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Supporting Information for

Unexpectedly efficient SO₂ capture and conversion to sulfur in novel imidazole-based deep eutectic solvents

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General information

All chemicals are analytically pure agents purchased from Chengjie Chemical Co. Ltd. with a purity of 99 wt% and are used without further purification unless otherwise indicated. The deuterated solvents, acetamide, choline chloride, glycerin, and glycol are purchased from TCI Chemical Company. SO₂ (99.9 and 1.0 vt.%) and N₂ (99.99 vt.%) are purchased from Nanjing Tianze Gas Center, Nanjing. The Bruker AV 400 spectrometer was used to conduct the NMR experiments. FTIR spectra were recorded on a Nicolet iS50 infrared spectrometer. TGA were recorded on a PerkinElmer Pyris 1 TGA from room temperature to 400 °C with a scanning rate of 5 °C·min⁻¹ under N₂ atmosphere to determine the decomposition temperatures of DESs. XRD spectra was recorded on a Shimadzu XRD-6000 instrument to confirm the structure of produced sulfur. The melting point was measured using a Yice WRS-2 Instrument to evaluate the purity of produced sulfur. The densities were determined using an DM40/DM45 DeltaRange/DM50 automatic densiometer with a precision of 0.0001 g·cm⁻³, which was calibrated using distilled water. Viscosities were measured on a HAAKE Rheostress 600 viscometer with an uncertainty of $\pm 1\%$ in relation to the full scale.

Preparation of DESs

All imidazole-based DESs were prepared by simply mixing imidazolium salts (EmimCl, BmimCl, HmimCl, and BmimBr) and acetamide (AA) with at the desired molar ratio at 80 °C until a homogeneous liquid was formed. The ChCl-urea, ChCl-glycerol, and EmimCl-EG were also prepared according to literatures.¹⁻³ All DESs were dried under vacuum for 24 h at 50 °C before use. The chemical structure of the DESs prepared in this work was confirmed by NMR spectra and FTIR spectra. No impurities were found in ¹H NMR spectra. The water contents of the DESs were determined with the Carl Fischer method, and the result showed that the water content of each DES is below 0.2 wt.%.

Characteristic information of DES

EmimCl-AA (2:1): ¹H NMR (400 MHz, CDCl₃) δ = 10.51 (s, 2H), 7.66 (dt, *J* = 5.6, 1.8 Hz, 4H), 6.99 (s, 1H), 5.92 (s, 1H), 4.42 (q, *J* = 7.4 Hz, 4H), 4.12 (s, 6H), 2.03 (s, 3H), 1.61 (t, *J* = 7.4 Hz, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 173.16 (s), 137.35 (s), 123.59 (s), 121.83 (s), 45.08 (s), 36.41 (s), 22.61 (s), 15.58 (s) ppm. IR: 3330, 3062, 1667, 1570, 1450, 1380, 1338, 1167, 756, 619, 452 cm⁻³.

EmimCl-AA (1:1): ¹H NMR (400 MHz, CDCl₃) δ = 10.42 (s, 1H), 7.74 – 7.51 (m, 2H), 7.02 (s, 1H), 6.08 (s, 1H), 4.41 (q, *J* = 7.4 Hz, 2H), 4.11 (s, 3H), 2.03 (d, *J* = 6.9 Hz, 3H), 1.60 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 173.30 (s), 137.26 (s), 123.56 (s), 121.81 (s), 45.06 (s), 36.38 (s), 22.59 (s), 15.53 (s) ppm. IR: 3308, 3144, 1660, 1569, 1450, 1381, 1340, 1168, 862, 752, 646, 619, 562, 447 cm⁻³.

EmimCl-AA (1:2): ¹H NMR (400 MHz, CDCl₃) δ = 10.36 (s, 1H), 7.57 (d, *J* = 1.5 Hz, 2H), 6.93 – 6.52 (m, 2H), 6.12 (s, 2H), 4.59 – 4.27 (m, 2H), 4.09 (s, 3H), 2.01 (s, 6H), 1.60 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 173.35 (s), 137.39 (s), 123.52 (s), 121.74 (s), 45.14 (s), 36.43 (s), 22.62 (s), 15.52 (s) ppm. IR: 3337, 3152, 1651, 1569, 1384, 1303, 1167, 1139, 750, 621, 560, 532, 457 cm⁻³.

BmimCl-AA (1:1): ¹H NMR (400 MHz, CDCl₃) δ = 10.55 (s, 1H), 7.61 (t, *J* = 1.7 Hz, 1H), 7.48 (t, *J* = 1.8 Hz, 1H), 6.79 – 6.47 (m, 1H), 6.00 – 5.69 (m, 1H), 4.33 (t, *J* = 7.4 Hz, 2H), 4.12 (s, 3H), 2.03 (s, 3H), 1.91 (dq, *J* = 12.8, 7.6 Hz, 2H), 1.50 – 1.29 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 173.10 (s), 137.89 (s), 123.53 (s), 121.92 (s), 49.76 (s), 36.50 (s), 32.11 (s), 22.64 (s), 19.42 (s), 13.39 (s) ppm. IR: 3308, 3144, 1660, 1569, 1451, 1381, 1340, 1168, 858, 757, 646, 616, 565, 451 cm⁻³.

HmimCl-AA (1:1): ¹H NMR (400 MHz, CDCl₃) δ = 10.45 (s, 1H), 7.59 (t, *J* = 1.7 Hz, 1H), 6.60 (s, 1H), 5.88 (s, 1H), 4.31 (t, *J* = 7.4 Hz, 2H), 4.12 (s, 3H), 1.98 (d, *J* = 29.9 Hz, 3H), 1.45 – 1.18 (m, 7H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 173.15 (s), 137.84 (s), 123.54 (s), 121.81 (s), 50.05 (s), 36.53 (s), 31.03 (s), 30.19 (s), 25.84 (s), 22.63 (s), 22.33 (s), 13.89 (s) ppm. IR: 3313, 3150, 1661, 1567, 1455, 1381, 1340, 1164, 863, 651, 623, 563, 451 cm⁻³.

BmimBr-AA (1:1): ¹H NMR (400 MHz, CDCl₃) $\delta = 10.25$ (s, 1H), 7.63 (t, J = 1.7 Hz, 1H), 7.53 (t, J = 1.8 Hz, 1H), 6.40 (s, 1H), 5.85 (s, 1H), 4.47 – 4.22 (m, 2H), 4.13 (s, 3H), 2.03 (d, J = 6.2 Hz, 3H), 1.97 – 1.81 (m, 2H), 1.49 – 1.26 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) $\delta = 173.09$ (s), 137.21 (s), 123.66 (s), 122.11 (s), 49.80 (s), 36.66 (s), 32.10 (s), 22.71 (s), 19.41 (s), 13.41 (s) ppm. IR: 3309, 3165, 2961, 1657, 1571, 1464, 1379, 1338, 1166, 864, 754, 651, 616, 554, 451 cm⁻³.

Details on absorption and desorption experiments

The absorption and desorption of SO2 were carried out using well-defined process according to literatures.⁴ In a typical procedure, the SO₂ of atmospheric pressure was bubbled through about 1.00 g EmimCl-AA (2:1) in a 10 mL Schlenk flask with a SO₂ bubbling rate of 100 ml·min⁻¹. The glass container was partly immersed in a circulation water bath of desirable temperature. The amount of SO₂ absorbed was determined at regular intervals by the electronic balance with an accuracy of \pm 0.1 mg. During the absorption of SO₂ under reduced pressure, SO₂ was diluted with N₂ in order to reduce the partial pressure of SO₂ passing through the system. The SO₂ partial pressure was controlled by changing the flow of SO₂ and N₂. The experiment was carried out by three repeated experiments, and the reliability was found to be satisfactory. In a typical desorption of SO₂, the desorption of SO₂ gas from EmimCl-AA (2:1) saturated was carried out and monitored in an analogous way as for the described absorption method. The EmimCl-AA (2:1) was regenerated by heating (80°C) and bubbling N₂ (50 mL·min⁻¹) through solvent. The release of SO₂ was determined by the electronic balance.

Details for calculating the theoretical uptake of ideal EmimCl-AA (1:1)

Firstly, the solubility of SO₂ in ethylene glycol (EG) was determined to be 0.28 g/g at 20 °C and 1.0 bar. At the same time, the solubility of SO₂ in EG + EmimCl and EG + AA were measured under the same conditions, respectively. Then, the solubility of SO₂ in neat EmimCl and AA could be calculated by deducting the solubility of SO₂ in EG. It gives the results that the solubilities of SO₂ in EmimCl and AA are 1.34 and 0.18 g/g, respectively. When EmimCl and AA were mixed with the molar ratio of 1:1, the theoretical SO₂ uptake for the ideal EmimCl-AA (1:1) solvent can be calculated.

Procedure for the Claus reaction in DESs

(Attention: Due to the high toxicity of H₂S gas, all experiment must be operated under good ventilation and protection conditions)

The DES-mediated Claus reaction were carried out according to our previous work,⁴ and the experimental device as shown in the illustration.



DES-mediated Claus reaction instrument; 1 storage tank of H_2S ; 2 storage tank of SO_2 ; 3 reaction kettle; 4 constant temperature bath; 5 pressure sensor; 6 real-time data acquisition instrument; 7 PC; 8 microthermometer; 9 vacuum pump

Typically, the reaction of SO₂ with H₂S in HmimCl-AA (1:1) was performed in a stainless steel reaction still coupling a magnetic stirrer. The temperature of the reaction system was controlled by a water bath with an uncertainty of \pm 0.1 °C. About 1.00 g of HmimCl-AA (1:1) was added in the reaction kettle and the air in the chamber was evacuated by vacuum pump. SO₂ (2.0 mmol) from the storage tank was introduced into the reaction still. After the absorption of SO₂ in HmimCl-AA (1:1) reached equilibrium, H₂S (4.0 mmol) from the another storage tank was then injected into the reaction kettle. The pressures of the storage tank and reaction kettle were recorded online to monitor the progress of the reaction with an uncertainty of \pm 0.001 bar. The reaction lasted at the desired temperature for 40 min. After the completion of reaction, the gas remained in the reaction chamber was introduced to NaOH aqueous solution by vacuum pump. Resulted solid sulfur was separated by centrifugation and filtration. The collected sulfur was rinsed with cold water, and then dried and weighed to calculate conversion of SO₂. The structure of produced sulfur was decided by XRD, and the melting point was measured to evaluate the purity of produced sulfur.

Chemicals	Absorption capacities of SO ₂ (g/g)	T(°C)	Con. of SO ₂ in Claus process $(\%)^a$	Ref.
Diglycol monomethylether (DGM)	0.53	20	69	This work
Diethylenetriamine (DETA)	0.62	20	51	This work
Sulfolane (SUF)	0.42	30	None	6
Ethylene glycol (EG)	0.20	30	None	6
Propylene carbonate (PC)	0.34	30	None	6
<i>N</i> -methylimidazole (NMI)	1.11	30	None	6
<i>N</i> -methylpyrrolidone (NMP)	0.80	30	None	6
11-(<i>N</i> , <i>N</i> -Di-n-butylamino)-1- undecanol (DBUA)	0.54	25	None	7
<i>N</i> -ethyl- <i>N</i> -(2-(2-(2- methoxyethoxy)ethoxy)ethyl)-2- aminoethanol (EE ₃ AE)	1.07	20	None	8
<i>N</i> -decyl- <i>N</i> -ethyl-2-aminoethanol (DEAE)	0.83	20	None	8

Table S1 Comparison of SO_2 absorption capacities in conventional absorbants and the conversion of SO_2 in Claus process.



Fig. S1 The densities and viscosities of DES. $\blacksquare C_2C_1Cl-AA(1:2)$, $\blacklozenge C_2C_1Cl-AA(1:1)$, $\blacktriangle C_2C_1Cl-AA(2:1)$, $\blacktriangledown C_4C_1Cl-AA(1:1)$, $\blacktriangleleft C_6C_1Cl-AA(1:1)$, $\triangleright C_4C_1Br-AA(1:1)$



Fig. S2 The TGA curves of the DESs investigated.



Fig. S3 The effect of water on the SO₂ absorption performance in EmimCl-AA (2:1) at 20 °C and 1.0 bar.



Fig. S4 FTIR spectra for EmimCl-AA (2:1), EmimCl-AA (1:1), BmimCl-AA (1:1) HmimCl-AA (1:1) before and after capture SO₂.



	11(d)	11(g)	n(g)
0.00	10.083	7.000	5.963
0.25	9.772	6.746	5.945
0.53	9.611	6.565	5.914
0.70	9.584	6.505	5.899
0.82	9.575	6.429	5.867

Fig. S5 The ¹H NMR spectra for EmimCl-AA (1:1) + SO₂ with increasing concentration of SO₂.



Fig. S6 Pressure-reaction time profile of the reaction of SO₂ absorbed with H₂S in EmimCl-AA (2:1).

Reaction conditions: EmimCl-AA (2:1) (1.00 g), room temperature, reaction time (40 min), SO₂ (2.0 mmol) and H_2S (4.0 mmol).



Fig. S7 XRD pattern of sulfur produced from the Claus reaction in EmimCl-AA (2:1)



Fig. S8 Pressure-reaction time profiles of the reaction of SO₂ absorbed with H₂S in different DESs.



Fig. S9 A: Illustrations of the solid sulfur (A); (B) Product agglomeration using ChCl-glycerol (1:1) as medium; (C) Product dispersed using HmimCl-AA (1:1) as medium.

The role of acetamide

In order to find out the role of acetamide, we have performed more NMR experiment and DFT calculation (Fig. S9-S11). It was found that both the C=O and NH₂ group of acetamide form hydrogen bond with EmimCl. The most stable structure of EmimCl-AA (2:1) indicates that the NH₂ group of acetamide binds with two different EmimCl and the two EmimCl also interacts with each other (Fig. S11). This is different from past DES (EmimCl-TEG) used as SO₂ absorbents ^{5f}, in which the two EmimCl cannot interact with each other. Further DFT calculations show that EmimCl-AA (2:1) can bind with 8 SO₂ (Fig. S12), which agrees well with the experimental results listed in Table 2.

Calculation methods

All the geometries were fully optimized with Gaussian 03 program using B3LYP method based on density functional theory ⁹. $6-311+G^*$ basis set was used for all atoms. Energy calculations as well as Zero-point energies (ZPE) correction have been performed at the same theory. All energies reported in this work are corrected by ZPE. The computed stationary points have been characterized as minima by diagonalizing the Hessian matrix and analyzing the vibrational normal modes. In this way, the stationary points can be classified as minima if no imaginary frequencies are shown.



Fig. S10 The ¹H-NMR of EmimCl-AA. From top to bottom, the molar contents of AA are 100, 89, 74, 51, 30, and 0%, respectively.



Fig. S11 The C=O part of the ¹³C-NMR of EmimCl-AA. From top to bottom, the molar contents of AA are 100, 89, 74, 51, 30, and 0%, respectively.



Fig. S12 The optimized structures of EmimCl-AA (2:1) obtained by B3LYP/6-311+G* method. The italic values are binding energies between Emim and AA. The other values are bond length in Å.



Fig. S13 The optimized structures of DESa-SO₂ obtained by B3LYP/6-311+G* method. The italic values are binding energies between DESa and SO₂. The other values are bond length in $_{\circ}^{\circ}$



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