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Guanidinium-based ionic liquids for sulfur dioxide sorption

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ABSTRACT

Three guanidinium-based ionic liquids (GBILs) including [1,1,3,3-tetramethylguanidinium][phenol] ([TMG][PHE]), [1,1,3,3-tetramethylguanidinium][2,2,2-trifluoroethanol] ([TMG][TE]) and [1,1,3,3-tetramethylguanidinium][imidazole] ([TMG][IM]) were synthesized and their absorption and desorption of sulfur dioxide were investigated, respectively. The saturated molar ratio of SO_2 to GBILs varied from 2.24 to 3.16 at 40 °C with high absorption rate. The absorption mechanism might be that SO_2 reacts with the $-NH_2$ group on the cation and then a new $-SO_2H$ group is formed. The new GBILs could absorb SO_2 by both physical and chemical interactions while physical absorption does play an important role at the experimental conditions under investigation.

1. Introduction

Air pollution from burning of fossil fuel has been the focus of the environmental problem, among which, sulfur dioxide could result in acid rain, corrosion of equipments and architectures, diseases [1–3]. On the other hand, SO_2 is an important and useful chemical intermediates in industry and need to be separated and recycled. Therefore, the research of the sorption and desorption behavior as well as the related mechanism of SO_2 is of great significance [4–8]. As one promising separation candidate media, ionic liquids (ILs) have been attracting extensive interest in recent years due to their unique properties, such as chemical stability, negligible vapor pressure and high thermal stability [9–12]. It was found that SO_2 has optimistic physical solubility in series of ionic liquids [13–18]. In order to improve the capacity as well as the sorption rate [1], [1,1,3,3-tetramethylguanidinium][lactate] as one special functional capturing reagent was designed and synthesized [11]. There exists one surprising phenomenon that the viscosity could decrease after 0.5 mol ratio of SO_2 absorbed [14]. As convincing cases, [TMG][BF_4], [TMG][BTA] and [$TMGB_2$][BTA] were demonstrated to be excellent SO_2 absorption reagent [9,12]. As an even promising innovation, poly(1,1,3,3-tetramethylguanidine acrylate) was polymerized and high selectivity, capacity and rapid sorption/desorption rate were realized [2,13]. In this manuscript, we changed the anion of this kind of guanidinium ILs to study the absorption and desorption behaviors of sulfur dioxide in [1,1,3,3-tetramethylguanidinium][phenol] ([TMG][PHE]), [1,1,3,3-tetramethylguanidinium][2,2,2-trifluoroethanol] ([TMG][TE]) and [1,1,3,3-tetramethylguanidinium][imidazole] ([TMG][IM]), which were obtained by direct neutralization of 1,1,3,3-tetramethylguanidine (TMG) with imidazole, 2,2,2-trifluoroethanol and phenol, respectively (see Scheme 1). The sorption/desorption behavior of SO_2 at different temperatures was investigated.

2. Experimental

2.1. Materials

1,1,3,3-Tetramethylguanidine (TMG) (99%, CAS no. 80-70-6, Alfa Aesar), 2,2,2-Trifluoroethanol (99%, CAS no. 75-89-8, Alfa Aesar), Imidazole (AR, CAS no. 288-32-4, Sinopharm Chemical Reagent Co. Ltd.) and Phenol (AR, CAS no. 108-95-2, Beijing Chemical Reagent Plant) were used without further purification. Sulfur dioxide (99.9%, CAS no.7446-09-5) was purchased from Beijing Hua Yuan Gas Chemical Industry Co. Ltd.

2.2. Synthesis and characterization of GBILs

[TMG][PHE] was synthesized via direct neutralization of TMG and phenol (see Scheme 1). To synthesize the [TMG][PHE], ethanol (250 mL) and TMG (24.763 g, 0.215 mol) were loaded into a dried 500 mL flask in a water bath of 25 °C. A solution of phenol (20.232 g,

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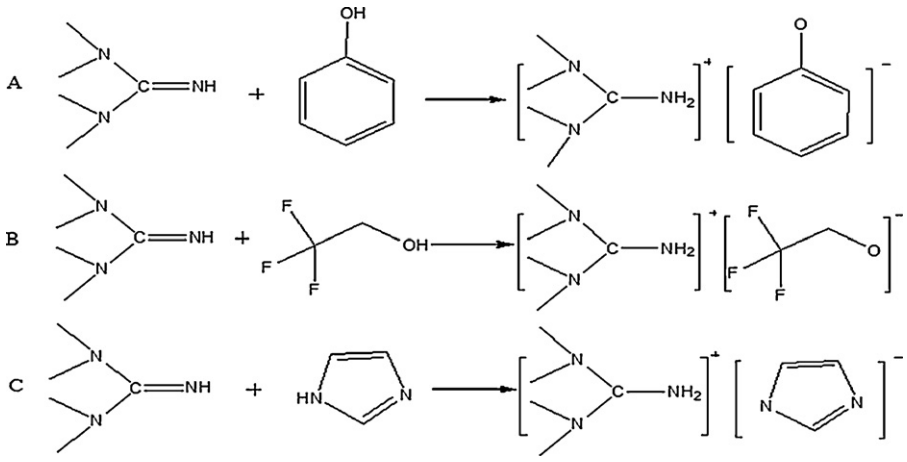


Scheme 1. The synthesis route of GBILs.

Table 1
Properties of the GBILs at 40 °C.

IL	Density (g/cm^3)	Viscosity (mPa s)	Conductivity ($\mu s/cm$)
[TMG][PHE]	1.02	31.3	923
[TMG][TE]	1.05	1.8	841
[TMG][IM]	0.99	5.4	3014

0.215 mol) in ethanol (100 mL) was then added, and the reaction was allowed to proceed for 12 h. The solvent was removed by rotary evaporation under vacuum at 65 °C, and finally, a hygroscopic product was obtained with a yield of 91.44%. The synthesis method for the product of [TMG][TE] and [TMG][IM] was similar as described for [TMG][PHE]. Herein, TMG (23.613 g, 0.205 mol) and 2,2,2-trifluoroethanol (20.218 g, 0.205 mol) were used to synthesized the [TMG][TE]. And TMG (28.281 g, 0.246 mol) and imidazole (16.712 g, 0.246 mol) were used for the synthesis of [TMG][IM].

The densities of the GBILs were measured by the Anton Paar DMA5000 Density Meter with an uncertainty of 1×10^{-5} g cm^{-3}, the viscosity data were obtained from Anton Paar AMVn Automated Mirco Viscometer, and the conductivity data from DDSJ-308A conductivity meter (Shanghai Precision & Scientific Instrument Co., LTD, accurate to ±0.01), respectively. The properties of GBILs at 40 °C in this work were tabulated in Table 1. The FTIR spectra of SO_2-free and SO_2-absorbed [TMG][IM], [TMG][TE] and [TMG][PHE] were measured on a Nicolet 380 infrared spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker MSL-600 NMR spectrometer using $(CD_3)_2SO$ as solvent and tetramethylsilane (TMS) as an internal reference, and the respective NMR data of GBILs could be found in the Supplementary data.

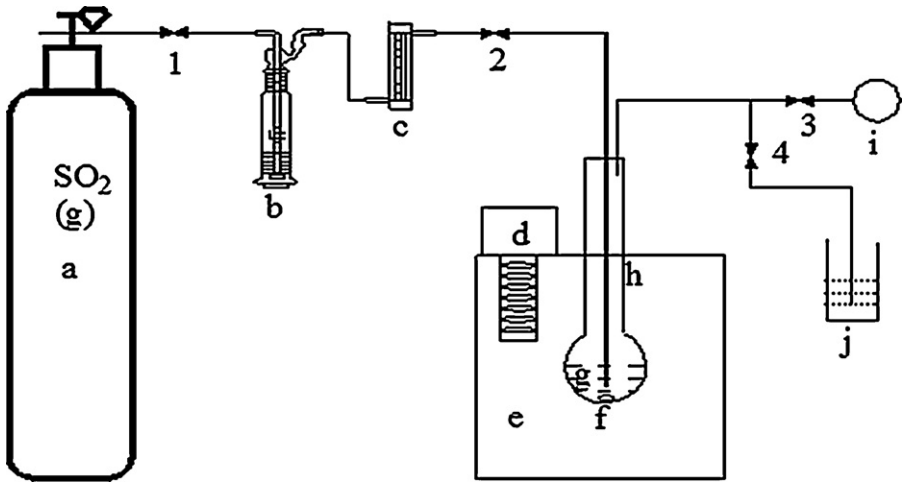
2.3. SO_2 absorption and desorption

The experiments on gas absorption were carried out under atmospheric pressure and at various temperatures, and the experimental diagram for SO_2 absorption of GBILs was illustrated in Scheme 2. The desorption was carried out at 40 and 100 °C under vacuum, respectively. The gas stream was bubbled through about 1 g of GBILs in a typical glass tubule with an inner diameter of 10 mm. The glass device was partly immersed in a constant temperature oil bath. The weight of the GBILs solution before and after sorption of SO_2 was determined at regular intervals.

3. Results and discussion

3.1. The behaviors of SO_2 absorption and desorption

The respective color change of the new GBILs before and after SO_2 absorption was shown in Fig. 1.



Scheme 2. Experimental diagram for SO_2 absorption of GBILs.
a, SO_2 gas cylinder; b, Dryer; c, Rotary flow meter; d, Temperature controller; e, Oil bath; f, A typical glass device; g, IL; h, Tubule; i, Pressure gauge; j, Gas outlet (absorbed by NaOH solution before venting); 1, 2, 3, 4, Valves.