THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

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What Are Functional Ionic Liquids for the Absorption of Acidic Gases?

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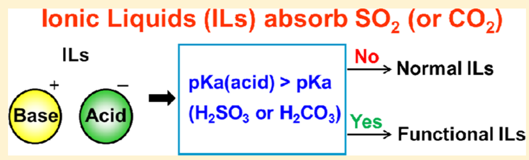
ABSTRACT: As a kind of novel and efficient material, ionic liquids (ILs) are used for capture of acidic gases including SO_2 and CO_2 from flue gas. Due to very low content of acidic gases in flue gas, it is important to find functional ILs to absorb the acidic gases. However, up to now, there is no criterion to distinguish if the ILs are functional or not before use, which greatly influences the design of functional ILs. In this work, a series of ILs were synthesized and used to determine functional or normal ILs for the capture of acidic gases. It has been found that the pK_a of organic acids forming the anion of ILs can be used to differentiate functional ILs from normal ILs for the capture of acidic gases from flue gas. If the pK_a of an organic acid is larger than that of sulfurous acid (or carbonic acid), the ILs formed by the organic acid can be called functional ILs for SO_2 (or CO_2) capture, and it can have a high absorption capacity of SO_2 (or CO_2) with low SO_2 (or CO_2) concentrations. If not, the IL is just a normal IL. The pK_a of organic acids can also be used to explain the absorption mechanism and guide the synthesis of functional ILs.



INTRODUCTION

The emission of acid gases from burning of fossil fuels causes environmental problems all over the world. The main acidic gases are SO_2 and CO_2. SO_2 can form acid rain and destroy plants, and CO_2 may cause the global warming and climate change. The most efficient way to reduce the emission of acidic gases has been proven to be SO_2 and CO_2 capture after the burning of fuels. For years, many kinds of materials have been used to capture SO_2 and CO_2, such as limestone for SO_2 absorption[1] and amines for CO_2 capture.[2,3] Although these materials can capture SO_2 and CO_2, the formation of waste byproducts and the evaporation of absorbents still exist during the processes.

Due to their extremely low vapor pressure, tunable structure, high thermal and chemical stability, and excellent solvent power, ionic liquids (ILs) are regarded as a kind of novel material for SO_2 and CO_2 capture. Until now, many types of ILs have been synthesized and used for SO_2 or CO_2 capture, especially functional ILs which can chemically absorb SO_2 and CO_2 at ambient pressure even when the volume fractions of SO_2 and CO_2 in flue gas are very low.

1,1,3,3-Tetramethylguanidinium lactate ([TMG]L),[4] regarded as the first functional IL, was broadly used for SO_2 absorption. This IL could absorb nearly 1 mol SO_2 per mol IL at 1 bar with 8% of SO_2 in simulated flue gas. Due to their excellent capacity and selectivity for SO_2 absorption, many TMG-based ILs were synthesized, such as tetramethylguanidinium tetrafluoroborate ([TMG][BF_4])[5,6] and tetramethylguanidium acrylate ([TMG]A).[7] Hydroxyl ammonium-, pyrimidine-, and imidazole-based ILs[8−12] were also synthesized to absorb SO_2 and had high capacities. Membrane and polymer technologies used in SO_2 capture by ILs could enhance the absorption.[13−16]

ILs are also used for CO_2 capture.[17−26] 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) can physically absorb CO_2 at high pressures.[17] The physical absorption of CO_2 in ILs depends on the partial pressures of CO_2. At ambient pressure, normal ILs can hardly absorb CO_2. As a result, these ILs cannot be used to capture CO_2 from flue gas. Therefore, Bates et al.[22] first synthesized a functional IL, 1-*n*-propylamine-3-butylimidazolium tetrafluoroborate, which could capture CO_2 at ambient pressure. After that, many kinds of functional ILs were synthesized, including tetraalkylammonium ILs[23] and tetrabutylphosphonium ILs.[24−26] These ILs can capture a large amount of CO_2 at ambient pressure.

As we know, flue gas is emitted at ambient pressure, and the volume fractions of SO_2 and CO_2 in flue gas are very low. To capture these acidic gases from flue gas, it is important to find functional ILs to chemically absorb acidic gases with high absorption capacities. It is obvious that the IL reported by Bates et al.[22] with a free amino on the cation can chemically absorb CO_2, and it belongs to a functional IL. However, almost all of ILs do not have free amino on the cation. It is difficult to distinguish them as functional or not before use. The experimental and simulative results showed that using cations to distinguish functional and normal ILs had some shortages, especially for SO_2 capture.[27−29] For instance, Han et al.[4] reported that the cation of [TMG]L as the functional group led to a chemical absorption, but Riisager et al.[5] found that [TMG][BF_4] that had the same cation as [TMG]L had no chemical absorption of SO_2.

Received: November 28, 2012
Revised: January 24, 2013
Published: January 29, 2013

Table 1. Acid pKa and Absorption Capacity (Mole Ratio) of SO_2 by Different ILs at 50 °C from a Simulated Gas Mixture with 3% SO_2 (Volume Fraction)

		TMG		MEA	
acids	pK_a[a]	ILs	absorption capacity	ILs	absorption capacity
acetic	4.76	[TMG][Ac]	0.49	[MEA][Ac]	0.28
benzoic	4.21	[TMG][Ben]	0.70	[MEA][Ben]	N/A[b]
lactic	3.85	[TMG]L	0.61/0.978[c]	[MEA]L	0.33
sulfurous	1.81				
trifluoroacetic	0.3	[TMG][Tfa]	0.05	[MEA][Tfa]	0.02
tetrafluoroboric	−0.4	[TMG][BF_4]	0.01/0.06[d]	[MEA][BF_4]	0.002
methanesulfonic	−0.6	[TMG][Msa]	0.01	[MEA][Msa]	0.01

[a]These data are from Wikipedia.org, which were measured at 25 °C and 100 kPa. [b]This IL cannot be synthesized by the base and the acid. [c]The experiment was carried out at 40 °C, 0.10 MPa, with 8% of SO_2 (volume fraction) reported by Han et al.[4] [d]The experiment was carried out at 25 °C, 0.10 MPa, with 10% of SO_2 (volume fraction) reported by Rasiiger et al.[5]

In our previous work,[30] we simply differentiated several ILs for SO_2 capture by pH values of the ILs. However, it is difficult to understand that, when its pH value is 5, monoethanolaminium lactate ([MEA]L) could also absorb SO_2 from flue gas.[31] Therefore, it is necessary to find the relation between ILs and capture of acidic gases. In this work, a series of ILs were synthesized and used to determine functional or normal ILs for acidic gas capture.

■ EXPERIMENTAL SECTION

Materials. SO_2 (99.95%) and N_2 (99.99%) were supplied from Beijing Haipu Gases. 1,1,3,3-Tetramethylguanidine was purchased from Baigui Chemical Co., Ltd. (Shijiazhuang, China), which was used after distillation. Monoethanolamine, lactic acid, acetic acid, benzoic acid, trifluoroacetic acid, tetrafluoroboric acid, methanesulfonic acid, tetraethylammonium hydroxide, and phenol were purchased from Shanghai Jingchun Chemical Co., Ltd. (Shanghai, China). All reagents and solvents were analytical reagents. [TMG]L and [MEA]L were synthesized and characterized following the procedure reported in the literature.[4,8] The other TMG-based and MEA-based ILs were synthesized similarly to [TMG]L and [MEA]L. N_{2222}-based ILs were synthesized following the procedure reported by Jiang et al.[23] All of the ILs were dried using the sweeping method[32] until their water contents were less than 0.1% in weight.

Apparatus and Procedures. A SO_2/N_2 gas mixture, with SO_2 content of 3% by volume, was prepared by mixing SO_2 and N_2 in a high-pressure cylinder of 40 L. The absorption experiment consisted mainly of the cylinder containing the SO_2/N_2 gas mixture, a test tube with an inner diameter of 12 mm and a length of 200 mm, a rotameter (Beijing Forth Automation Meter Factory, China), and a constant temperature water bath.

In a typical experiment, the SO_2/N_2 gas mixture bubbled through a tested IL loaded in the test tube, and the flow rate was monitored by the rotameter and calibrated by a soap film fluid meter. The test tube was partially immersed into the water bath, the temperature of which was maintained within ±0.1 °C by a temperature controller (model A2, Beijing Changliu Co., Ltd., China). After a given time for absorption, the weight of the test tube was measured, and the content of absorbed SO_2 in the IL was calculated by the weight difference. If water was present in the IL, after a given time, a small amount of IL was sampled and the content of SO_2 in IL was measured following the standard iodimetry (HJ/T 56-2000, a standard method of State Environmental Protection Administration of China). The reproducibility of the measurements was better than ±2.5%, and it was estimated that the data were accurate to ±5%.

■ RESULTS AND DISCUSSION

Functional ILs for SO_2 Absorption. The ILs used for SO_2 capture are shown in Table 1. They were synthesized by neutralization of tetramethylguanidine (TMG) or monoethanolamine (MEA) with a series of organic acids. The pK_a of the organic acids and absorption capacities of SO_2 by the ILs are also listed in Table 1.

As shown in Table 1 and Figure 1, when the base is TMG, the first three kinds of ILs, formed by acetic acid, benzoic acid, and lactic acid, can get high absorption capacities of SO_2. For instance, when [TMG]L was used to absorb 3% of SO_2 at 50 °C, the mole ratio of SO_2 to IL could reach 0.61. Han et al.[4] also reported that the mole ratio of SO_2 to IL could reach 0.978 with 8% of SO_2 at 40 °C. However, the other three ILs almost have no absorption capacity of SO_2. The mole ratio of SO_2 to [TMG][BF_4] is just 0.01 with 3% of SO_2. Compared with [TMG]L, the absorption of SO_2 by [TMG][BF_4] can be ignored. The same phenomenon also appears in MEA-based ILs, as shown in Table 1 and Figure 2. [MEA]L can absorb 0.33 mol SO_2 per mole IL, but [MEA][Msa], which is synthesized by neutralization of MEA and methanesulfonic acid, can only absorb 0.01 mol SO_2 per mole IL.

In our previous study, the absorption of SO_2 in ILs was investigated and the solubilities of SO_2 in functional ILs by

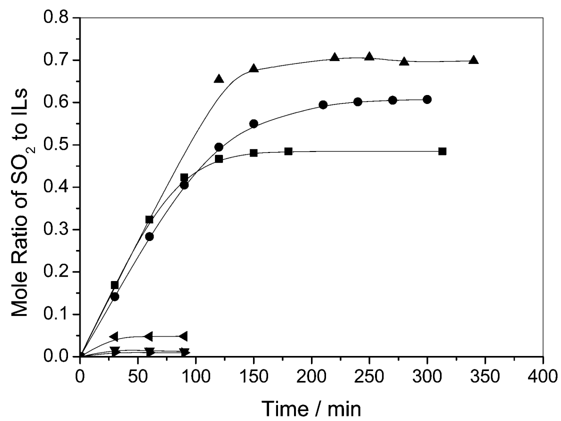


Figure 1. Absorption of SO_2 in TMG-based ILs at 50 °C: ■, [TMG]Ac; ●, [TMG]L; ▲, [TMG]Ben; ▼, [TMG]Msa; ◀, [TMG]Tfa; ▶, [TMG]BF_4.

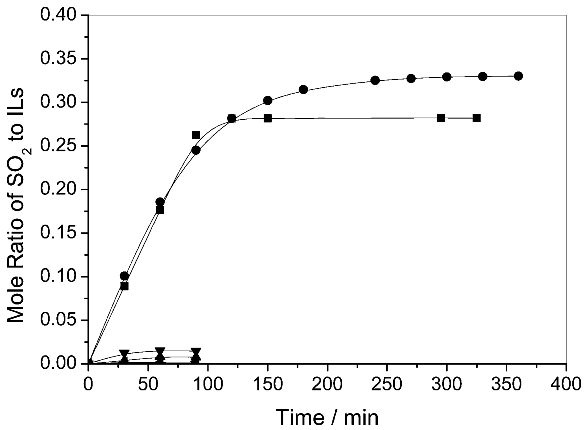


Figure 2. Absorption of SO_2 in MEA-based ILs at 50 °C: ■, [MEA]Ac; ●, [MEA]L; ▲, [MEA]Msa; ▼, [MEA]Tfa; ◀, [MEA] BF_4.

physical absorption and chemical absorption were differentiated.[33] The contribution of physical absorption of SO_2 is very small when the volume fraction of SO_2 is very low. The main factor for ILs to absorb SO_2 with 3% volume fraction is the chemical interaction between SO_2 and ILs. As a result, when an IL possesses a high absorption capacity from a gas mixture with 3% of SO_2, the IL can chemically absorb SO_2 and it is a functional IL for SO_2 capture.

Interestingly, when the pK_a of organic acids is compared with that of sulfurous acid and related to the absorption capacities of SO_2 by the ILs in Table 1, it can be seen that the pK_a of acids can be used to differentiate functional ILs from normal ILs for SO_2 capture and has relation with the absorption of SO_2. If the pK_a of an acid is larger than that of sulfurous acid, the ILs formed by the acid can be called functional ILs and it can absorb low-concentration SO_2 with high absorption capacity of SO_2. For example, the pK_a of acetic acid is 4.76, higher than that of sulfurous acid, so [TMG][Ac] is a functional IL and it can absorb a large amount of SO_2 with 3% of SO_2, but if not, the IL is just a normal IL and it has almost no absorption capacity of SO_2 with low SO_2 concentration. For example, the pK_a of trifluoroacetic acid is 0.3, much less than that of sulfurous acid, so [TMG][Tfa] is a normal IL and it can hardly absorb SO_2 with 3% of SO_2.

The above conclusion can also be obtained from the results reported previously.[4,5] For example, Han et al.[4] found the chemical interaction between SO_2 and [TMG]L from the FT-IR and NMR spectra before and after the absorption. [TMG]L is a functional IL. Rasiiger et al.[5] found that there was no chemical interaction between [TMG][BF_4] and SO_2. [TMG]-[BF_4] is a normal IL.

Why can the pK_a of the acid be used to distinguish functional ILs from normal ILs for SO_2 capture? It may be deduced from the mechanism of the SO_2 absorption by ILs, shown as follows. In our previous work,[30] it was found that the absorption of functional ILs and normal ILs was different. For functional ILs based on lactic acid, the mechanism proposed is shown in Scheme 1.

Two IL molecules can theoretically absorb one SO_2 molecule by chemical interaction, and two molecules of organic acid can be recovered. The chemical absorption amount follows the chemical equilibrium. As SO_2 can replace the organic acids in IL, the interaction between SO_2 and cation should be stronger than that between organic acid and cation. For these functional ILs, the acidity of organic acids is weaker than that of sulfurous acid. Then the organic acids are replaced, and the ILs can chemically react with SO_2. For normal ILs, as the acids forming anions are stronger than sulfurous acid, they have no chemical interaction with SO_2, and the reaction shown in Scheme 1 cannot happen. Hence, during the absorption of SO_2, only physical absorption exists. When the volume fraction of SO_2 in gas becomes very low, the absorption capacity of SO_2 by normal ILs also becomes very low, as it obeys Henry's law.

The production of organic acids during the absorption of SO_2 in functional ILs can be proven by the following evidence. [TMG][Ben] is a solid IL, and a little water, which had no effect on SO_2 absorption by IL,[34] was added in the IL to dissolve it. During the absorption, a solid product was formed. The solid product was demonstrated to be benzoic acid by FT-IR and NMR analysis shown in Figure 3 and Figure 4. This

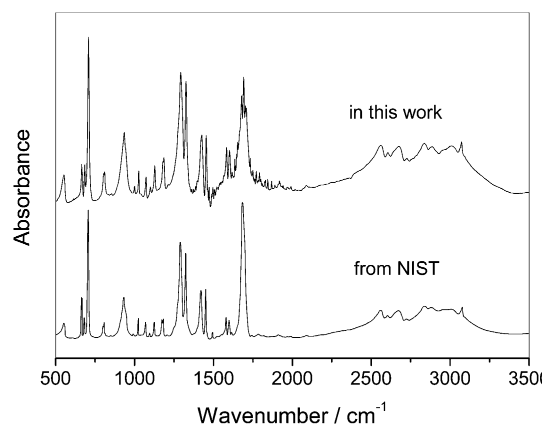
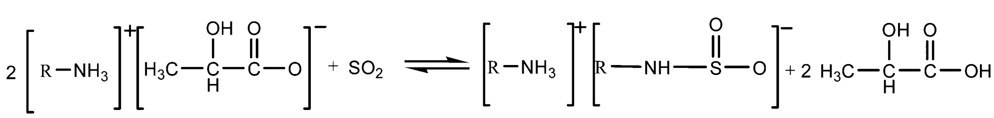


Figure 3. FT-IR spectrum of benzoic acid from web book of NIST and the solid substance in this work from the absorption of SO_2 by [TMG]Ben.

means that the IL can chemically absorb SO_2, and SO_2 can replace the organic acid in the IL. Moreover, Lee et al.[35] reported that when [BMIM][Ac] was used to absorb SO_2 from a gas stream, acetic acid was found in the outlet stream, which further proved that organic acid in the functional IL was replaced by sulfurous acid during the absorption of SO_2.

Functional ILs for CO_2 Absorption. The above method used for differentiating functional ILs from normal ILs for SO_2 capture can also be used to differentiate functional ILs from normal ILs for CO_2 capture. Table 2 shows the pK_a of acids and the capacity of CO_2 by different ILs at 50 °C with pure CO_2 at

Scheme 1. Proposed Mechanism of the Absorption of SO_2[a]



[a] $[R\text{-}NH_3]^+$ stands for cations, such as TMG^+ or MEA^+.[30]

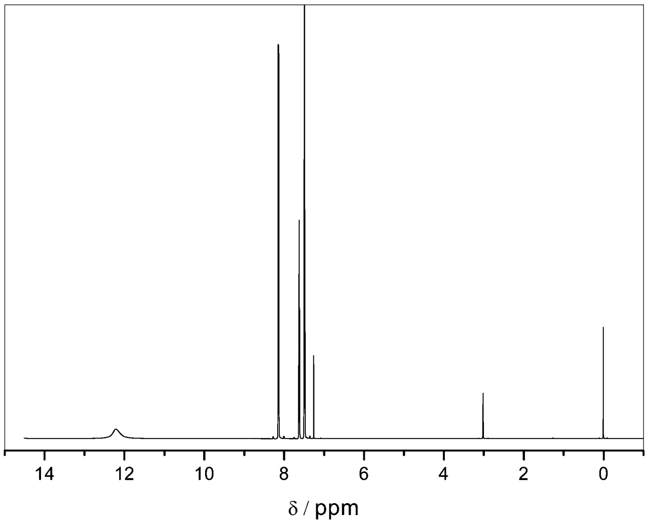


Figure 4. ^{1}H NMR spectrum of the solid substance in this work from the absorption of SO_2 by [TMG]Ben.

0.10 MPa. The ILs were synthesized from tetraethylammonium hydroxide ([N_{2222}]OH) and tetrabutylphosphonium hydroxide ([P_{4444}]OH) as bases.

It has been reported that for normal ILs, such as [BMIM][PF_6] and [BMIM][BF_4],[19,20] CO_2 can dissolve in them at high pressures. For instance, CO_2 has a solubility of 0.16 mol fraction in [BMIM][PF_6] at 1.0 MPa and 25 °C, while at 0.10 MPa, it has a solubility of about 0.018 mol fraction.[19] At ambient pressure, there is almost no absorption of CO_2 in normal ILs due to their physical absorption. Hence, ambient pressure of CO_2 was used to learn the physical and chemical absorption and determine functional ILs.

It can be seen from Table 2 that, if the pK_a of the organic acid is larger than that of carbonic acid, the IL synthesized from the organic acid can absorb large amounts of CO_2, indicating that CO_2 is chemically absorbed. The ILs can be called functional ILs for CO_2 capture. If the pK_a of the organic acid is smaller than that of carbonic acid, the IL can absorb small amounts of CO_2, indicating that CO_2 is physically absorbed by normal ILs. The ILs can be called normal ILs. For instance, as the pK_a of tetrafluoroboric acid is smaller than carbonic acid, [BMIM][BF_4] is a normal IL and can only absorb about 0.02 mol CO_2 per mole IL at 25 °C and ambient pressure. The pK_a of imidazole is 14.5, which is larger than that of carbonic acid; hence, ILs, [P_{66614}][Im][26] and [MTBDH][Im],[36] are functional ILs and can absorb more than 1 mol CO_2 per mole IL at 23 °C and ambient pressure.

CONCLUSIONS

In summary, a series of ILs were synthesized and used to absorb acidic gases with low partial pressures, and it was found that the pK_a of the organic acids was related to the absorption of acidic gases and could be used to differentiate functional from normal ILs. If the pK_a of acids is larger than sulfurous acid, the IL synthesized from the acid is a functional IL and can chemically absorb SO_2 with a large absorption capacity. If not, the IL is a normal IL and can only physically absorb SO_2. This method can also be used to determine functional ILs for CO_2 capture. On the basis of this work, to synthesize a functional IL to chemically capture SO_2 or CO_2, an organic acid that has a larger pK_a than sulfurous acid or carbonic acid should be chosen and neutralized with a strong base.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank professors Zhenyu Liu and Qingya Liu for valuable suggestions and the support of the Natural Science Foundation of China (No. 21176020) and the Program for New Century Excellent Talents in University (NCET-08-0710).

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Table 2. Acid pKa and the Absorption Capacity (Mole Ratio) of CO_2 by Different ILs at 50 °C with Pure CO_2

		[N_{2222}]OH		[P_{4444}]OH		[P_{66614}]OH	
acids	pK_a^{a}	ILs	absorption capacity	ILs	absorption capacity	ILs	absorption capacity
imidazole	14.5					[P_{66614}][Im]	1.00^d
glycine	9.60			[P_{4444}][Gly]	0.50^c		
β-/L-alanine	9.87	[N_{2222}][Ala]	0.47^b				
phenol	9.95	[N_{2222}][Pho]	0.64			[P_{66614}][Pho]	0.50^d
carbonic	6.36						
acetic	4.76	[N_{2222}][Ac]	0.24				
benzoic	4.21	[N_{2222}][Ben]	0.01				
lactic	3.85	[N_{2222}]L	0.05				

^{a}These data are from Wikipedia.org, which were measured at 25 °C and 100 kPa. ^{b}The experiment was carried out at 40 °C, 0.10 MPa, with CO_2 reported by Jiang et al.[23] ^{c}The experiment was carried out at room temperature and ambient pressure with IL supported on porous SiO_2.[24] ^{d}The experiment was carried out at 23 °C and ambient pressure for 20 min reported by Wang et al.[26]

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