NJC

PAPER



Cite this: DOI: 10.1039/c6nj03563a



View Article Online

Investigation of furoate-based ionic liquid as efficient SO₂ absorbent

Dongshun Deng,* Yaotai Jiang and Xiaobang Liu

A series of furoate anion-functionized ionic liquids (ILs) were synthesized and applied as new absorbents for SO₂. Results showed that these ILs possessed satisfactory performance for SO₂ absorption. At 293.15 K, the maximum absorption capacity was 0.69 and 0.24 g SO₂ per g P_{4442} [FA] under 1.0 and 0.1 bar, respectively. The SO₂ enriched ILs were easily regenerated by bubbling N₂ at 343.15 K and recycled five times without obvious loss of absorption performance. The influences of temperature, SO₂ partial pressure, and water content in ILs on SO₂ absorption performance were systematically explored. The absorption capacity of ILs is discussed from aspects of the structure of cations, anions, and the interaction of cation–anion. The absorption mechanism was analyzed using NMR and FTIR methods. The selectivities of SO₂/CO₂, SO₂/N₂ and SO₂/O₂ were studied and [P₄₄₄₂][FA] achieved relatively high selectivity for SO₂ compared to other gases. Present furoate ILs demonstrate potential application as a SO₂ absorbent owing to their good performance.

Received 15th November 2016, Accepted 22nd January 2017

DOI: 10.1039/c6nj03563a

rsc.li/njc

Introduction

Sulfur dioxide (SO₂), largely emitted into the atmosphere from fossil-fuel-fired power plants, is widely regarded as a vital component of acid rain and smog, which cause serious harm to ecology, environment, health, etc.¹ Ways to control and reduce SO₂ release at low cost have attracted extensive attention because of stringent policies for environmental protection.² To date, many commercial Flue Gas Desulfurization (FGD) technologies have been utilized to remove SO₂ from exhaust flue gas with aqueous slurries of limestone as the most efficient and typical absorbent.³ However, a valuable sulfur resource is transferred into a by-product of CaSO₄ and wastewater is produced in abundance during that process. Moreover, some organic solvents have also been reported to absorb SO2, but secondary pollution caused from their volatility is a simultaneous obstacle.⁴ Thus, exploring a renewable and efficient absorbent for removal and recovery of SO₂ is still highly in demand.

Recently, Ionic Liquids (ILs) have manifested efficacy as absorbents for acidic gas because of their good absorption capacity as well as superior properties of high thermal stability, chemical inertness, negligible volatility, and structure diversity.^{5–8} Generally, the absorption capacity of SO₂ in conventional ILs is not high. Fortunately, the most attractive feature of ILs is the introduction of functional groups into cations or anions to adjust performance of gas absorption. Since Wu *et al.* reported the first

functionalized IL of 1,1,3,3-tetramethylguanidinium lactate ([TMG][L]) for chemisorption of SO₂,⁹ many anion-functionalized ILs have been developed for efficient and reversible SO₂ capture. For example, Shang et al.¹⁰ combined 1,1,3,3-tetramethylguanidinium with phenolate, 2,2,2-trifluoroethanoxide, or imidazolate to form ILs as efficient SO₂ absorbents. Wang's group¹¹⁻¹⁴ designed a series of azole-based, phenol-based, and acylamido-based ILs as efficient materials to capture SO₂ through multiple-site chemical and physical absorption, with the highest absorption capacity of 0.95 g SO₂ per g IL at 293.15 K and 0.1 MPa. Huang et al.¹⁵ reported six dicarboxylic acid salt ILs as reversible absorbents for SO2 with the best performance from 0.456 g SO_2 per g IL at 1.0 bar and 313.15 K. Cui et al.¹⁶ developed halogenated carboxylate ILs to capture SO₂. Although ILs demonstrated satisfactory performance as SO₂ absorbents, the abovementioned functionalized anions still encountered limitations of uncertain toxicity and poor biodegradability.

The emergence of Green Chemistry, replacing hazardous reagents by "green" chemicals, has become important,¹⁷ and the preparation of ILs from renewable ("green") materials is completely in accordance with the concept of Green Chemistry. By developing a bio-based anion to form functionalized IL, 2-furoic acid is a good alternative to traditional carboxylic acids and can be conveniently obtained by oxidation of furaldehyde, which is a typical platform chemical from biomass; this was highlighted by the United States Department of Energy in 2004 and again in 2010 as a promising building block for chemistry.¹⁸ 2-Furoic acid has a pK_a value of 3.16. It was reported that an organic acid with a larger pK_a value than sulfurous acid (pK_a = 1.81 at 298 K) would be chosen and neutralized to

Zhejiang Province Key Laboratory of Biofuel, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China. E-mail: dengdsh@zjut.edu.cn

synthesize a functional IL for chemically capturing SO₂.¹⁹ Furthermore, 2-furoic acid has the merit of a high normal boiling point of 403-405 K.²⁰ For example, even if there is some water exited in the furoated IL or flue gas, the derived 2-furoic acid, due to a neutralization reaction, can still be kept in the system during the regeneration of SO₂-saturated ILs by heating. Based on above considerations, here we describe a new strategy to build an anion-functionalized furoate-based IL. Previous research indicated that a halo atom in carboxylates is helpful for improving their absorption capacity with SO2.¹⁶ Therefore, 5-bromo-2-furoic acid was also selected to prepare anionfunctionalized ILs for a comparative study. To investigate the relationship between a structure and absorption performances, and to design a more competitive absorbent for SO₂, a serial group of two furoate-based chemicals with four different cations were synthesized and their physicochemical properties, as well as the performances of SO₂ absorption, were systematically investigated for the first time. Meanwhile, effects of temperature, partial pressure of SO2 and the water content in ILs on the absorption capacity, and recyclability of the P4442[FA] were further investigated.

Experimental

Materials

SO₂ and N₂ (0.999, mass fraction purity, with the same below) were supplied by Jingong Special Gas Co., Ltd (Hangzhou, China). 2-Furoic acid (FA), tributylphosphine (P₄₄₄, 0.95), bromoethane (0.99), and tetraethylammonium bromide ([N₂₂₂₂]Br, 0.98) were purchased from Aladdin Industrial Co., Ltd (Shanghai, China). 5-Bromo-2-furoic acid (BFA, 0.99) and trihexyl(tetradecyl) phosphonium bromide ([P₆₆₆₁₄]Br, 0.95) were obtained from J&K Scientific Ltd (Beijing, China). Choline hydroxide (ChOH, 0.99) was supplied by Shouguang Jinyu Industrial Co., Ltd (Jinan, China). 201 × 7(OH) Anion-exchange resin was obtained from the Chemical Plant of NanKai University. The exchange capacity of anion-exchange resin was 3.41 mmol g^{-1} (dry resin). All the reagents were used without further purification.

Synthesis and characterization of ionic liquids

All ILs were synthesized by neutralizing an equimolar corresponding base with FA or BFA. Here, the detailed procedure is described by taking $[P_{4442}]$ [FA] as an example. The intermediate of $[P_{4442}]$ Br was first prepared according to the literature procedure.¹² In a typical run, P_{444} (2.02 g, 10 mmol) in MeCN (10 cm³) was charged into a 100 cm³ flask. Subsequently, bromoethane (1.20 g, 11 mmol) in MeCN (10 cm³) was added dropwise into the flask *via* a syringe within 30 min at room temperature. The mixture was then heated to 60 °C in a water bath and stirred for 24 h. MeCN was distilled off under reduced pressure at 70 °C. Finally, the product was washed with ethyl acetate (3 × 20 mL) and dried at 80 °C under high vacuum for 24 h. The product of $[P_{4442}]$ Br was obtained as white solid with a yield of 87%.

 $[P_{4442}][OH]$, $[P_{66614}][OH]$, and $[N_{2222}][OH]$ were obtained using an anion-exchange resin from $[P_{4442}]Br$, $[P_{66614}]Br$, and

 $[N_{2222}]Br$, respectively. $[P_{4442}][FA]$ was obtained by direct neutralization of equimolar FA and $[P_{4442}][OH]$ according to the literature method.¹ $[N_{2222}][FA]$, $[N_{2222}][BFA]$, and Ch[FA] presented as solids; the other ILs with different combinations of cations and anions were clear, bright, and viscous liquids at room temperature.

The water content of the ILs was measured by Karl Fischer analysis (SF-3 Karl-Fischer Titration, Zibo Haifen Instrument Co., Ltd) with a mass fraction of $\leq 0.3\%$ in all cases. An electronic balance (Mettler-Toledo ME204E) with an accuracy of ± 0.0002 g was used to determine weights of the materials. Thermogravimetric analysis (TGA) was performed on a PerkinElmer instrument Q50 under N2 atmosphere with a heating rate of 10 K min⁻¹, and the decomposition temperatures (T_d) were determined according to the TGA curves. Bruker AVANCE III (500, 126, 202 MHz) and Nicolet 6700 FT-IR spectrometers were used to characterize the structures of ILs, and no obvious impurity peaks were found. Electrospray ionization-MS (ESI-MS) characterization was performed on a Waters 2695 Thermo LCQ Deca XP plus LCMS spectrometer. The samples were stored in a desiccator to avoid any effect of atmospheric humidity. The ¹H NMR chemical shift data for the ILs were listed as follows.

[Ch][FA]. ¹H NMR (500 MHz, DMSO-d₆, TMS), δ /ppm: 7.74 (1H, dd, O-CH=CH), 6.98–6.97 (1H, dd, CH-CH=C), 6.54–6.53(1H, t, CH=CH-CH), 3.86–3.84 (2H, t, OCH₂), 3.44–3.42 (2H, t, NCH₂), 3.13 (9H, s, 3 × NCH₃), 2.51–2.50 (1H, s, COH). ¹³C NMR (126 MHz, CDCl₃, TMS), δ /ppm: 147.32, 145.20, 116.50, 111.65, 68.16, 56.21, 54.50. ESI-MS: m/z = 103.9 ([Ch]⁺), 318.2 ([Ch][FA] + [Ch]⁺).

[N₂₂₂₂][FA]. ¹H NMR (500 MHz, DMSO-d₆, TMS), δ /ppm: 7.46 (1H, dd, O-*CH*=CH), 6.53 (1H, dd, CH-*CH*=C), 6.35–6.34 (1H, t, CH=*CH*-CH), 3.23–3.19 (8H, m, 4 × NCH₂), 1.17–1.13 (12H, t, 4 × CH₃). ¹³C NMR (126 MHz, CDCl₃, TMS), δ /ppm: 164.08, 153.17, 142.24, 111.78, 110.77, 52.42, 52.40, 7.49. ESI-MS: *m*/*z* = 130.2 ([N₂₂₂₂]⁺), 369.8 ([N₂₂₂₂][FA] + [N₂₂₂₂]⁺).

[**P**₆₆₆₁₄][**FA**]. ¹H NMR (500 MHz, DMSO-d₆, TMS), δ/ppm: 7.40 (([P₆₆₆₁₄]⁺), 1077.7 ([P₆₆₆₁₄][**FA**] + [P₆₆₆₁₄]⁺) 1H, dd, O–CH—CH), 6.45–6.44 (1H, dd, CH–CH—C), 6.31–6.30 (1H, t, CH—CH–CH), 2.23–2.17 (8H, m, 4 × PCH₂), 1.49–1.24 (48H, m, 24 × CH₂), 0.89–0.84 (12H, m, 4 × CH₃). ¹³C NMR (126 MHz, CDCl₃, TMS), δ/ppm: 163.76, 153.56, 141.37, 110.92, 110.21, 31.57, 30.77, 30.49, 30.37, 30.17, 30.06, 29.33, 29.30, 29.27, 29.17, 29.01, 28.96, 28.64, 22.34, 22.00, 21.55, 21.52, 18.76, 18.38, 13.78, 13.59. ³¹P NMR (202 MHz, CDCl₃, H₃PO₄), δ/ppm: 33.07. ESI-MS: m/z = 483.9 ([P₆₆₆₁₄]⁺), 1077.7 ([P₆₆₆₁₄][FA] + [P₆₆₆₁₄]⁺).

[**P**₄₄₄₂][FA]. ¹H NMR (500 MHz, CDCl₃, TMS), δ/ppm: 7.41 (1H, dd, O–C*H*=CH), 6.66 (1H, dd, CH–C*H*=C), 6.33 (1H, t, CH=C*H*–CH), 2.61 (2H, t, PCH₂), 2.52 (6H, t, 3 × PCH₂), 1.69–1.43 (12H, d, 6 × CH₂), 1.26-1.15 (3H, t, CH₃), 0.95–0.89 (9H, t, 3 × CH₃). ¹³C NMR (126 MHz, CDCl₃, TMS), δ/ppm: 162.11, 156.15, 141.13, 110.27, 110.00, 24.29, 24.19. 24.02, 23.90, 23.65, 23.62, 18.92, 18.03, 17.65, 13.72, 13.46, 12.30, 11.91, 5.95, 5.91. ³¹P NMR (202 MHz, CDCl₃, H₃PO₄), δ/ppm: 34.95. ESI-MS: m/z = 231.4 ([P₄₄₄₂]⁺), 573.1 ([P₄₄₄₂]FA] + [P₄₄₄₂]⁺).

[**P**₄₄₄₂][**BFA**]. ¹H NMR (500 MHz, DMSO-d₆, TMS), δ/ppm: 6.47-6.45 (1H, d, CH-CH=C), 6.41-6.40 (1H, d, CBr=CH-CH),

2.52–2.50 (2H, t, PCH₂), 2.27–2.18 (6H, t, 3 × PCH₂), 1.49–1.37 (12H, d, 6 × CH₂), 1.16–1.04 (3H, t, CH₃), 0.92 (9H, t, 3 × CH₃). ¹³C NMR (126 MHz, CDCl₃, TMS), δ /ppm: 162.29, 155.58, 120.70, 113.30, 112.26, 23.91, 23.72, 23.60, 23.48, 23.45, 23.40, 23.36, 18.21, 18.14, 17.76, 13.32, 13.14, 12.45, 12.07, 5.77, 5.73. ³¹P NMR (202 MHz, CDCl₃, H₃PO₄), δ /ppm: 35.07. ESI-MS: m/z = 231.2 ([P₄₄₄₂]⁺), 652.3 ([P₄₄₄₂][BFA] + [P₄₄₄₂]⁺).

[**P**₆₆₆₁₄][**BFA**]. ¹H NMR (500 MHz, DMSO-d₆, TMS), δ/ppm: 6.47–6.45 (1H, d, CH–CH=C), 6.40 (1H, d, CBr=CH–CH), 2.28– 2.17 (8H, m, 4 × PCH₂), 1.50–1.26 (48H, m, 24 × CH₂), 0.89– 0.86 (12H, m, 4 × CH₃). ¹³C NMR (126 MHz, CDCl₃, TMS), δ/ppm: 162.09, 154.15, 121.94, 114.69, 112.64, 31.80, 31.00, 30.73, 30.61, 30.40, 30.28, 29.56, 29.53, 29.50, 29.42, 29.23, 29.20, 28.88, 22.56, 22.23, 21.79, 21.75, 19.02, 18.65, 13.99, 13.82. ³¹P NMR (202 MHz, CDCl₃, H₃PO₄), δ/ppm: 33.11. ESI-MS: m/z = 483.8 ([P₆₆₆₁₄]⁺), 1157.2 ([P₆₆₆₁₄][BFA] + [P₆₆₆₁₄]⁺).

Experiments for SO₂ absorption and desorption

Absorption and desorption experiments were carried out using a bubble method under atmospheric pressure, in which the former processes were carried out at various temperatures and the latter were carried out at 343.15 K. The gas mixtures under experimental conditions were assumed as ideal gases; namely, the partial pressure of SO₂ is proportional to its volume fraction in the gas mixtures. Therefore, by changing the flow rates of SO₂ and N₂ with rotometers (Changzhou Shuanghuan Thermo-Technical Instrument Co., Ltd, LZB-3WB), the SO₂ at various partial pressures were obtained. In the release experiment, pure N₂ flowed through a 4A molecular sieve column and then bubbled through the SO₂ saturated ILs phase.

Effect of water on SO₂ absorption

To the best of our knowledge, water existing in either ILs liquid phase or SO₂ gas phase may change the SO₂ absorption capacity and mechanism of ILs. Accordingly, two glass tubes containing ILs and water, respectively, were immersed in the same thermostatic water bath at 30 °C. Pure N₂ was then bubbled through water and ILs successively. The amount of water loaded into the ILs was determined at regular intervals with an electronic balance (Mettler-Toledo ME204E). After 30 min of wet N₂ absorption, the ILs was exposed to dry SO₂ and the amount of SO₂ captured by the ILs was determined in the same manner.

Results and discussion

In this work, the chemical structures of four cations and two anions in the furoate ILs we used are depicted in Scheme 1.

The choice of cation has evident influence on several physical properties for ILs. For example, the ILs of $[N_{2222}]$ [BFA], Ch[BFA], and $[N_{2222}]$ [FA] are solid states at room temperature. Therefore, the present study does not include the ILs of $[N_{2222}]$ [BFA] and Ch[BFA]. However, $[N_{2222}]$ [FA] still remained to compare the influence of different cations on absorption performance in spite of the fact that $[N_{2222}]$ [FA] was also a solid at experimental temperatures.



Scheme 1 Chemical structures of cations and anions used in present ILs.

A similar effect of cations on IL's properties was also reported in Seo's work.²¹

The thermal stability of the ILs

TGA curves of six ILs based on the furoate anion are illustrated in Fig. 1. It can be seen from the curves that all the ILs are stable below 195 °C, and no obvious loss of weight was observed with heating. When the temperature was raised to 240 °C, the four phosphonium-based ILs began to decompose rapidly. In all, the T_d (thermal decomposition temperatures) were 289, 281, 198, 216, 243, and 240 °C for $[P_{4442}]$ [FA], $[P_{66614}]$ [FA], $[N_{2222}]$ [FA], Ch[FA], $[P_{4442}]$ [BFA], and $[P_{66614}]$ [BFA], respectively. Cations have an evident effect on the thermal stability of the ILs. For example, the ILs with quaternary ammonium cations of $[N_{2222}]^+$ and Ch⁺ are less stable than those with quaternary phosphonium of $[P_{4442}]^+$ and $[P_{66614}]^+$, while the influence of anions was relatively small. A high thermal stability gives our ILs good operation flexibility for the absorption/desorption of SO₂.

Absorption of SO₂ by furoate ILs

To investigate relationships between the structure of cations and anions as well as absorption performance, time-dependent absorption profiles of SO₂ in six ILs at 293.15 K under atmospheric pressure are illustrated in Fig. 1, with a mass-based scale (gram SO₂ per gram IL) selected. Similar profiles based on molar ratio were omitted due to the overlap of several curves. We point out that the performance of $[N_{2222}]$ [FA] was obtained



Fig. 1 TGA graphs of six ILs. Black, [P₄₄₄₂][FA]; red, [P₆₆₆₁₄][FA]; blue, Ch[FA]; orange, [N₂₂₂₂][FA]; magenta, [P₄₄₄₂][BFA]; cyan, [P₆₆₆₁₄][BFA].



Fig. 2 SO₂ absorption profiles in six furoate ILs as a function of time at 293.15 K and atmospheric pressure. \Rightarrow , green, [N₂₂₂₂][FA]; \bigcirc , blue, [P₄₄₄₂][FA]; \Box , cyan, [P₄₄₄₂][BFA]; \diamondsuit , black, Ch[FA]; \triangle , red, [P₆₆₆₁₄][FA]; \bigtriangledown , magenta, [P₆₆₆₁₄][BFA].

as the deviation of absorption capacity between [N2222][FA]-PEG-200 solution and PEG-200 because [N2222] [FA] was a solid at 293.15 K. Generally, the absorption process was basically completed within thirty minutes for all the ILs. However, the absorption capacity demonstrated evident differences, along with the structure of the cations, for each kind of ILs. When absorption capacity was compared with molecular structure, the molar ratio provided a direct insight. The changing sequence was $[P_{4442}]$ [FA] (3.72, molar ratio of SO₂ to IL, and the same below) > $[P_{66614}]$ [FA] (3.65) > $[P_{4442}]$ [BFA] (3.58) > $[N_{2222}]$ FA] (2.87) > $[P_{66614}]$ BFA] (2.80) > Ch[FA] (1.49). For the same anion of furoate, the abovementioned sequence means that the cation-anion interaction plays a more critical role than the SO₂-anion in capturing SO₂. This phenomenon was also reported in CO₂ capture by several anion-functioned ILs.^{21,22} If the mass-based scale (gram SO_2 per gram IL) was selected, then the sequence of absorption capacity for furoate based IL changed to be $[N_{2222}][FA] > [P_{4442}][FA] > Ch[FA] > [P_{66614}][FA]$. This order included the comprehensive effects of molecular mass and cation-anion interactions. Among the ILs, [P4442][FA] demonstrated the best performance for SO₂ absorption from the absorption rate as well as capacity. When a Br atom was introduced into the furan ring at the position of C-5, the derived BFA had lower pK_a value ($pK_a = 2.80$) than FA ($pK_a = 3.27$).²³ Then, the furoate possessed higher basicity than 5-bromofuroate. Although the addition of a halo atom into the anion in an ordinary chain carboxylate or benzoate will enhance their absorption capacity for SO₂, because of the additional effect of halo atom and SO₂ interaction,^{16,24} the additional effect of a Br atom in the furan ring was discounted by the decreased basicity of the carboxylate anion, and the formed IL of [P4442][BFA] as demonstrated by a slightly lower absorption capacity than [P₄₄₄₂][FA] (Fig. 2).

Effect of temperature and partial pressure on SO₂ absorption

The temperature and pressure dependence of SO_2 absorption capacity was also investigated. [P₄₄₄₂][FA] was selected as the best candidate owing to its relatively high absorption capacity



Fig. 3 Effect of temperature (at 1.0 bar, a) and partial pressure (at 303.15 K, b) on $[P_{4442}]$ [FA] performance for SO₂ absorption.

and low viscosity among the six ILs. As shown in Fig. 3a, the SO_2 absorption capacity decreased from 0.711 to 0.332 g SO_2 per g IL when the temperature increased from 293.15 to 333.15 K. Fig. 3b shows the pressure dependence of SO_2 absorption capacity at 303.15 K. Absorption capacity increased significantly as the pressure increased. When pressure increased from 0.096 bar to 1.0 bar, the SO_2 absorption capacity increased from 0.209 to 0.565 g SO_2 per g IL. This result means that low temperature is favorable for higher absorption of SO_2 , while a high temperature is helpful for stripping out the absorbed SO_2 and regeneration of the absorbents. Moreover, pressure swelling is also an alternative way to regenerate SO_2 -saturated IL.

Effect of water on the performance of ILs for SO₂ absorption

It is well known that water as steam is an accompanying component with SO₂ in fuel gas emissions and that it will also be absorbed by hydrophilic ILs. Thus, it is necessary to explore the influence of water on the absorption performance of the ILs. In the present study, the capture performances of dry and wet SO₂ (100% humidity) by $[P_{4442}][FA]$ under 1.0 bar and 303.15 K were systematically compared. Results showed that the SO₂ absorption capacity decreased when water was added to the IL, presumably due to re-protonation of the anion. For example, SO₂ absorption capacity of $[P_{4442}][FA]$ decreased from 0.565 to 0.530 g SO₂ per g IL when dry SO₂ was saturated with water to 100% humidity SO₂, which means that the addition of water depressed the absorption capacity by possibly changing the absorption mechanism or its solution structure. This result is also similar to other carboxylate based ILs in the literature.¹⁶

Selectivity of SO_2 to CO_2 or N_2

Gas absorption is generally related to gas separation in practical applications. Gas separation technology always involves the gas mixture. For example, SO_2 and CO_2 are two major acidic gases coexisting in real flue gas. Thus, selectivity of different gases in a selected gas absorbent is an essential parameter with high priority for consideration. It is important to remove SO_2 prior to carbon capture with flue gas because SO_2 is a relatively stronger acidic gas than CO_2 , and what's worse is that the absorbed SO_2 can hardly be released with the regeneration of



Fig. 4 Different gas absorption behaviours in $[P_{4442}][FA]$ as a function of time at 293.15 K and 1.0 bar. \bigcirc , SO₂; \triangle , CO₂; \square , N₂.

an absorbent for CO_2 .²⁵ To investigate the potential suitability of our ILs for the above applications, the absorption capacity of CO2 and N2 in [P4442] FA] at 293.15 K and 1.0 bar were also determined, as illustrated in Fig. 4. It is evident that the absorption capacity of SO_2 is much higher than that of CO_2 and N₂ with [P₄₄₄₂][FA]. Furthermore, the selectivity of SO₂/CO₂ and SO₂/N₂ (defined as the absorption capacity ratio of SO₂ to CO2 or N2) are calculated to be 37 and 114, respectively. The selectivity of SO₂/N₂ is higher than that of *N*-butylpyridinium thiocyanate ([C₄Py][SCN]) and N-butylpyridinium tetrafluoroborate ([C₄Py][BF₄]).²⁶ The selectivity of SO₂/CO₂ is similar with that of 1-(2-diethylaminoethyl)-3-methyl-imidazolium tetrazolate ([Et₂NEMim][Tetz]),²⁷ while slightly lower than that of 1-{2-[2-(2methoxyethoxy]ethyl}pyridinium chloride ([E₃Py]Cl).²⁸ These results indicated that furoate based ILs have the potential to capture or be useful with pretreatment of SO₂ from CO₂ in flue gas.

The changes of physical property before and after absorption

It is well known that physical property data are important and essential for industrial applications and engineering designs with ILs. In our present study, the density and dynamic viscosity data of virgin and SO2 saturated [P4442][FA] at various temperatures were also determined, as shown in Fig. 5. As can be seen from Fig. 5, the dissolution of SO₂ increased the density of the ILs at each temperature, and the density of pure and mixture systems decreased with increasing temperature. Two possibilities may explain this phenomenon. On one hand, the absorbed SO₂ would reinforce the attractive interactions between ion pairs. On the other hand, the pores between cations and anions would just accommodate the gas molecule. It is noteworthy that the dynamic viscosity of [P₄₄₄₂][FA] changed to be half of the initial value after saturation by SO₂ at each temperature. For example, the initial and final viscosity values of [P₄₄₄₂][FA] at 303.15 K was 117.5 and 60.6 mPa, respectively. For functionalized ILs, the behaviour of viscosity along with the absorption of SO₂ was complicated.^{6,29} Thus, changes of dynamic viscosity of [P4442][FA] with increasing absorption amount of SO₂ needs further research.



Fig. 5 The density (a) and dynamic viscosity (b) of virgin and SO₂ saturated [P₄₄₄₂][FA] at various temperatures. \Box , \blacksquare : before absorption; \bigcirc , \blacksquare : after absorption.

Regeneration and recycling of ILs

Reusability is a critical property for IL as gas absorbents in practical applications, because it directly relates to operation, cost, and economic efficiency and thus determines the frequency of a IL's replacement.³⁰ Therefore, five SO₂ absorption/ desorption cycles by [P4442] [FA] was investigated, and the results are presented in Fig. 6. The absorption/desorption procedures were carried out at 303.15 K, 1.0 bar, SO₂ of 30 cm³ min⁻¹ and 343.15 K, 1.0 bar, and N₂ at 60 cm³ min⁻¹, respectively. As shown from Fig. 6, the regeneration process was completed within thirty minutes. After 5 absorption/desorption cycles, the absorption ability remained at almost the same level, indicating that [P₄₄₄₂][FA] is satisfactory for repeated SO₂ absorption/desorption uses. If an anion with stronger basicity relative to furoate was used to capture SO₂, then the absorption capacity may be higher, but the desorption of SO₂ would become more difficult and the neat absorption capacity would be even lower than with a furoate-based IL. For example, as [P66614][C5H11COO] was mentioned, the desorption of SO₂ was not complete even at 393.15 K and the real absorption capacities were depressed during the recycling of IL due to its strong interactions with SO2.16

Spectroscopic investigations comparing SO₂ and ILs

Spectroscopy is a useful approach to get an insight of the structure of a solution *in situ*.³¹ To investigate the interaction



Fig. 6 Five consecutive SO₂ absorption (303.15 K, 1 atm, 30 cm³ min⁻¹) and desorption (343.15 K, N₂, 60 cm³ min⁻¹) cycles by [P₄₄₄₂][FA]. \bullet , absorption; \bigcirc , desorption.



Fig. 7 FT-IR spectra of $[P_{4442}][FA]$ (black), $[P_{4442}][FA] + SO_2$, (red) and $[P_{4442}][FA] + 100\%$ humidity SO₂ (blue).



Fig. 8 $\,^{1}$ H NMR (upper) and 13 C NMR (below) spectra of [P_{4442}][FA] before and after absorption of SO_2.

between SO₂ and IL in [P₄₄₄₂][FA], FTIR and NMR spectroscopy were used to characterize the structures of virgin and SO₂-saturated [P₄₄₄₂][FA], with the results illustrated in Fig. 7 and 8. By comparing the two FT-IR spectra in Fig. 7, two new absorption peaks at 1266 and 1098 cm⁻¹ were assigned to the asymmetric stretching and symmetric vibration of S=O bonds, respectively, and a peak at 969 cm⁻¹ attributable to S-O stretches, formed *via* the absorption of SO₂. Furthermore, the band at 1604 cm⁻¹ was assigned to C=O vibration in the carboxyl group (-COO⁻) of fresh IL [P₄₄₄₂][FA]; this same mode was blue-shifted by 101 cm⁻¹ in SO₂-saturated [P₄₄₄₂][FA] to 1705 cm⁻¹ because of the electrophilic environment due to SO₂.^{15,16} Another new peak at 527 cm⁻¹ was regarded as a scissor bending vibration (δ) of dissolved SO₂.³² Furthermore, a

new band at 2441 cm⁻¹ was assigned to the S=O/H-C hydrogen bonding interactions between furoate anion and SO₂. When water is present in ILs or gas, SO₂ will react with it to from H₂SO₃. Tracking [P₄₄₄₂][FA] as an example, since 2-furoic acid ($pK_a = 3.16$) is weaker than H_2SO_3 ($pK_{a1} = 1.81$), the anion of [FA] would be transferred to 2-furoic acid in the presence of H_2SO_3 . Then, $[P_{4442}]$ [FA] would react with H_2SO_3 to form $[P_{4442}]$ [HSO₃]. As seen from the FTIR spectrum of $[P_{4442}]$ [FA] + 100% humidity SO₂, another new band at 1032 cm^{-1} should be attributed to the O-S stretching mode of HSO₃^{-,14} indicating the rationality of the proposed mechanism. Moreover, as illustrated in Fig. 8 of the ¹H NMR spectra for free and SO₂ treated $[P_{4442}]$ [FA], the chemical shifts of the hydrogen atom in the ring moved down-field from 7.41, 6.66, and 6.33 ppm to 7.92, 7.31, and 6.82 ppm, respectively. The typical peak of the carboxyl group on the anion of furoate in ¹³C NMR spectra moved up-field from 162.1 ppm to 161.8 ppm, indicating the interaction of SO₂ with the carboxyl group in the anion. For the carbon atom adjacent to carboxyl group and oxygen atom, a larger ¹³C NMR shift from 156.1 ppm to 148.1 ppm means the synergistic absorption of SO_2 by the carboxyl group and oxygen atom in the furan ring. The $\pi \cdots S$ interaction¹¹ between the furan ring and SO₂ results in down-field movement of ¹³C NMR

 $\label{eq:stable} \begin{array}{ll} \mbox{Table 1} & \mbox{Comparison of O_2 absorption capacities in different functionalized ILs} \end{array}$

		SO_2 absorption capacity ²		
Ionic liquids ^a	T/K	At 1 bar	At 0.1 bar	Ref.
[P ₄₄₄₂][FA] [P ₄₄₄₂][FA]	293.15 293.15	0.69(3.70) 0.39(3.64)	0.24(1.31) 0.15(1.38)	This work This work
$[N_{2222}][FA]$	293.15	0.76(2.87)	0.34(1.29)	This work
[P ₄₄₄₂][BFA]	293.15 293.15	0.37 (1.24) 0.55 (3.59)	0.10(0.33) 0.19(1.27)	This work
$\begin{bmatrix} P_{66614} \\ N_{2224} \end{bmatrix} \begin{bmatrix} dimalonate \end{bmatrix}$	293.15 313.15	0.27(2.80) 0.46(1.88)	0.12(1.30) 0.15(0.61)	15
$\begin{array}{c} [P_{66614} \ DAA] \\ [P_{66614}] [6-BrC_5 H_{10} COO] \end{array}$	293.15 293.15	0.49(4.47) 0.41(4.34)	$0.18\ (1.60)\ 0.15\ (1.61)$	14 16
$[P_{66614}][C_5H_{11}COO]$ $[P_{66614}][4-BrC_6H_4COO]$	293.15 293.15	$0.41 (3.82) \\ 0.39 (4.12)$	0.18(1.70) 0.16(1.66)	16 24
[P ₆₆₆₁₄][Tetz] [P ₆₆₆₁₄][Im]	293.15 293.15	0.43(3.72) 0.46(4.00)	0.18(1.54) 0.24(2.07)	33 34
[Emim][SCN] [Emim][C(CN) ₂]	293.15 293.15	1.13(2.99) 0.74(2.33)	0.37(0.98) 0.07(0.23)	34 34
$[P_{444E3}][Tetz]$	293.15 293.15	0.75 (4.87) 0.62 (1.96) ^c	$0.29 (1.87) \\ 0.32 (1.03)^d$	35
[MEA]L	293.15	$0.02 (1.90)^{c}$ $0.42 (0.99)^{c}$	$0.32 (1.03)^d$ $0.21 (0.53)^d$	36
[N ₂₂₂₂]L [Bmim]L	313.15	_	$0.23 (0.79) \\ 0.19 (0.67)^e$	37

^{*a*} [N₂₂₂₄][dimalonate], triethylbutylammoniumdimalonate; [P₆₆₆₁₄][DAA], trihexyl(tetradecyl)phosphonium diacetamide; [P₆₆₆₁₄][6-BrC₅H₁₀COO], trihexyl(tetradecyl)phosphonium6-bromo-*n*-hexanoic acid; [P₆₆₆₁₄][C₅H₁₁COO], trihexyl(tetradecyl)phosphonium hexanoic acid; [P₆₆₆₁₄][C₅H₁₁COO], trihexyl(tetradecyl)phosphonium 4-bromobenzoic acid; [P₆₆₆₁₄][4-BrC₆H₄COO], trihexyl(tetradecyl)phosphonium 4-bromobenzoic acid; [P₆₆₆₁₄][Tetz], trihexyl(tetradecyl)phosphonium tetrazole; [P₆₆₆₁₄][Im], trihexyl(tetradecyl)phosphonium imidazole; [Emim][SCN], 1-ethyl-3-methylimidazolium thiocyanate; [Emim][C(CN)₃], 1-ethyl-3-methylimidazolium tricyanomethanide; [P_{444E3}][Tetz], tri-*n*-butyl{2-[2-[2-[2-methoxyethoxy]ethyl]phosphonium tetrazolate; [TMG]L, 1,1,3,3-tetramethylguanidinium lactate; [MEA]L, monoethanolaninium lactate; [N₂₂₂₂]L, tetraethylamnonium lactate; [Bmim]L, 1-butyl-3-methylimidazolium lactate, ^{*b*} Values given in units of g SO₂ per g IL (mol SO₂ per mol IL). ^{*c*} At 101.3 kPa. ^{*d*} At 6.08 kPa. ^{*e*} At 0.03 bar.

shifting from 141.1, 110.3 and 110.0 ppm to 145.7, 116.5 and 112.2 ppm for other carbon atoms in the furan ring, respectively. These results imply that the dissolved SO₂ interacted physically and chemically with the anion of $[P_{4442}][FA]$. Combined with the easy regeneration property, the capture of SO₂ by $[P_{4442}][FA]$ could be regarded as basically a reversible process.

Comparison with other functionalized ILs

Throughout investigations of present furoate based ILs as a SO_2 absorbent, the absorption capacity of SO_2 was compared with those in other functionalized ILs reported in the literature, with results listed in Table 1 based on molality and molarity scales. Present furoate-based ILs demonstrate competitive or superior absorption capacity of SO_2 on a molality scale compared with fatty acid salt based ILs. However, their performance was slightly inferior to thiocyanate, lactate, imidazole, and tetrazolate-based ILs. It should be noted that functionalized [Emim][SCN] is susceptible to oxidization by SO_2 , which possesses relatively strong oxidization ability, especially in the presence of water. Besides, the alkalinity of [Tetz]- and [Im]-based ILs is very strong, which may result in difficult desorption of SO_2 . Thus, the present furoate-based ILs are regarded as more promising SO_2 absorbents due to their high absorption capacity and easy regeneration.

Conclusions

In this work, a new kind of furoate-based functionalized ILs were prepared and evaluated for SO₂ capture from absorption performance, physical property, gas selectivity, absorption mechanism, and comparisons with other ILs. After comprehensive consideration, $[P_{4442}][FA]$ is regarded as the most satisfactory and competitive anion-functionalized IL with a maximum absorption capacity of 0.69 and 0.24 g SO₂ per g IL at 293.15 K under 1.0 bar and 0.1 bar, respectively. Furthermore, the high selectivity of SO₂/CO₂ in $[P_{4442}][FA]$ provides an attractive way to selectively separate SO₂ from CO₂ in flue gas. The high efficiency, reasonable cost, low energy consumption and ease of operation make the present furoate-based ILs very promising absorbents for SO₂.

Acknowledgements

The research was supported by the Natural Science Foundation of Zhejiang Province (LY17B060010).

Notes and references

- 1 S. J. Smith, J. van Aardenne, Z. Klimont, R. J. Andres, A. Volke and S. Delgado Arias, *Atmos. Chem. Phys.*, 2011, **11**, 1101–1116.
- 2 Environmental Protection Agency (EPA), Primary National Ambient Air Quality Standard for Sulfur Dioxide, Final Rule, Washington, 2010.
- 3 X. X. Ma, T. Kaneko, T. Tashimo, T. Yoshida and K. Kato, *Chem. Eng. Sci.*, 2000, **55**, 4643–4652.
- 4 K. Huang, S. Xia, X. M. Zhang, Y. L. Chen, Y. T. Wu and X. B. Hu, *J. Chem. Eng. Data*, 2014, **59**, 1202–1212.

- 5 Z. G. Lei, C. N. Dai and B. H. Chen, *Chem. Rev.*, 2014, **114**, 1289–1326.
- 6 S. H. Ren, Y. C. Hou, W. Z. Wu, Q. Y. Liu, Y. F. Xiao and X. T. Chen, J. Phys. Chem. B, 2010, 114, 2175–2179.
- 7 J. E. Bara, D. E. Camper, D. L. Gin and R. D. Noble, Acc. Chem. Res., 2010, 43, 152–159.
- 8 S. J. Zeng, H. S. Gao, X. C. Zhang, H. F. Dong, X. P. Zhang and S. J. Zhang, *Chem. Eng. J.*, 2014, **251**, 248–256.
- 9 W. Z. Wu, B. X. Han, H. X. Gao, Z. M. Liu, T. Jiang and J. Huang, Angew. Chem., Int. Ed., 2004, 43, 2415–2417.
- 10 Y. Shang, H. P. Li, S. J. Zhang, H. Xu, Z. X. Wang, L. Zhang and J. M. Zhang, *Chem. Eng. J.*, 2011, 175, 324–329.
- 11 G. K. Cui, W. J. Lin, F. Ding, X. Y. Luo, X. He, H. R. Li and C. M. Wang, *Green Chem.*, 2014, 16, 1211–1216.
- 12 K. H. Chen, W. J. Lin, X. N. Yu, X. Y. Luo, F. Ding, X. He, H. R. Li and C. M. Wang, *AIChE J.*, 2015, 61, 2028–2034.
- 13 G. K. Cui, J. J. Zheng, X. Y. Luo, W. J. Lin, F. Ding, H. R. Li and C. M. Wang, *Angew. Chem., Int. Ed.*, 2013, 125, 10814–10818.
- 14 G. K. Cui, F. T. Zhang, X. Y. Zhou, Y. J. Huang, X. P. Xuan and J. J. Wang, *ACS Sustainable Chem. Eng.*, 2015, 3, 2264–2270.
- 15 K. Huang, G. N. Wang, Y. Dai, Y. T. Wu, X. B. Hu and Z. B. Zhang, *RSC Adv.*, 2013, 3, 16264–16269.
- 16 G. K. Cui, Y. J. Huang, R. N. Zhang, F. T. Zhang and J. J. Wang, *RSC Adv.*, 2015, 5, 60975–60982.
- 17 P. Anastas and N. Eghbali, *Chem. Soc. Rev.*, 2010, **39**, 301–312.
- 18 J. J. Bozell and G. R. Petersen, Green Chem., 2010, 12, 539-554.
- 19 S. Ren, Y. Hou, S. Tian, X. Chen and W. Wu, *J. Phys. Chem. B*, 2013, **117**, 2482–2486.
- 20 P. Freundler, Bull. Soc. Chim. Fr., 1897, 3, 610-613.
- 21 S. Seo, M. A. DeSilva, H. Xia and J. F. Brennecke, J. Phys. Chem. B, 2015, 119, 11807–11814.
- 22 R. Babarao, S. Dai and D. E. Jiang, *J. Phys. Chem. B*, 2011, 115, 9789–9794.
- 23 S. M. Zhang, J. Baker and P. Pulay, J. Phys. Chem. A, 2010, 114, 432–442.
- 24 G. K. Cui, J. J. Zheng, X. Y. Luo, W. J. Lin, F. Ding, H. R. Li and C. M. Wang, Angew. Chem., Int. Ed., 2013, 52, 10620–10624.
- 25 R. Tailor and A. Sayari, Chem. Eng. J., 2016, 289, 142-149.
- 26 S. J. Zeng, H. S. Gao, X. C. Zhang, H. F. Dong, X. P. Zhang and S. J. Zhang, *Chem. Eng. J.*, 2014, **251**, 248–256.
- 27 D. Z. Yang, M. Q. Hou, H. Ning, J. Ma, X. C. Kang, J. L. Zhang and B. X. Han, *ChemSusChem*, 2013, 6, 1191–1195.
- 28 J. Wang, S. J. Zeng, L. Bai, H. S. Gao, X. P. Zhang and S. J. Zhang, *Ind. Eng. Chem. Res.*, 2014, 53, 16832–16839.
- 29 S. J. Zeng, X. C. Zhang, H. S. Gao, H. Y. He, X. P. Zhang and S. J. Zhang, *Ind. Eng. Chem. Res.*, 2015, 54, 10854–10862.
- 30 A. Sayari and Y. Belmabkhout, J. Am. Chem. Soc., 2010, 132, 6312.
- 31 Z. Z. Yang, L. N. He, Q. W. Song, K. H. Chen, A. H. Liu and X. M. Liu, *Phys. Chem. Chem. Phys.*, 2012, 14, 15832–15839.

- 32 Z. F. Zhang and G. E. Ewing, Spectrochim. Acta, Part A, 2002, 58, 2105–2113.
- 33 C. M. Wang, G. K. Cui, X. Y. Luo, Y. J. Xu, H. R. Li and S. Dai, J. Am. Chem. Soc., 2011, 133, 11916–11919.
- 34 C. M. Wang, J. J. Zheng, G. K. Cui, X. Y. Luo, Y. Guo and H. R. Li, *Chem. Commun.*, 2013, **49**, 1166–1168.
- 35 G. K. Cui, C. M. Wang, J. J. Zheng, Y. Guo, X. Y. Luo and H. R. Li, *Chem. Commun.*, 2012, **48**, 2633–2635.
- 36 M. J. Jin, Y. C. Hou, W. Z. Wu, S. H. Ren, S. D. Tian, L. Xiao and Z. G. Lei, *J. Phys. Chem. B*, 2011, 115, 6585–6591.
- 37 S. D. Tian, Y. C. Hou, W. Z. Wu, S. H. Ren and C. Zhang, *RSC Adv.*, 2013, 3, 3572–3577.