1,1,3,3-tetramethylguanidinium lactate) which could absorb 1 mole of SO<sub>2</sub> at 1 bar by formation of the guanidinium sulfurous acid cation. However, a relatively low thermal stability of the IL limited its general practical use, as only part of the absorbed gas could be released upon heating before IL degradation occurred.

In this Communication, we report that several ILs—most likely as a general feature—are found to be excellent solvents for SO<sub>2</sub> gas, providing physical absorption of the gas. ILs based on both 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]) and the analogous bis(trifluoromethanesulfonyl)amide ([BMIM][BTA]) and new ILs based on TMG prepared here, [TMG][BF<sub>4</sub>], [TMG][BTA] and [TMGB<sub>2</sub>][BTA] (see Scheme 1), were found to readily absorb 1–2 mole SO<sub>2</sub> per mole of IL reversibly at ambient pressure and room temperature without any chemical transformation.

The [TMG][BF<sub>4</sub>] and [TMG][BTA] ILs were prepared by neutralization of TMG with fluoroboric acid (HBF<sub>4</sub>) and HBTA in ethanolic solution (see Supporting Information).<sup>3a</sup> The IL [TMGB<sub>2</sub>][BTA] was synthesized by alkylation of TMG with *n*-iodobutane (C<sub>4</sub>H<sub>9</sub>I)<sup>10</sup> followed by anion exchange (see Supporting Information). [BMIM][BF<sub>4</sub>]<sup>11</sup> and [BMIM][BTA]<sup>12</sup> were prepared by literature procedures. For the SO<sub>2</sub> gas absorption experiments the gas stream was bubbled through about 3.0 g of IL loaded into a glass tube with inner diameter of 10 mm with a flow rate adjusted to 50 ml min<sup>-1</sup>. When the IL was saturated with SO<sub>2</sub> gas the weight became constant. For SO<sub>2</sub> desorption the glass tube was partly immersed in an oil bath with a temperature controller. During desorption the weight of the IL solution was determined periodically at different set-temperatures. When no SO<sub>2</sub> gas was released at the set-temperature, the solution was weighed.



**Scheme 1** The novel ILs based on TMG (1,1,3,3-tetramethylguanidine) which were prepared and examined in this study: [TMG][BF<sub>4</sub>], [TMG][BTA] and [TMGB<sub>2</sub>][BTA].

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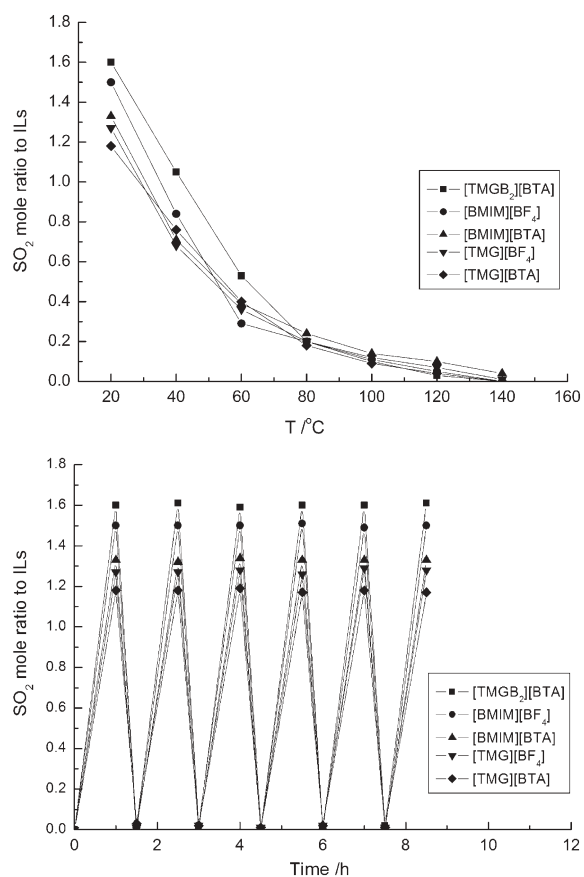
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The ILs examined were found to absorb a large amount of SO<sub>2</sub> gas corresponding to molar ratios of SO<sub>2</sub> to ILs of 1.33, 1.50, 1.27, 1.18, 1.60, (wt %: 20.4%, 40.0%, 40.1%, 19.2% and 20.1%) for [BMIM][BTA], [BMIM][BF<sub>4</sub>], [TMG][BF<sub>4</sub>], [TMG][BTA] and [TMGB<sub>2</sub>][BTA], respectively, after being saturated with SO<sub>2</sub> gas at 1 bar and 20 °C. Desorption of the absorbed SO<sub>2</sub> was carried out by heating the saturated ILs, while the weight loss was monitored periodically. In Fig. 1 (top) the SO<sub>2</sub> content in the ILs (as molar ratio of SO<sub>2</sub> to IL) is shown as a function of the desorption temperature. For all the ILs examined the SO<sub>2</sub> gas can be completely desorbed when heated to about 140 °C.

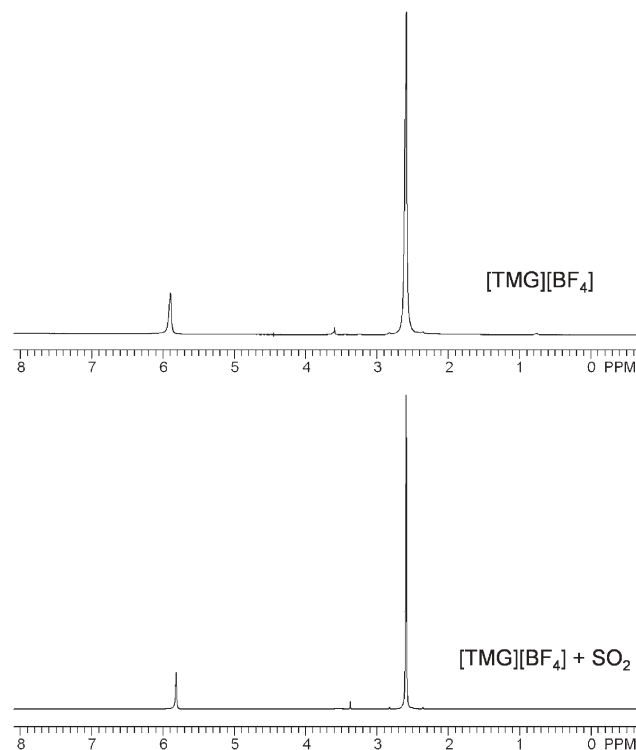
Both absorption and desorption of SO<sub>2</sub> gas in the five examined ILs (*i.e.* [BMIM][BTA], [BMIM][BF<sub>4</sub>], [TMG][BF<sub>4</sub>], [TMG][BTA], [TMGB<sub>2</sub>][BTA]) were relatively fast, providing complete absorption in one hour with pure SO<sub>2</sub> gas (50 ml min<sup>-1</sup>, 200 rpm stirring), and complete gas desorption in half an hour at room temperature and 20 Pa vacuum. However, the absorption and desorption times are very dependent on the exposed surface area of the IL, thus making room for considerable improvement. Moreover, the ILs can be reused many times without any loss of absorption capability. In Fig. 1 (bottom) six consecutive absorption cycles with the ILs are shown.

There is no difference in the proton chemical shift or  $\Delta\delta_{\text{H}}$  of the [TMG]<sup>+</sup> cation in the <sup>1</sup>H NMR spectra of the ILs [TMG][BF<sub>4</sub>], [TMG][BTA] and [TMGB<sub>2</sub>][BTA] and the ILs saturated with SO<sub>2</sub>

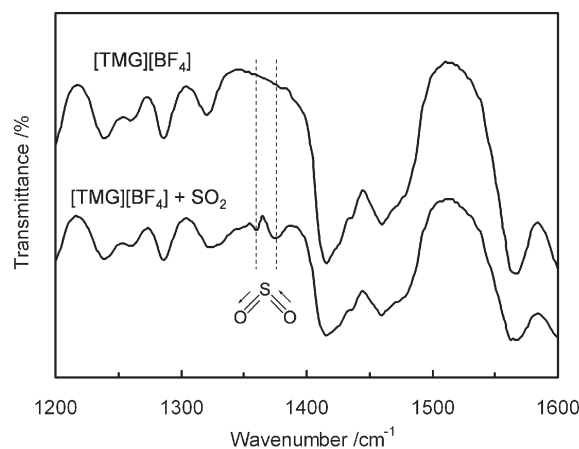


**Fig. 1** SO<sub>2</sub> desorption by heating shown as mole ratio of SO<sub>2</sub> to IL versus temperature (top). Consecutive absorption and desorption (20 °C, 20 Pa vacuum) of SO<sub>2</sub> gas in recycled ILs against time (bottom). Standard deviations of the ratios are  $\pm 0.03$ .

gas, which means there is no new chemical (covalent) bond involving hydrogens formed between the IL cations and SO<sub>2</sub> during absorption (Fig. 2, exemplified with comparison of the spectra of [TMG][BF<sub>4</sub>]). Similarly, in FT-IR spectra recorded of the ILs and the SO<sub>2</sub> saturated ILs, only additional bands assignable to molecular SO<sub>2</sub> ( $\nu_{\text{max}} = 1376$  and  $1360$  cm<sup>-1</sup>, O–S–O asym. str.)<sup>13</sup> were observed (Fig. 3, comparison of the spectra of [TMG][BF<sub>4</sub>], as example). From these results, it is evident that the SO<sub>2</sub> gas must be purely physically absorbed in the ILs (governed only by weak interactions, such as hydrogen bonds, van der Waals forces,  $\pi$ - $\pi$  interactions and Coulombic interactions), providing no



**Fig. 2** <sup>1</sup>H-NMR spectra (300 Hz) of ILs [TMG][BF<sub>4</sub>] (top) and [TMG][BF<sub>4</sub>] with SO<sub>2</sub> gas (bottom) (solvent-free, d<sup>6</sup>-DMSO capillary as internal standard).



**Fig. 3** FT-IR spectra (KBr tablet) in the range 1200–1600 cm<sup>-1</sup> of ILs [TMG][BF<sub>4</sub>] and [TMG][BF<sub>4</sub>] with absorbed SO<sub>2</sub> gas.

chemical bond between the ILs and SO<sub>2</sub>. Possibly, the presence of two S–O stretching bands, as also found in solid-state spectra of SO<sub>2</sub>,<sup>13</sup> could indicate a restricted movement of the captured SO<sub>2</sub> resulting in two different S–O bond distances with one being notably short (*i.e.* shift of  $\nu_{\max}$  towards higher frequency).

Also, from comparison of the SO<sub>2</sub> absorption curves (Fig. 1) and identical <sup>1</sup>H-NMR and FT-IR spectra (Supporting Information and Fig. 2) of [TMG][BF<sub>4</sub>] and [TMG][BTA], it is apparent that the anion did not influence the interaction of SO<sub>2</sub> with the ILs. In contrast, the nature of the cation did influence the absorption capability slightly.

When attempts were made to get 10% SO<sub>2</sub> gas (10 mole percent in N<sub>2</sub>) absorbed in the ILs in order to simulate flue gas removal, only 0.007, 0.005, 0.064, 0.061, 0.080 (SO<sub>2</sub> molar ratio to ILs) SO<sub>2</sub> gas was absorbed in [BMIM][BTA], [BMIM][BF<sub>4</sub>], [TMG][BF<sub>4</sub>], [TMG][BTA] and [TMGB<sub>2</sub>][BTA], respectively, due to competing N<sub>2</sub> absorption (no measurable weight increase was observed when ILs were exposed to pure N<sub>2</sub>). The absorption capability probably relates to the strength of the electrostatic force between IL cation and SO<sub>2</sub> gas. Thus, the interaction between ILs based on [TMG]<sup>+</sup> and SO<sub>2</sub> is stronger than that of the ILs based on the [BMIM]<sup>+</sup> cation. A more conclusive examination of the interaction between IL cations and SO<sub>2</sub> gas and the cation effect on absorption capability will be the subject of later studies.

The local structure (see above) in ILs could provide a possible explanation for the pronounced SO<sub>2</sub> gas dissolution in ILs. Previous experimental and computational reports on CO<sub>2</sub> gas absorption in ILs suggest that CO<sub>2</sub> is taking up free space from void cavities already available in the rigid and intricate topography of ILs when CO<sub>2</sub> dissolves in ILs.<sup>2,5b</sup> As SO<sub>2</sub> is a polar gas, the void space originally available in ILs should be taken up much more easily by SO<sub>2</sub> gas. The volume of ILs increased significantly during gas absorption (about 22%, 45%, 45%, 23% and 25% volume increase for [BMIM][BTA], [BMIM][BF<sub>4</sub>], [TMG][BF<sub>4</sub>], [TMG][BTA] and [TMGB<sub>2</sub>][BTA], respectively). This could relate to the fact that the molecular radius of SO<sub>2</sub> is larger than the cavities – in particular for the ILs containing the smaller [BF<sub>4</sub>]<sup>−</sup> anion where the volume increase is about twice that for the analogous [BTA]<sup>−</sup> anion-based ILs, most likely due to the smaller cavities present. On-line thermal measurements (*i.e.* TGA, DSC) of the physical absorption of SO<sub>2</sub> by the ILs at different temperatures and SO<sub>2</sub> partial pressures are in progress to provide additional insight into the structural re-ordering of the ILs during gas exposure.

In summary, we have demonstrated that ILs most likely as a general feature (shown here for ILs based on the [BMIM]<sup>+</sup>- and the [TMG]<sup>+</sup>-cation) can physically absorb large amounts of SO<sub>2</sub> gas (1.1–1.6 moles SO<sub>2</sub> per mole IL) at room temperature and ambient SO<sub>2</sub> pressure. The absorbed SO<sub>2</sub> gas remains in the

molecular state without any chemical reaction during absorption in all the ILs [BMIM][BTA], [BMIM][BF<sub>4</sub>], [TMG][BF<sub>4</sub>], [TMG][BTA] and [TMGB<sub>2</sub>][BTA]. The absorbed SO<sub>2</sub> gas can be readily desorbed from the ILs by applying a vacuum or by heating, allowing the ILs to be reused several times for consecutive absorption/desorption cycles without loss of capability. It is believed that ILs may be useful for SO<sub>2</sub> removal regarding pollution control. Furthermore, studies using SO<sub>2</sub> as a guest molecule in ILs could provide important information about the structural details of ILs. Additionally, the ILs may be designed with optimal type and number of functional groups with respect to selective SO<sub>2</sub> capture and appropriate desorption conditions. This approach will be examined in future work.

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