

## The Sulfur Dioxide–1-Butyl-3-Methylimidazolium Bromide Interaction: Drastic Changes in Structural and Physical Properties

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The contact between minor amounts of SO<sub>2</sub> and crystalline 1-butyl-3-methyl-imidazolium bromide (BMIBr) causes the almost immediate melting of the ionic liquid (mp 45 °C) as well as a dramatic decrease in its viscosity in comparison to the pure molten phase. The same behavior was observed for other halide ionic liquids of higher melting points (70, 135, and 220 °C). The Raman spectrum of BMIBr–SO<sub>2</sub> clearly indicates a specific charge transfer interaction involving SO<sub>2</sub> and the halide. The measurements of ionic conductivity and diffusion coefficients obtained for the neat BMIBr (molten phase) and for the BMIBr–SO<sub>2</sub> strongly suggest a higher degree of ionic association in the presence of SO<sub>2</sub>. Molecular dynamic simulations indicate that although the cation–anion distance is preserved in the short range, there is a variation in the interionic distances in the second shell, leading to a less organized structure in the long range. The modulation of the structural and physical properties of ionic liquids by SO<sub>2</sub> and the convenient choice of the ions for gas absorption are suggested.

Sulfur dioxide is a conspicuous atmospheric pollutant, representing a major concern for public health in modern society.<sup>1</sup> Consequently, its monitoring, quantification, and removal have been the subject of several studies. Much of them have focused on the use of ionic liquids for the selective absorption of sulfur dioxide.<sup>2–5</sup> In a very recent work<sup>6</sup> involving the use of imidazolium ionic liquids supported on polyether-sulfone membranes, it is reported that the selectivity of SO<sub>2</sub> absorption is up to 19 times greater in comparison with CO<sub>2</sub>. On the other hand, few reports in the literature concern the nature of the molecular interactions of SO<sub>2</sub> and ionic liquids. Such knowledge could provide the rationale for optimizing the SO<sub>2</sub> absorption capability by the judicious choice of the cations and anions. The crystalline 1-butyl-3-methylimidazolium bromide (BMIBr) is capable to absorb 80% mol of SO<sub>2</sub> at 1 bar (25 °C). In this letter, experimental (density, viscosity, conductivity, diffusion coefficients) and theoretical (molecular dynamics simulations) data are shown to interpret how the SO<sub>2</sub> molecules effectively shield the main Coulombic attraction that maintains the BMIBr in the solid state.

When a rather small flow of SO<sub>2</sub> is passed close to the surface of the crystalline BMIBr (mp 45 °C), it melts almost instantaneously, giving rise to a yellowish liquid whose viscosity (5.2 cP at 50 °C) is much smaller than of the pure molten ionic liquid<sup>7</sup> (1486 cP at 25 °C). It must be mentioned that BMIBr, as many other ionic liquids, shows supercooling effects, standing

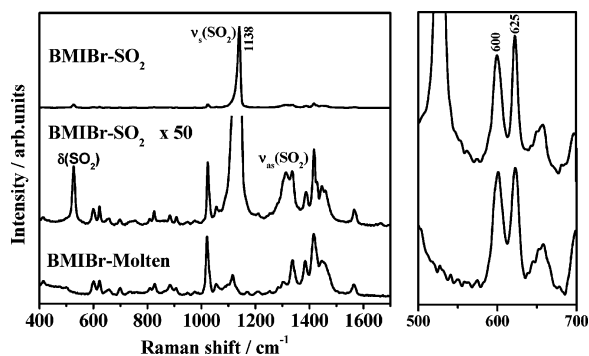
as a liquid at temperatures much lower than the normal melting point. A similar behavior was observed for other synthesized<sup>8</sup> halide ionic liquids, that is, immediately yellowish low viscosity liquids are formed. The ionic liquids submitted to SO<sub>2</sub> were 1-butyl-3-methylimidazolium chloride (BMICl) with mp 70 °C, 1-ethyl-3-methylimidazolium chloride (EMICl) with mp 135 °C, and finally *N*, *N*-butyl-methylpiperidinium bromide (BMPBr) with a much higher melting point of ca. 220 °C. It is well known that the appearance of a yellowish to orange color in the sulfur dioxide solvates of halides and pseudohalides are assigned to a charge transfer interaction, where SO<sub>2</sub> acts as an electron acceptor species.<sup>9</sup> It is worth mentioning that when bromide is changed for bis(trifluoromethanesulfonyl)imide, (BMITFSI, mp –3 °C), a much more delocalized anion, the behavior concerning the interaction with SO<sub>2</sub> is qualitatively different, that is, even with the saturation of absorbed SO<sub>2</sub> there is no change in color and the decrease in viscosity is quite small.

In the Raman spectra of the neat BMIBr (in molten phase at 50 °C) and BMIBr–SO<sub>2</sub> (Figure 1), one can observe that the symmetric stretching of the SO<sub>2</sub>,  $\nu_s(\text{SO}_2)$ , shows up as a very strong band at 1138 cm<sup>–1</sup>, to be compared with ca. 1148 cm<sup>–1</sup> for SO<sub>2</sub> dissolved in hexane. This shift to lower wavenumbers is a consequence of electrostatic and charge-transfer (CT) effects<sup>9</sup> between Br<sup>–</sup> and SO<sub>2</sub>. In addition, one can notice that there is not any significant change in the Raman spectra of the BMI<sup>+</sup> cation, confirming its minor interaction with the SO<sub>2</sub> molecules. The only significant change is the relative intensity of the bands at ca. 600 and 625 cm<sup>–1</sup>, assigned by Katayanagi et al.<sup>10</sup> to gauche and trans BMI<sup>+</sup> isomers, respectively. The author reported that the relative intensity of these bands depends

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**Figure 1.** Raman spectra of neat BMIBr (molten phase) and of BMIBr-SO<sub>2</sub>.

**TABLE 1: Physical Properties of BMIBr and BMIBr-SO<sub>2</sub> at 50 °C**

	density g cm <sup>-3</sup>	viscosity cP	diffusion coefficient <sup>a</sup> cm <sup>2</sup> s <sup>-1</sup>	conductivity ( $\sigma^{\text{exp}}$ ) S cm <sup>-1</sup>	$\sigma^{\text{exp}}/\sigma^{\text{NE}}$
BMIBr	1.28	1486 (25 °C)	$3.5 \times 10^{-8}$	$4.5 \times 10^{-4}$	0.6
BMIBr-SO <sub>2</sub>	1.38	5.2	$5.5 \times 10^{-5}$	$2.5 \times 10^{-1}$	0.2

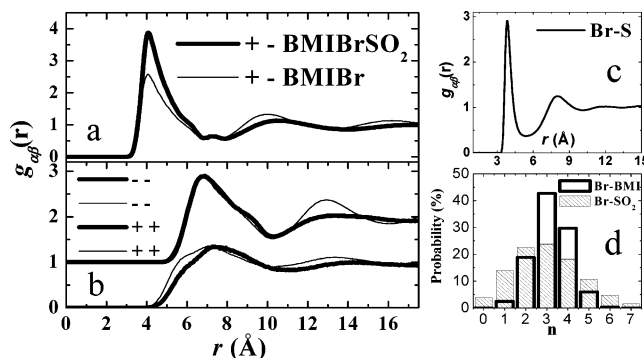
<sup>a</sup> Diffusion coefficients for BMI<sup>+</sup> cation.

on the halide anion (Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>). In our case, the relative intensities in BMIBr-SO<sub>2</sub> spectrum are quite similar to the observed for BMI<sup>+</sup>I<sup>-</sup> (mp -3 °C), suggesting that the Br<sup>-</sup>/3SO<sub>2</sub> solvate behaves similarly to I<sup>-</sup> anions concerning the interaction with BMI<sup>+</sup> cations.

Such facts point to the specific charge transfer (CT) interaction of SO<sub>2</sub> and Br<sup>-</sup> in BMIBr as one of the main factors responsible for the expressive values of its transport properties. In Table 1 are shown the set of experimental values for density, viscosity, diffusion coefficients, and conductivity for BMIBr and BMIBr-SO<sub>2</sub> at 50 °C.

It is worth mentioning that the dramatic decrease in the viscosity of the ionic liquid in the presence of SO<sub>2</sub> cannot be explained by the difference in temperature (25 and 50 °C), because the available data in the literature for ionic liquid viscosities at several temperatures indicate with certainty that the decrease in the viscosity is no greater than a factor of 3 in this temperature range. The diffusion coefficient increased by 3 orders of magnitude in the presence of SO<sub>2</sub>, and the same trend was observed for the ionic conductivity. Such changes can be understood from a single root, namely, the clustering of a substantial number of SO<sub>2</sub> molecules around the bromide anions, which leads to a shielding effect on the Coulombic interactions. The ratio of the experimental ionic conductivity ( $\sigma^{\text{exp}}$ ) and the one estimated from diffusion coefficients by the Nernst-Einstein equation ( $\sigma^{\text{NE}}$ ) is extensively used to access the degree of ionic association in a solution. For the neat IL, the value is ca. 0.6, that is, in line with the reported values for this kind of electrolyte. However, for the BMIBr-SO<sub>2</sub> the value of  $\sigma^{\text{exp}}/\sigma^{\text{NE}}$  is ca. 0.2, which in principle suggests a rather strong ionic association in the BMIBr-SO<sub>2</sub> that precludes the independent transport of charge in the system. This seems to be in contradiction with the shielding effect caused by the clustering by the SO<sub>2</sub> molecules around bromide ions. At the moment, we do not have a consistent explanation for such apparently contradictory results.

In fact, molecular dynamics (MD) simulations reveal that the average cation-anion distance is not altered in the short range, indicating that close interaction between BMI<sup>+</sup> and Br<sup>-</sup> still exists in the presence of SO<sub>2</sub>. However, in the next neighbor shell there is an increase in such distance, and the ionic



**Figure 2.** Radial distribution functions of cation-anion (a), anion-anion and cation-cation (b), and bromide-sulfur (c) calculated for BMIBr-SO<sub>2</sub> and BMIBr. Distribution of the nearest neighbor around Br<sup>-</sup> (d).

arrangement becomes less organized (Figure 2) because one is able to observe the smoothing in all the second peaks in  $g(r)$ . These features indicate that the structure of BMIBr-SO<sub>2</sub> is mainly dominated by ionic clusters and/or ion pairs in accordance to the large ion correlation observed ( $\sigma^{\text{exp}}/\sigma^{\text{NE}} = 0.2$ ), which reflects in a large mass transport but not in the charge transport.

The significant interaction between SO<sub>2</sub> and Br<sup>-</sup>, evidenced by the shifting in  $\nu_s(\text{SO}_2)$  to lower wavenumbers (Figure 1), is also observed in MD (Figure 2c) whose peak is centered at 3.60 Å, which is in line with the equilibrium ab initio distance of Br<sup>-</sup>/4SO<sub>2</sub> cluster, 3.82 Å. The average first neighbor shell of Br<sup>-</sup> (Figure 2d) comprises 3 SO<sub>2</sub> molecules and 3 BMI<sup>+</sup> cations, instead of the 5 cations in the neat BMIBr. Because BMI<sup>+</sup> cations are replaced by SO<sub>2</sub> in the Br<sup>-</sup> first neighborhood, some of them are more separated from each other, as can be seen in Figure 2b. Such results, together with the smoothing of the all second neighbor shells in the presence of SO<sub>2</sub>, are an important clue to understand the increased fluidity observed experimentally.

Anderson et al.<sup>3</sup> showed for two ionic liquids, 1-*n*-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide and 1-*n*-hexyl-3-methylpyridinium bis(trifluoromethanesulfonyl)imide, that the SO<sub>2</sub> absorption is thermodynamically favorable in comparison with CO<sub>2</sub>. It seems that the charge-transfer interaction between anions and SO<sub>2</sub> plays a key role to explain such difference. While the polar SO<sub>2</sub> molecules interact specifically with the anions, changing the ionic liquid (IL) structure, the nonpolar CO<sub>2</sub> molecules fill the IL cavities without any change in the interionic distances. As an example, the molecular dynamic simulations<sup>11</sup> of the system BMIPF<sub>6</sub>-CO<sub>2</sub> show no alteration of the IL structure in the presence of CO<sub>2</sub>, which possibly would not be the case of BMIPF<sub>6</sub>-SO<sub>2</sub>.

It is our contention that this work opens the possibility of using SO<sub>2</sub> to modulate important physical properties of ionic liquids, provided that a judicious choice of the anions is made, as this will reflect in CT interactions of different magnitude with SO<sub>2</sub>. By the same token, the potential use of cations bearing substituents like -NH<sub>2</sub>, -NHR, and -NR<sub>2</sub> groups, which are efficient electron donors toward SO<sub>2</sub>, would certainly imply a very efficient gas removal process.

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**Supporting Information Available:** Experimental conditions, transport properties determination, and simulation details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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