



## REVIEW

### Ionic Liquids for SO<sub>2</sub> Capture: Development and Progress

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Removal of SO<sub>2</sub> from flue gas has attracted increasing interests under worldwide environmental pressure. In this paper, the recent progress of ionic liquids for SO<sub>2</sub> capture, including the absorption capacity, the desorption performance and the absorption mechanisms of guanidinium based ionic liquids, hydroxyl ammonium ionic liquids, imidazolium based ionic liquids and quaternary ammonium based ionic liquids, are reviewed. In addition, some strategies recently developed to enhance the absorption processes have been briefly introduced, such as ionic liquids mixtures, solidified ionic liquids and supported ionic liquids membranes. Moreover, the drawbacks for the industrial application of this technology have been proposed.

**Keywords:** Ionic liquids, SO<sub>2</sub>, Absorption, Mechanism.

#### INTRODUCTION

Sulfur dioxide (SO<sub>2</sub>), mainly emitted from the burning of fossil fuels, brings out severe air pollution such as acid rain. Thus SO<sub>2</sub>-emitting industries worldwide are under pressure to reduce their sulfur emissions. The technologies for the capture of SO<sub>2</sub> have attracted increasing interests, among which flue gas desulfurization (FGD) is the most efficient way. The conventional Flue gas desulfurization technologies include wet scrubbing<sup>1,2</sup> using calcium-based absorbents, dry scrubbing<sup>3</sup> and absorption by aqueous amines. However, there are large amounts of non-renewable by products such as calcium sulfate<sup>4</sup> and the consumption of water is huge during the wet scrubbing process. The dry scrubbing process is simple, but limited in industry due to the high ratio of Ca/S, low efficiency in removal of SO<sub>2</sub> and the high cost in recovery of desulfurizer. In addition, secondary pollution is the biggest problem to be solved for the absorption by aqueous amines, as the amines are easy to volatilize to flue gas with water.

Ionic liquids are molten organic salts consisting of large organic cations and inorganic or organic anion at ambient temperature. Due to the unique properties such as negligible vapour pressure, high thermal stability and excellent solvent power for a wide range of both organic and inorganic materials, ionic liquids have been considered environmental friendly solvents as water and supercritical CO<sub>2</sub>. So far, ionic liquids have been widely used in organic synthesis<sup>5</sup>, extraction separation<sup>6</sup>, analytical chemistry<sup>7</sup>, biocatalysts and nanophase materials<sup>8</sup>.

In recent years, ionic liquids have been proposed to remove acid gases such as CO<sub>2</sub><sup>9</sup>, SO<sub>2</sub> and H<sub>2</sub>S. Compared to the traditional industrial solvents, ionic liquids present significant advantages, especially in complex systems, as they could be tuned by appropriate selection of the structures of their cations and anions. In this work, ionic liquids used for SO<sub>2</sub> capture and separation from flue gas or mixed gas have been briefly summarized.

**Ionic liquids used for SO<sub>2</sub> capture:** Ionic liquids used for removal of SO<sub>2</sub> was first synthesized in 2004<sup>10</sup>, after which much attention has been drawn to the development of ionic liquids for removal of SO<sub>2</sub>. According to cations, the ionic liquids can be classified as guanidinium based, hydroxyl ammonium, imidazolium based and quaternary ammonium based ionic liquids. The performance of absorption and desorption of SO<sub>2</sub> has been studied. In addition, some strategies to improve the performance have been developed, such as ionic liquids mixtures, solidified ionic liquids and supported ionic liquids membranes.

**Guanidinium based ionic liquids:** The first ionic liquids used for capture of SO<sub>2</sub> was synthesized by direct neutralization of 1,1,3,3-tetramethylguanidine (TMG) and lactic acid<sup>10</sup>. The solubility of SO<sub>2</sub> in the ionic liquids [TMG][LAC] (Fig. 1) was as high as 1.7 mol SO<sub>2</sub>/mol ionic liquids at 40 °C and 120 KPa. However, when the ionic liquids ([TMG][LAC]) was used to remove SO<sub>2</sub> from the simulated flue gases, a mixture of N<sub>2</sub> and SO<sub>2</sub> with a SO<sub>2</sub> content of 8 % by volume, it exhibit a lower absorption capacity of 0.978 mol SO<sub>2</sub>/mol ionic liquids

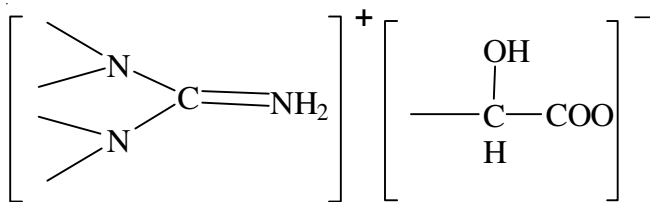


Fig. 1. Structure of ionic liquids [TMG][Lac]

at 40 °C, 101.325 KPa. The absorption capacity decreased with temperature increasing and the molar ratio of SO<sub>2</sub> to ionic liquids at 60 and 94 °C were only 0.775 and 0.512, respectively. However, this ionic liquid is limited in practice because of relatively low thermal stability, which results in that only a fraction of the absorbed gas could be thermally released before degradation of the ionic liquids occurs.

The absorption of CO<sub>2</sub> by ionic liquids [TMG][Lac] was also studied in their work. The result showed that this ionic liquid presents high selectivity towards SO<sub>2</sub>, as the absorption capacity of CO<sub>2</sub> by the ionic liquid was very low (0.012 mol CO<sub>2</sub>/mol ionic liquid). The selectivity of [TMG][Lac] towards CO<sub>2</sub> and SO<sub>2</sub> was also studied using molecular dynamics simulations<sup>11</sup>. The simulation result showed that CO<sub>2</sub> has relatively poor interaction with the cations and the anions of the ionic liquids, while SO<sub>2</sub> has high interaction, especially with the [LAC] anion. Therefore, the ionic liquid [TMG][Lac] has a low absorption capacity towards CO<sub>2</sub>, while the solubility of SO<sub>2</sub> is fairly high. This study lays the basic theory foundation for improvement of ionic liquids used for capture of SO<sub>2</sub>. Prasad *et al.*<sup>12</sup> also studied the interaction between SO<sub>2</sub> and the ionic liquids [TMG][Lac] from first-principle calculations. The result indicated that the key factor on the solubility of SO<sub>2</sub> is the interaction between SO<sub>2</sub> and the anion in ionic liquids. So the relatively high solubility of SO<sub>2</sub> in [TMG][Lac] is attributable to the strong association of SO<sub>2</sub> with the anion [Lac].

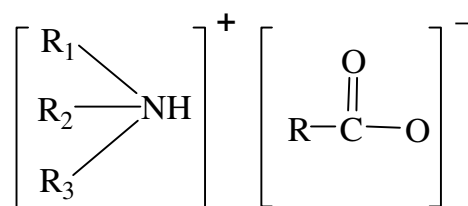
Huang *et al.*<sup>13</sup> prepared three new guanidinium based ionic liquids used for SO<sub>2</sub> capture. The ionic liquids, [TMGH][BF<sub>4</sub>] and [TMGH][Tf<sub>2</sub>N], were prepared by direct neutralization of TMG solution with aqueous fluoroboric acid and HBTa respectively, while the ionic liquid ([TMGB<sub>2</sub>][BTA]) was synthesized by alkylated TMG solution. The ionic liquids were found to absorb a large amount of SO<sub>2</sub> gas corresponding to molar ratios of SO<sub>2</sub> to ionic liquids of 1.27, 1.18, respectively at 20 °C, 101.325 KPa. The SO<sub>2</sub> gas can be completely desorbed by heating to about 140 °C. However, when the ionic liquids were used to remove SO<sub>2</sub> from simulated flue gases (N<sub>2</sub> and SO<sub>2</sub> with a SO<sub>2</sub> molar content of 10 %), the absorption capacity was fairly low due to competing N<sub>2</sub> absorption.

Later, the strategy that hydroxyl group was grafted on the cations was proposed to improve the absorption performance of the ionic liquids<sup>14</sup>. A series of modified ionic liquids with alcohol-containing alkyl chains on the cations were synthesized and used for SO<sub>2</sub> capture. The ionic liquids ([TMGHPO][Tf<sub>2</sub>N] and [TMGHPO<sub>2</sub>][Tf<sub>2</sub>N]) exhibited high solubility with a ratio of SO<sub>2</sub> to ionic liquids of 2.01, which illustrated that hydroxyl groups on the cations favour the absorption of SO<sub>2</sub>. This result also indicated that the premier interaction was found between the cations of the ionic liquids and SO<sub>2</sub>. However, when the

two ionic liquids were used to remove SO<sub>2</sub> from 10 % SO<sub>2</sub> gas (10 mole % in N<sub>2</sub>), the absorption capability were still relatively low with the ratio of SO<sub>2</sub> to ionic liquids being 0.15 and 0.20 for [TMGHPO][Tf<sub>2</sub>N] and [TMGHPO<sub>2</sub>][Tf<sub>2</sub>N], respectively.

It can be concluded that the guanidinium based ionic liquids have good performance in absorption of pure SO<sub>2</sub> gas and that the absorbed SO<sub>2</sub> can be released by heating or vacuum. However, the absorption capability of SO<sub>2</sub> from simulated flue gases is lower. Since the key interaction exists between the cations and SO<sub>2</sub>, improvement can be made based on the cations.

**Hydroxy ammonium ionic liquids:** Hydroxy ammonium ionic liquids are basically prepared by neutralization of organic amine with different organic acids. Yuan *et al.*<sup>15</sup> synthesized a series of hydroxy ammonium ionic liquids (Fig. 2), which present a high solubility of SO<sub>2</sub>. Among these ionic liquids, 2-hydroxyethyl ammonium exhibited the highest absorption capacity with a value of 1.04 mol SO<sub>2</sub>/mol ionic liquids. The absorbed SO<sub>2</sub> could be released under vacuum or by heating and the ionic liquids can be recycled for 4 times with a recovery larger than 90 %. The absorption capability of these ionic liquids showed close association both with the cations and the anions. The study showed that the effect of cations on the solubilities of SO<sub>2</sub> followed the sequence: 2-hydroxyethylammonium > tri-(2-hydroxyethyl) ammonium > 2-(2-hydroxyethoxy) ammonium, while the effect of anions is lactate > acetate > formate.



R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>: H or HO-CH<sub>2</sub>-CH<sub>2</sub>- or HO-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-  
R: H, CH<sub>3</sub> and CH<sub>3</sub>-CH(OH)

Fig. 2. Structure of the hydroxy ammonium ionic liquids

Compared with guanidinium based ionic liquids, hydroxy ammonium ionic liquids show a relatively lower absorption capability for SO<sub>2</sub>. However, the decomposition temperature of the hydroxy ammonium ionic liquids is mostly higher than that of guanidinium based ionic liquids, meaningly that the hydroxy ammonium ionic liquids have higher thermal-stability.

**Imidazolium based ionic liquids:** Imidazolium based ionic liquids are based on the imidazole ring and have attracted much attention due to their unique properties. The imidazolium based ionic liquids, [BMIM][BTA] and [BMIM][BF<sub>4</sub>], were firstly used for SO<sub>2</sub> capture<sup>12</sup>. The ionic liquids can physically absorb large amounts of SO<sub>2</sub> with a capacity of 1.1-1.6 mol SO<sub>2</sub>/mol ionic liquids and the SO<sub>2</sub> can be completely desorbed by heating to about 140 °C. However, the absorption capability of SO<sub>2</sub> from the simulated flue gases is similarly low.

Jessica *et al.*<sup>16</sup> measured the solubility of SO<sub>2</sub> in the ionic liquids [HMIM][Tf<sub>2</sub>N] and [HMPY][Tf<sub>2</sub>N]. The result suggested that the solubility in [HMIM][Tf<sub>2</sub>N] was extremely high and that the absorption capacity can be as high as 1.6 mol

SO<sub>2</sub>/mol ionic liquids at 25 °C and 3.44 atm. Additionally, the Henry's law constants were also calculated in their work. Compared to that of CO<sub>2</sub>, there was over an order of magnitude decrease in the Henry's law constants for SO<sub>2</sub>. This result illustrated that these ionic liquids present high selective towards SO<sub>2</sub>.

A series of imidazolium based ionic liquids with halide anions, such as [BMIM][Cl], [BMIM][Ac], [BMIM][BF<sub>4</sub>], [BMIM][PF<sub>6</sub>] and [BMIM][MeSO<sub>4</sub>], were also prepared for SO<sub>2</sub> capture and the effect of different anions was also investigated<sup>17</sup>. These ionic liquids exhibited high solubility within the range of 1.91-2.22 mol SO<sub>2</sub>/mol ionic liquids at 50 °C and the solubility followed the order: Br > Cl > I. However, the SO<sub>2</sub> absorbed by [BMIM][Cl] and [BMIM][Ac] couldn't be completely released when heated. It is due to the strong interaction between SO<sub>2</sub> and the relative strong basic anions such as [Ac].

In order to improve the absorption capability of ionic liquids with a less basic anion, the cations were functionalized with ether groups, considering that SO<sub>2</sub> could interact with oxygen atoms in the ether groups. The ionic liquids, ether-functionalized imidazolium methanesulfonates (Fig. 3), were found to have pretty high SO<sub>2</sub> solubility with a value of at least 2 moles SO<sub>2</sub>/mol ionic liquids at 30 °C and 1 atm<sup>18</sup>. The SO<sub>2</sub> can be readily and completely desorbed by heating at 100 °C in a N<sub>2</sub> flow and the ionic liquids can be reused for 5 times without loss of absorption capability.

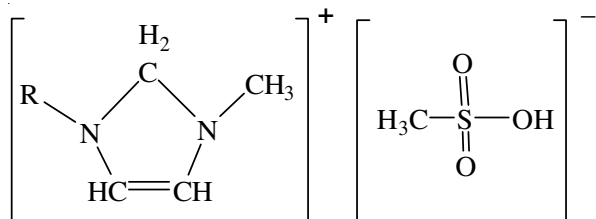


Fig. 3. Structure of ionic liquids [EMIM][MeSO<sub>3</sub>]

Another strategy to improve the absorption capacity is to increase the number of interaction sites between the ionic liquids and SO<sub>2</sub>. Two azole-based ionic liquids, [P<sub>6614</sub>][Tetz] and [P<sub>6614</sub>][Im], were prepared by neutralization of tetrazole (Tetz) or imidazole (Im) and solution of phosphonium hydroxide in ethanol<sup>19</sup>. The molar ratios of SO<sub>2</sub> to ionic liquids for [P<sub>6614</sub>][Tetz] and [P<sub>6614</sub>][Im] decreased from 3.72 to 1.54 and 4.80 to 2.07, respectively, as the pressure decreased from 1.0 to 0.1 atm. The ionic liquids, [P<sub>6614</sub>][Tetz], can be reused for 28 times.

Since the thermal stability of some ionic liquids is low, the degradation of the ionic liquids may occur during the desorption processes of SO<sub>2</sub> at high temperatures. For the purpose of improving thermal stability, several novel ionic liquids were prepared and used to separate SO<sub>2</sub> from the simulated flue gases<sup>20</sup>. The ionic liquids were stable below 150 °C without any loss of weight. The effect of the cations on the SO<sub>2</sub> absorption capacity followed the order: [N<sub>2222</sub>] > [BMIM] ≈ [HMIM] > [TMG] > [MEA]. The absorption capacity of [BMIM][Lac] was 0.807 mol SO<sub>2</sub>/mol ionic liquids at 40 °C and the ionic liquids could be recycled for 5 times without obvious loss of capacity.

In summary, much work has been done on the development of iminazolium based ionic liquids. Efforts have been made to improve the absorption capacity of the ionic liquids as well as thermal stability.

**Quaternary ammonium based ionic liquids:** Guo *et al.*<sup>21</sup> synthesized a series of caprolactam tetrabutyl ammonium bromide ([CPL][TBAB]) ionic liquids and the solubility of SO<sub>2</sub> was measured. The absorption capacity of SO<sub>2</sub> in the ionic liquids at 35 °C and 101.325KPa can be as high as 1.84 mol/mol ionic liquids. The ionic liquids can be reused for 6 times with a high efficiency of desorption (99 %). A mixture of ionic liquids [CPL][TBAB] and sodium humate (HA-Na) solution was also used to remove SO<sub>2</sub> from flue gas<sup>22</sup>. The result showed that the maximum absorption efficiency of SO<sub>2</sub> approached almost 95 %, allowing this mixed solution to be used repeatedly for 5 cycles at 25 °C and atmospheric pressure.

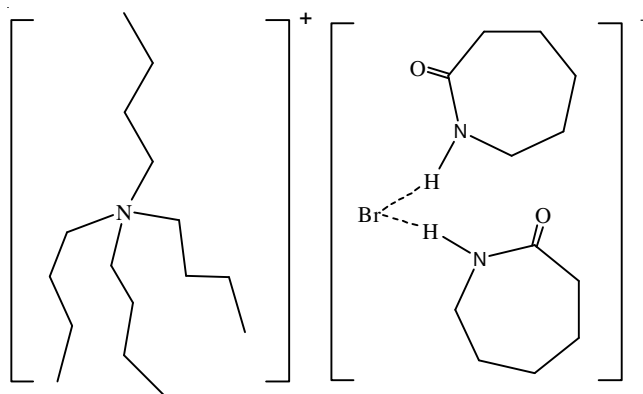


Fig. 4. Structure of ionic liquids [CPL][TBAB]

**Ionic liquids mixtures:** Ionic liquids have attracted extensive interests from the research community and are considered to be of potential use in flue gas desulfurization processes. However, currently available ionic liquids are all expensive. In addition, the high viscosity of ionic liquids induces the low heat and mass transfer performance in SO<sub>2</sub> absorption processes. These two factors limit the industrial application of ionic liquids in flue gas desulfurization processes. So, it is necessary to develop ionic liquids with low viscosity and low cost as well as high SO<sub>2</sub> absorption capacity and absorption rate. A new strategy to solve this problem is to blend ionic liquids with water or other organic solvent to form hybrid absorbents, which has been adopted in CO<sub>2</sub> capture<sup>23-26</sup>.

The solubility of SO<sub>2</sub> in [CPL][TBAB] was measured and the ionic liquids exhibited a high affinity for SO<sub>2</sub>. However, the viscosity of the ionic liquids is high, which makes the mass and heat transfer difficult. So the mixture of [CPL][TBAB] and water was designed to remove SO<sub>2</sub>, as the viscosity decreased with the water content increased<sup>27</sup>. Two phases appeared when SO<sub>2</sub> was introduced into the mixture. The SO<sub>2</sub> was concentrated in the lower phase and the absorption capacity can be as high as 52.29 g/100 g solution. After the two phases were separated, the absorbed SO<sub>2</sub> can be released by heating under reduced pressure.

Three hydroxyl ammonium dicarboxylate ionic liquids were also used to absorb SO<sub>2</sub> with DMEA<sup>28</sup>. The hybrid solvents exhibited very low viscosity, which was beneficial to

the transfer of SO<sub>2</sub> absorption. The solubility of SO<sub>2</sub> increased with the DMEA content increased, but the desorption became difficult. So there existed optimal DMEA / ionic liquids molar ratio. Due to the low viscosity, the SO<sub>2</sub> can be absorbed by the mixture very rapidly. After the two layers were separated, the SO<sub>2</sub> can also be released from the lower layer by heating under reduced pressure.

Recently, another eutectic mixture has caused wide interest. The eutectic ionic liquids are made up of organic quaternary ammonium salts and low molecular weight amides. These eutectic ionic liquids exhibit significant properties such as low viscosity and high solubility. Five amide-thiocyanates eutectic ionic liquids, acetamide-KSCN (3:1), caprolactam (CPL)-KSCN (3:1), acetamide-NH<sub>4</sub>SCN (3:1), CPL-NH<sub>4</sub>SCN (3:1) and urea-NH<sub>4</sub>SCN (3:2), were prepared for SO<sub>2</sub> capture<sup>29</sup>. The solubility of SO<sub>2</sub> in these ionic liquids was quite high and the absorption capacity of acetamide-KSCN (3:1) could reach 5.17 mol SO<sub>2</sub> / mol ionic liquids at 20 °C and 1 atm. The absorbed SO<sub>2</sub> can be easily released at 70 °C under vacuum and the ionic liquids can be reused for at least 5 times without any loss of absorption capacity.

**Solidified ionic liquids:** Ionic liquids have been widely used in flue gas desulfurization, but the high viscosity could be operational drawback as well as a cause for slow sorption rate because of relatively small gas-liquid interface and slow diffusion rate of gas molecules in viscous media. Ionic liquids are solidified as ionic polymers or porous silica supported ionic liquids so as to enlarge the gas-liquid interface.

To improve the absorption capacity and rate, crosslinked porous particles based on the ionic copolymer of 1,1,3,3-tetramethylguanidine acrylate and N,N-methylenebisacrylamide were prepared<sup>30</sup>. The particles demonstrated high absorption capacity for SO<sub>2</sub>, 0.26 g SO<sub>2</sub> per g P(TMGA-co-MBA) and high absorption rate. The absorbed SO<sub>2</sub> can be released by heating under vacuum and the SO<sub>2</sub> absorption properties kept unchanged during the SO<sub>2</sub> absorption/desorption cycles.

[TMG][Lac] was immobilized into porous silica particles by a simple impregnation-vaporization method. The [TMG][Lac] supported particles present large specific surface area and high absorption capacity for SO<sub>2</sub><sup>31</sup>. The result showed that the absorption capacity increased from 0.61 g SO<sub>2</sub>/g [TMG][Lac] at 30 °C to about 0.88 g SO<sub>2</sub>/g [TMG][Lac] at 20 °C for [TMG][Lac]-SiO<sub>2</sub> 1/1 and from 0.67 to 0.95 for [TMG][Lac] 0.5/1. The solid ionic liquids particles can be recycled for several times without loss of absorption capability. In addition, the silica supported ionic liquids exhibit good mechanical strength and thermal stability. So the ionic liquids particles are expected to be widely used in flue gas desulfurization.

**Supported ionic liquids membranes:** The supported liquid membranes (SLMs) are porous materials whose pores are filled with liquids. Supported ionic liquids membranes (SILMs) are developed for SO<sub>2</sub> absorption or separation, as the nonvolatility and incredible stability of ionic liquids enable the membrane separation process to avoid the loss of the supported liquid.

The permeability of SO<sub>2</sub> in five imidazolium based ionic liquids supported on the polyethersulfone microfiltration membranes was measured at 25-45 °C and atmospheric

pressure<sup>32</sup>. The SO<sub>2</sub> selectivity using supported ionic liquids membranes was 9-19 times that of CO<sub>2</sub>. So the supported ionic liquids membranes are expected to have widely application in recovery of SO<sub>2</sub> from flue gas or gas mixtures.

Two kinds of supported ionic liquids membranes used for SO<sub>2</sub> separation were prepared using porous membranes made of PVDF with hydrophobic materials. The membranes were soaked in the ionic liquids [MIM][ace] and [BIM][ace]<sup>33</sup>. The permeabilities of air, CO<sub>2</sub>, 10 vol. % SO<sub>2</sub>-air were obtained. The permeability of air was one order of magnitude lower than that of CO<sub>2</sub> and it was also lower than that of the mixture of air and 10 vol. % SO<sub>2</sub>. The supported ionic liquids membranes made of hydrophilic PVDF and [BIM][ace] showed the highest permeability and are expected to be used in SO<sub>2</sub> separation processes.

In order to enhance the selectivity, α-D-glucose pentaacetate (GPA) was impregnated in supported ionic liquids membranes and used for the separation of CO<sub>2</sub> and SO<sub>2</sub> or separation of SO<sub>2</sub> from flue gas stream<sup>34</sup>. It was found that selectivities of CO<sub>2</sub>/N<sub>2</sub> and SO<sub>2</sub>/N<sub>2</sub> were obviously improved compared with supported ionic liquids membranes without GPA. So the supported ionic liquids membranes with GPA are expected to have a potential application for the separation of CO<sub>2</sub> and SO<sub>2</sub> from a flue gas stream.

**Mechanism of SO<sub>2</sub> absorption by ionic liquids:** In order to design more effective ionic liquids for industrial application, it is necessary to get a clear understanding of the mechanism of the SO<sub>2</sub> absorption processes. The mechanism has been extensively discussed using detection means such as FT-IR, NMR and UV. The mechanism of absorption by some ionic liquids having been studied so far is presented in Table-1.

TABLE-1  
MECHANISM OF SO<sub>2</sub> ABSORPTION  
IN DIFFERENT IONIC LIQUIDS

Ionic liquids	Mechanism
[TMG][Lac] <sup>10</sup>	Physical and chemical absorption
[HMIM][Tf <sub>2</sub> N]	Physical <sup>16</sup> or Chemical <sup>35</sup> absorption
[HMPY][Tf <sub>2</sub> N] <sup>16</sup>	Physical absorption
[TMG][BF <sub>4</sub> ] <sup>12</sup>	Physical absorption
[TMG][BTA] <sup>12</sup>	Physical absorption
[BMIM][BF <sub>4</sub> ] <sup>12</sup>	Physical absorption
[BMIM][BTA] <sup>12</sup>	Physical absorption
[TMGB <sub>2</sub> ][BTA] <sup>12</sup>	Physical absorption
Hydroxyl ammonium ILs <sup>15</sup>	Physical and chemical absorption
[TMGHPO][BF <sub>4</sub> ] <sup>14</sup>	Physical absorption
[TMGHPO <sub>2</sub> ][BF <sub>4</sub> ] <sup>14</sup>	Physical absorption
[P <sub>66614</sub> ][Tetz] <sup>19</sup>	Chemical absorption
[P <sub>66614</sub> ][Im] <sup>19</sup>	Chemical absorption
[TMGHH][Tf <sub>2</sub> N] <sup>30</sup>	Physical absorption
[TMGHH][Lac] <sup>36</sup>	Physical absorption and chemical absorption
[BMIM][Ac] <sup>35</sup>	Chemical absorption
[BMIM][MeSO <sub>4</sub> ] <sup>35</sup>	Chemical absorption
[EMIM][C(CN) <sub>3</sub> ] <sup>37</sup>	Physical absorption
[EMIM][SCN] <sup>27</sup>	Chemical absorption
[Acetamide][KSCN] <sup>27</sup>	Physical absorption
[CPL][KSCN] <sup>27</sup>	Physical absorption
[Acetamide][NH <sub>4</sub> SCN] <sup>27</sup>	Physical absorption
[CPL][NH <sub>4</sub> SCN] <sup>27</sup>	Physical absorption
[Urea][NH <sub>4</sub> SCN] <sup>27</sup>	Physical absorption

**Physical and chemical absorption:** The absorption processes of SO<sub>2</sub> by ionic liquids [TMG][Lac] were discussed under different pressures by Wu *et al.*<sup>10</sup>. It was considered to be chemical absorption lower than 100 KPa and both physical and chemical absorption higher than 120 KPa. The mechanism of chemical absorption process is showed in Fig. 5. It was considered that SO<sub>2</sub> reacts with the NH<sub>2</sub> group on the cation, while the O atom on S=O probably forms intramolecular hydrogen bond with the H atom of the amine.

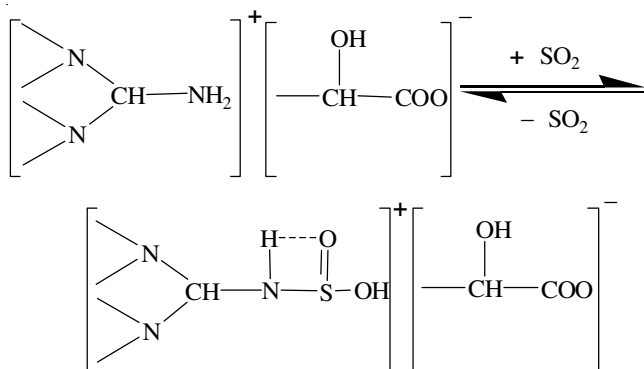


Fig. 5. Reaction between the ionic liquids [TMG][Lac] and SO<sub>2</sub>

The absorption of SO<sub>2</sub> by hydroxyl ammonium ionic liquids were also considered to be both physical and chemical absorption processes<sup>15</sup>. The mechanism was considered that the SO<sub>2</sub> molecule attacks the -NH group in the cations of the ionic liquids and forms the N-S bond and that simultaneously the carboxylate is turned to carboxylic acid (Fig. 6).

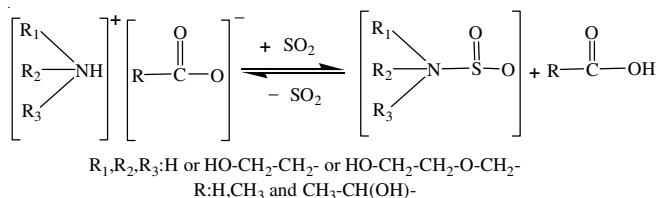


Fig. 6. Reaction between hydroxyl ammonium ionic liquids and SO<sub>2</sub>

**Physical absorption:** Anderson *et al.*<sup>16</sup> studied the solubility of SO<sub>2</sub> in [HMIM][Tf<sub>2</sub>N] and [HMPY][Tf<sub>2</sub>N]. The high solubility was considered to be based on physical sorption processes. The absorption processes by amide-thiocyanates eutectic ionic liquids are also found to be physical processes. But the mechanism of the interaction between ionic liquids and SO<sub>2</sub> have not been discussed<sup>27</sup>.

The absorption processes by ionic liquids [TMGH][Tf<sub>2</sub>N], [TMGHPO][Tf<sub>2</sub>N] and [TMGPO<sub>2</sub>][Tf<sub>2</sub>N] *etc* had been analyzed. It was concluded that no new chemical bonds appeared during the absorption process according to the Raman and UV spectra. The primer interaction was suggested to be vander Waals type of bonding between the delocalized π bonding systems in the cations and SO<sub>2</sub>. The physical absorption processes were explained using the local structure in ionic liquids. Due to the polarity of SO<sub>2</sub> molecule, the void space originally available in ionic liquids could be taken up much more easily by SO<sub>2</sub>. Since the molecular radius of SO<sub>2</sub> is larger than the cavities in ionic liquids, the volume of ionic liquids increased significantly during gas absorption<sup>13,14</sup>.

**Chemical absorption:** Shiflett *et al.*<sup>35</sup> studied the chemical absorption by ionic liquids [Bmim][Ac], [Bmim][MeSO<sub>4</sub>], [Hmim][Tf<sub>2</sub>N] systematically. The pressure-temperature-composition (PTx) data was measured and analyzed using an equation-of-state model. Then, excess thermodynamic functions and Henry's constants obtained from the PTx data were used to classify whether the absorption is physical or chemical type. According to the excess Gibbs, enthalpy functions and the magnitude of the Henry's constants, the absorption processes were considered to be chemical absorption processes.

## Conclusion

In summary, much work has been done on the synthesis and characterization of ionic liquids used for removal of SO<sub>2</sub> as well as the mechanism of the absorption processes. Different kinds of ionic liquids have been prepared and some of them exhibit high absorption capacity for SO<sub>2</sub>. In addition, several strategies have been proposed to improve the performance of ionic liquids, such as solid ionic liquids, supported ionic liquids membranes and ionic liquids mixtures. However, the technology has not been widely used in industry due to the high cost of ionic liquids, complexity of flue gas and other factors. So there is still much work to be done:

(1) It is of great necessary to find a way to reduce the high cost of ionic liquids.

(2) Considering flue gas in practice is about 110-160 °C, high thermal-stable ionic liquids are expected to be developed and the performance of SO<sub>2</sub> absorption to be studied systematically.

(3) Many ionic liquids so far exhibit high absorption capability for pure SO<sub>2</sub>, but low absorption capacity for SO<sub>2</sub> from the simulated flue gases. So the effect of other gases in flue gas on the performance of ionic liquids needs to be investigated so as to design more effective ionic liquids.

(4) There is not a common or clear understanding of the mechanism of the sorption of SO<sub>2</sub> by ionic liquids.

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