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Hydroxyl Ammonium Ionic Liquids: Synthesis, Properties, and Solubility of SO_2

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To explore environmentally benign solvents for absorbing SO_2, a series of hydroxyl ammonium ionic liquids (ILs) was synthesized and characterized, and the solubilities of SO_2 in these synthesized ILs were determined. It was found that the solubilities of SO_2 in these ILs at ambient pressure are quite high, for example, the solubility of SO_2 in tri-(2-hydroxyethyl)ammonium lactate is 0.4957 mole fraction and decreases sharply as temperature increase. The absorption and desorption are practically reversible in the synthesized ILs. Comparing with the conventional absorbents such as calcium carbonate ($CaCO_3$), calcium oxide (CaO), and sodium hydroxide (NaOH), the synthesized ILs show two advantages: one is that the ILs can be recycled and repeatedly used, another is that the absorbed SO_2 can be reversibly released and recovered as a sulfur resource.

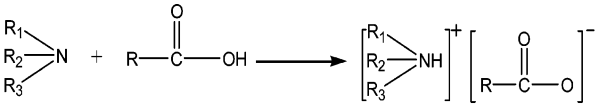
Introduction

Emission of SO_2 from combustion of sulfur-containing fossil fuels causes serious pollution problems such as the formation of acid rain that is harmful to the environment and the human being; therefore, removal and recovery of SO_2 from flue gas is a crucial subject in the recent decades. Although there are some commercial processes for flue gas desulfurization (FGD),[1] for example, dry or wet FGD with lime scrubbing, the disadvantages of these processes are obvious. For example, low efficiency and a huge amount of gypsum waste are two disadvantages.[2] In fact, most of the conventional desulfurization processes are discarding approaches resulting in discarding the product, which is not consistent with the sustainable development principles. In order to recover SO_2 from flue gas, the first step is to obtain concentrated and pure SO_2. For achieving such a goal, there are several approaches such as pressure-swing adsorption, solvent scrubbing, etc.,[3] among which solvent scrubbing is proven to be a promising technology where a potentially good solvent is of critical importance.

In recent years, ionic liquids (ILs) have attracted much attention in various fields[4−12] due to their unique properties such as negligible vapor pressure and stability. More interesting is that the properties of ILs could be tailored by adjusting the structures of their cations and anions, which further increases the unique features and applicability of ILs in complex systems and challenging conditions compared to the conventional organic solvents. It is expected that ILs would be good solvents for absorbing SO_2 through designing the desired structures of the cations and anions. Reference work[13] showed a potential solvent, 1,1,3,3-tetramethylguadium lactate, in absorption of SO_2.

Considering the acidity of SO_2 and the environmental benign properties of the ILs, in this work a series of hydroxyl ammonium ILs were synthesized, and the solubilities of SO_2 in them were determined at atmospheric pressure. The effects of different cations and anions on their capacity for absorption of SO_2 were systematically investigated, and the recovery of SO_2 and recycle of the synthesized ILs were also conducted by increasing temperature or under vacuum. In order to understand the mechanism of absorption of SO_2 by these ILs, FTIR spectrum was used to analyze the microstructure of SO_2-absorbed ILs and SO_2-free ILs.

Scheme 1. Formation of the Hydroxyl Ammonium Ionic Liquids



R_1, R_2, R_3: H or OH-CH_2-CH_2- or OH-CH_2-CH_2-O-CH_2-CH_2-

R : H, CH_3 and CH_3-CH(OH)-

Experimental Procedures

Materials. 2-Aminoethanol (AR grade, 99 %), triethanolamine (AR grade, 98 %), and formic acid (AR grade, 95 %) were all purchased from Beijing Chemical Reagent Co. and were distilled under reduced pressure. Lactic acid (AR grade, 90 %) and 2-(2-aminoethoxy) ethanol (AR grade, 90 %) were purchased from J&K Chemical Co. and were purified under reduced pressure before use. Acetic acid (AR grade, 99.5 %) was also purchased from Beijing Chemical Reagent Co. and used without further purification. Ethanol, acetone, acetic ether, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), 1,2-dihydroxypropane, and *N*,*N*-dimethyl formamide are all AR grade and were used as received. All reagents purified are no less than 99 % before use.

Synthesis of ILs. Hydroxyl ammonium ionic liquids were prepared by neutralization of ethanolamine in ethanol with different acids. As an example, the synthesis procedure of 2-hydroxyethylammonium lactate is described here: 0.5 mol of 2-aminoethanol was dissolved in 100 mL of ethanol to form a liquid mixture and loaded into a 500 mL flask. The flask was placed in a water bath of 298.2 K and equipped with a reflux condenser under vigorous stirring with a magnetic stirrer. A mixture of 0.5 mol of lactic acid dissolved in 100 mL of ethanol

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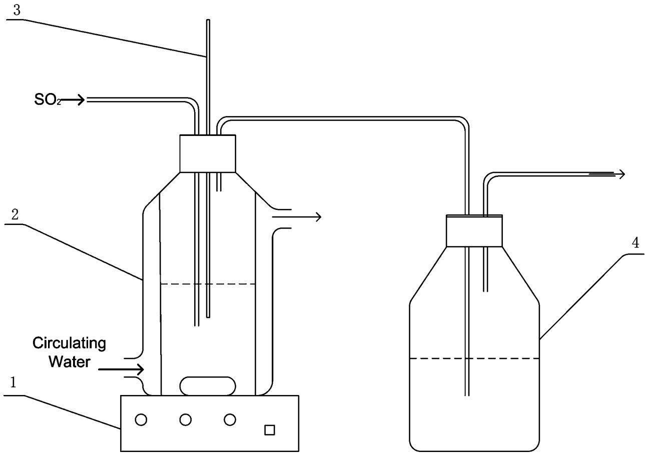


Figure 1. Apparatus of absorption of SO_2 using ionic liquids: 1, magnetic stirrer; 2, jacketed glass vessel; 3, precision thermometer; 4, off-gas absorption.

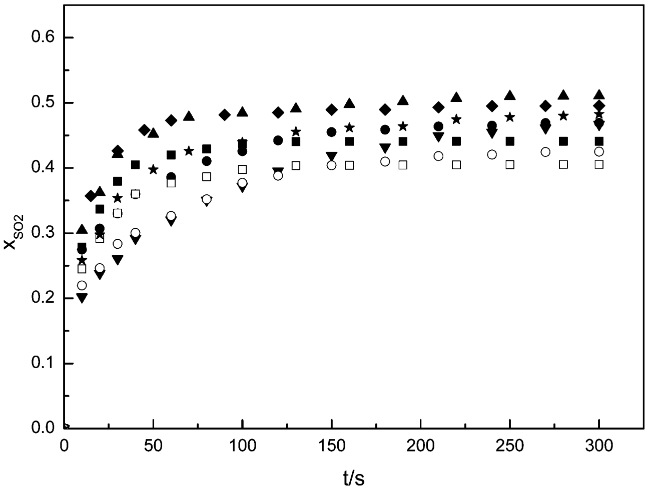


Figure 2. Dissolution of SO_2 in ILs at 298.2 K and 101.3 kPa as a function of time: ■, 2-hydroxyethylammonium formate; ●, 2-hydroxyethylammonium acetate; ▲, 2-hydroxyethylammonium lactate; ▼, tri-(2-hydroxyethyl)-ammonium acetate; ♦, tri-(2-hydroxyethyl)ammonium lactate; □, 2-(2-hydroxyethoxy)ammonium formate; ○, 2-(2-hydroxyethoxy)ammonium acetate; ★, 2-(2-hydroxyethoxy)ammonium lactate.

was added dropwise to the flask in about 90 min. The reaction lasted for 2 h. The solvent was removed by evaporation under vacuum. The resulting crude residue was dissolved in 100 mL of ethanol, treated with active carbon, and filtered. A colorless product was obtained after evaporation and dried under vacuum at 323.2 K for 48 h. The water mass fraction in the ILs after drying was less than 10^{-4} measured by 787 KF Titrino (a titrator for water determination according to Karl Fisher). The synthesized reaction for the hydroxyl ammonium ILs is expressed in Scheme 1. The synthesized ILs are 2-hydroxyethylammonium formate, 2-hydroxyethylammonium acetate, 2-hydroxyethylammonium lactate, tri-(2-hydroxyethyl)ammonium formate, tri-(2-hydroxyethyl)ammonium acetate, tri-(2-hydroxyethyl)-ammonium lactate, 2-(2-hydroxyethoxy)ammonium formate, 2-(2-hydroxyethoxy)ammonium acetate, and 2-(2-hydroxyethoxy)-ammonium lactate.

Characterization of ILs. ^{1}H NMR spectra were measured on a Bruker AM 400 MHz spectrometer, using DMSO as a solvent with TMS as the internal standard. FT−IR spectra were taken by a Perkin-Elmer IR spectrometer, using a NaCl disk.

Determination of Physical Properties of ILs. Viscosities were determined using a NDJ-1 rotary type viscometer, conductivities were measured by a DDS-307 conductivity meter, and densities were determined using pycnometers of 5 mL. All these determinations are in a water bath of 298.2 K with a temperature uncertainty of ± 0.1 K. Uncertainties of viscosities, densities, and conductivities are ± 1, ± 0.001, and ± 0.1, respectively. Melting temperature and decomposition temperature were characterized by a Perkin-Elmer DSC-7 differential scanning calorimetry (DSC) and Perkin-Elmer TGA-7 themogravimetric analysis (TGA).

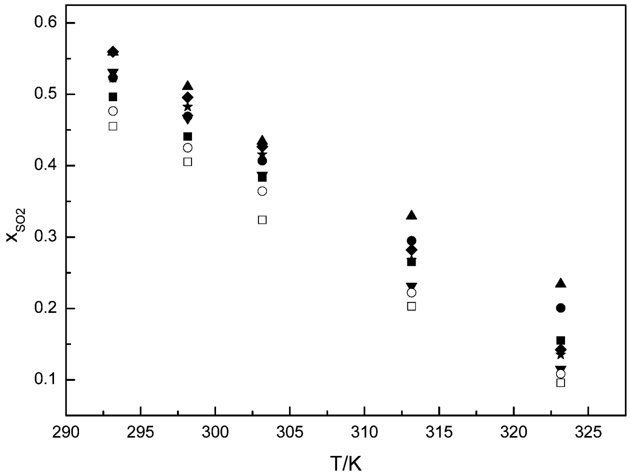


Figure 3. SO_2 solubility in ILs at 101.3 kPa as a function of temperature: ■, 2-hydroxyethylammonium formate; ●, 2-hydroxyethylammonium acetate; ▲, 2-hydroxyethylammonium lactate; ▼, tri-(2-hydroxyethyl)ammonium acetate; ♦, tri-(2-hydroxyethyl)ammonium lactate; □, 2-(2-hydroxyethoxy)ammonium formate; ○, 2-(2-hydroxyethoxy)ammonium acetate; ★, 2-(2-hydroxyethoxy)ammonium lactate.

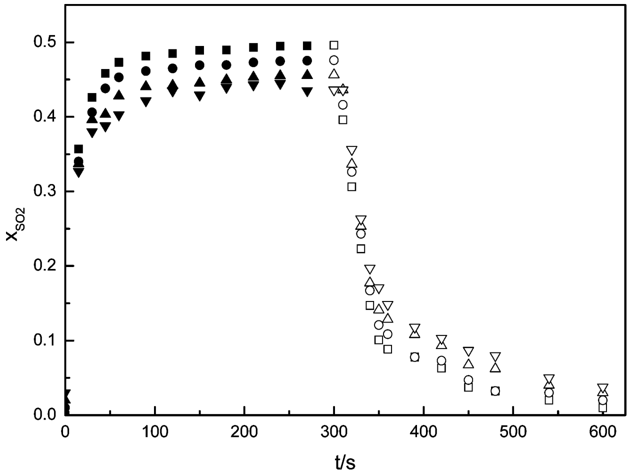


Figure 4. Cycle of SO_2 absorption and desorption in tri-(2-hydroxyethyl)-ammonium lactate (F) at 298.2 K: ■, first absorption at atmospheric pressure; □, first desorption under vacuum; ●, second absorption at atmospheric pressure; ○, second desorption under vacuum; ▲, third absorption at atmospheric pressure; △, third desorption under vacuum; ▼, fourth absorption at atmospheric pressure; ▽, fourth desorption under vacuum.

Absorption of SO_2 in ILs. The apparatus of absorption of SO_2 in these ILs is showed in Figure 1, which mainly consisted of a jacketed glass vessel maintained at the desired temperature through circulating water. The water temperature was controlled by a workstation with a temperature accuracy of ± 0.1 K. Continuous stirring was achieved by a magnetic stirrer, and a thermometer with an uncertainty of ± 0.01 K was used to determine the temperature of the system. SO_2 gas was bubbled with a flow rate of 100 mL/min through predetermined amounts of the ILs (about 5 g) loaded in a glass vessel. There is a valve

Table 1. Properties of the Synthesized ILs[a]

ionic liquids	T_m/K	T_g/K	T_d/K	$T = 298.2$ K		
				$\sigma/\mu S\cdot cm^{-1}$	$\rho/g\cdot cm^{-3}$	$\eta/mPa\cdot s$
2-hydroxyethylammonium formate	190.9	187.2	444.5	3291.0	1.204	118
2-hydroxyethylammonium acetate	202.2	197.3	439.1	692.0	1.120	640
2-hydroxyethylammonium lactate	214.6	209.4	520.2	377.5	1.202	1200
tri-(2-hydroxyethyl)ammonium formate	340.7		506.7	---	---	---
tri-(2-hydroxyethyl)ammonium acetate	200.9	194.3	510.0	495.8	1.120	342
tri-(2-hydroxyethyl)ammonium lactate	218.3	213.7	511.2	90.0	1.222	455
2-(2-hydroxyethoxy)ammonium formate	198.3	194.4	517.9	194.4	1.133	371
2-(2-hydroxyethoxy)ammonium acetate	212.4	208.5	445.9	289.2	1.119	2893
2-(2-hydroxyethoxy)ammonium lactate	217.6	213.2	547.8	1784.1	1.149	3040

[a] T_m, melting temperature; T_g, glass transition temperature; T_d, decomposition temperature; σ, conductivity; ρ, density; η, viscosity.

in the inlet and outlet lines of gas and circulating water, respectively. These valves were closed, and the glass vessel was weighed using a balance with an uncertainty of ± 0.001 g to get the mass of SO_2 absorbed, through which the ratio of SO_2 to ILs can be calculated. The absorption concentration of SO_2 in ILs versus time was determined at 298.2 K and 101.3 kPa, and that versus temperature was determined at 101.3 kPa and temperature from (293.2 to 323.2) K. Considering the absorption rate, the equilibrium can be considered to be reached after 3 h in the thermodynamic experiments.

Recycle of ILs. The absorption and desorption cycles were conducted to study the recovery of SO_2 and recycle of these synthesized ILs. To get the effects of temperature on desorption of SO_2, the solubilities of SO_2 in these ILs with temperature increasing were determined at atmospheric pressure. ILs saturated with SO_2 were slowly heated with a 5 K increase per hour (to make SO_2 in ILs being equilibrium) with stirring at ambient atmosphere. The residual absorption amount of SO_2 was also determined by weighing at 30 min intervals.

Results and Discussions

Characterization of ILs. In this work, nine hydroxyl ammonium ILs were synthesized and characterized. ^{1}H NMR spectra of 2-hydroxyethylammonium formate are presented, which are in good agreement with that reported by Bicak.[14]

^{1}H NMR(400 MHz, DMSO, δ): 8.4 ppm (s, 1H, H-COO$^-$); 6.0−7.6 ppm (broad signal, 4H, -NH_3 + OH); 3.5 ppm (t, 2H, -CH_2-N); 2.8 ppm (t, 2H, -O-CH_2).

Properties of ILs. Physical properties of the synthesized ILs were presented in Table 1. The properties of 2-hydroxyethylammonium formate are in good agreement with that reported by Bicak.[14] The other eight ILs were synthesized for the first time in this work, and there are no data reported in the literature. For tri-(2-hydroxyethyl)ammonium formate, there is no glass transition temperature in the scanning temperature range from (173.2 to 373.2) K, and its conductivity, density, and viscosity are not given in Table 1 because it is solid at room temperature.

From Table 1 it can be seen that the viscosities increase as the chain lengths of anions increase and decreases as the radius of cations increases. The relation between conductivities of these ILs and their structures is not clear. To ILs containing cations like 2-hydroxyethylammonium or tri-(2-hydroxyethyl)ammonium, the conductivities of ILs decrease when viscosities increase, while to ILs containing 2-(2-hydroxyethoxy)ammonium cations, the conductivities of ILs increase when viscosities increase. To ILs containing anions like formate and acetate, the conductivities decrease when viscosities increase, while to ILs containing lactate anions, the conductivities of ILs increase as viscosities increase. From Table 1, we can see that the conductivity of 2-hydroxyethylammonium formate is so high and that the viscosity of it is so small, which makes it potentially applicable for use in industry. All these ILs except for tri-(2-hydroxyethyl)ammonium formate are liquids at room temperature, and the temperature ranges of liquid state are comparatively large. For example, the melting temperature of tri-(2-hydroxyethyl)ammonium lactate is 217.6 K, and its decomposition temperature is 547.8 K.

Absorption of SO_2 in ILs. The dissolution of SO_2 in the synthesized ILs was determined versus time at 298.2 K and 101.3 kPa except for tri-(2-hydroxyethyl)ammonium formate, which is solid at 298.2 K. The results are presented in Figure 2. It can be seen absorption takes about 1 h to reach the equilibrium state. The saturated solubilities of SO_2 in these synthesized ILs are quite high, for example, the solubility of SO_2 in tri-(2-hydroxyethyl)ammonium lactate is 0.4957 (mole fraction), corresponding to 0.208 (mass fraction).

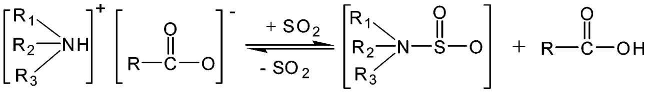
The equilibrium solubilities of SO_2 in these eight ILs versus temperature at 101.3 kPa are presented in Figure 3. It can be seen that the solubilities of SO_2 in these eight ILs decrease sharply when the temperature increases. For example, the solubility of SO_2 in tri-(2-hydroxyethyl)ammonium lactate at 293.2 K is 0.5596 (mole fraction) while it decreases to 0.1423 (mole fraction) at 323.2 K.

There are three kinds of cations and anions that have been investigated respectively in this work. From Figures 2 and 3, we can see that the effect of cations on the solubilities of SO_2 follow the sequence 2-hydroxyethylammonium > tri-(2-hydroxyethyl)ammonium > 2-(2-hydroxyethoxy)ammonium and that the effect of anions is lactate > acetate > formate. As an overall result of the cation and anion, 2-hydroxyethylammonium lactate shows the highest capacity for absorption of SO_2, and the equilibrium concentration of SO_2 in it reaches a value of 0.5107 (mole fraction). Therefore, 2-hydroxyethylammonium lactate can be regarded as the most potential absorbent of SO_2 for FGD.

Recycle of ILs. Experiments showed that the solubilities of SO_2 in these synthesized ILs are almost zero at the atmospheric pressure when the temperature rises to 353.2 K. When SO_2-saturated ILs are vacuumed with stirring at 298.2 K, it can be found that the solubilities of SO_2 in all these synthesized ILs decreased rapidly and approached zero after 2 h. As an example, Figure 4 shows the recycle of SO_2 of absorption and desoprtion in tri-(2-hydroxyethyl)ammonium lactate. These recycling experiments were repeated for four times, and the decreasing of the absorption ability was very little. Experiments showed that the absorption ability of the ionic liquid was 40 % after 30 times. The above results indicated that the ILs can be recycled and used repeatedly and that recovery of SO_2 in four times is 97.9 %, 95.8 %, 93.4 %, and 91.3 %, respectively.

Mechanism of Absorption. FTIR spectra of SO_2-absorbed ILs were compared with those of SO_2-free ILs. The compared results showed that in all these FTIR of SO_2-absorbed ILs there

Scheme 2. Proposed Reactions between the Synthesized ILs and SO_2



R_1, R_2, R_3: H or OH-CH_2-CH_2- or OH-CH_2-CH_2-O-CH_2-CH_2-

R: H, CH_3 and CH_3-CH(OH)-

were two new absorptions at about 1718 cm^{-1} (specific absorptions of —C═O—OH) and 1227 cm^{-1} (N—S═O—), while the peak of about 1580 cm^{-1} (—C═O—O^{-}) disappeared. From the above results, it can be deduced that the SO_2 molecule attacks the group of —NH in the cation of the ILs and forms the N—S bond and that simultaneously the carboxylate was turned to carboxylic acid. Reversibly the N—S bond breaks down, and the absorbed SO_2 is released when they were under vacuum or being heated. The reversible reactions of ILs with SO_2 can be expressed as in Scheme 2.

From the mechanism, we can see that the ratio of ionic liquid to SO_2 is 1 when these ionic liquids absorb SO_2 and that the ratio of $CaCO_3$, CaO, and NaOH is 1, 1, and 2, respectively. The absorption of SO_2 using these ILs is both physical absorption and chemical absorption, which showed that the solubilities of SO_2 in these ILs are lager than in the solvents commonly used.

Conclusions

A series of hydroxylammonium ILs were synthesized, and the properties such as density and viscosity were determined. From the mechanism of absorption, we can see that the cation is less and the branches are less, that the SO_2 molecule attacks the group of -NH in the cation of the ILs more easily, and that the solubilities are higher, which are all in good agreement with the solubility results detailed above. More interesting is that the absorbed SO_2 can be simply released under vacuum or by heating and that the recycled ILs show stable capability in the absorption of SO_2 after recycling of absorption and desorption. This is the greatest advantage of the present approach as compared to the traditional processes by using calcium carbonate ($CaCO_3$), calcium oxide (CaO), and sodium hydroxide (NaOH). Therefore, the synthesized ILs show great potential as alternative solvents for the recovery of SO_2 in the industrial process of FGD.

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