

**Supporting Information for “The Sulfur Dioxide – 1-Butyl-3-Methylimidazolium
Bromide Interaction: Drastic Changes in Structural and Physical Properties.”**

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Complexos

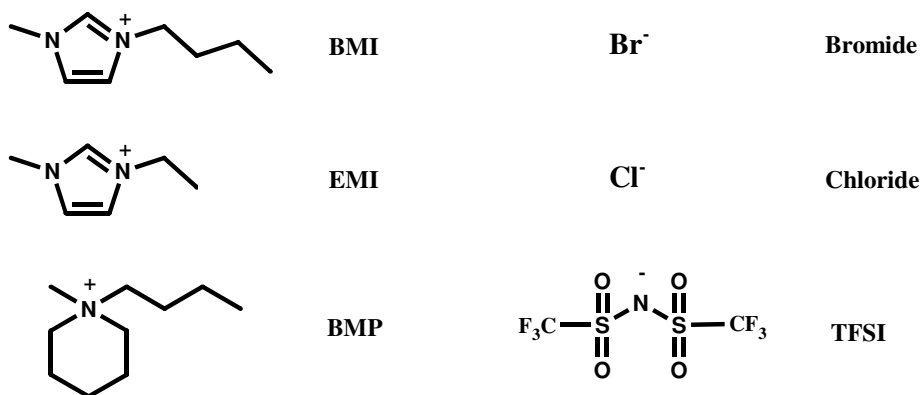
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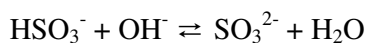
Materials

The 1-butyl-3-methylimidazolium bromide (BMIBr, 99%), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMITFSI, 99%) and N,N-butyl-methylpiperidinium bromide (BMPBr, 99%) were synthesized and purified by Fernanda C. Bazito. The 1-butyl-3-methylimidazolium chloride (BMICl, 99%) and 1-ethyl-3-methylimidazolium chloride (EMICl, 98%) were purchased from Solvent Innovations and sulfur dioxide (SO₂, 99.9%) was purchased from White Martins. All the operations were undertaken in anaerobic dry conditions in a glove box.



Experimental

The relative molar concentration of BMIBr/SO₂ was systematically determined by acid/base titration, considering the follow equilibrium:



The Raman spectra were obtained in a RFS 100/S FT-Raman Bruker spectrometer with the 1064 nm radiation from an air-cooled diode-pumped Nd:YAG

laser. The laser beam was focused on the sample in backscattering geometry at ca. 300 mW of laser power.

Ionic conductivity (σ^{exp}) was measured by the impedance method with the Autolab PGSTAT 30 (Eco Chemie) equipment within the frequency range 0.1 - 100 kHz. The cell constant was calibrated with KCl standard aqueous solution. The conductivity measurements of the neat BMIBr and BMIBr-SO₂ were done in the 5-95°C temperature range, describing a Vogel-Tammann-Fulcher (VTF) regime (equation 1):

$$\ln \sigma = \ln \sigma_0 - \frac{\beta}{T - T_0} \quad (1)$$

where β is a parameter related to the activation energy, T is the absolute temperature and T_0 is the ideal glass transition temperature.

Viscosity (η) and density (ρ) measurements (at 50°C) were undertaken using Anton Paar Stabinger SVM 3000 and DMA 4500 equipments, respectively.

Diffusion coefficients (D) of the BMI⁺ was measured by pulsed gradient spin echo nuclear magnetic resonance (PGSE-NMR) in a Varian INOVA 500 MHz spectrometer equipped with a 5 mm Indirect Detection Probe (50 G cm⁻¹ max), calibrated with water, $D = 2.299 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 298 K. A stimulated spin-echo pulse sequence, i.e. 90° - τ_1 - 90° - τ_2 - 90° - τ_1 - acquisition, incorporating a gradient pulse in each τ_1 period was used. The echo attenuation was fit by the equation (2):

$$\ln \left(\frac{I}{I_0} \right) = - \gamma^2 g^2 \delta^2 D \left(\Delta - \frac{\delta}{3} \right) \quad (2)$$

where g is the gradient strength, I_o is the echo amplitude when g tends to zero, γ is the gyromagnetic ratio, δ is the duration of the gradient pulse, and Δ is the time between gradient pulses. Experiments were conducted with $50 < \Delta < 150$ ms and $\delta = 1 - 5$ ms.

The values of conductivities (σ^{NE}) estimated by the diffusion coefficients were determined by the Nernst-Einstein equation:

$$\sigma^{NE} = \frac{q^2}{kT} (n_{cation} * D_{cation} + n_{anion} * D_{anion}) \quad (3)$$

where q is the electron charge (1.602×10^{-19} C), k is the Boltzmann constant (1.38065×10^{-23} J/K), T is the temperature, n is the number of ions and D is the diffusion coefficients. The conductivities were obtained considering the same values of diffusion coefficients for BMI^+ and Br^- , since it was not possible to obtain the D_{Br^-} by the PGSE-NMR method.

Molecular Dynamics Simulations

Table I. Computational details.

	No. cation	No. anion	No. SO ₂	Temperature (K)	Density
BMIBr-SO ₂	125	125	500	330	1.36
BMIBr	200	200	-	400	1.28
	Equil. Run		Prod. run	Time step	Long range forces
BMIBr-SO ₂	1ns		1ns	5	Ewald summation
BMIBr	1ns		2 ns	5	Ewald summation

The intermolecular potential used was follow (equation 4):

$$U = \sum_{\substack{i,j \\ i < j}} \left\{ B_{ij} e^{-\alpha_{ij} r_{ij}} - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}} \right\} + \sum_{\text{bonds}} k_r (r - r_{eq})^2 + \sum_{\text{angles}} k_{\theta} (\theta - \theta_{eq})^2 + \sum_{\text{dihedrals}} \sum_{n=1}^3 k_{\psi,n} [1 + \cos(n\psi - \delta_n)] , \quad (4)$$

Table II. Parameters of intermolecular potential used in BMIBr and BMIBr-SO₂ simulations.

	Epsilon (10 ⁻²⁰ J)	Sigma (Å)	Charge (e)
N1	0.71	3.25	-0.400
N2	0.71	3.25	-0.394
C3	0.443	3.88	0.5999
C4	0.443	3.88	0.2516
C5	0.443	3.88	0.2243
C6	0.865	3.775	0.3448
C7	0.493	3.905	0.2671
C8	0.493	3.905	0.0327
C9	0.493	3.905	0.0374
C10	0.326	3.905	0.0358
Br ⁻	0.09	4.62	-1.00
S ^b	0.213	3.585	0.467
O ^b	0.086	2.993	0.235

^a S. M. Urahata, M. C. C. Ribeiro, *J. Chem. Phys.* 120, 1855 (2004).

^b In SO₂ bonds and angle were kept rigid by rattle constraint, LJ parameters were taken from Ribeiro, M.C.C., *J. Phys. Chem. B*, XXX.

Table III. Parameters of intramolecular potential used in the simulation of BMIBr and BMIBr-SO₂.^a

	k_b (kJ/mol Å ⁻²)	r_{eq} (Å)		k_θ (kJ mol ⁻¹ rad ⁻²)	θ_{eq}
N1-C3	1674.7	1.34	N1-C3-N2	544.3	109.1
N2-C3	1674.7	1.34	C3-N2-C7	544.3	125.9
N1-C4	1674.7	1.38	C5-N2-C7	544.3	125.9
N2-C5	1674.7	1.38	C3-N1-C5	544.3	108.3
N1-C6	921.1	1.47	C3-N1-C4	544.3	108.3
N2-C7	921.1	1.48	N2-C5-C4	544.3	107.2
C4-C5	1716.6	1.36	N1-C4-C5	544.3	107.2
C7-C8	837.4	1.53	C3-N1-C6	544.3	125.8
C _i -C _{i+1} (i>8)	931.6	1.53	C4-N1-C6	544.3	125.8
			N2-C7-C8	586.2	112.6
			C _i C _{i+1} C _{i+2}	244.5	111.6
	$k_{\psi,n}$ (kJ mol ⁻¹)	N	δ (degree)		
C6-N1-C4-C5	58.6	1	0		
C7-N2-C5-C4	58.6	1	0		
C7-N2-C3-N1	58.6	1	0		
C6-N1-C3-N2	58.6	1	0		
C5-N2-C3-N1	58.6	2	180		
N2-C3-N1-C4	58.6	2	180		
N2-C5-C4-N1	58.6	2	180		
C4-C5-N2-C3	58.6	2	180		
C3-N1-C4-C5	58.6	2	180		
C3-N2-C7-C8	0.42	1	180		
C5-N2-C7-C8	0.84	1	0		
C _i -C _{i+1} -C _{i+2} -C _{i+3} (i>6)	0.63	1	0		

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***Ab initio* Calculations**

Ab initio calculations were performed in a cluster comprising 4 SO₂ molecules and 1 Br⁻ by using DFT methods with functional B3LYP and basis set 6-31+G*.