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Absorption and desorption of SO_2 in aqueous solutions of diamine-based molten salts

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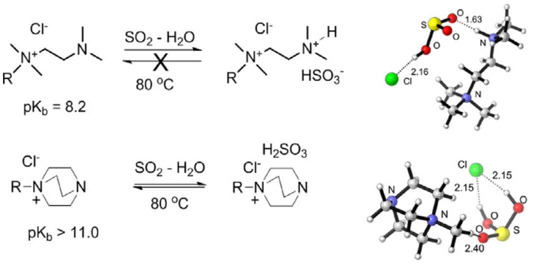
HIGHLIGHTS

- Diamine-based molten salts having two different basic sites were synthesized.
- Weakly basic molten salts reversibly interact with SO_2 in aqueous media.
- The SO_2 absorption mode was greatly affected by the basicity of molten salts.

GRAPHICAL ABSTRACT



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ABSTRACT

SO_2 absorption and desorption behaviors were investigated in aqueous solutions of diamine-derived molten salts with a tertiary amine group on the cation and a chloride anion, including butyl-(2-dimethylaminoethyl)-dimethylammonium chloride ([BTMEDA]Cl, $pK_b = 8.2$), 1-butyl-1,4-dimethylpiperazinium chloride ([BDMP]Cl, $pK_b = 9.8$), and 1-butyl-4-aza-1-azoniabicyclo[2,2,2]octane chloride ([BDABCO]Cl, $pK_b = 11.1$). The SO_2 absorption and desorption performance of the molten salt were greatly affected by the basicity of the molten salt. Spectroscopic, X-ray crystallographic, and computational results for the interactions of SO_2 with molten salts suggest that two types of SO_2-containg species could be generated depending on the basicity of the unquaternized amino group: a dicationic species comprising two different anions, HSO_3^- and Cl^-, and a monocationic species bearing Cl^- interacting with neutral H_2SO_3.

1. Introduction

Stringent environmental regulations regarding SO_2 emissions from the flue gases of fossil fuel-fired power plants and other industrial facilities have been enacted in many developed and developing countries [1–5]. Currently, SO_2 generated from fossil fuel combustion is mostly being removed by flue gas desulfurization (FGD) processes using alkaline sorbents such as calcium-based lime (CaO) and limestone ($CaCO_3$) [6–8]. Although these alkaline scrubbing processes are highly attractive in terms of SO_2 absorption efficiency and sorbent cost, they possess several drawbacks such as the generation of large amounts of waste water and the loss of SO_2 as waste solid salts.

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As alternatives to alkaline sorbents, ionic liquids (ILs) have received great interest recently because they possess favorable properties for dissolving SO_2 through interactions of anions and cations; further, the absorbed SO_2 can be desorbed at mild temperatures below 100 °C [9–13]. Accordingly, a great number of ILs have been developed as SO_2 absorbents, and significant advances have been made especially in terms of molar SO_2 absorption capacity. Nonetheless, practical application of ILs to the desulfurization of flue gases has not been realized, because the basicities of ILs are too weak to capture SO_2 present at extremely low concentrations of approximately 500–2500 ppm [14]. In principle, the interaction of SO_2 with ILs can be enhanced to a great extent by increasing the basicity of the ILs. It is possible to achieve this by introducing a basic amino group on the ILs. Another important aspect in the application of ILs to the flue gas desulfurization is that the ILs should exhibit high water tolerance during SO_2 sorption and desorption processes because flue gases contain 10–15 wt% water. However, SO_2 absorption in aqueous solutions of ILs has only rarely been investigated [15,16].

Herein, we report on an investigation of the SO_2 absorption and desorption behaviors in aqueous solutions of diamine-based molten salts with a tertiary amino group on the cations, which have been prepared from 1:1 reactions of diamines with butyl chloride. The effect of the basicity of molten salts is discussed in detail on the basis of ^1H NMR, IR, and Raman spectroscopic results as well as X-ray crystallogrpahic and computational results.

2. Experimental

2.1. Materials

All reagents were purchased from Aldrich Chemical Co. and used without further purification. SO_2 (99.99%) was obtained from Shin Yang Gas Chemical Co.

2.2. Instrumentation

^1H NMR spectra were recorded on a Varian 500 Unity plus (400 MHz). The pH values of diamines and molten salts were measured in water at 25 °C using a 0.1 N HCl aqueous solution as a titrant by means of an AT-700 automatic potentiometric titrator equipped with a pH meter fitted with glass electrode (KEM, Japan). The pK_a values were determined by a half-neutralization technique using an AT-Win titration software [17], from which the pK_b values were obtained ($pK_b = 14 - pK_a$). FT-IR spectra were recorded on a Nicolet FT-IR spectrometer (iS10, USA) equipped with a SMART MIRACLE accessory. Thermogravimetric analysis data were obtained using a Metter TGA 50 system and a TA Instruments Q10 differential scanning calorimeter (see Supplementary data (SD) for details). Raman spectra were measured using a TruScan GP (Thermo Scientific, 785 nm). Single crystal X-ray diffraction data were collected on a Bruker SMART APEXII diffractometer equipped with a CCD area detector using graphite monochromated MoK radiation ($\lambda = 0.71073$ Å) (see SD).

2.3. Synthesis of diamine-based molten salts bearing a chloride anion

Diamine-based molten salts were prepared by reacting diamines with *n*-butyl chloride. A typical synthesis of a diamine-based molten salt with a chloride anion is as follows: in a 250 mL one-necked flask, a mixture of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (11.69 g, 100.6 mmol) and *n*-butyl chloride (9.51 g, 102.7 mmol) in acetonitrile (100 mL) was refluxed for 5 h under a nitrogen atmosphere. After the completion of the reaction, diethyl ether was added into the mixture at room temperature to precipitate white solid. The solid was dried under vacuum for 6 h to afford butyl-(2-dimethylaminoethyl)-dimethylammonium chloride ([BTMEDA]Cl). Yield: 85.2%.

Other diamine-based ionic salts, 1-butyl-1,4-dimethylpiperazinium chloride ([BDMP]Cl) and 1-butyl-4-aza-1-azoniabicyclo[2,2,2]octane chloride ([BDABCO]Cl) were prepared in a similar manner to that employed in the synthesis of [BTMEDA]Cl. The elemental analysis and ^1H NMR spectroscopic results of [BTMEDA]Cl, [BDMP]Cl, and [BDABCO]Cl are provided in SD.

2.4. SO_2 absorption and desorption

Adsorption and desorption of SO_2 were conducted using a similar apparatus described elsewhere [18]. In a typical experiment, a molten salt (2 g) dissolved in 7 g of water was loaded into the absorption glass tube equipped with an electrical heater, temperature controller, and inlet and outlet valves. SO_2 (99.9%) was introduced into the absorption tube at 30 °C at a rate of 20 mL/min. The weight change during the SO_2 adsorption was monitored using a balance (accuracy: 0.001) and recorded on a computer until equilibrium was attained. The amount of SO_2 absorbed by the molten salt was calculated by subtracting the amount of SO_2 absorbed by water from the total absorbed amounts of SO_2 by the aqueous solution of the molten salt. Once the absorption was completed, the absorbed SO_2 was desorbed at 50 or 80 °C by flowing N_2 into the SO_2 loaded solution at a rate of 20 mL/min.

SO_2 concentration in the simulated flue gas before and after SO_2 absorption was analyzed by a non-dispersive infrared gas analyzer (Rosemount NGA 2000). To a glass tube containing [BDABCO]Cl (2 g) in water (8 g), A mixture gas of N_2 (80%), O_2 (5%), and CO_2 (15%) containing 1980 ppm of SO_2 was bubbled through a glass tube loaded with [BDABCO]Cl (2 g) in water (8 g) at a rate of 100 cc/min, and the exit gas was analyzed every 15 min.

2.5. Computational calculations

The interactions of amines with SO_2 were theoretically investigated using the Gaussian 03 program [19]. The geometry optimizations and thermodynamic corrections were performed with the hybrid Becke 3-Lee–Yang–Parr (B3LYP) exchange–correlation functional with the 6-31 + G* basis sets for C, H, N, O, and S. In order to obtain the most stable geometries, all kinds of possible interaction patterns were optimized. All stationary points were verified as minima by full calculation of the Hessian and a harmonic frequency analysis [20,21].

3. Results and discussion

3.1. Synthesis and physicochemical properties of diamine-derived molten salts

Three types of diamine-derived molten salts having a tertiary amine functionality were synthesized from the 1:1 reaction of diamine with butyl chloride (Scheme 1). Table 1 shows some of the physicochemical properties of the prepared molten salts. Only [BTMEDA]Cl exists as a liquid below 100 °C, whereas [BDMP]Cl and [BDABCO]Cl melt at significantly higher temperatures of 170.0 and 144.3 °C, respectively. All three of these molten salts exhibited relatively high thermal stabilities up to at least 180 °C (Figs. S-1 and S-2 in SD), suggesting that these molten salts could be stable under desorption condition.

The pK_b values of the amines and diamine-based molten salts were compared to find out a correlation between the basicity and the SO_2 absorption capacity ($pK_a + pK_b = 14$). As can be seen in Table 1, the pK_b values of [BTMEDA]Cl and [BDMP]Cl were found as