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Investigation of deep eutectic solvent formed by levulinic acid with quarternary ammonium salt as efficient SO$_2$ absorbent

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Efficient and reversible absorption of SO$_2$ in six new deep eutectic solvents (DESs) composed of levulinic acid (LA) and quarternary ammonium salts (choline chloride, CC; choline acetyl chloride, CAC; tetraethylammonium chloride, TEAC; tetraethylammonium bromide, TEAB; tetrabutylammonium chloride, TBAC; tetrabutylammonium bromide, TBAB) was sysmatically investigated. The molar ratio of LA to quarternary ammonium salt was fixed at 3:1. The results showed that all DESs possessed satisfactory performance for SO$_2$ absorption, with the maximum absorption capacity of 0.625 g SO$_2$ per g DES of LA-TEAC at 293.15 K under ambient pressure. The absorbed SO$_2$ was easily released by bubbling N$_2$ at 323.15 K and the regenerated DES was recycled five times without obvious loss of absorption performance. The solubility of SO$_2$ in DES of LA-CC at T = (293.15, 303.15, 313.15, and 323.15) K under subatmospheric pressures were also determined. The relative thermodynamic parameters of absorption enthalpy, absorption entropy, and absorption Gibbs free energy were further calculated with the results of small negative values. The influence of water content on the SO$_2$ absorption was also investigated. According to NMR and FTIR analysis, the absorption of SO2 in DES was a physical process. Moreover, all the DESs exhibited high selectivity of SO$_2$/CO$_2$. Present DESs emergy as promising absorbents for SO$_2$ because of their high absorption capacity and good reversibility.

Introduction

The combustion of fossil fuels releases large amount of sulfur dioxide (SO$_2$) into atmosphere. SO$_2$ is a major contributor to smog and acid rain, which generates serious harm to public health, ecological balance, agricultural production, architectures and equipment. The removal and reduction of SO$_2$ from the exhaust flue gases have attracted increasing interest because of the stringent environmental regulation [1]. Therefore, many commercial Flue Gas Desulfurization (FGD) technologies have been developed [2], with the lime/limestone-based FGD is regarded as the most efficient technology in industry [3]. Despite its high efficiency, lime/limestone-based FGD still represents several inherent drawbacks such as the production of large waste solid (CaSO$_4$) and wastewater, high energy penalty and equipment corrosion. Moreover, the valuable sulfur resource is completely transferred into almost worthless CaSO$_4$. Hence, lime/limestone-based FGD is inconsistent with sustainable development and circular economy. Besides, amine-based absorbents and some organic solvents have also been utilized or reported to capture SO$_2$, the second pollution arisen from the high volatility of solvents is hard to avoid [4-6]. So, developing green, efficient, economical, reversible absorbent for SO$_2$ is still highly desirable.

In recent decades, Ionic liquids (ILs) have been widely recognized as new reactive and gas absorptive mediums owing to their advantageous properties such as high thermal and chemical stability, extremely low volatility, non-flammability and high salvation capacity for different kinds of substances [7-10]. Since Wu et al firstly reported efficient and reversible capture of SO$_2$ using task-specific 1, 1, 3, 3-tetramethylguanidinium lactate ([TMG][L]) [11], the research on ILs as SO$_2$ absorbent has attracted persistent attentions and a serial of ordinary and functionalized ILs were developed[12-24]. Although ILs demonstrated satisfactory performance for SO$_2$ capture, there still existed some limitation including high price, tedious preparation or purification technology, uncertain toxicity and poor biodegradability [25]. The recent emerging deep eutectic solvents (DESs), also known as IL analogues or an advanced generation of ILs, seem to be good alternative because they share many unusual characteristics similar to the traditional ILs [26] and overcome the shortcoming as mentioned above [27]. Moreover, DESs can be directly prepared by mixing hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA) with high purity at considerably lower cost than ILs [28, 29]. Up to date, various polyhydric alcohols [30, 31], organic acids [32-34], amides [35, 36], and sugars [37] a as HBD and quaternary ammonium salts [38, 39], quaternary phosphium salts [40], and inorganic salts [41, 42] as HBA have been developed. The application of DESs in various fields, such as extraction separation [43, 44], chemical reaction [45, 46] and CO2 capture [47-49] have been widely investigated. Recently, Liu et al [42] reported five inorganic thiocyanate-based DESs to capture SO$_2$, while the DES of acetamide-KSCN (3:1) possesses the maxium SO$_2$ solubility of 0.588 g SO$_2$/g DES at 293.15 K and 1 bar. The DESs can be easily regenerated under vacuum at 343.15 K and recycled five times without apparent loss of absorption efficient. Yang et al [50] reported renewable DESs of choline chloride-glycerol as SO$_2$ absorbent, with the highest capture capacity of 0.678 g SO$_2$/ g DES

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for choline chloride-glycerol (1:1) at 293.15 K and 1 bar. The proposed mechanism demonstrated that the chloride anion played as the main physical absorption site for SO_2. Such two typical DESs presented encouraging and comparable SO_2 capture capacity with many task-specific ILs at the same conditions, such as [P_{66614}][Tetz] (0.431 g SO_2 / g IL) [51]. However, the stability of thiocyanate-based DESs is susceptible in the existence of SO_2 and the high viscosity of choline chloride-glycerol mixtures also hinders mass transfer in the gas absorptive process. Now, utilizing renewable biobased materials as HBD is an important trend for preparing DES. LA has been highlighted by the United States Department of Energy in 2004 and again in 2010 as a promising building block for chemistry [52]. LA is also a nonreductive platform chemical industrially produced by Biofine process [53]. Compared with the hydroxyl group in glycerol, the carbonyl group presented in the LA is more helpful for binding acidic gases [54]. Previously, we have determined the solubility of CO_2 in the DESs of LA-ChCl with good results [55]. In this work, LA is selected as HBD and further paired with various quaternary ammonium salts to form DESs for SO_2 absorption. The molar ratio of levulinic acid to quaternary ammonium was fixed at 3:1 and the quaternary ammonium salts included choline chloride (CC), choline acetyl chloride (CAC), tetraethylammonium chloride (TEAC), tetraethylammonium bromide (TEAB), tetrabutylammonium chloride (TBAC), and tetrabutylammonium bromide (TBAB). The influence of temperature, partial pressure of SO_2, water content in DESs on the absorption efficiency was systematically investigated. The selectivity of SO_2/CO_2, regeneration and recyclability were also included. Henry's law constants and thermodynamic parameters in DES of CC-LA were also determined. Moreover, the interaction between SO_2 and present DESs was analyzed using spectroscopy (FT-IR and NMR).

Experimental

Materials

SO_2 (0.999, mass fraction purity, the same below) gas was supplied by Jingong Special Gas Co., Ltd. (Hangzhou, China). Anhydrous CC (0.985) was purchased from Jinan Hualing Pharmaceutical Co., Ltd. (Shandong, China). LA (AR grade, 0.99), CAC (AR grade, 0.99), TEAC (AR grade, 0.98), TEAB (AR grade, 0.99), TBAC (CP grade, 0.97) and TBAB (AR grade, 0.99) were obtained from Aladdin Chemical Company (Shanghai, China). All the chemicals were used as received without any further purification.

Preparation of levulinic acid-based DESs

The DESs were prepared by direct mixing LA with various quaternary ammonium salts at suitable temperature and dried under vacuum at 353 K for 48 h before use. The molar ratio of LA to quaternary ammonium salt was fixed at 3:1 for each DES. The water content of each DES was determined by Karl Fischer analysis (SF-3 Karl-Fischer Titration, Zibo Zifen Instrument Co. Ltd.) with the mass fraction of less than $1.2\cdot10^{-3}$ in all cases. An electronic balance (Mettler-Toledo AL204) with the accuracy of ± $2*10^{-4}$ g was used to determine the weight of the materials. ^1H NMR spectra were recorded on a Bruker AVANCE □ (500 MHz) spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the standard. FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer.

Absorption and desorption of SO_2 in DESs

The absorption and desorption experiments were carried out using a bubble method. In a typical experiment, an accurate mass of DES (about 2.0 g) was charged into a glass tube with an inner diameter of 12 mm and length of 200 mm, while the glass tube was immersed in a thermostatic water bath with the desired temperature. SO_2 was bubbled into the DES at the flow rate of 20 $cm^3.min^{-1}$ using a long stainless needle. The total weight of glass tube as well as the needle was determined at regular intervals during the absorption process by electronic balance (Mettler-Toledo AL204). For the absorption of SO_2 under reduced partial pressure, a mixture of SO_2 and N_2 of known composition was passed through the absorption system. The SO_2 partial pressure was controlled by changing the composition of the gas mixtures. In desorption of SO_2, atmospheric N_2 was bubbled through the solutions at 323.15 K at the flow rate of 30 $cm^3.min^{-1}$. The total weight of the glass tube was also determined at regular intervals during desorption process by the electronic balance.

Results and discussion

In present work, six new DESs prepared by direct mixing bio-based levulinic acid and quaternary ammonium salt (with the fixed molar ratio of 3:1) were used to comparatively study the absorption and separation performances for SO_2.

Absorption of SO_2 by DESs and structure of quaternary ammonium salts and temperature on their absorption capacity

In order to investigate the structure of quaternary ammonium salts on the absorption behavior for present DESs, the time-dependent absorption curves of SO_2 in six DESs at 303.15 K and 1 atm was depicted in Fig.1. Generally, the rate of absorption was fast and fifteen minutes was enough to reach equilibrium at the flow rate of 20 $cm^3.min^{-1}$. However, the absorption capacity demonstrated evident difference along with the structure changing of the quaternary ammonium salts. For example, the DESs containing bromide ion possessed higher absorption capacity than those with chloride ion. As mentioned previously [50], the absorption of SO_2 was mainly ascribed to the performance of the anions. Therefore, the relatively larger bromide ion could bind more SO_2 than chloride ion. Similarly, the tetrabutylammonium salt-based DESs possessed higher absorption capacity than tetraethylammonium salt-based counterparts.

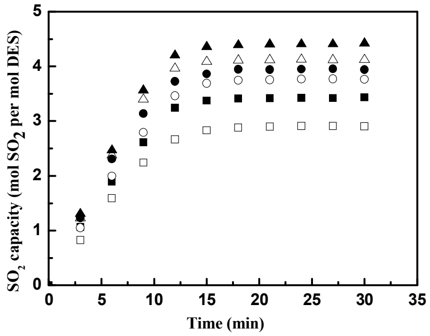

Figure 1. Absorption of SO_2 by DESs at 303.15 K and 1atm as a function of time.□, LA-CC; ■, LA-ACC; ○, LA-TEAC; ●, LA-TBAC; △, LA-TEAB; ▲, LA-TBAB.

When the hydroxyl group in CC was transferred to be acetyl ester in ACC, the absorption capacity in the corresponding two DESs was enhanced evidently from 2.91mol SO_2/mol CC-LA to 3.43 mol SO_2/ mol ACC-LA. The enhancement of absorption capacity may come from the performance of the ester group, which is believed to be more effective than hydroxyl group for the absorption of SO_2 [56].

The solubility of SO_2 in six DESs at temperatures of (293.15-343.15) K and 1 atm was also determined, with the results listed in Table 1 and graphically presented in Fig.2 with two DESs of LA-TEAC and LA-TBAC as representatives. It was obvious that the solubility of SO_2 decreased rapidly with increasing temperature. For example, the solubility of SO_2 varied from 0.625 to 0.172 g/g LA-TEAC when the temperature increased from 293.15 K to 343.15 K. Such result means that low temperature is favorable for high absorption amount of SO_2, while high temperature is helpful for stripping of the absorbed SO_2 and regeneration of the absorbents.

Table 1 Gravimetric capacity of SO_2 in the DESs at different temperatures [a]

T (K)	LA-CC	LA-ACC	LA-TEAC	LA-TEAB	LA-TBAC	LA-TBAB
293.15	0.557	0.567	0.625	0.622	0.541	0.547
303.15	0.384	0.417	0.472	0.475	0.402	0.425
313.15	0.285	0.310	0.363	0.370	0.296	0.332
323.15	0.214	0.237	0.287	0.290	0.220	0.264
333.15	0.162	0.186	0.223	0.234	0.162	0.213
343.15	0.123	0.145	0.172	0.184	0.116	0.169

[a] g SO_2 / g DES

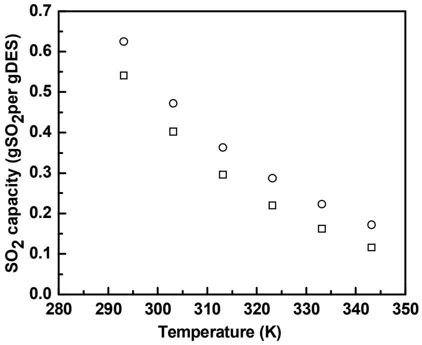

Figure 2. The effect of temperature on SO_2 capacity at 1atm for DESs of LA-TEAC (○) and LA-TBAC (□).

Regeneration and recycling of DESs

Regeneration and recyclability of the absorbent are two important properties related directly to the produce cost and equipment investment in gas absorption and separation process. For simplification, LA-CC was selected as the representative system to investigate the regeneration and recycling of DESs. In a typical regeneration operation, the SO_2 treated LA-CC was heated to 323.15 K and bubbled with N_2 to strip out the absorbed SO_2. The regenerated eutectic mixture was a colorless liquid and reused to capture SO_2 again. Such recycling experiment was carried out five times with the results illustrated in Fig. 3. As shown from Fig. 3, the regeneration process was completed within fifteen minutes. The absorption rate and capacity of the regenerative CC-LA had been barely influenced after five cycles of absorption and regeneration operation, meaning that the capture of SO_2 by CC-LA could be regarded as a basically reversible process.

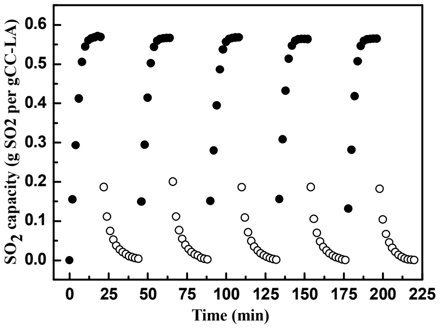

Figure 3. Five consecutive cycles of SO_2 absorption (20°C, 1atm, 30 $cm^3.min^{-1}$) and desorption (50°C, N_2, 30 $cm^3.min^{-1}$) for LA-CC. ●, Absorption; ○, Desorption.

Effect of water on the performance of DES for SO_2 absorption

It is well known that water vapor always coexists with SO_2 in the real fuel gas and will be simultaneously absorbed by the hydrophilic absorbents. Therefore, it is necessary to understand the influence of water on absorption rate and capacity of the absorbents. In present work, three groups of LA-CC containing different amount of water were compared in capturing SO_2 at 293.15 K and 1 atm, with the results illustrated in Fig.4. As can be seen from Fig.4, the absorption rate was little affected by changing the water content in the mixtures. The absorption capacity decreased slightly with increasing contents of water, with 0.56, 0.52, and 0.46 gSO_2 / g CC-LA mixture without water, with 5.0 and 10.0% water, respectively. If the amount of SO_2 absorbed by water (0.271g SO_2/g H_2O at 293.15 K) in the LA-CC was deducted [57], the absorption capacity of SO_2 was 0.56, 0.53, 0.48 gSO_2 per g LA-CC, which means that the addition of water maybe produces little change in the structure and performance of the LA-CC.

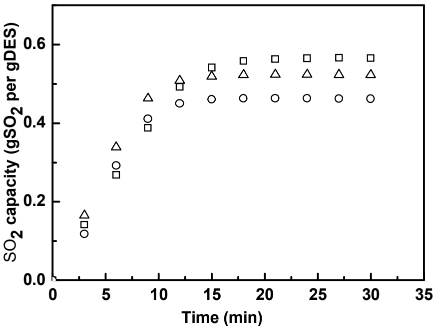

Figure 4. Effect of water on the performance of LA-CC for SO_2 absorption at 293.15 K and 1 atm. □, LA-CC; △, LA-CC with 5.0 wt% water; ○, LA-CC with 10.0 wt% water.

Selectivity of SO_2 to CO_2

SO_2 and CO_2 are two major acid gases coexisted in real flue gas. Substantial effort has been focused on separating SO_2 from CO_2 in pretreatment of flue gas [58], which were associated with the selectivity of SO_2/CO_2 (derived as the absorption capacity ratio of SO_2 to CO_2) in the absorbent. To investigate the potential suitability of present DESs in above application, the absorption capacity of CO_2 in present six DESs at 303.15 K and 1 atm were also determined. Table 2 illustrates absorption capacity of two gases and the calculated selectivity of SO_2/CO_2 in present DESs as well as other functionalized ILs. As expected, CO_2 have much lower solubility than SO_2 in present DESs, thus resulting in high selectivity in all the DESs, which offer an attractive way for the separation of SO_2 from CO_2. Moreover, the selectivities of SO_2/CO_2 in DESs are 3-4 times higher than those in many functionalized ILs included in Table 2. These results indicated that these DESs have the potential to be used as candidates for selective capture or pretreatment of SO_2 from CO_2 in flue gas.

Table 2 SO_2/CO_2 absorption capacity and selectivity in DESs and some ILs at 293.15 K and 1 atm.

Absorbents [a]	Absorption capacity of gas [b]		Selectivity of	References
	SO_2	CO_2	SO_2/CO_2	
LA-CC	8.703	0.056	155	This work
LA-ACC	8.859	0.057	155	This work
LA-TEAC	9.766	0.049	199	This work
LA-TEAB	9.719	0.053	183	This work
LA-TBAC	8.453	0.060	141	This work
LA-TBAB	8.547	0.064	134	This work
[P_{66614}][Tetz]	6.719	0.143	47	[51]
[Et_2NEMim][Tetz] [c]	17.188	0.441	39	[59]
[Et_2NEMim][Tf_2N] [c]	6.094	0.152	40	[59]
[E_3Py]Cl	16.515	0.332	49	[60]
[C_4Py][SCN]	13.140	0.235	56	[14]

[a] [P_{66614}][Tetz], trihexyl-(tetradecyl)phosphonium tetrazolate; [Et_2NEMim][Tetz], 1-(2-diethylaminoethyl)-3-methyl-imidazolium tetrazolate; [Et_2NEMim][Tf_2N], 1-(2-diethyl-aminoethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [E_3Py]Cl, 1-{2-[2-(2-methoxyethoxy)ethoxy]ethyl} pyridinium chloride; [C_4Py][SCN], N-butylpyridinium thiocyanate; [b] mol of gas per (kg of DES or IL); [c] At 0.101 MPa and 20℃;

The interaction mechanism between SO_2 and DES

In order to understand the interaction between SO_2 and DES of LA-CC, FTIR and NMR spectroscopy techniques were applied to characterize the structures of LA-CC before and after the absorption of SO_2. The recorded FT-IR spectra of pure LA-CC and LA-CC+SO_2 are depicted in Fig.5. By comparing the two spectra in Fig.5, a new absorption peak at 1326.4 cm^{-1} was assigned to be the asymmetric stretching of S=O band (V_{as}) because of the dissolution of SO_2. However, the V_{as} shifts toward lower 17.5 cm^{-1} than 1343.9 cm^{-1} reported in noncomplexing CCl_4 system [61]. This phenomenon can be ascribed to the lengthening of S=O bond due to the intermolecular interaction of the electropositive sulfur atom of SO_2 with electronegative chloride or oxygen atom in the CC-LA. Furthermore, the symmetric stretching of S=O band (V_s) at 1164.3 cm^{-1} has widened the original band at 1163.9 cm^{-1}. Another new peak at 527.8 cm^{-1} was regarded as scissor bending vibration (δ) of dissolved SO_2 [62]. Moreover, as illustrated in Fig.6 of the NMR spectra for free and SO_2 treated LA-CC, All the original chemical shifts were also kept unchanged and no peak with new chemical shift appeared. These results mean that the dissolved SO_2 interacted physically with LA and the cation of the quarternary ammonium salts. Such phenomena were consistent with those for DESs of CC-glycerol reported previously by Yang et al. [50]

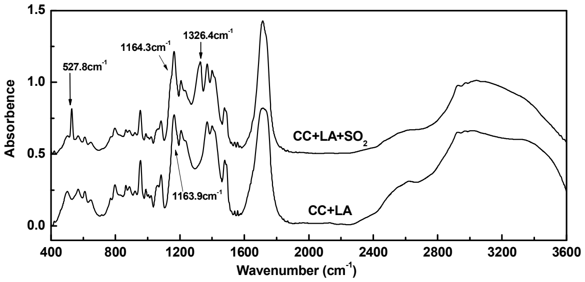

Figure 5. FT-IR spectra of LA-CC before and after absorption of SO_2.

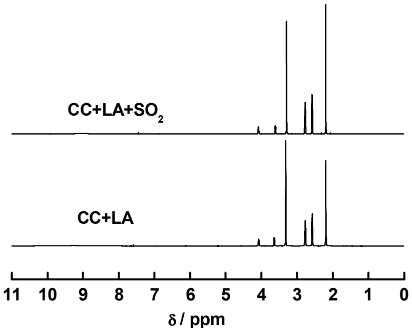

Figure 6. ^{1}H NMR spectra of LA-CC before and after absorption of SO$_2$.

Thermodynamic properties

CC-LA was chosen to investigate the dependence of absorption capacity on various SO$_2$ partial pressures at various temperatures, with the results illustrated in Fig.7. It was evident that the absorption capacity and SO$_2$ partial pressure demonstrated strong correlation. The absorption capacity increased continuously from 0.124 to 0.557 gSO$_2$ per gDES when the partial pressure changed from 0.1 to 1.0 atm. Such results mean that the absorbed SO$_2$ can be easily stripped out through the reduction of pressure.

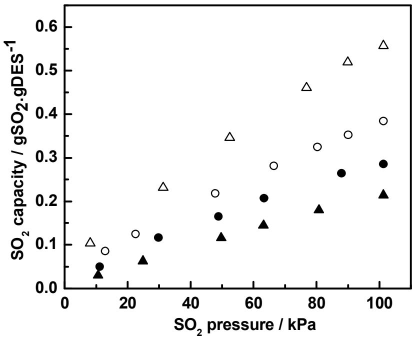

Figure 7. The effect of partial pressure of SO$_2$ on SO$_2$ capacity in the DES of LA-CC at different temperatures. △, 293.15K; ○, 303.15K; ●, 313.15K; ▲, 323.15K.

According to above analysis, the dissolution capacity can be described using the Henry's law constant based on molar fraction as following [63],

$$k_H = \lim_{x_1 \to 0} \frac{f_1}{x_1} \approx \frac{p_1}{x_1} \tag{1}$$

where k_H is the Henry's constant; f_1 and $p_1$are fugacity and partial pressure of SO$_2$ in the vapor phase, respectively; x_1 is the mole fraction of SO$_2$ in the liquid phase. The fugacity is simplified to be partial pressure of SO$_2$ because of the low experimental pressure and negligible vapor pressure of DES. Therefore, k_H was obtained from the intercept by extrapolating the p_1/x_1 vs. p_1 curves to zero of pressure. The k_H of LA-CC at 293.15-323.15 K were listed in Table 3, which decreased continuously with decreasing temperatures.

Thermodynamic properties are helpful for quantitative understand of SO$_2$ dissolution into DESs and the process design of capture. Three thermodynamic properties can be calculated from the Henry's law constants as following,

$$\Delta_{dis}G^0 = RT\ln(\frac{H(T,p)}{p^0}) \tag{2}$$

$$\Delta_{dis}H^0 = R(\frac{\partial \ln(H(T,p)/p^0)}{\partial(1/T)})_p \tag{3}$$

$$\Delta_{dis}S^0 = (\frac{\Delta_{dis}H^0 - \Delta_{dis}G^0}{T}) \tag{4}$$

where $\Delta_{dis}G^0$, $\Delta_{dis}H^0$, $\Delta_{dis}S^0$ are the standard Gibbs free energy, dissolution enthalpy and dissolution entropy for SO$_2$ in DESs under pressure p^0 = 0.1 MPa, respectively. The values of $\Delta_{dis}G^0$, $\Delta_{dis}H^0$, $\Delta_{dis}S^0$ at 303.15K were also listed in Table 3. $\Delta_{dis}H^0$ provides a pathway to quantitatively evaluate the strength of interaction between SO$_2$ and DES of LA-CC and the energy consumption in the regeneration of the used DES. As can be seen from Table 3, the small $\Delta_{dis}H^0$ value of -35.25kJ.mol^{-1} indicates weak interactions between DES and SO$_2$ and the absorption can be easily reversed. The negative value of $\Delta_{dis}S^0$ means that a higher ordering degree in DES solution is obtained after the capture of SO$_2$ from molecular points. The negative $\Delta_{dis}G^0$ indicates that the capture of SO$_2$ by DES is a spontaneous process.

Comparison with other DESs and some ILs

For throughout investigation of present DESs as SO$_2$ absorbent, we hope to compare the absorption capacity of SO$_2$ in present DESs with that in other DESs as well as some ILs reported in the literatures, with the results listed in Table 4 on the basis of molality scale. It can be found that present DESs demonstrates similar absorption capacity of SO$_2$ with thiocyanate or glycerol based DESs, while slightly superior to the ordinary ILs and inferior to functionalized ILs. It should be noted that the thiocyanate based DESs and functionalized [C$_4$Py][SCN] are susceptible to be oxidized by SO$_2$ which possesses relatively strong oxidizability, especially in the presence of water. Besides, the functionalized ILs surfers from multi-step synthesis and high cost [65]. Thus, the present DESs are regarded as more promising SO$_2$ absorbents due to their high absorption capacity, low absorption enthalpy, and reasonable cost.

Table 3 Henry's law constants at four temperatures and thermodynamics properties at 303.15 K for LA-CC.

k_H (kPa)				$\Delta_{dis}G^0$ (kJ mol^{-1})	$\Delta_{dis}H^0$ (kJ mol^{-1})	$\Delta_{dis}S^0$ (J mol^{-1} K^{-1})
293.15	303.15	313.15	323.15			
46.18	78.19	112.08	187.84	-0.62	-35.25	-114.24

Table 4 Comparison of SO_2 absorption capacity in present DESs to other DESs and some ILs at 1 atm and 313.15 K

Absorbents [a] (mole ratio)	SO_2 absorption capacity at 1 atm		References
	molSO_2/mol absorbent	g SO_2/g absorbent	
LA-CC	2.171	0.285	This work
LA-ACC	2.567	0.310	This work
LA-TEAC	2.915	0.363	This work
LA-TEAB	3.229	0.370	This work
LA-TBAC	2.896	0.296	This work
LA-TBAB	3.479	0.332	This work
CC-glycerol(1:3)	1.266	0.195	[50]
Acetamide-KSCN (3:1)	1.572	0.367	[42]
Acetamide-NH_4SCN (3:1)	1.348	0.341	[42]
Urea-NH_4SCN (3:2)	1.465	0.282	[42]
[C_4Py][BF_4]	1.014	0.291	[14]
[Bmim][BF_4]	0.86	0.229	[13]
[TMG] [BF_4]	0.68	0.214	[13]
[TMG] [Tf_2N]	0.76	0.122	[13]
[Bmim][$MeSO_4$]	1.11	0.284	[64]
[Hmim] [Tf_2N]	0.775	0.110	[18]
[E1mim][$MeSO_3$]	2.09	0.563	[24]
[Et_2NEMim][Tetz]	3.01	0.767	[59]
[P66614][BenIm]	4.381	0.465	[23]
[TMG][L]	1.70 [b]	0.53 [b]	[11]
[C_4Py][SCN]	1.973	0.650	[14]

[a] [C_4Py][BF_4], N-butylpyridinium tetrafluoroborate; [Bmim][BF4], 1-butyl-3-methylimidazolium tetrafluoroborate; [TMG] [BF4], 1,1,3,3-tetramethyguandinium tetrafluoroborate; [TMG][Tf2N], 1,1,3,3-tetramethyguandinium bis(trifluoromethylsulfonyl)imide; [Bmim][$MeSO_4$], 1-butyl-3-methylimidazolium methylsulfate; [Hmim] [Tf_2N], 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [E1mim][$MeSO_3$], 1-ethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate; [Et_2NEMim][Tetz], 1-(2-diethylaminoethyl)-3-methyl-imidazolium tetrazolate; [P66614][BenIm], trihexyl(tetradecyl)phosphonium benzimidazolate; [TMG][L], 1,1,3,3-tetramethylguanidinium lactate; [C_4Py][SCN], N-butylpyridinium thiocyanate; [b] At 1.2 bar.

Conclusions

In present work, six deep eutectic solvents were prepared from bio-based levulinic acid and quarternary ammonia salts and used to evaluate the absorption performance for SO_2. The results illustrate that levulinic acid-tetraethylammonium chloride demonstrates the maximum absorption capacity of 0.625 g SO_2 / g absorbent among the investigated ones at 293.15 K under ambient pressure. Furthermore, the high selectivity of SO_2/CO_2 in present deep eutectic solvents provides an attractive way to selectively separate SO_2 from CO_2 in flue gas. The existence of water in levulinic acid-choline chloride has slightly negative effect on its SO_2 absorption capacity. The spectroscopic investigation suggests the physical interaction between dissolved SO_2 and deep eutectic solvent. The high efficient, reasonable cost, low energy consumption and ease of operation makes the present deep eutectic solvents to be promising absorbents for SO_2.

Acknowledgements

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Notes and references

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