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Absorption of SO₂ by renewable ionic liquid/polyethylene glycol binary mixture and thermodynamic analysis

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Separation and removal of SO₂ before atmospheric release of the flue gas is essential to combat acid rain formation. Traditional chemical absorbents and conventional ionic liquids (ILs) suffer from several shortcomings including waste, second pollution, high viscosity, poor biodegradability and low absorption capacity. In this work, two renewable ILs where both cation and anion come from biogradable materials,2-hydroxyethyl-trimethylammoniume levulinate ([Choline][LA]) and 2-hydroxyethyl-trimethylammoniume lactate ([Choline]L), were synthesized and mixed with polyethylene glycol 200 (PEG200) to form 40 w% ILs binary mixture as SO₂ absorbents. Solubilities of SO₂ in the above two mxitures were measured under the temperature range of 303.15-333.15 K and the pressure up to 1.2 bar, with the result of 6.97-7.24 mol/kg absorbents at 1.0 bar and 303.15 K. When the SO₂ pressure is reduced to 0.039bar, the solubilities are still 1.77-1.84 mol/kg absorbents. Reaction Equilibrium Thermodynamic Model (RETM) was used analysis the thermodynamic behavior of SO₂ in present ILs mxitures. The obtained absorption enthalpies are as low as -39.81 and -51.69 kJ·mol⁻¹ for the two binary mixtures, respectively. The two mixtures possess one or more improvements over commonly reported ILs in the aspects of biodegradability, absorption capacity, cost and energy consumption for regeneration of absorbents.

Introduction

Sulfur dioxide (SO₂), a major atmospheric pollutant emitted from the combustion of fossil fuel [1], has caused a series of environmental problems affecting public health and human productive activity. Therefore, removal or reduction of SO₂ from flue gas has attracted extensive attention. Many commercial processes for flue gas desulfurization (FGD) have been developed in recent decades, such as ammonia method [2], limestone method [3] and seawater method [4]. The inherent drawbacks of these processes include second pollution, high operation cost and intensive energy consumption. Accordingly, the new processes with high efficiency, low cost and without by-products are still highly desirable.

In the past decade, ionic liquids (ILs) have become the research hot spot in gas capture and separation [5] due to their unique properties of negligible vapor pressure, tunable structure [6-8] and good solubility for acidic SO₂[9-11], CO₂[6-8, 12] and H₂S [13]. Since Wu et al [14] firstly reported the task-specific IL of 1, 1, 3, 3-tetramethylguanidinium lactate ([TMG]L) as SO₂ absorbent with the absorption capacity of 1.0 mol SO₂ per mol IL at 313.15K, many ordinary ILs [15-20] and functionalized ILs [21-30] were developed for SO₂ absorption. Ordinary ILs, such as guanidinium-based ILs [19] ([TMG][BF₄], [TMG][BTA], [TMGB₂][BTA]) and immidazolium-based ILs [20] ([hmim] [Tf₂N]) absorb SO₂ only through physical interaction. Thus, the absorption capacity of SO₂ is relatively small, especially in the region of low SO₂ partial pressure. A good strategy to enhance the absorption capacity of SO₂ with low pressure is introducing various weak basic anions to form functionalized ILs. Recently, Zhang et al [30] reported 1,1,3,3-tetramethylguanidinium phenolate

([TMG][PHE]), 1,1,3,3-tetramethylguanidinium 2,2,2-trifluoroethanoxide ([TMG][TE]) and 1,1,3,3-tetramethylguanidinium imidazolate ([TMG][IM]) to capture SO₂. Besides, acid salt ILs [21], novel ether functionalized ILs [22], and tunable azole-based ILs [23, 24, 31] were also reported as highly efficient absorbents for SO₂. However, most functionalized ILs are troubled by the high viscosity, which is disadvantageous for industrial applications. In order to overcome t the high viscosity of ILs, a direct way is to pair the functionalized anions with big quaternary ammonium or phosphonium cations. However, the gravimetric absorption capacity of the ILs will decrease because of their increasing molecular weights. Another simple and cheap method is the addition of organic solvent with high boiling point. For example, PEG200 [32] and sulfolane [33] were used to dilute carboxylic acid based ILs to form efficient absorbents for CO₂ or SO₂.

In recent years, synthesis of ILs using renewable materials has been attractive. Levulinic acid and lactic acid have been highlighted by the United States Department of Energy in 2004 and again in 2010 as a promising building block for chemistry [34]. Levulinic acid is also a nonreductive platform chemical industrially produced by Biofine process [35]. Lactic acid is another large-scale, organic commodity chemical from sugar. Polyethylene glycol (PEG) has been used widely in pharmaceutical, food and cosmetic industries. PEGs have many attractive properties including low volatility, nontoxicity, biodegradability, and available sources. As a continuous works of developing excellent absorbents for acidic gases, two new ILs of choline levulinate ([Choline][LA]) and choline lactate ([Choline]L) were synthesized and blended withPEG200 to form ILs/ PEG200 mixtures. The feature of present two ILs is that both the cation and anions come from renewable materials. PEG200 also has some unusual properties, such as nonvolatile, nontoxic, biodegradable, inexpensive, widely available. Unlike other aqueous ILs solutions reported in literature [36, 37]. ILs/PEG200 mixtures have negligible

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vapour pressure and thus avoid volatilization loss and lower energy consumption during the regeneration of absorbents. The SO_2 absorption performances of the two binary mixtures were systematically investigated and thermodynamic properties were also calculated by correlating the experimental data with Reaction Equilibrium Thermodynamic Model (RETM).

Experimental

Materials

SO_2 (0.999, mass fraction purity, the same below besides special statement) gas was supplied by Jingong Special Gas Co., Ltd. (Hangzhou, China). 2-Hydroxyethyl-trimethylammoniume hydroxide aqueous solution ([Choline][OH], AR grade, 0.3468 w%) was purchased from Jinan Jin Hui Chemical Co., Ltd. (Jinan, China). Levulinic acid (AR grade, 0.99), lactic acid (ACS grade, 0.85) and PEG200 (with the average molecular weight of 200 g mol^{-1}, AR grade) were obtained from Aladdin Chemical Company (Shanghai, China). All the chemicals were used without any further purification.

Preparation of ILs

[Choline[LA] and [Choline]L were prepared by direct neutralization reaction of [Choline][OH] with corresponding acids according to the literature method [38]. For example, equimolar levulinic acid was slowly added into the aqueous [Choline][OH], and the mixture was stirred magnetically for 2 h at room temperature. Then, the water was distilled off under reduced pressure. Finally, the [Choline][LA] as a light yellow viscous product was obtained under vacuum at 353 K for 48 h to remove possible trace of water and volatile impurities.

Characterization of ILs

Bruker AVANCE Ⅲ (500 MHz) and Nicolet 6700 FT-IR spectrometer were used to characterize the structure of the ILs, with the ^1H NMR, ^{13}C NMR, and FT-IR spectra results as following,

[Choline]L, ^1H NMR (500 MHz, DMSO-d$_6$, 25℃, TMS), δ/ppm: 3.00 (9H, s, 3×NCH$_3$), 3.83-3.85 (2H, m, OCH$_2$), 3.45-3.47 (2H, t, NCH$_2$), 1.09-1.10 (3H, d, CH$_3$), 3. 58-3.62 (1H, m, OCH), 5.48 (2H, s, 2×COH); ^{13}C NMR (500 MHz, DMSO-d$_6$, 25℃, TMS), δ/ppm: 21.65, 53.17, 64.41, 67.28, 72.34, 178.28; FT-IR: 666.5, 852.1, 924.4, 956.4, 1038.8, 1086.4, 1123.5, 1351.4, 1415.1, 1478.8, 1589.0, 2976.3, 3471.6 cm^{-1}.

[Choline][LA], ^1H NMR (500 MHz, DMSO-d$_6$, 25℃, TMS), δ/ppm: 3.00 (9H, s, 3×NCH$_3$), 3.82-3.83 (2H, d, OCH$_2$), 3.43-3.45 (2H, t, NCH$_2$), 2.44-2.46 (2H, t, COCH$_2$), 2.07-2.08 (2H, d, COOCH$_2$), 2.05-2.06 (3H, d, CH$_3$), 7.77 (1H, s, CH$_2$OH); ^{13}C NMR (500 MHz, DMSO-d$_6$, 25℃, TMS), δ/ppm: 29.80, 32.57, 39.61, 53.01, 64.27, 67.24, 174.99, 210.25; FT-IR: 573.6, 699.4, 865.8, 956.3, 1056.3, 1086.3, 1168.7, 1238.1, 1305.8, 1402.0, 1479.8, 1567.5, 1651.0, 1704.7, 3417.5 cm^{-1}.

Measurement of physical properties

The densities of two ILs/PEG200 mixtures were measured at atmospheric pressure and temperatures ranging from 303.15 to 333.15 K with 10 K intervals by Anton Paar DMA4500 with an uncertainty of ± 0.00001 g·cm^{-3}. The instrument was calibrated periodically with double-distilled water and dried air. The viscosity was detected by Pinkevitch method. The uncertainty of viscosity was ± 0.2%.

### Apparatus and procedure to determine solubility of SO_2 in ILs/PEG200

The solubility experiments were carried out using an isochoric saturation method. The apparatus was illustrated in Fig. 1 and the experimental procedure was described in detail in our previous works [39-42]. The apparatus was mainly made up of a SO_2 cylinder, constant temperature water baths with a precision of ± 0.05 K, a SO_2 Gas Reservoir (4, GR), Equilibrium Chamber (5, EC) with magnetic stirrer, pressure transmitter and digital indicator. The volumes of EC and GR were measured in our previous reported method [39] with the results of 141.61 cm^3 and 370.99 cm^3, respectively. Two pressure transmitters (Fujian WIDEPLUS Precision Instruments Co., Ltd. WIDEPLUS-8) with a precision of ± 0.6 kPa were used to record pressure change during absorption process. In a typical determination procedure, the temperature of water bath 2 was always maintained at 293.15 K. After a known mass (w) sample was placed into EC, the air of two chambers and all pipelines was evacuated to be p_0 with valve 12 closed and valve 9, 10, 13 opened. Then, with valve 12 opened, GR was charged with SO_2 from cylinder and the initial pressure was recorded as p_1. The temperature of water bath 3 was set to the desired value of T. Subsequently, SO_2 was brought into the EC from GR to contact with the absorbent with valve 12 closed and needle-type valve 11 opened. Absorption equilibrium was supposed to be reached when the pressure of the EC remained constant for at least 2 h. The equilibrium pressures were recorded as p_2 for the GR and p_3 for the EC. Therefore, the equilibrium pressure of SO_2 in EC was expressed as following:

$$p_s = p_3 - p_0 \tag{1}$$

The SO_2 uptake, $n\,(p_s)$ was calculated by the following equation:

$$n(p_s) = \rho_g(p_2,T)V_{GR} - \rho_g(p_1,T)V_{GR} - \rho_g(p_s,T)(V_{EC} - w/\rho_L) \tag{2}$$

where $\rho_g(p_i, T)$ represents the density of SO_2 in mol/cm^3 at p_i (i=1, s) and T, and is obtained from NIST standard reference data [43]. ρ_L is the density of binary mixture in g/cm^3 at T. V_{EC} and V_{GR} represent the volumes of EC and GR in cm^3, respectively. Continual measurements at the same equilibrium temperature were carried out by introducing more SO_2 into EC to reach new equilibrium.
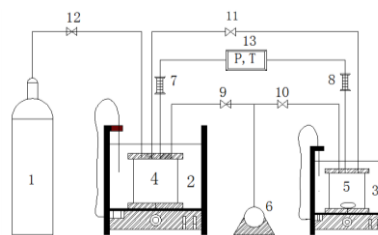
Fig. 1 Schematic diagram of the SO_2 solubility apparatus. 1, SO_2 gas cylinder; 2, 3, thermostatic water bath and magnetic stirrer; 4, SO_2 gas reservoir; 5, SO2 gas equilibrium cell; 6, vaccum; 7, 8, pressure transmitter; 9, 10, 11, 12 valve; 13, digital indicator.

Apparatus and procedure to study absorption and desorption of SO_2 in ILs/PEG200

The absorption experiments were carried out using a bubble method. In a typical experiment, an accurate mass of ILs/PEG200 mixture (about 4.0 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 mixture at the flow rate of 30 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 by

electronic balance (Mettler-Toledo AL204) until a constant value. In desorption of SO_2, the SO_2 saturated mixture was heated at 323.15 K under vacuum of 0.01 bar for 0.5 hr.

Results and discussion

Physical properties of ILs/PEG200 binary mixtures

The density and viscosity of two ILs/PEG200 mixtures containing 40 w% ILs at the temperature range of (303.15 to 333.15) K were systematically measured with the values presented in Table 1. As can be seen, the density and viscosity decreased with increasing temperature. [Choline]L/PEG200 possesses lower density and viscosity than [Choline][LA]/PEG200 at each same temperature level. The viscosities of two ILs/PEG200 binary mixtures are less than 80 mPa·s at 323.15 K, which would be helpful for promoting the gas absorption and desorption process.

Table 1 Densities and viscosities of the ILs/PEG200 binary mixtures

Temper-ature (K)	ρ (g·cm^{-3})		η (mPa·s)	
	[Choline]L /PEG200	[Choline][LA] /PEG200	[Choline]L /PEG200	[Choline][LA] /PEG200
303.15	1.17212	1.18804	173.31	305.78
313.15	1.16504	1.17798	94.37	138.26
323.15	1.15807	1.16803	62.04	79.54
333.15	1.15123	1.15821	40.93	46.83

SO_2 absorption in ILs/ PEG200 binary mixtures

Absorption capacity and recycling of ILs/PEG200 binary mixtures

Table 2 Solubilities of SO_2 in [Choline]L/PEG200 [a]

The solubilities of SO_2 in two ILs/PEG200 binary mixtures were measured at T = (303.15, 313.15, 323.15 and 333.15) K and pressure up to 1.2 bar. The experimental results are presented in Tables 2 and 3, where m_{SO_2} stands for the molality in the liquid phase and p for SO_2 equilibrium pressure above the absorbents. m_{SO_2} can be easily calculated by following equation,

$$m_{SO_2} = n_{SO_2} / w \qquad (3)$$

where w is the mass of binary mixture used in the experiment. Figs. 2 and 3 show SO_2 solubility profiles in ILs/PEG200 binary mixtures at different temperatures. As can be seen, the solubility of SO_2 grows rapidly with increasing SO_2 partial pressure at low pressure (below 0.1 bar), while grows slowly with the increasing pressure at the higher pressure range. Such phenomenon indicates that chemical absorption may take place during the region of low pressure, while physical absorption may dominate during the relatively higher pressure rang of (0.1-1.2 bar). For example, the solubilities of SO_2 in [Choline]L/PEG200 and [Choline][LA]/PEG200 at 303.15K and 1.0 bar were 6.9652mol/kg (0.4462 g/g), 7.2393mol/kg (0.4638 g/g), respectively. Even when the SO_2 partial pressure is only 0.04 bar, the solubilities are 1.7661 mol/kg (0.1131 g/g) and 1.8442 mol/kg (0.1181 g/g) for [Choline]L/PEG200 and [Choline][LA]/PEG200, respectively. According to the literature [44], pure PEG200 is only a physical absorbent for SO_2. Thus, the solubility of SO_2 in PEG200 under low pressure is very low. For example, solubility of SO_2 in PEG200 at 0.039 bar and 303.15K is 0.3075 mol/kg (0.0197 g/g), Therefore, the majority of the absorption capacity comes from the chemical absorption of ILs in ILs/PEG200 binary mixtures at low SO_2 partial pressure region.

303.15 K		313.15 K		323.15 K		333.15 K	
p (bar)	m_{SO_2} (mol/kg)	p (bar)	m_{SO_2} (mol/kg)	p (bar)	m_{SO_2} (mol/kg)	p (bar)	m_{SO_2} (mol/kg)
0.041	1.9736	0.039	1.7962	0.024	1.4267	0.040	1.2787
0.077	2.3006	0.070	1.9947	0.046	1.6066	0.062	1.4682
0.109	2.4991	0.104	2.1819	0.078	1.7944	0.096	1.6593
0.155	2.7940	0.151	2.4129	0.107	1.9332	0.150	1.8729
0.206	3.0971	0.212	2.6851	0.154	2.1278	0.208	2.0487
0.306	3.6552	0.311	3.0956	0.213	2.3402	0.348	2.4067
0.404	4.1493	0.400	3.4345	0.333	2.7200	0.425	2.5814
0.513	4.6871	0.503	3.8099	0.423	2.9769	0.505	2.7549
0.601	5.1103	0.603	4.1653	0.505	3.2068	0.603	2.9591
0.706	5.5943	0.710	4.5299	0.607	3.4804	0.706	3.1696
0.807	6.0525	0.818	4.8877	0.703	3.7268	0.805	3.3615
0.912	6.5136	0.930	5.2462	0.806	3.9855	0.900	3.5407
1.015	6.9702	1.014	5.5400	0.903	4.2243	1.003	3.7343
1.105	7.4099	1.107	5.8331	1.017	4.5021	1.101	3.9129
1.203	7.8418	1.218	6.1813	1.116	4.7391	1.206	4.1040
				1.206	4.9500		

[a] Standard uncertainties u are $u(T)$ = 0.05 K, $u(p)$ = 0.006 bar, $u_r(m)$ = 0.02.

Table 3 Solubilities of SO_2 in [Choline][LA]/PEG200 [a]

303.15 K		313.15 K		323.15 K		333.15 K	
p (bar)	m_{SO_2} (mol/kg)	p (bar)	m_{SO_2} (mol/kg)	p (bar)	m_{SO_2} (mol/kg)	p (bar)	m_{SO_2} (mol/kg)

|							
0.021	1.5524	0.023	0.9230	0.027	0.6790	0.024	0.3095
0.039	1.7902	0.047	1.7045	0.043	1.5061	0.046	1.3289
0.070	2.0582	0.073	1.8702	0.075	1.7266	0.070	1.6060
0.100	2.2932	0.098	2.0144	0.112	1.8941	0.135	1.8637
0.154	2.6775	0.150	2.2798	0.153	2.0476	0.154	1.9203
0.209	3.0402	0.203	2.5283	0.207	2.2399	0.202	2.0515
0.303	3.6163	0.307	2.9982	0.314	2.5902	0.300	2.2965
0.403	4.1884	0.406	3.4133	0.418	2.9077	0.405	2.5440
0.501	4.7112	0.509	3.8206	0.507	3.1713	0.503	2.7609
0.605	5.2557	0.617	4.2337	0.604	3.4463	0.611	2.9962
0.702	5.7268	0.725	4.6349	0.709	3.7358	0.706	3.1980
0.813	6.2686	0.805	4.9198	0.819	4.0316	0.806	3.4021
0.901	6.6873	0.901	5.2587	0.900	4.2464	0.906	3.6063
1.005	7.1939	1.005	5.6179	1.007	4.5205	1.008	3.8119
1.107	7.6914	1.100	5.9482	1.099	4.7561	1.108	4.0071
1.205	8.1492	1.202	6.2964	1.210	5.0377	1.241	4.2651

[a] Standard uncertainties u are $u(T)$ = 0.05 K, $u(p)$ = 0.006 bar, $u_r(m)$ = 0.02.
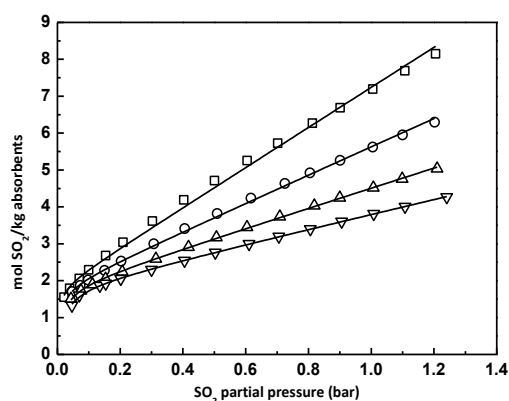
Fig. 2 Dependence of **s**olubility of SO_2 on pressure and temperature in [Choline][LA]/PEG200. (□ 303.15K; ○ 313.15K; △ 323.15K; ▽ 333.15K; Lines: fitting results)
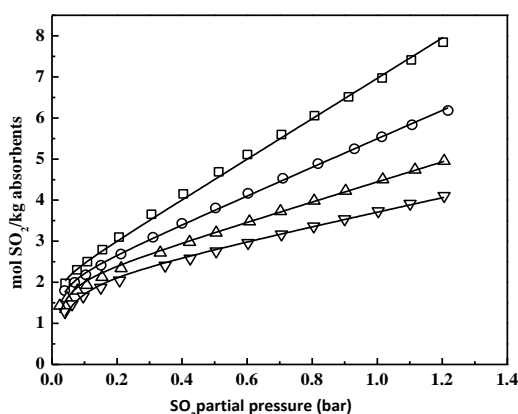
Fig. 3 Dependence of **s**olubility of SO_2 on pressure and temperature in [Choline]L/PEG200. (□ 303.15K; ○ 313.15K; △ 323.15K; ▽ 333.15K; Lines: fitting results)
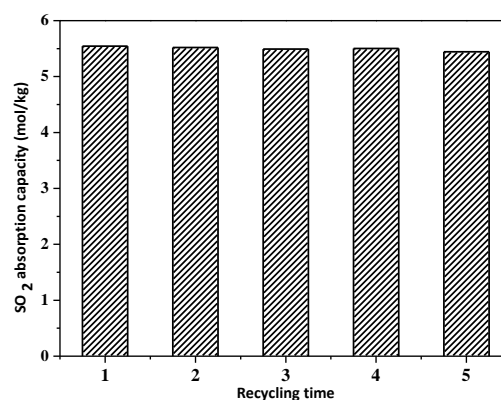

Fig. 4 SO_2 absorption in [Choline]L/PEG200 for 5 cycles (Absorption: 313.15K, 1.0 bar; Desorption: 353.15K, 0.01 bar).

As a gas absorbent, regeneration and recyclability are related directly to the comprehensive cost and equipment investment in gas absorption and separation process. In order to evaluated the recycling of the s ILs/PEG200 binary mixtures used in this work, the SO_2-saturated [Choline]L/PEG200 was heated to 353.15K under vacuum of 0.01 bar for 0.5 hr to release the dissolved SO_2. Then, the renewed [Choline]L/PEG200 was reused to capture SO_2 under 313.15K and 1.0 bar using a bubble method. Such recycling experiment was carried out five times with the results illustrated in Fig. 4. As shown in Fig. 4, the absorption capacity was barely influenced after five cycles of absorption-regeneration process, revealing that the capture of SO_2 by ILs/PEG200 binary mixtures could be regarded as a basically reversible process.

Thermodynamic analysis

Thermodynamic analysis is helpful for understanding absorption mechanism and designing excellent absorbents. According to the discussion in previous section, the dependence of solubility of SO_2 on the pressure strays away from the ideal behaviour, especially in the low pressure region. Such phenomenon was ascribed to the chemical interaction between SO_2 and ILs. On the basis of reports in the literatures[33, 45], a Reaction Equilibrium Thermodynamic Model

(RETM) including the physical and chemical absorptions was used to correlate the experimental solubility data. The Henry's law constants, reaction equilibrium constants, chemical absorption capacity, physical absorption capacity and thermodynamic properties were derived for the present two mixtures. The total absorption capacity could be divided into two parts, physical dissolution and chemical reaction. They were interdependent and controlled by dissolution equilibrium and reaction equilibrium expressed as equations (4) and (5) as following,

$$SO_2(g) \rightarrow SO_2(l) \tag{4}$$

$$SO_2(l) + IL(l) \rightarrow SO_2IL(l) \tag{5}$$
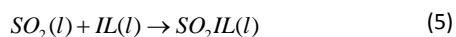
Thus, the overall reaction is expressed as equation (6),

$$SO_2(g) + IL(l) \rightarrow SO_2IL(l) \tag{6}$$
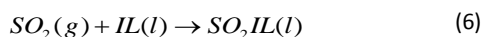
Here, Henry's law constant (H), equilibrium constant (K_1°), and over reaction equilibrium constant (K°) were used to qualitatively describe the equations (4)-(6), respectively. The three constants could be correlated using equations (7) and (8) as following,

$$m_t = (\frac{m_{IL_0}}{p + \frac{H}{K_1^\circ}} + \frac{1}{H})p \tag{7}$$

$$K^\circ = \frac{K_1^\circ}{H}p^\circ \tag{8}$$

where m_t is total concentration of SO_2 in ILs/PEG200 in mol/kg, m_{IL_0} is the initial concentration of ILs and it should be a constant, p refers to the SO_2 partial pressure in bar and p^0 refers to the standard pressure of 1.0 bar.

By fitting the experimental data in [Choline][LA]/PEG200 and [Choline]L/PEG200 mxitures, the values of K°, H were obtained and presented in Table 4. As seen from Table 4, [Choline][LA]/PEG200 possesses larger K° and smaller H than [Choline]L/PEG200, which indicates that [Choline] [LA]/PEG200 exhibits a higher SO_2 absorption capacity than [Choline] L/PEG200. Moreover, the good fitting results were also displayed graphically in Figs. 1 and 2, respectively ($R^2 > 0.99$).

The Henry's law constants in terms of molar fraction and molality in pure ILs and PEG200 could be obtained by following equations [33], [46],

$$H_{2,m}(T,p) = \lim_{m_{SO_2} \rightarrow 0} \frac{f^{gas}}{m_{SO_2}} \approx \frac{p}{m_{SO_2}/m^0} \tag{9}$$

$$\frac{p}{H} = \frac{0.4 \cdot p}{H_{1,m}} + \frac{0.6 \cdot p}{H_{2,m}} \tag{10}$$

$$H_{1,x} = \frac{H_{1,m}}{M_1/m^0} \tag{11}$$

where $H_{1,m}$ and $H_{2,m}$ are Henry's law constants of SO_2 absorption in pure ILs and PEG200 in terms of molality in bar, respectively. $H_{1,x}$ is the Henry's law constant of SO_2 absorption in terms of molar fraction in bar, M_1 is the molar mass of ILs in mol/kg and m^0 is the standard molality (1 mol/kg). f^{gas} is the gas phase fugacity of SO_2 in kPa, P is the gasous partial pressure of SO_2 at equilibrium. The estimated Henry's law constants were presented in Table 5. Both $H_{1,m}$ and $H_{1,x}$ in [Choline][LA] are lower than those

in [Choline]L , meaning that [Choline][LA] has a stronger physical interaction with SO_2 than [Choline]L.

The total solubility of SO_2 in ILs/PEG200 binary mixtures (m_t) could be divided into physically absorbed SO_2 (m_{phy}) and chemically absorbed SO_2 (m_{chem}),

$$m_t = m_{phy} + m_{chem} \tag{12}$$

where m_{phy} can be obtained by Henry's law, m_{chem} can be subsequently obtained by equation (12). Calculated values of physical absorption and chemical absorption of SO_2 in [Choline][LA]/PEG200 and [Choline]L/PEG200 at 313.15 K were presented in Figs. 5 and 6, respectively. In the case of [Choline][LA]/PEG200, chemical absorption capacity is mainly constrained by the stoichiometric ratio in chemical reaction. Therefore, the increasement of chemical absorption capacity was very small with the increasing SO_2 partial pressure even at relatively high-pressure area. On the contrary, the physical absorption capacity proportional to the SO_2 partial pressure as expressed by Henry's law. It is evident in Fig. 5 that chemical solubility is larger than physical solubility under low pressures (below 0.51 bar), while physical solubility surpasses the chemical solubility under high pressures (above 0.51 bar). This phenomenon indicates that present mixture also possesses good absorption ability even at low SO_2 partial pressure, which is a necessary requirement to absorbent for the removal of SO_2 in flue gas. Similar phenomenon is observed in the case of [Choline]L/PEG200.
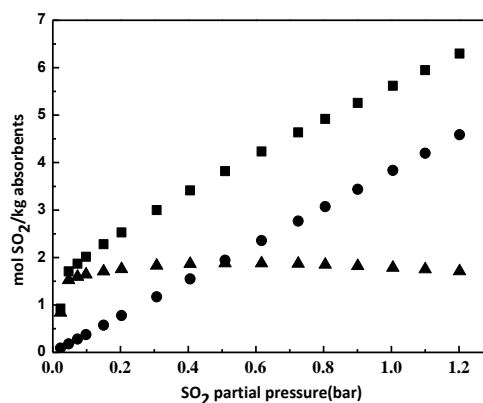
Fig. 5 Calculated chemical and physical solubilities of SO_2 in [Choline][LA]/PEG200 at 313.15K. (■ overall solubilities; ▲ chemical solubilities; ● physical solubilities)

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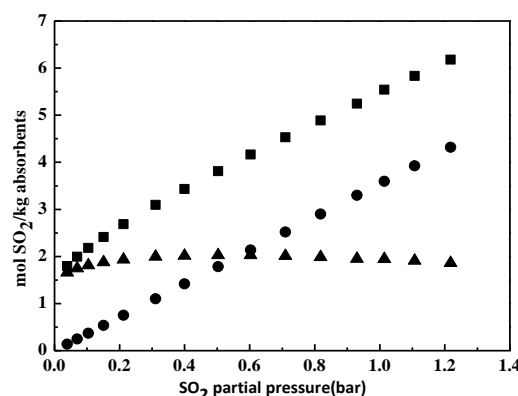
Fig. 6 Calculated chemical and physical solubilities of SO_2 in [Choline]L/PEG200 at 313.15K. (■ overall solubilities; ▲ chemical solubilities; ● physical solubilities)

Table 4 Standard equilibrium constants of overall reaction and Henry's law constants of SO_2 absorption in ILs/PEG200 binary mixtures.

Temperature(K)	[Choline]L/PEG200		[Choline][LA]/PEG200	
	K^0	H(bar)	K^0	H(bar)
303.15	191.2	0.204	206.6	0.184
313.15	91.3	0.282	109.1	0.262
323.15	56.8	0.415	68.7	0.369
333.15	28.7	0.586	49.9	0.499

Table 5 Estimated Henry's constants of SO_2 absorption in pure ILs

Temperature(K)	[Choline]L		[Choline][LA]	
	$H_{1,m}$(bar)	$H_{1,x}$(bar)	$H_{1,m}$(bar)	$H_{1,x}$(bar)
303.15	0.642	3.323	0.351	1.599
313.15	1.143	5.913	0.640	2.919
323.15	1.621	8.386	0.733	3.343
333.15	2.107	10.902	0.821	3.743

Thermodynamic properties are helpful for understanding gas dissolution and reaction equilibrium between SO_2 and the liquids. Thus, thermodynamic properties such as molar reaction Gibbs energy $\Delta_r G^0_m$, molar reaction enthalpy $\Delta_r H^0_m$ and molar reaction entropy $\Delta_r S^0_m$ were calculated. In this work, molar reaction enthalpy $\Delta_r H^0_m$ can be calculated using equation (13) from the slope of linear fitting of $\ln K^0$ with $1/T$ (as shown in Fig. 7).

$$\frac{\partial \ln K^0}{\partial (1/T)} = -\frac{\Delta_r H^0_m}{R} \quad (13)$$

Two other thermodynamic properties $\Delta_r G^0_m$ and $\Delta_r S^0_m$ can further be calculated from equations (14) and (15).

$$\Delta_r G^0_m = -RT \ln K^0 \quad (14)$$

$$\Delta_r S^0_m = (\Delta_r H^0_m - \Delta_r G^0_m)/T \quad (15)$$

The thermodynamic property changes at T = 313.15 K are presented in Table 6. As shown in Table 6, molar reaction enthalpy were found to be -51.69 and -39.81 kJ·mol^{-1} for [Choline]L/PEG200 and [Choline][LA]/PEG200, respectively. The negative values indicate that absorption process is exothermic and favourable from the view of enthalpy. The absolute value of $\Delta_r H^0_m$ for SO_2 absorption in [Choline][LA]/PEG200 is less than that in [Choline]L/PEG200, suggesting [Choline][LA]/PEG200 is weaker to interact with SO_2 than [Choline]L/PEG200. Thus, the absorbed SO_2 could be stripped out easily. From molecular points, the negative value of $\Delta_r S^0_m$ means that a higher ordering degree in ILs/PEG200 is obtained after the capture of SO_2. The negative $\Delta_r G^0_m$ indicates that the capture of SO_2 by ILs/PEG200 is a spontaneous process.
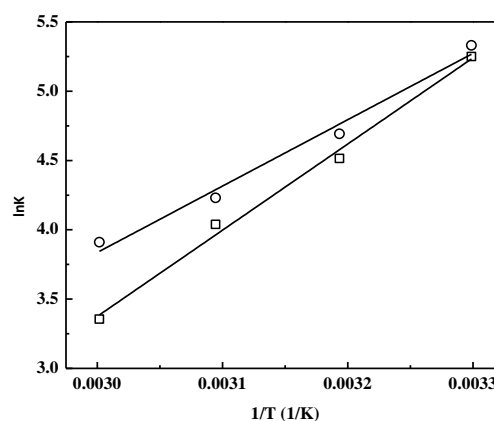
Fig. 7 Linear fit of ln K^0 and $1/T$. (○ [Choline][LA]/PEG200; □ [Choline]L/PEG200).

Table 6 Molar reaction Gibbs energy, molar reaction enthalpy and molar reaction entropy of SO_2 absorption in ILs/PEG200 binary mixtures at 313.15 K

Absorbents	$\Delta_r G^0_m$ (kJ·mol^{-1})	$\Delta_r H^0_m$ (kJ·mol^{-1})	$\Delta_r S^0_m$ (J·K^{-1}·mol^{-1})
[Choline]L/PEG200	-11.75	-51.69	-127.53
[Choline][LA]/PEG200	-12.22	-39.81	-88.13

Comparison with other ILs

For throughout investigation of present renewable ILs as SO_2 absorbent, the suppositional solubilities of SO_2 in present ILs were compared with those in other ILs reported in literatures, as illustrated in Table 7. It can be found that present ILs demonstrates similar absorption capacity of SO_2 with [TMG]L [29], [DMEA][diglutarate] [33], and [Et$_2$NEMim][Tf$_2$N] [26], while superior to [MEA]L [29], [Bmim][SO$_4$] [47], [Bmim][BF$_4$] and [TMG] [Tf$_2$N] [19] and inferior to functionalized ILs of [P$_{66614}$][IM], [P$_{66614}$][Tetz] [23] and [Et$_2$NEMim][Tetz] [26]. Although ILs with tetrazolate and imidazolate anion exhibit higher SO_2 capacity, they also suffer from intensive energy consumption during regeneration (the enthalpies for the absorption in [P$_{66614}$][IM] and [P$_{66614}$][Tetz] are -124.6 and -89.4 kJ·mol^{-1}, respectively), expensive cost and doubtful biodegradability. [TMG]L also encounters the same question of energy consumption because the $\Delta_r H^0_m$ of SO_2 absorption in [TMG]L is -71.78 kJ·mol^{-1}.

In addition, present two ILs can be prepared from inexpensive and biodegradable materials. In addition, the lower $\Delta_r H^0_m$ of SO_2 absorption in [Choline][LA]/PEG200 (-39.81 kJ·mol^{-1}) and [Choline]L/PEG200 (-51.69 kJ·mol^{-1}) means less energy penalty in the regeneration of absorbents. Thus, with the overall consideration of absorption capacity, regeneration energy consumption, cost and biodegradability, [Choline]L/PEG200 and [Choline][LA]/PEG200 are thought to be an attractive alternative to pure ILs for SO_2 absorption.

Table 7 Comparison of the suppositional solubility of SO_2 in pure ILs with other ILs.

ILs	Tempera-ture(K)	Solubility of SO$_2$ at 0.004 bar (mol/mol)	Solubiliy of SO$_2$ at 1.0 bar (mol/mol)	Reference
[Choline]L	313.15	0.241	1.533	This work

[Choline][LA]	313.15	0.274	1.770	This work
[Bmim][BF$_4$]	313.15	NA[a]	0.86	[19]
[TMG] [Tf$_2$N]	313.15	NA	0.76	[19]
[DMEA][diglutarate]	313.15	0.370	1.382	[33]
[TMG]L	313.15	0.52[b]	1.56	[29]
[MEA]L	313.15	0.17	0.82	[29]
[Bmim][SO$_4$]	313.15	NA	1.11	[47]
[Et$_2$NEMim][Tf$_2$N]	313.15	NA	1.85	[26]
[Et$_2$NEMim][Tetz]	313.15	NA	3.01	[26]
[P$_{66614}$][IM]	293.15	2.07[c]	4.80	[23]
[P$_{66614}$][Tetz]	293.15	1.54[c]	3.72	[23]

[a] NA: Not available, [b] at 0.00343 bar, [c] at 0.1 bar

Conclusions

In present work, two renewable carboxylic acid-based ionic liquids were prepared and further blended with PEG200 to form binary mixtures containing 40 w% ILs. Their physical properties as well as performances for SO$_2$ absorption were also investigated. RETM was used to correlate the experimental data and calculate the Henry's law constants, reaction equilibrium constants, chemical/physical absorption capacity and thermodynamic properties of SO$_2$ absorption in the mixtures. Compared with many ILs reported in literature, [Choline][LA]/PEG200 and [Choline]L/PEG200 can be regarded as good alternative due to their one or more advantages in the aspects of absorption capacity, biodegradability, cost, and energy consumption during regeneration of absorbents.

Acknowledgements

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