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# Unexpectedly efficient SO<sub>2</sub> capture and conversion to sulfur in novel imidazole-based deep eutectic solvents

Received 00th January 20xx, Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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Published on 07 July 2018. Downloaded by University of Cambridge on 7/9/2018 7:32:40 PM

An innovative strategy for sustainable SO<sub>2</sub> capture and conversion in novel imidazole-based deep eutectic solvents (DESs) is demonstrated in this work. These DESs exhibit an extremely high SO<sub>2</sub> loading capacity (up to 1.39 g/g) and excellent reversibility (15 recycles). The absorbed SO<sub>2</sub> can be rapidly converted in situ to sulphur (up to 99% conversion) in the presence of H<sub>2</sub>S at room temperature without any additives.

Controlling the SO<sub>2</sub> concentration in the atmosphere has been a worldwide urgent issue to be solved.<sup>1</sup> Up to now, SO<sub>2</sub> capture is still highly desirable from the viewpoint of sustainable development strategy of environment. Although many conventional methods had been developed, they are always accompanied with some inevitable shortcomings.<sup>2</sup> Typically, amines scrubbing and limestone-gypsum methods have been widely used for SO<sub>2</sub> capture in industry. However, the former suffers from solvent loss because of the high volatility of solvents.<sup>2a-e</sup> Limestone-gypsum bears huge amounts of CaSO<sub>4</sub> and waste-water, resulting in secondary pollution to the environment.<sup>2f.g</sup> Therefore, development of efficient and reversible materials for the capture of SO<sub>2</sub> is of critical importance.

lonic liquids (ILs)<sup>3</sup> have been widely used in the field of acid gas separation (SO<sub>2</sub>, <sup>3a</sup> CO<sub>2</sub>, <sup>3b</sup> H<sub>2</sub>S, <sup>3c</sup> NO<sup>3d</sup> etc.) because of their unique properties, such as high thermal stability, negligible vapor pressure, and adjustable chemical structure. Among these ILs, azole-based, <sup>4a</sup> ether-functionalized, <sup>4b</sup> and guanidine-functionalized<sup>4c</sup> ILs show considerable SO<sub>2</sub> absorption capacity. Although significant progresses have been made in improving the absorption of SO<sub>2</sub> in ILs, the gravimetric capacities of SO<sub>2</sub> in these ILs are still relatively low. For example, 0.75 g SO<sub>2</sub> per gram IL was obtained in ether-functionalized imidazolium methanesulfonates [E<sub>3</sub>Mim][H<sub>3</sub>CSO<sub>3</sub>].<sup>4b</sup> Nevertheless, the synthesis of these functional ILs is not easy, and the application of ILs in SO<sub>2</sub> removal is also limited by the high expenses.<sup>4a,b</sup>

Deep eutectic solvents (DESs)<sup>5</sup> are known as a kind of green solvents and IL analogues because of the similar characteristics and properties. It allows DES to replace or improve upon ILs in many applications. Because of their advantages of low volatility, low price, and easy preparation, DESs have been widely used in extractions, metal processing, organic synthesis, and gas separation applications.<sup>5</sup> Though some DESs, such as choline chloride (ChCl)glycerol,<sup>6a</sup> ChCl-thiourea,<sup>6b</sup> betaine-ethylene glycol (EG),<sup>6c</sup> 1-ethyl-3methylimidazolium chloride (EmimCl)-EG<sup>6d</sup>, and azole-based deep eutectic solvents7b have been reported as efficient absorbent for SO2, the method to convert DESs absorbed SO2 in situ is still unknown.<sup>6,7</sup> Furthermore, SO<sub>2</sub> absorption and conversion in the same medium is a more effective strategy to solve the problem induced by SO<sub>2</sub> emission. To the best of our knowledge, even for ILs, only few works concern the conversion of SO<sub>2</sub>, not to mention the SO<sub>2</sub> capture and conversion in the same medium.<sup>8,9</sup> Herein, we develop an innovative strategy for SO<sub>2</sub> capture and conversion to sulfur in imidazole-based DESs containing acetamide (AA) with unexpectedly high efficiency.

All imidazole-based DESs were prepared by simply mixing imidazolium salts (EmimCl, BmimCl, HmimCl, and BmimBr) and AA with stirring and heating at 80 °C (See ESI ‡). Though melting points of AA and EmimCl are 81 and 78 °C respectively, the EmimCl-AA (2:1) can exist as a liquid at room temperature. Correspondingly, no phase transition was discovered in the temperature range of room temperature to -30 °C for EmimCl-AA (2:1, mole ratio) from the result of DSC. Others DESs are also liquids even at 5 °C, meaning that these DESs can be used directly for SO<sub>2</sub> capture at room temperature. The significant change of melting point may be caused by the strong interaction of intermolecular hydrogen bonding.<sup>5e</sup> The density and viscosity of these DESs were measured and the results are listed in Fig. S1. It was found that the densities of these DESs decrease linearly with increasing of temperature, whereas the viscosities of DESs decrease in an exponential manner. The onset decomposition temperatures of the DESs investigated are above 120 °C according to the TGA curves (Fig. S2). The thermal stabilities are thus enough to ensure SO<sub>2</sub> desorption at 80 °C.

The capture of  $SO_2$  was carried out according to the method reported in literature.<sup>4a</sup> As shown in Fig. 1, among these DESs, the EminCl-AA (2:1) exhibits unexpectedly the best performance with a

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 $<sup>\</sup>pm$ Electronic supplementary information (ESI) available: Details on preparation of DESs, SO<sub>2</sub> absorption and desorption, and DES-mediated Claus process.

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loading capacity of 1.39 g/g (7.63 mol/mol) (Table 1), obviously higher than those previously reported values of DESs,<sup>6,7</sup> ILs,<sup>4</sup> or classical absorbents (See Table S1).<sup>2a-e</sup> The SO<sub>2</sub> absorption amount increases with the EmimCl concentration in the DESs, and the better loading capacities for imidazole chloride salts [BmimCl-AA (1:1) vs BmimBr-AA (1:1)] may be due to the strong charge transfer interaction of acidic SO<sub>2</sub> with Cl<sup>-.10</sup> The results indicated that the imidazole-based DESs are appreciable both in terms of gravimetric and molar absorption capacities of SO<sub>2</sub>. Because water vapor always coexists with SO<sub>2</sub> in real fuel gas, the effect of water on SO<sub>2</sub> absorption in EmimCl-AA (2:1) was thus evaluated (Fig. S3). The absorption rate was slightly affected by the water content, while absorption capacity decreased with increasing contents of water. Moreover, we also studied the SO<sub>2</sub> absorption capacities of EmimCl and AA. Since the EmimCl and AA are solid at 20 °C and 1.0 bar, both were dissolved in ethylene glycol and the absolute uptakes of SO2 were calculated. The solubilities of SO2 in EmimCl and AA are 1.34 and 0.18 g/g, respectively, giving a theoretical uptake of 0.98 g/g for the ideal EmimCl-AA (1:1) solvent. Interestingly, it is significantly lower than that of the real EmimCl-AA (1:1) solvent (1.25 g/g), indicating that coexistence of EmimCl and AA is crucial to increase the absorption of SO<sub>2</sub>.



Fig. 1 Comparison of  $SO_2$  absorption in imidazole-based DESs as a function of time at 20 °C and 1.0 bar.

Table 1 Comparison of  $SO_2$  absorption capacities in different DESs and some ILs at 20 °C.

Solvents (mole ratio)	Absorption capacities of SO <sub>2</sub> <sup>a</sup>		Ref.
	1.0 bar	0.1 bar	_
EmimCl-AA (2:1)	1.39 (7.63)	0.49 (2.70)	This
EmimCl-AA (1:1)	1.25 (4.01)	0.46 (1.48)	work
EmimCl-AA (1:2)	1.13 (4.69)	0.27 (1.12)	
BmimCl-AA (1:1)	1.17 (4.28)	0.44 (1.61)	
HmimCl-AA (1:1)	1.02 (4.16)	0.38 (1.55)	
BmimCl-AA (1:1)	1.00 (4.35)	0.30 (1.30)	
EmimCl-EG (2:1)	1.15 (6.38)	0.42 (2.33)	6d
EmimCl-EG (1:1)	1.03 (3.36)	0.31 (1.01)	6d
EmimCl-EG (1:2)	0.82 (3.47)	0.22 (0.55)	6d
ChCl-EG (1:2)	0.70 (2.88)		6b
ChCl-Thiourea (1:1)	0.89 (2.96)		6b
ChCl-Malonic acid (1:1)	0.49 (1.88)		6b
ChCl-Glycerol (1:1)	0.678 (2.45)	0.153 (0.55)	6a
ChCl-LA (1:1)	0.557 (4.687)		7a
ACC-LA (1:1)	0.567 (4.695)		7a
ACC-Im (1:2)	0.989 (5.56) <sup>b</sup>	0.381 (2.14) <sup>b</sup>	7b
P <sub>66614</sub> Im	0.559 (4.80)	0.241 (2.07)	4a
P <sub>66614</sub> Tetz	0.413 (3.72)	0.179 (1.54)	4a
P <sub>444</sub> E <sub>3</sub> Tetz	0.75 (4.87)	0.29 (1.87)	4d
E₃minTetz	0.95 (4.43)	0.34 (1.58)	4d
$Et_2NemimNTf_2$	0.389 (2.81)	0.123 (0.89)	4e
Et <sub>2</sub> NemimTetz	1.102 (4.32)	0.427 (1.85)	4e

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<sup>a</sup> The absorption capacities in g/g (mol/mol). <sup>b</sup> At 30 °C.

To investigate the effects of temperature and pressure on the SO2 absorption, EmimCl-AA (2:1), EmimCl-AA (1:1), BmimCl-AA (1:1), and HmimCl-AA (1:1) are selected because of their excellent absorption properties of  $SO_2$ . In Fig. 2A, as the temperature increases, the SO<sub>2</sub> absorption capacities of all DESs decrease. For example, the SO<sub>2</sub> absorption capacity in EmimCl-AA (2:1) decreases from 1.39 g/g at 20 °C to 0.49 g/g at 80 °C, indicating that most captured SO<sub>2</sub> can easily be released by heating the absorption system, and low temperatures are favorable for the capture of SO<sub>2</sub> in DESs. Fig. 2B shows that the loading capacities of SO<sub>2</sub> are elevated continuously with the increasing partial pressure of SO<sub>2</sub>. In addition, the absorption of diluted SO<sub>2</sub> (1.0 vt.%) in EmimCl-AA (2:1) was also investigated. It is satisfactorily found that the mass ratio of SO<sub>2</sub> to EmimCl-AA (2:1) can still exceed 0.22, indicating EmimCl-AA (2:1) are also efficient even under very low concentration of SO<sub>2</sub>. Compared with those functionalized ILs (0.05 g/g in P<sub>4442</sub>HFA, 0.16 g/g in P4442TTFA, and 0.19 g/g in P4442BTFA,4f) EmimCl-AA (2:1) exhibits a better absorption performance.



Fig. 2 The effects of temperature at 1.0 bar (A) and  $SO_2$  partial pressure at 20 °C (B) on  $SO_2$  absorption.

The excellent absorption capacity of SO<sub>2</sub> in EmimCl-AA (2:1) enables the DES an attractive substitute for the removal of SO<sub>2</sub> in flue gas desulfurization. However, for practical application, the – reusability of EmimCl-AA (2:1) is very important. As expected, the absorbed SO<sub>2</sub> can be released completely by bubbling N<sub>2</sub> at 80 °C – (Fig. 3A) in five absorption-desorption cycles, illustrating that the solvent can be recycled and reused. Notably, the experimental results of 15 absorption/desorption cycles justify further the highly reversible SO<sub>2</sub> absorption process in EmimCl-AA (2:1) (Fig. 3B). It is therefore concluded that EmimCl-AA (2:1) is promising candidate for the removal of SO<sub>2</sub> due to its excellent SO<sub>2</sub> absorption capacity and favorable recyclability.



**Fig. 3** A: Five consecutive cycles of SO<sub>2</sub> absorption and release in EmimCl-AA (2:1); B: SO<sub>2</sub> absorption in EmimCl-AA (2:1) for 15 cycles. SO<sub>2</sub> absorption was carried out at 20 °C for 30 min, and the desorption was performed at 80 °C under N<sub>2</sub> for 30 min.

To explore the absorption mechanism, FTIR and NMR were carried out. From the comparison of the FTIR spectra before and after SO<sub>2</sub> absorption in EmimCl-AA (2:1) (Fig. 4) and others (Fig. S4),

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three new peaks were identified at about 1296, 1130, and 528 cm<sup>-1</sup> being corresponding to the asymmetrical, symmetrical stretching vibration, and bending vibration of SO<sub>2</sub>, respectively.<sup>11</sup> Particularly, no other new peaks or significant shifts of peaks can be observed, implying that SO<sub>2</sub> is absorbed in these DESs physically but not chemically. In addition, the chemical shifts of all hydrogen atoms of EmimCl-AA (2:1) moved downfield (Fig. 5A), because of the charge-transfer interactions between SO<sub>2</sub> and solvent molecule.<sup>6d,12b</sup> Meanwhile, the chemical shifts of active protons (a and g + g') shifted significantly with the increase in SO<sub>2</sub> concentration, indicating that strong hydrogen-bond interactions occurred between SO<sub>2</sub> and these protons (Fig. S5). No obvious changes are found in <sup>13</sup>C NMR (Fig. 5B), suggesting that SO<sub>2</sub> interacts physically with imidazole-based DESs. The results of NMR are in agreement with the conclusions of FTIR and absorption experiments.



**Fig. 4** FTIR spectra for EmimCI-AA (2:1) before and after the capture of SO<sub>2</sub>.



Fig. 5 The NMR spectra for EmimCl-AA (2:1) before and after the capture of  $\mathsf{SO}_{2}.^{13}$ 

Preparation of sulfur through the Claus process is one of the most important ways to convert SO<sub>2</sub>.<sup>3c</sup> The liquid-phase Claus process is a significant advance because the reaction of SO<sub>2</sub> with H<sub>2</sub>S can usually be performed under relatively mild conditions. The polyethylene glycol ethers have been industrially applied as solvents in the liquidphase Claus reaction and organic bases such as *N*,*N*-dimethylaniline are used as catalysts to accelerate the reaction of SO<sub>2</sub> with H<sub>2</sub>S in PEGEs.<sup>12a</sup> The metal containing ILs serving as catalyst and solvent was also employed in the process of oxidative absorption of H<sub>2</sub>S.<sup>12b</sup> Recently, we have demonstrated ILs-mediated Claus process,<sup>9</sup> and the absorbed SO<sub>2</sub> can be completely converted to sulfur. However,

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due to the lower solubility of  $SO_2$  in the ILs, the efficiency of this process is still not satisfactory. If the SO2 adsorbed IA/DESS car4be converted into sulfur in situ, the process efficiency will be greatly improved because of the high SO<sub>2</sub> loading capacity in these DESs. To determine the possibility of SO<sub>2</sub> conversion in DESs, the pressurereaction time profile of the Claus process in EmimCl-AA (2:1) was accomplished by detecting pressure change of the reaction system (Fig. 6). Interestingly, after introducing H<sub>2</sub>S to SO<sub>2</sub>-saturated EmimCl-AA (2:1), the pressure in the reaction chamber decays sharply to a very low level, due to the rapid and complete reaction between H<sub>2</sub>S and SO<sub>2</sub>. The reaction almost completes within 5 min. The produced sulfur can be separated by centrifugation and filtration. The final conversion of SO2 was calculated to be 88% according to mass of collected sulfur. The XRD result suggested that the isolated sulfur has a rhombic sulfur (S<sub>8</sub>) crystalline phase (Fig. S6). Furthermore, the melting range of the resulted sulfur was determined to be 116.1~116.2 °C, which also proves the high purity of the sulfur product due to the very narrow melting range.



**Fig. 6** Pressure-reaction time profile of the reaction of SO<sub>2</sub> absorbed with  $H_2S$  in EmimCl-AA (2:1). Reaction conditions: EmimCl-AA (2:1) (1.00 g), room temperature, reaction time (40 min), SO<sub>2</sub> (2.0 mmol) and  $H_2S$  (4.0 mmol).

More results of Claus process in different imidazole-based DESs are showed in Table 2. The reactions in three well-known DESs (ChCl-urea, ChCl-glycerol, and EmimCl-EG) were also studied for comparison. The pressure-reaction time profiles of the Claus process in these solvents are presented in Fig. S7. The time of the turning point  $(t_{tp})$  was an indicator to evaluate the reaction rate of SO<sub>2</sub> with H<sub>2</sub>S in DESs, which was defined by the largest curvature on the pressure-reaction time curve.9 The HmimCl-AA (1:1) has the highest activity for the liquid-phase Claus process among all the DESs investigated (Entries 1~9, Table 2). These DESs-mediated Claus reactions showed more impressive results, as compared to a single ILs or conventional diethylene glycol monomethyl ether (DGME).9 The reaction proceeds slightly faster in EmimCl-AA (1:2) (Entry 3) than that in HmimCl-AA (1:1) (Entry 5). It is attributed to the lower viscosity of EmimCl-AA (1:2), which makes the transfer of H<sub>2</sub>S from the gas phase to the liquid phase and the diffusion of H<sub>2</sub>S and SO<sub>2</sub> in EmimCl-AA (2:1) more rapid. Particularly, classical ChCl-urea (1:2) and ChCl-glycerol (1:1) are inferior to imidazole-based DESs, due to the product agglomeration in ChCl-glycerol (1:1) (Fig. S8) and the much lower solubility of SO<sub>2</sub>. Temperature has a slightly positive effect on conversion ratio of SO<sub>2</sub> (Entry 5 vs Entry 10). The input of H<sub>2</sub>S is usually in excess to ensure the complete conversion of SO<sub>2</sub> in industrial application. We thus investigated the case of slightly excess H<sub>2</sub>S reacting with SO<sub>2</sub> in HmimCl-AA (1:1). The conversion of SO<sub>2</sub> can arrive at 99% in comparison with 88% of the stoichiometric case (Entry 5 vs Entry 11). In fact, excess unreacted H<sub>2</sub>S will also be

recovered and completely converted in the actual Claus process. Since CO<sub>2</sub> and H<sub>2</sub>O are inevitably present in industrial streams, the effects of  $CO_2$  and  $H_2O$  on the Claus process in DESs were investigated. The result showed the CO<sub>2</sub> has no obvious influence on the Claus process in HmimCl-AA (1:1) (Entry 12). Considering that H<sub>2</sub>O is a product of the Claus process, it presents in the reaction system throughout the whole process. Therefore, the effect of equimolar water on the Claus process in DES is insignificant (Entry 13). In addition, the recycling of HmimCl-AA (1:1) was also tested. The used DES can be regenerated by drying under vacuum. It was found that HmimCl-AA (1:1) can be reused three times without obvious loss of activity (Entry 14).

Table 2 The conversion of 502 in different DE5s in claus process.				
Entry	DES	t <sub>tp</sub> (min)	Con. of SO <sub>2</sub> (%) <sup>a</sup>	
1	EmimCl-AA (2:1)	3.4	88	
2	EmimCl-AA (1:1)	3.1	86	
3	EmimCl-AA (1:2)	2.5	75	
4	BmimCl-AA (1:1)	4.2	83	
5	HmimCl-AA (1:1)	3.8	94	
6	BmimBr-AA (1:1)	4.0	83	
7 <sup>b</sup>	ChCl-Urea (1:2)	8.6	72	
8 <sup>b</sup>	ChCl-Glycerol (1:1)	4.5	65	
9	EminCl-EG (1:1)	3.7	87	
10 <sup>b</sup>	HmimCl-AA (1:1)	4.0	95	
11 <sup>c</sup>	HmimCl-AA (1:1)	4.0	99	
12 <sup>d</sup>	HmimCl-AA (1:1)	4.3	97	
13 <sup>e</sup>	HmimCl-AA (1:1)	4.0	99	
14 <sup>f</sup>	HmimCl-AA (1:1)	5.1	91	

Table 2 The conversion of SO<sub>2</sub> in different DESs in Claus process

Conditions: DES (1.00 g), room temperature, reaction time (40 min),  $SO_2$  (2.0 mmol) and  $H_2S$  (4.0 mmol) from the storage tank were introduced into the reaction kettle, respectively. The pressure of the storage tank and reaction kettle was recorded online to monitor the progress of the reaction. <sup>a</sup>The conversions of SO<sub>2</sub> are calculated from the mass of collected sulfur. <sup>b</sup> Reaction temperature (40 °C); <sup>c</sup> SO<sub>2</sub> (2.0 mmol) and H<sub>2</sub>S (4.4 mmol);  $^{d}$  SO<sub>2</sub> (2.0 mmol), H<sub>2</sub>S (4.4 mmol), and CO<sub>2</sub> (0.12 bar); <sup>e</sup> SO<sub>2</sub> (2.0 mmol), H<sub>2</sub>S (4.4 mmol), and  $H_2O$  (2.0 mmol); <sup>f</sup>The DES was reused for the third time.

In summary, we have demonstrated a highly efficient strategy for the sustainable capture and conversion of SO2 using the novel imidazole-based DESs. The highest absorption ability of these imidazole-based DESs can be 1.39 g/g at 20 °C and 1.0 bar, and the captured  $SO_2$  can be easily released by bubbling  $N_2$  and heating. Furthermore, the absorbed SO<sub>2</sub> can be completely transformed to sulfur via imidazole-based DESs-mediated Claus process at room temperature without any additives. We believed that imidazolebased DESs provide a potential opportunity for the green and sustainable SO<sub>2</sub> capture and conversion.

#### Acknowledgement

This work was supported by National Natural Science Foundation of China (No.21376115, and 21676134).

#### Conflicts of interest

There are no conflicts to declare.

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