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Functional ionic liquids for SO_2 capture and conversion

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Owing to their many unique properties, ionic liquids (ILs) have emerged as novel solvents and catalysts for gas capture and utilization compared with conventional organic solvents. SO_2, an acidic gas, is usually emitted during the combustion of fossil fuels and leads to the formation of acid rain and haze. In the last few decades, many types of ILs, especially functional ILs, have been developed and their corresponding absorption mechanisms were investigated. Besides, SO_2 can be used to produce various value-added chemicals, including sulfur (S_8), cyclic sulfites, and benzenesulfinic acids, from green chemistry and engineering viewpoints. In this critical review, we focus on the design of task-specific ILs for SO_2 capture and conversion. Initially, we present a brief introduction on ILs and then systematically summarize the different active sites and active groups in task-specific ILs. In contrast to other reviews, we discuss the absorption models, mechanisms, influencing factors, and several strategies for the design of active sorbents. For SO_2 conversion to value-added products, this review, for the first time, highlights IL-based catalysts that are also absorbents. Finally, the future directions and prospects for SO_2 capture and conversion using ILs are outlined. This work will open the door to the development of novel task-specific IL-based materials for gas capture, separation, and conversion.

Introduction

It is known that SO_2 is a type of acidic gas that causes a series of environmental problems, including acid rain and haze. Thus, it is harmful to human health and social economy. SO_2 is usually emitted during the combustion of fossil fuels. There are several traditional flue-gas desulfurization (FGD) technologies for SO_2 capture, such as semi-dry FGD and wet FGD.[1] However, these technologies have shortcomings, such as high energy consumption, low capacity, high equipment corrosion rate, high cost, low reversibility, and secondary pollution, all of which do not conform to the principles of sustainable and green chemistry. Therefore, it is highly important to develop novel technologies to overcome the disadvantages of traditional technologies and improve the performance of SO_2 capture and conversion.[2]

Ionic liquids (ILs), which are composed of organic/inorganic anions and organic cations, are liquid at room temperature or below 100 °C.[3] In recent years, ILs have been widely used to separate gases such as CO_2,[4–6] SO_2,[7] NH_3,[8–10] NOx,[11,12] and CO.[13–15] For SO_2 absorption, Han *et al.*[16] reported the first example of SO_2 capture in 2004 using a task-specific IL, 1,1,3,3-tetramethylguanidine lactate ([TMG][L]), which showed a high sorption capacity of 0.978 molar SO_2 per molar IL at 40 °C under 8% SO_2 in N_2. Subsequently, there has been rapid development in the design and synthesis of green solvents based on ILs, especially task-specific ILs for SO_2 absorption or adsorption, in the past 20 years. IL-based absorbents can be classified into conventional ILs and task-specific ILs with active sites or active groups. Among these, we mainly focus on the active sites of task-specific ILs, which can provide strategies for designing other IL-based solvents for SO_2 capture. Besides, it is known that the utilization or conversion of captured acid gas to value-added chemicals is the goal to achieve a green world. To date, several attempts have been reported on SO_2 conversion, including the synthesis of sulfur (S_8), cyclic sulfites, and benzenesulfinic acids, and more attempts are underway. There are several review articles published on SO_2 capture by ILs.[17–21] However, none of them have discussed the conversion of SO_2, and the most recent review article was published 5 years ago.

Thus, in this critical review, we mainly focus on the recent advances in SO_2 capture and conversion using task-specific ILs

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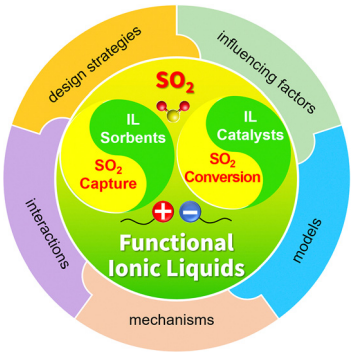

Fig. 1 Summary on functional ILs for SO_2 capture and conversion.

as efficient absorbents and catalysts from the viewpoint of active sites and active groups. This review includes the following main sections: (1) definition and synthesis of functional ILs, (2) SO_2 capture using task-specific ILs with functional anions and cations, (3) SO_2 absorption models, mechanisms, influencing factors, and design strategies, and (4) SO_2 conversion by ILs. Finally, the future directions and prospects for SO_2 capture and conversion by ILs are outlined (Fig. 1). This review will be beneficial for academic researchers to obtain an overall understanding of the current developments and future trends of SO_2 capture and conversion. This work will open the door to the development of novel task-specific materials for gas capture, separation, and conversion.

Definition and synthesis of functional ILs

Definition of ILs

Ionic liquids (ILs) are a type of salt with organic cations and organic or inorganic anions in the liquid state. The typical cations include imidazolium, pyridinium, quaternary ammonium, and quaternary phosphonium through quaternization. The typical inorganic anions include halogen anions (*e.g.* [F], [Cl], [Br], and [I]) and some halogen-containing anions such as tetrafluoroborate ($[BF_4]$) and hexafluorophosphate ($[PF_6]$), while organic anions are prepared from a huge number of organic compounds, which can serve as proton donors, such as carboxylic acids, phenols, azoles, and some alcohols. Theoretically, there are about 10^{18} types of ILs as a result of the different assembles of cation and anion.[22] Traditional ILs are liquid compared with ionic solids such as NaCl, which is composed of an inorganic cation and anion. Thereby, the traditional definition of ILs is salts with a melting point below 100 °C. For example, a type of red oil was first observed in the mid-19th century as an "early ionic liquid" with the arenium cation and heptachlorodialuminate anion.[23] The second example, ethylammonium nitrate, has a melting temperature of 12 °C, which was found in the early 20th century. However, ionic compounds (m.p. > 100 °C) with organic cations and organic or inorganic anions, as mentioned above, are all classified as ILs. Thus, ILs include liquid-state ILs (or low-temperature molten salts) and solid-state ILs. The structures of the typical cations and anions forming ILs are presented in Fig. 2.

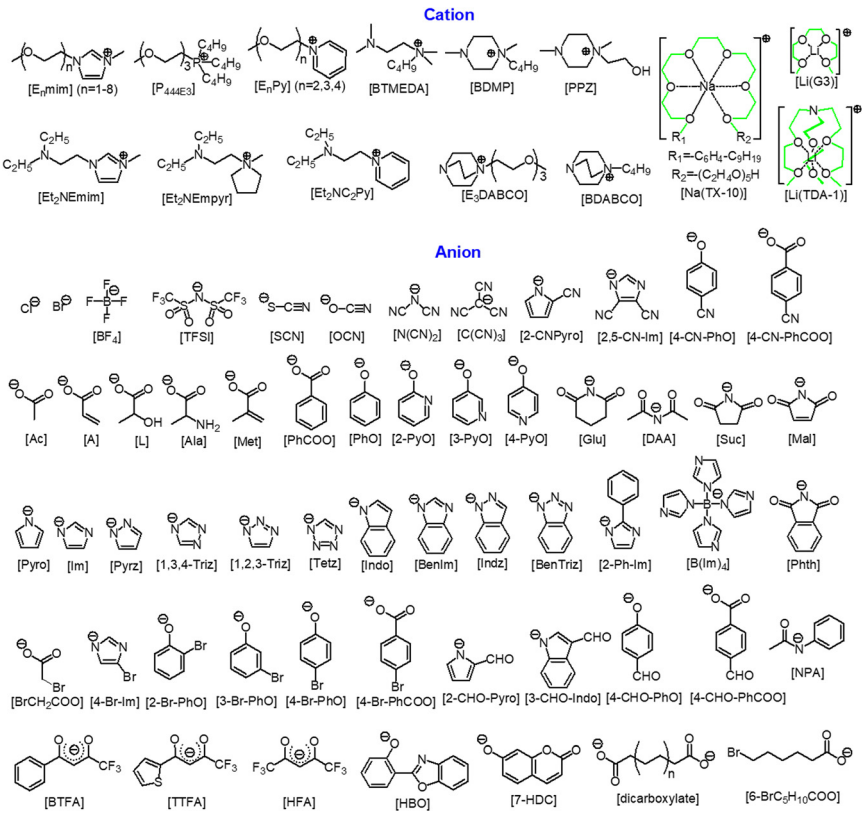

Fig. 2 Structures of typical cations and anions forming ILs for SO_2 capture and conversion.

SO_2-philic ILs

SO_2-philic ILs are defined as stimuli-responsive ILs responding to SO_2. Specifically, SO_2-philic ILs exhibit a response to adsorb or catalyze SO_2 when it moves towards them. There are various types of task-specific IL-based SO_2-responsive structures containing functional groups that can efficiently interact with SO_2. The functional groups are mainly grafted on the cations and anions. The interactions between SO_2 and ILs include physical interactions, quasi-chemical interaction, and chemical interaction. The efficient SO_2-philic ILs (functional ILs) are mainly based on the quasi-chemisorption and chemisorption of SO_2.

Typical synthesis of cation-functionalized ILs

Many strategies have been developed for the synthesis of cation-functionalized ILs (Fig. 3). The easiest method for both ether-functionalized ILs and amino-functionalized ILs is the coordination method, using Li, Na, and K salts and multi-amino or multi-ether organic compounds as the raw materials.[24–26] Another widely used method is quaternization, using ether or amino-containing alkyl halides and tri-substituted amines, *N*-methyl imidazole, pyridine, or tri-substituted phosphines as the raw materials.[27–30]

Typical synthesis of anion-functionalized ILs

Compared with ether sites and amino sites on the cations, there are numerous functionalized anions with various structures that can be used for SO_2 capture and separation. The general synthesis of anion-functionalized ILs includes three steps, quaternization, anion-exchange, and acid–base neutralization.[5] Firstly, quaternization results in initial ILs with halide anions, while anion-exchange results in ILs with hydrophobic functional anions or an [OH] anion. The key step is acid–base neutralization, in which ILs with an [OH] anion react with numerous types of proton donors (precursors of anions), such as azoles, amides, imides, carboxylic acids, acetylacetone, and phenols.

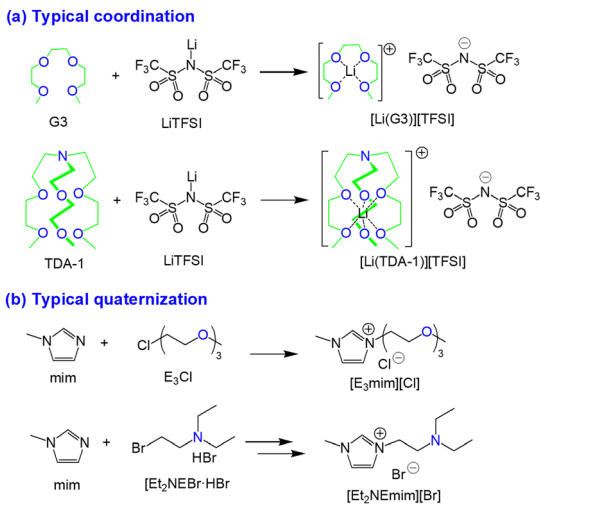

Fig. 3 Typical synthesis of SO_2-philic cation-functionalized ILs through (a) coordination and (b) quaternization.

Classification of functional ILs

It is known that functional ILs can provide active sites and result in high SO_2 sorption capacity through efficient interactions between their active sites and SO_2. These interactions not only include very strong interactions (such as chemical interactions), but also moderate-strength interactions (such as quasi-chemical interactions). Functional ILs can be classified into cationic functional ILs, anionic functional ILs, and bifunctional ILs according to the location of their functional sites. Unlike the variety of functionalized anions, there are only a few types of functionalized cations due to the small number of functional groups that can efficiently interact with SO_2, including ether groups and amine groups. Deprotonation (or dehydrogenation) is the removal or transfer of a proton from a Brønsted–Lowry acid in an acid–base reaction. The formed anions are the conjugate base of the proton donors. The less acidic the proton donor, the less likely the proton donor is to be deprotonated, leading to strong interactions between the functional anion and SO_2. Besides, according to the number of active sites, functional ILs can be classified into single-site functional ILs and multi-site functional ILs.

SO_2 capture by ILs with functional cations

Ether functional groups

The ether group is defined as an O atom connected to two alkyl or aryl groups (R–O–R′). Ether-based ILs refer to ILs containing one or more ether groups (also named PEG groups) on their cations. Jung *et al.*[31] prepared a series of ether-based functionalized ILs [E_nMIm][$MeSO_3$] (n = 1–8) by introducing ether groups into imidazolium cations. These ILs exhibited a good performance in SO_2 absorption, and their absorption capacity increased with an increase in the number of ether groups due to the stronger physical interaction between the ether group and SO_2. Subsequently, Sun *et al.*[32] prepared ether-based functionalized bisimidazolium ILs with a lower viscosity for the uptake of SO_2. Zhang *et al.*[27] showed that at 20 °C and 0.1 MPa, 1 mol [E_2Py][Cl], [E_3Py][Cl], and [E_4Py][Cl] could uptake 3.924, 4.289, and 4.594 mol SO_2, respectively. Wei *et al.*[33,34] studied SO_2 physisorption by ethylene glycol derivatives or a series of metal chelate ILs obtained by mixing different types of glymes, such as glyme (G1), diglyme (G2), triglyme (G3), and tetraglyme (G4), and different types of lithium salts, including LiTFSI, $LiClO_4$, LiOTf, and $LiBF_4$.

Amine-functional groups

Amine-functionalized ILs refer to ILs containing primary amine (–NH_2), secondary amine (–NHR), or tertiary amine (–NRR′) on their cations or anions. Among them, tertiary amine-based cation-functionalized ILs are common. For example, Park *et al.*[35] showed that at 30 °C and 1 bar, 1 mol [Bztmeda][$MeSO_3$] with a tertiary amine group could absorb 1.329 mol SO_2. Wu *et al.*[36] reported the synthesis of two hydrophobic ILs,

$[Et_2NEmim][PF_6]$ and $[Et_2NEmim][PF_6]$, with tertiary amine groups, and fund that $[Et_2NEmim][PF_6]$ showed high SO_2 absorption capacities of up to 2.03 mol SO_2 per mole IL (pure SO_2) and 0.356 mol SO_2 per mole IL (3% SO_2) under hydrous conditions at 30 °C.

SO_2 capture by ILs with functional anions

Carboxylate anions

Organic acid anions are formed through the deprotonation of organic acids, including saturated or unsaturated carboxylic acids (R–COOH), and sulfonic acid (R–SO_3H). However, considering the interactions between these anions and SO_2, carboxylate anions ([R–COO]) can be functional groups for efficient SO_2 capture. 1,1,3,3-Tetramethylguanidine lactate IL ([TMG][L]), reported by Han *et al.*,[16] is the first carboxylate anion-functionalized IL used in the absorption and separation of SO_2. The results showed that 1 mol [TMG][L] could absorb 0.978 mol SO_2 per mol IL at 40 °C under 8% SO_2 in N_2. Due to its high SO_2 capacity at a low SO_2 concentration, the absorption process was believed to be chemical absorption. Subsequently, Li *et al.*[37,38] and Chen *et al.*[39] used quantum chemical calculations and molecular simulation studies to reveal that the [L] anion may be the main factor influencing the absorption. Thus, the negatively charged oxygen atom on the anion is the key factor in the process of SO_2 absorption.

Besides the lactate anion, other saturated carboxylic acids (*e.g.* formic acid and acetic acid), as well as unsaturated carboxylic acids (*e.g.* benzoic acid and acrylic acid), including their substituted counterparts, can also be used to form anion-functionalized ILs. Wu and Hu *et al.*[40] showed that the formation of hydrogen bonds between the C–H bond of the dicarboxylate anions and SO_2 was the reason for SO_2 absorption by ILs with malonate, succinate, and maleate anions. Wu *et al.*[41,42] believed that the type of cation also had a great effect on the absorption of SO_2 by [L]-based ILs. Zhang *et al.*[37] showed that at 25 °C and 0.1 MPa, 1 mole of [MEA][HCOO], [MEA][Ac], and [MEA][L] could absorb 0.724, 0.786, 1.041 mole of SO_2, respectively. Zhong *et al.*[43] and Li *et al.*[44] also studied SO_2 absorption by alcoholamine ILs. Deng *et al.*[45] reported that the SO_2 absorption capacity of [choline][L] and [choline][levulinate] at 40 °C and 0.1 MPa was 1.533 and 1.770 mol mol^{-1}, respectively; when the partial pressure of SO_2 was reduced to 0.0004 MPa, the capacity could still reach 0.241 and 0.274 mol mol^{-1}, respectively. Shiflett *et al.*[46] measured the SO_2 sorption by [Bmim][Ac] and Lee *et al.*[47] showed that the regeneration of [Bmim][Ac] was difficult after the sorption of SO_2. Wang *et al.*[48] investigated the dual-tuning property of a series of ILs such as $[P_{66614}]$[R–PhCOO], $[P_{66614}]$[R–Ac], and $[P_{66614}]$[R–$PhSO_3$] on SO_2 capture. Wu *et al.*[49] believed that when the pK_a value of the hydrogenated anion is greater than that of the sulfurous acid, the IL can absorb SO_2 chemically. Deng *et al.*[50] showed that at 293.15 K, the SO_2 absorption capacity of $[P_{4442}]$[FA] with an anion formed from 2-furoic acid was 3.72 and 1.29 mol SO_2 per mol IL at 1.0 and 0.1 bar, respectively. Recently, Gomes *et al.*[51] reported that 1*H*-tetrazole-1-acetate, $[P_{4444}][TetrazC_1COO]$, is promising for the selective and reversible absorption of SO_2 at low pressures (0.77 mol SO_2 per mol IL under 0.02 bar) and in the presence of CO_2 (0.01 mol CO_2 per mol IL under 0.25 bar) at 303 K. However, Xu *et al.*[52] reported that the SO_2 capacities of ILs with deprotonated methacrylic acid and crotonic acid as their anions were low, and the interactions between SO_2 and the ILs were physical.

Cyanate anions

Acid anions are formed through the dehydrogenation of inorganic acids, including cyanic acid (HOCN), thiocyanic acid (HSCN), sulfuric acid (H_2SO_4), nitric acid (HNO_3), carbonic acid (H_2CO_3), tetrafluoroboric acid (HBF_4), hexafluorophosphoric acid (HPF_6), and hydrochloric acid (HCl). Among these anions, the cyanate ([OCN]) and thiocyanate ([SCN]) anions can act as functional groups for efficient SO_2 capture. Wang *et al.*[53,54] studied SO_2 capture by cyano-containing $[P_{66614}]$[SCN], $[P_{66614}]$[OCN], [Emim][SCN], and [Emim][$C(CN)_3$] ILs. Their results showed that the [SCN] and [OCN] anions have high sorption capacity for low concentrations of SO_2 due to the strong interaction between their negatively charged S or O atoms and SO_2. Subsequently, Deng *et al.*[55] showed that SO_2 absorption by [SCN]-based betainium ILs was better than that by their [TFSI]- and $[N(CN)_2]$-based counterparts through chemical interaction. However, Zhang *et al.*[56–58] found that $[C_4CNPy]$[SCN], $[C_4OPy]$[SCN], and $[C_4Py]$[SCN] as well as $[C_4Py][BF_4]$ were physical absorbents for SO_2 capture through the change in viscosity and FT-IR data during absorption.

Alcoholate and phenolate anions

The deprotonation of alcohols is very difficult due to their high pK_a values in water (pK_a = 15–20) compared with pure water (pK_a = 15.7). However, several special alcohols with F substituents can be easily deprotonated by superbases due to their decreased pK_a compared with their F-free counterparts. For example, the pK_a values of 2,2,2-trifluoroethanol (TFE) and ethanol in water are 12.4 and 15.9, respectively. Additionally, the pK_a value of phenol (PhOH) in water is 10, which is stronger than that of alcohols. Thus, phenols are acidic in nature and easily deprotonated. Zhang *et al.*[59] reported the preparation of several protic ILs [TMG][TFE] and [TMG][PhO] with deprotonated 2,2,2-trifluoroethanol and phenol as the anions. Their results showed that these ILs could capture 4.13 and 2.58 mole of SO_2 per mole of IL at 20 °C and atmospheric pressure, respectively. However, the regeneration of these ILs was more difficult.

Azolate anions

Azole compounds are aromatic compounds containing a five-membered aromatic ring structure with two heteroatoms (N, O, S, *etc.*), at least one of which must be an N atom. This also means that an azole is a pyrrole (Pyro) with at least one heteroatom in its ring. The common azole compounds include pyrazole, imidazole, triazole, tetrazole, thiazole, oxazole, and

isoxazole. Different from the above-mentioned ILs, which exhibit single-site chemical absorption under low SO_2 partial pressure conditions, ILs with functional azolate anions exhibit excellent SO_2 absorption capacity through multiple site chemical interaction. Wang *et al.*[54,60] showed that the molar absorption capacities of 0.01 MPa SO_2 by $[P_{66614}][Pyro]$, $[P_{66614}][Im]$, and $[P_{66614}][Tetz]$ at 20 °C were 0.84, 2.07, and 1.54, respectively. It was found that the multiple electronegative N atoms on the azolate anions were the main reason for the efficient absorption of low-concentration SO_2. Subsequently, the same authors reported that $[P_{4442}][Tetz]$ with a low molecular weight showed the absorption capacity of 0.18 g SO_2 per g IL for 2000 ppm SO_2.[61] Cui *et al.*[62] investigated the effect of different substituents in the [Im] anion on SO_2 absorption. It was reported that up to 5.3 and 2.4 mole capacity could be achieved by the IL with the methylimidazolate anion at 0.1 and 0.01 MPa, respectively, through the tuning multiple N···S interactions with different substituents. Recently, Wang *et al.*[63] reported that although [Bentriz]-based ILs exhibited high SO_2 capacity at 30 °C under 2000 ppm of SO_2 ($\sim$1 mol mol^{-1}), their desorption residue capacity was as high as $\sim$0.6 mol mol^{-1}. Thus, the available absorption capacity was only 0.4 mol mol^{-1}.

Acetylacetonate anions

Acetylacetone (pK_a = 8.9) is a β-diketone compound with two carbonyl (C═O) groups linked to methylene (–CH_2–). It exists as an equilibrium mixture of tautomeric keto and enol forms. In basic solution, it is deprotonated to form the acetylacetonate anion, a resonance-stabilized carbanion. Cui *et al.*[64] prepared and characterized a series of functionalized aprotic ILs with fluorinated acetylacetonate anions, such as benzoyltrifluoroacetonate ([BTFA]), thenoyltrifluoroacetonate ([TTFA]), hexafluoroacetylacetonate ([HFA]). These ILs exhibited remarkable SO_2 capacity and good desorption performance. For example, the molar capacities of SO_2 by $[P_{66614}][BTFA]$ and $[P_{66614}][HFA]$ were 1.82 and 1.10, respectively. Clearly, these capacities were significantly greater than the 1 : 1 stoichiometry, which is to the multiple-site interactions between SO_2 and the acetylacetonate anions.

Amide and imide anions

Amides and lactams have a –CO–NH– configuration, while imides have a –CO–NH–CO– configuration. Thereby, imides are monoacyl derivatives of amides or lactams, and more acidic than the corresponding amides and lactams but less acidic than carboxylic acids. Amide anions and imide anions are produced *via* the deprotonation of –NH– on the corresponding proton donors. Similarly, sulfonimide anions that include a highly conjugated anionic center (–SO_2–N^-–SO_2–) are generated through the deprotonation of the corresponding sulfonimides. The most popular sulfonimide anions used for preparing hydrophobic ILs are bis(fluorosulfonyl)imide ([FSI]) and bis(trifluoromethylsulfonyl)imide ([TFSI]) anions. However, these ILs cannot be used as functional ILs for efficient SO_2 capture. For example, the molar capacities of SO_2 absorption by [Emim][TFSI] and $[P_{4442}][TFSI]$ were only 1.49[65] and 1.43,[64] respectively, at 20 °C and 1 bar, which decreased to about 0.2 mol mol^{-1} when the partial pressure decreased to 0.1 bar.

The first functionalized ILs with amide and imide anions for efficient SO_2 sorption were reported by Wang *et al.*[66] They prepared ILs with maleimide ([Mal]), *o*-phthalimide ([Phth]), glutarimide ([Glu]), diacetamide ([DAA]), succinimide ([Suc]), and *N*-phenylethanamide ([NPA]) anions. Their results showed that the absorption capacities of $[P_{66614}][DAA]$, $[P_{66614}][Phth]$, $[P_{66614}][Glu]$, $[P_{66614}][Suc]$, $[P_{66614}][Mal]$, and $[P_{66614}][NPA]$ at 20 °C and 1 bar were 4.47, 4.40, 4.12, 4.10, 4.15, and 3.59 mol SO_2 per mole IL, respectively. It was concluded that compared with carbonyl-free ILs, the SO_2 absorption capacity of these ILs is significantly enhanced, which is due to the multi-site N···S, C═O···S interactions and C–H···O hydrogen bonding between their anion and SO_2.

SO_2 capture by ILs *via* multi-functionalization

Multi-functional anions

ILs containing a single functional group are still insufficient for tuning their SO_2 absorption performance. Considering (1) the absorption capacity and (2) absorption enthalpy, increasing the absorption capacity and decreasing the absorption enthalpy to obtain efficient and reversible absorption are highly desirable. Thereby, ILs based on bifunctional anions, bifunctional cations, or functional anions plus functional cations have been developed for SO_2 capture. Anions with more than one functional group can be classified as bifunctional anions. Here, functional groups mean groups with active sites that can interact with SO_2 efficiently. The activity of these sites on the anion is affected by (1) the structure and electrical charge of the anions in ILs, and (2) the absorption conditions (temperature and SO_2 partial pressure).

To obtain an increased absorption capacity under a low concentration of SO_2, derivatives of azole compounds were developed by Wang *et al.*[65] For example, after introducing a benzene ring structure on azolate anions, the ILs with benzimidazolate ([BenIm]) and 2-phenylimidazolate ([2-Ph-Im]) could absorb 2.46 and 2.59 mole SO_2 per mol IL, respectively, at 20 °C and 0.1 bar through N···S interactions and additional strong π···S interactions. Lu and Wu *et al.*[67–69] designed and prepared a series of tri-branched anion-functionalized ILs for SO_2 capture. Their results showed that up to 5.8 mol SO_2 per mol IL or 1.05 g SO_2 per g IL could be captured by [BMim][H-B(im)$_3$]. Cui *et al.*[70,71] measured the SO_2 capacities of a series of pyridinolate ([PyO]) aprotic and protic ILs. Pyridinolate anions can be regarded as a composition of phenolate anions and negatively charged pyridine. The results indicated that the simultaneous cooperative interactions of N···SO_2 and O···SO_2 between the anion and SO_2 were the main reason for the efficient absorption at a low partial pressure. The same authors also investigated SO_2 absorption by ILs with a pyridinecarboxylate anion ([PyCOO]) and pyridinesulfonate anion ([PySO_3]).

To achieve an increase in absorption capacity and decrease in absorption enthalpy, Wang *et al.*[48] developed a "dual-tuning" strategy by adding electro-withdrawing groups on anions with different functional main groups. For example, a series of aprotic ILs $[P_{66614}][R–PhO]$ with R = Br, CF_3, and CN was prepared and used for SO_2 absorption.[48,72] The substituents on [PhO] resulted in higher SO_2 absorption capacity by the ILs, especially at low temperature or high partial pressure, indicating the weak interaction between the CN group and SO_2 as well as strong interaction between the negative-charged O and SO_2. Besides, the effect of the CN group on SO_2 absorption was associated with the pK_a of the main groups on the anion. Thus, the CN group and halogens could not only improve the absorption capacity but also decrease the absorption enthalpy under certain conditions. The C ≡ N···S interaction as well as halogen···S interaction and C═O···S interaction are quasi-chemical interactions for efficient SO_2 capture.[73] Besides, Wang *et al.*[74] showed that –CHO was another quasi-chemical site for efficient SO_2 capture, especially under 10% SO_2.

Compared with multiple functional groups on one anion, which has one negative charge, Hu *et al.*[75,76] prepared several types of bianion-based ILs with two $[TMG]^+$ cations and a functional bicarboxylate anion ($[^-OOC–(CH_2–CH_2)_n–COO^-]$, n = 1, 3, 5) or PEG-linked bicarboxylate anion ([PBE]). These anions have two negative charges. The molar ratios of SO_2 to $[TMG]_2[SUC]$ (n = 1), ($[TMG]_2[SUB]$) (n = 3), $[TMG]_2[DOD]$ (n = 5), and $[TMG]_2[PBE]$ were 4.76, 5.96, 5.96, and 8.74, respectively, at 20 °C and 1 bar.

Multi-functional cations

Cations with more than one functional group can be classified as bifunctional cations. As mentioned above, ether groups and tertiary amine groups can be used to obtain ILs for efficient and reversible SO_2 absorption. He *et al.*[30] first reported that the SO_2 absorption capacities of $[E_3DABCO][TFSI]$ with three ether groups and a tertiary amine group on its cation at 0.1 MPa and 0.01 MPa at 25 °C were 4.38 and 1.01 mole SO_2 per mole IL, respectively. Tris(3,6-dioxaheptyl)amine (TDA-1) containing a tertiary amine group and six ether groups could act as a polydentate ligand to coordinate with the Li^+ cation.[77] Cui *et al.*[25] prepared a type of environmentally friendly chelate-based IL [Li(TDA-1)][TFSI] through the easy mixing of TDA-1 and LiTFSI. Their results showed that 1 mol [Li(TDA-1)][TFSI] could absorb 4.00 or 1.31 mol SO_2 at 20 °C and 0.1 MPa or 0.01 MPa, respectively, while its ether-containing counterpart [Li(G3)][TFSI] could only absorb 1.50 and 0.5 at 0.1 MPa and 0.01 MPa, respectively. This indicated that the ether groups were physical active sites and tertiary amine groups were chemical active sites. Thus, the capacities were significantly greater than a 1 : 1 stoichiometry (SO_2 : amine).

Functional anion plus functional cation

Given that an IL is composed of an anion and cation, a combination of a functional anion and functional cation is a common strategy for designing dual-functionalized ILs. Wang *et al.*[24,28] developed a class of dual-functionalized ILs composed of ether-based cations (physical interaction sites) and azolate anions (chemical interaction sites). The results showed that at 20 °C and 0.1 MPa, the reversible absorption capacities of 5.0 mol and 4.43 mol could be obtained by $[P_{444E3}][Tetz]$ and $[E_3mim][Tetz]$, respectively; when the SO_2 partial pressure decreased to 0.01 MPa, these ILs could still absorb 1.87 and 1.58 mol mol^{-1} SO_2, respectively. It was concluded that physical absorption was obvious at atmospheric pressure, whereas chemical absorption was obvious at low partial pressure. Kang *et al.* reported several types of dicationic ILs with the combination of an ether-functionalized dication and two azolates,[78] [SCN] or [Cl] anions.[79] For example, the SO_2 capacity of $[E_3EIm_2][Im]_2$, $[E_3EIm_2][SCN]_2$, and $[E_3EIm_2][Cl]_2$ was 3.178, 0.186, 0.378 mol SO_2 per mol IL at 20 °C and 2000 ppm SO_2, indicating the interaction between SO_2 and the former IL was chemisorption and the latter two ILs was physisorption. Recently, Wang *et al.*[80] reported the preparation of azolate anion-functionalized PEG400-based cation-functionalized ILs for highly efficient SO_2 separation at low concentration in flue gas. In their research, [Na(PEG400)][Tetz] exhibited a high absorption capacity for SO_2 (0.57 mol mol^{-1}), and excellent selectivity (63 under 2000 ppm SO_2/15% CO_2). Han *et al.*[29] investigated the SO_2 absorption behavior of a dual-functionalized $[Et_2NEMim][Tetz]$ IL composed of a tertiary amine cation and tetrazolate anion. Fu *et al.*[81] investigated the mechanism of SO_2 capture by the $[Et_2NEMim][Tetz]$ IL using density functional theory (DFT) methods. Zhang *et al.*[56] investigated SO_2 absorption by dual-functionalized ILs composed of a tertiary amine cation and thiocyanate anion.

ILs with trifunctional groups on both their anion and cation have also been developed for SO_2 absorption. Wu and Hu *et al.*[82] reported the preparation of a series of ILs with ether and tertiary amine groups on their cations and carboxylate anions. For example, the SO_2 absorption capacities of [DMDEEH][MEAAc] at 1 bar or 0.1 bar SO_2 were 6.12 and 2.14 mole SO_2 per mole IL, while its mass capacities were 1.04 and 0.36 g SO_2 per g IL at 20 °C, respectively. Cui *et al.*[25] reported the preparation of a series of metal-containing chelate-based ILs containing TDA-1 as the ligand. It was found that the SO_2 absorption capacities of [Li(TDA-1)][SCN] at 0.1 MPa or 0.01 MPa SO_2 at 20 °C were 5.50 and 2.36 mol mol^{-1}, respectively. Subsequently, Zhao *et al.*[83,84] reported the preparation of several types of ILs with TDA-1-functionalized cation and carboxylate anions or azolate anions for SO_2 absorption. Recently, Moosavi *et al.*[85,86] studied the effect of the functional group of the cation and anion on SO_2 acidic gas absorption by some designed amino acid ILs.

SO_2 sorption models

The ability of ILs to respond to SO_2 depends on the interactions between them and SO_2. Here, we focus on the sorption models and sorption mechanisms of pure ILs. Then, the influencing

factors are investigated, and design tips for active sorbents are presented.

Interactions

ILs can be divided into two categories, conventional and functional ILs. Conventional ILs only capture SO_2 through weak interactions such as van der Waals, while functional ILs can absorb SO_2 through relatively strong physical interactions or chemical interactions. The classification of interactions and approximate energies can be found in Table 1. The active sites can be on the cations or anions. The interactions between these active sites and SO_2 can be classified into three types including physical interaction, quasi-chemical interaction, and chemical interaction.[87] Generally, conventional ILs are based on physical interaction, while functional ILs are based on quasi-chemical interaction and chemical interaction, especially chemical interaction.

Physisorption model

Physisorption is physical sorption for short. Physisorption is caused by physical interaction, which is intermolecular force and exists between ILs and SO_2. As mentioned above, physical interaction is van der Waals force and physisorption is also called van der Waals absorption. van der Waals force exists between any two molecules, resulting in physisorption in any absorbent. The range of its binding energy is 0.1–1 kcal mol^{-1}. Thus, the binding force is very weak and it does not need to heat. Additionally, the physical absorption rate and desorption rate are fast. Henry's law constant, k_H, is often used to assess the degree of gas solubility in a solvent.[89]

Han *et al.*[90] reported the first example of SO_2 absorption by a [Cl]-based sorbent through the physical mechanism. They expressed Henry's constant as follows:

$$k_H = \lim_{x_1 \to 0} \frac{f_1}{x_1} \approx \frac{P_1}{x_1} \quad (1)$$

where x_1 is the mole fraction of physisorbed gas in the liquid phase, f_1 is the fugacity of the gas in the vapor phase, and P_1 is the pressure of the gas. Henry's constant could be obtained by extrapolation of the P_1/x_1 *vs.* pressure curves to zero pressure, and Henry's constants were 31.2, 72.5, 114.4, and 133.3 kPa. The increased Henry's constant with a decrease in the [Ch][Cl] concentration was probably due to the charge-transfer interaction of SO_2 with $[Cl]^-$.

Chemisorption model

Chemisorption is chemical sorption for short. A strong chemical interaction and new chemical bond are formed between ILs and SO_2. Thus, it is more difficult to reverse, and thus requires more energy to remove the absorbed SO_2 than physisorption. Chemical bonding includes N···SO_2 interaction, O···SO_2 interaction, and S···SO_2 interaction. For example, Wang *et al.*[61] studied anion-functionalized ILs such as $[P_{66614}][Tetz]$ for SO_2 chemisorption under 2000 ppm. Considering the negligible physical absorption because of the very low concentration of SO_2, a model could be obtained to fit the isotherm data according to the following equation:

$$K = \frac{x_{SO_2}}{P_{SO_2}(1 - x_{SO_2})} \quad (2)$$

where K is the equilibrium constant in bar^{-1}, x_{SO_2} is the SO_2 chemisorption capacity on a molar ratio basis and P_{SO_2} is the SO_2 pressure in bar. Thus, the SO_2 absorption enthalpy (ΔH = −53.2 kJ mol^{-1}) for $[P_{66614}][Tetz]$ was obtained from the temperature-dependence of K according to the van't Hoff equation.

Quasi-chemisorption model

Quasi-chemisorption is quasi-chemical sorption for short. Quasi-chemical sorption is caused by quasi-chemical interaction, which is a strong physical interaction (hydrogen bonding and electrostatic bonding) or a weak chemical interaction (coordination, complexation, and charge-transfer).[87] The key point is that the interaction strength needs to be within a certain range. Too strong interaction will result in difficult desorption, while too weak interaction will result in difficult absorption. Quasi-chemical interaction exists not only among molecules, groups, and atoms, but also between molecules and ions.

Charge transfer is a typical quasi-chemical interaction. It was reported by Jung *et al.*[91] that halogen anion ($[X]^-$)-based ILs could efficiently absorb SO_2 because of the electrostatic and charge-transfer effects between $[X]^-$ and SO_2. Han *et al.*[90] and Li *et al.*[92] investigated SO_2 capture by [Ch][Cl]:Gly through the charge-transfer interaction of $[X]^-$···S. Thornton *et al.*[93] and

Table 1 Classification of interactions and their approximate energies

General classification	Specific interaction	Energy range[a] (kJ mol^{-1})
Physical/van der Waals	London dispersion force	0.4–4
	Dipole-induced dipole	0.4–4
	Dipole–dipole	0.4–4
Physical/chemical	Hydrogen bonding	13–29
Physical/chemical	Electrostatic bonding	8–50
Weak chemical	Coordination/complexation/charge-transfer bonding	8–209
Chemical	Covalent/ionic bonding	105–1046

[a] Interaction energies are given on a per-bond basis and have been transformed in kJ mol^{-1} from the original unit in kcal mol^{-1}. Thus, large molecules forming a large number of van der Waals, hydrogen, or other types of bonds can have cumulative interaction energies many times that given in the table. Reprinted with permission from ref. 88. Copyright 1997, Academic Press.

Farmer *et al.*[94] demonstrated that SO_2 could cluster with the iodide reagent ion and form $(SO_2)I^-$. Thus, the $[X]^-\cdots SO_2$ charge transfer interaction was a strong physical interaction, and can be considered as 1 : 1 quasi-chemical interaction as follows:

$$\text{physisorption: } SO_2(g) \rightarrow SO_2(l)$$

$$\text{quasi-chemisorption: } SO_2(g) + [X]^-(l) \rightarrow [X]^-SO_2(l)$$

Thus, Cui *et al.*[95] expressed a quasi-chemisorption model to fit the isotherm data according to the following equation:

$$K_q = \frac{Z_{\text{quasi-chem}}}{\left(1 - Z_{\text{quasi-chem}}\right)\frac{P}{P^{\theta}}} \quad (3)$$

where K_q is the dimensionless quasi-chemical equilibrium constant, $Z_{\text{quasi-chem}}$ is quasi-chemisorption capacity in mol mol^{-1}, and P is the partial pressure of SO_2 in bars. In addition, the following equations represent physical absorption:

$$P = k_H m \quad (4)$$

$$Z_{\text{phys}} = \frac{MP}{K_H} \quad (5)$$

where k_H is Henry's constant for SO_2 physisorption in bars kg mol^{-1}, m is the solubility of SO_2 in mol kg^{-1}, and M is the molar weight of the sorbent in kg mol^{-1}, and the total SO_2 capacity, Z (in mol mol^{-1}), can be deduced as follows:

$$Z = Z_{\text{phys}} + Z_{\text{quasi-chem}} = \frac{MP}{k_H} + \frac{K_q\frac{P}{P^{\theta}}}{1 + K_q\frac{P}{P^{\theta}}} \quad (6)$$

The formyl group, –C(=O)–H, is another type of quasi-chemical site. In the case of the –CHO functional group, Wang *et al.*[74] showed that –CHO on the anion could efficiently capture SO_2, especially under 10% SO_2 *via* the cooperative interactions of C=O···S interaction and C–H···O hydrogen bonding. In fact, C–H alone is not an effective site because the C–H···O hydrogen bond is weak to interact with SO_2. Thus, the equimolar 1 : 1 reaction of –CHO with SO_2 may be applicable to the quasi-chemical model. Another functional group, –C(=N)–H, also has a similar performance.[70] However, the SO_2 affinities of these functional groups are limited by the negative charge on their anions.

Equilibrium thermodynamic model (RETM)

Wu and Hu *et al.*[40] studied SO_2 absorption using task-specific ILs based on dicarboxylate anions, and derived an equilibrium thermodynamic model (RETM) to analyze their absorption behavior based on the physical and chemical absorption mechanisms, as follows:

$$\text{physisorption: } SO_2(g) \rightarrow SO_2(l)$$

$$\text{chemisorption: } SO_2(l) + IL(l) \rightarrow SO_2IL(l)$$

$$\text{overall reaction: } SO_2(g) + IL(l) \rightarrow SO_2IL(l)$$

The overall reaction equilibrium was expressed as follows:

$$m_t = \frac{P}{k_H} + \left(\frac{K^{\circ}\frac{P}{P^{\circ}}}{1 + K^{\circ}\frac{P}{P^{\circ}}}\right) m_{IL_0} \quad (7)$$

$$K^{\circ} = \frac{K_1^{\circ}}{k_H} P^{\circ} \quad (8)$$

where K° is the equilibrium constant of the overall reaction, K_1° is the equilibrium constant of chemisorption, m_t is the total concentration of SO_2 in the liquid phase in mol kg^{-1}, m_{IL_0} is the initial concentration of IL in mol kg^{-1} and it should be a constant (m_{IL_0} = 1000/M), and P° is the standard pressure (1 bar). It can be seen that eqn (6) and (7) have a similar formation, and the difference between these models is that the equilibrium constant of the overall reaction K° is related to Henry's constant k_H.

It should be noted that the distinction between chemisorption and quasi-chemisorption is challenging because the absorption equations vary significantly across different studies under different conditions. For example, Wang *et al.*[60] calculated the interaction of [Tetz] with multiple SO_2, and the DFT results indicated that the interactions in [Tetz]–SO_2 and [Tetz]–$2SO_2$ are mainly chemical interactions, with absorption enthalpies larger than 50 kJ mol^{-1}. Subsequently, they showed that equimolar capacity was obtained under 2000 ppm SO_2 *via* 1 : 1 chemisorption, and it decreased from 0.87 to 0.07 mol SO_2 per mol IL when the temperature increased from 20 °C to 85 °C.[61] Clearly, different reaction mechanisms lead to the different calculation of the equilibrium constants. Besides, quasi-chemical interaction can be regarded as chemical interaction under some conditions, and can also be regarded as physical interaction under other conditions. Thus, choosing an appropriate model based on specific experimental data to explain experimental phenomena is important and can provide a necessary reference for future studies.

SO_2 sorption mechanisms

The SO_2 sorption mechanisms by ILs, especially functionalized ILs, can be investigated through theoretical calculations and spectroscopic analysis.

SO_2-philic ILs were reported to absorb SO_2 *via* physical interaction or chemical interaction. It is safe to indicate that physical active sites only interact with SO_2 at high SO_2 partial pressure and/or low absorption temperature, while chemical active sites can react with SO_2 at low SO_2 partial pressure and/or high absorption temperature. The typical physical active sites are O atoms in ether groups, while the typical chemical active sites are N atoms in azole-based anions.[28] Recently, Cui *et al.*[87,95] summarized a type of quasi-chemisorption by ILs through quasi-chemical interactions, including charge-transfer (CT), hydrogen bonding (HB), and halogen bonding (XB).

The typical mechanisms of SO_2–IL reactions can be found in Fig. 4. It can be seen that these active sites are mainly

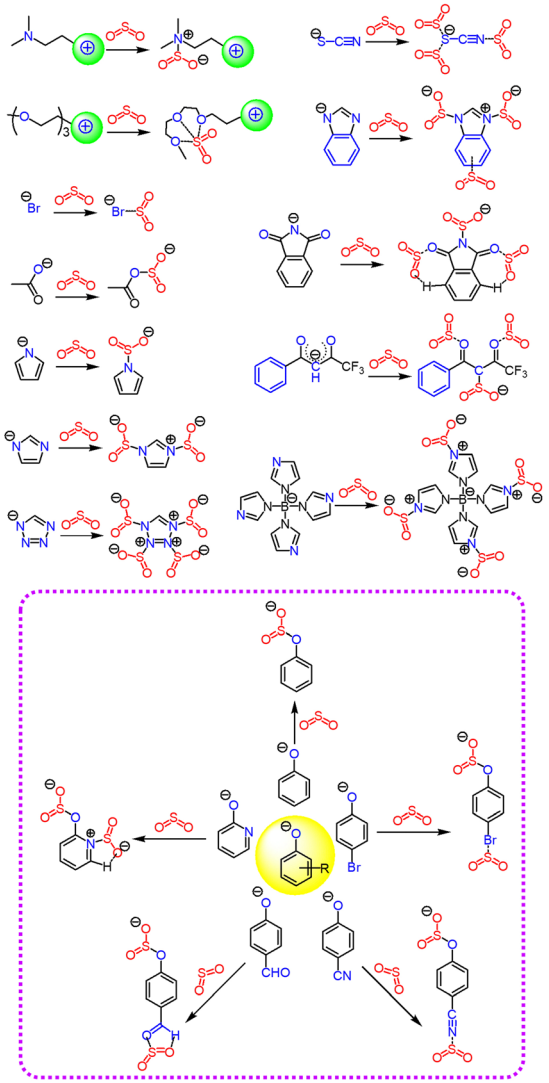

Fig. 4 Typical chemical and quasi-chemical mechanisms of SO_2–IL reactions.

electronegative-charged sites that can interact with the S in SO_2 through chemical interactions and physical interactions, while some H atoms can synergistically interact with the O in SO_2 through hydrogen bonds under certain conditions. Among the anion-functional ILs, Wang *et al.*[60] first reported efficient SO_2 capture by azolate-based ILs *via* multiple-site chemical interactions to obtain a 1 IL:2SO_2 capacity under low-concentration SO_2 or at a high absorption temperature. Subsequently, they also reported a series of dual-tuning strategies to increase the absorption capacity and decrease the desorption residual capacity using halogen-, cyano-containing anion-functionalized ILs *via* halogen···SO_2, cyano···SO_2 quasi-chemical interactions, respectively.[48,54] However, more potential sites did not mean more active sites for the better absorption of SO_2. Cui *et al.*[64] reported alternative functional ILs with a limited number of active sites that could achieve high SO_2 capacity. Moreover, Wu *et al.*[49] believed that when the pK_a value of the hydrogenated anion is greater than that of the sulfurous acid, the IL can absorb SO_2 chemically.

Theoretical calculations

Theoretical studies are performed through quantum chemical (QC) calculations, wave function (WF) analysis and molecular dynamics (MD) simulation. Among these methods, QC calculations have been used to investigate the interaction between SO_2 and ILs for a long time. After the [TMG][L] IL was reported for efficient SO_2 capture, Li *et al.*[37,38] first used QC calculations and MD simulation studies to investigate the interaction between SO_2 and [TMG][L]. Their results showed that the S···O interaction was 3.5–8.8 times that of the N–H···O hydrogen bonds, revealing that the [L] anion was the key factor affecting the absorption (Fig. 5). A similar conclusion was reported by Chen *et al.*[39] Thus, different types of anion-functionalized ILs were developed for efficient SO_2 capture.

Wang *et al.*[60] developed a type of azolate-based IL for efficient SO_2 capture under low concentration SO_2 (10 vol%). Their QC calculations showed multiple-site chemical interaction between [Im] or [Tetz] and SO_2 (Fig. 6). The absorption enthalpies for [Im]-SO_2, [Im]-2SO_2, [Tetz]-SO_2, and [Tetz]-2SO_2 were −124.6, −75.7, −89.3, and −59.9 kJ mol^{-1}, respectively. Generally, the absorption enthalpy is larger than 50 kJ mol^{-1} for chemisorption and lower than 50 kJ mol^{-1} for physisorption.[53] Thus, their calculations indicated the multiple-site chemisorption of SO_2, resulting in the absorption capacities of [P_{66614}][Im] and [P_{66614}][Tetz] at 20 °C and 0.1 bar of 2.07 and 1.54 mol SO_2 per mol IL, respectively.

Another efficient functional anion for SO_2 capture by ILs is [SCN]. Wang *et al.*[53] studied the SO_2 capture mechanisms of [Emim][SCN] and [Emim][$C(CN)_3$] ILs by QC calculations (Fig. 7). The optimized structures reflected the [SCN]···SO_2 and [$C(CN)_3$]···SO_2 interactions. The calculated absorption enthalpies of [SCN]···SO_2 and [$C(CN)_3$]···SO_2 were −73.0 and −32.3 kJ mol^{-1}, respectively, resulting in the chemisorption of SO_2 by the [SCN]-based IL. However, Kirchner *et al.*[96] carried out an *ab initio* molecular dynamics study on the SO_2 solvation in [Emim][SCN], and observed that both the cation and anion played an essential role in the solvation of SO_2. Recently, Gui *et al.*[97] investigated the thermodynamic feasibility, micro mechanism and molecular dynamic characteristics of SO_2 removal from fuel gas by an [Emim][Cl] + [Emim] (1 : 1) mixture by means of QC calculation, WF analysis and MD simulation. The interaction energy of [SCN]···SO_2 was the largest and favored an increase in SO_2 absorption capacity.

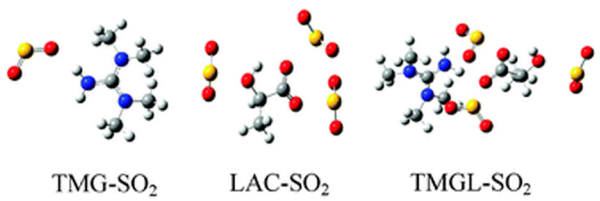

Fig. 5 Interaction between SO_2 and [TMG][L]. Reprinted with permission from ref. 37. Copyright 2008, the Royal Society of Chemistry.

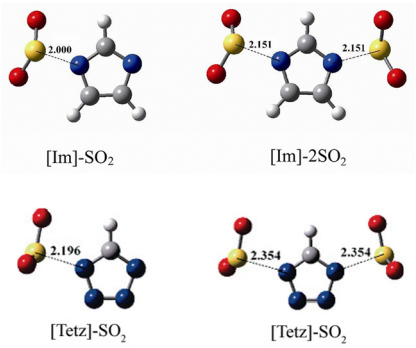

Fig. 6 Optimized structure of [Im]-SO_2, [Im]-$2SO_2$, [Tetz]-SO_2, and [Tetz]-$2SO_2$. Reprinted with permission from ref. 60. Copyright 2011, the American Chemical Society.

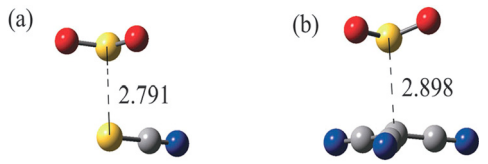

Fig. 7 Optimized structure of (a) [SCN]-SO_2 and (b) [$C(CN)_3$]-SO_2. Reprinted with permission from ref. 53. Copyright 2013, the Royal Society of Chemistry.

Quasi-chemical sites were designed for SO_2 capture by functionalized ILs through quasi-chemical interaction. Wang *et al.*[48,72] developed a "dual-tuning" strategy by adding electron-withdrawing groups (–Br and –CN) to anions with different functional main groups, such as [PhCOO], [PhO], and [$PhSO_3$] (Fig. 8). Their QC calculations showed that these electron-withdrawing groups shared negative charge on the anions and quasi-chemical Br···SO_2 or CN···SO_2 interactions resulted in an increase absorption capacity. Balasubramanian *et al.*[98] studied six anion-functionalized [P_{2221}]-based ILs ([XPhO], [XPhCOO], [Tetz], [$N(CN)_2$], and X = Br and CN) for SO_2 absorption by employing QC calculations and MD simulations. Their QC calculations indicated that the basicity of the anions resulted in enhanced anion···SO_2 interactions and high uptake of SO_2, while the MD simulations revealed the crucial role of both the cations and anions in SO_2 dissolution. Wang *et al.*[66,74] investigated that C═O and –CHO were other efficient quasi-chemical sites for SO_2 capture under low-concentration SO_2 through QC calculations. The above-mentioned quasi-chemical sites were affected by the basicity of the anion, where strong basicity resulted in strong quasi-chemical interaction (or chemical interaction). Different from the sites on the anions, Jung *et al.*[91] showed that electrostatic and charge-transfer effects, a quasi-chemical interaction, between $[Br]^-$ and SO_2 were the reason for efficient SO_2 absorption by halogen anion-based ILs using QC calculations.

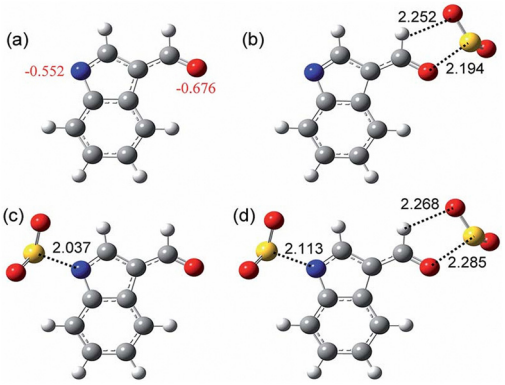

Fig. 8 Optimized structures of [3-CHO-Indo] (a) and [3-CHO-Indo]–SO_2 complexes (b)–(d) at the B3LYP/6-31++G(d,p) level. (b) O atom in [3-CHO-Indo] with the closest SO_2 molecule, [3-CHO-Indo]·SO_2, ΔH = −97.1 kJ mol^{-1}; multiple-site chemical interactions between [3-CHO-Indo] and SO_2 molecule: (c) N atom in [3-CHO-Indo] with the closest SO_2 molecule, [3-CHO-Indo]–SO_2, ΔH_1 = −115.3 kJ mol^{-1} and (d) [3-CHO-Indo]–$2SO_2$, ΔH_2 = −76.3 kJ mol^{-1}. Reprinted with permission from ref. 74. Copyright 2016, the Royal Society of Chemistry.

The O sites of ether groups and N sites of tertiary amine groups can endow ILs with efficient and reversible SO_2 absorption capacity under different absorption conditions. Jung *et al.*[31] optimized the structures and calculated the interaction enthalpies of ether-based [E_nMIm][$MeSO_3$] + $(2 + n)SO_2$ (n = 1–8) complexes (Fig. 9). For example, the interaction enthalpies of [E_1MIm][$MeSO_3$] + $3SO_2$, [E_2MIm][$MeSO_3$] + $4SO_2$, [E_3MIm]-[$MeSO_3$] + $5SO_2$ were calculated to be −89.5, −114.2, −130.1 kJ mol^{-1}, respectively. Although the calculations predicted that the maximum capacity was ∼$(2 + n)$ mol SO_2 per mol IL, the experimental results revealed that the maximum values could only be achieved at 2 bar SO_2 or higher, indicating the physical interaction between the ether groups and SO_2. Cui *et al.*[25] optimized the structure of a tertiary amine and ether group-functionalized chelate-based IL [Li(TDA-1)][TFSI] before and after interaction with SO_2 under low-concentration SO_2. The optimized structure indicated the triple helix of [Li(TDA-1)] with six O atoms coordinated with the lithium ion, while the free N atom could interact with SO_2 chemically. Recently, Lu and Wu *et al.*[99] reported a theoretical study on screening ILs for SO_2 capture at a low SO_2 partial pressure and high temperature.

According to the discussion above, it can be seen that functional ILs can interact with multiple SO_2 molecules under certain conditions not only through chemical interactions but also through quasi-chemical interactions due to their multiple

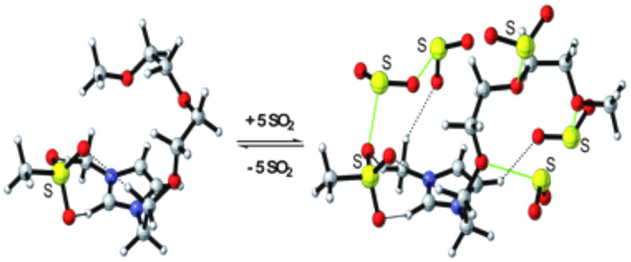

Fig. 9 Optimized structure showing the interactions between [E_3MIm][-$MeSO_3$] and SO_2 molecules. Reprinted with permission from ref. 31. Copyright 2011, the Royal Society of Chemistry.

active sites, mainly (negatively charged) O and N atoms. For example, the [L] anion has two carbonyl oxygen atoms and one hydroxyl oxygen atom, the [3-CHO-Indo] anion has one carbonyl oxygen atom and one negatively charged nitrogen atom, and the [E_3MIm] cation has three ether oxygen atoms. All these atoms can interact with the sulfur atom of the SO_2 molecule.

Spectroscopic analysis

FT-IR and NMR spectroscopy are the two common methods employed to study the capture mechanism. Especially, FT-IR spectroscopy shows bonding information, which is beneficial to verify the interaction between the active sites and SO_2 and predict the absorption mechanism. The IR and Raman spectra and geometry of SO_2 have been known for a long time.[100] For example, Anderson[101,102] investigated the IR and Raman spectra of crystalline and liquid SO_2. Allavena *et al.*[103] studied the IR spectra and geometry of SO_2 isotopes in solid krypton matrices. Schriver-Mazzuoli *et al.*[104] the reported IR spectra of SO_2 and SO_2:H_2O ice at low temperature. The typical absorption modes of amorphous SO_2 at 30 K of ν_1 (S═O, symmetric stretch), ν_2 (S═O, bending mode), and ν_3 (S═O, asymmetric stretch) were 1145.8, 520.1, and 1315.5 cm^{-1}, respectively.[104]

The first functional IL [TMG][L] for SO_2 sorption was reported by Han *et al.*, and the interaction between [TMG][L] and SO_2 was also analyzed through FT-IR and NMR spectroscopy.[16] The band at 957 cm^{-1} in the FT-IR spectrum was assigned to the S–O stretching, which is a feature of chemisorption. To show the interaction between SO_2 and azolate-based ILs, Wang *et al.*[60] investigated the absorption mechanism of [P_{66614}][Tetz] using *in situ* FT-IR spectroscopy during absorption at 20 °C and 1 bar, and a new absorption band 935 cm^{-1} attributed to S–O stretches was observed (Fig. 10). Subsequently, although different types of functionalized ILs with different structures have been developed for the chemisorption of SO_2, the main active sites are negatively charged N atom and O atom, and the typical new band is in the range of 900 to 1000 cm^{-1}, which is attributed to S–O stretching.

The NMR spectra before and after the absorption of SO_2 by ILs are also used to verify their absorption mechanism. For

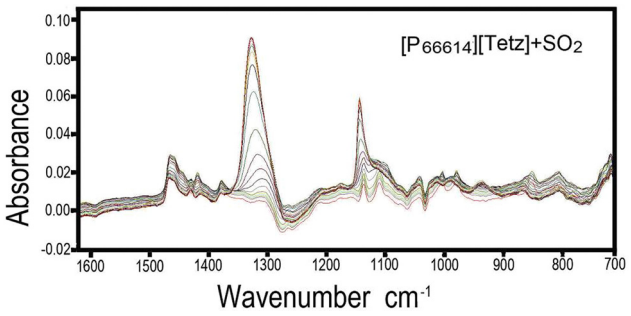

Fig. 10 Stack plot of the *in situ* FT-IR spectra collected at 1 min intervals for SO_2 capture using [P_{66614}][Tetz] in 30 min at 20 °C and 1 bar. Reprinted with permission from ref. 60. Copyright 2011, the American Chemical Society.

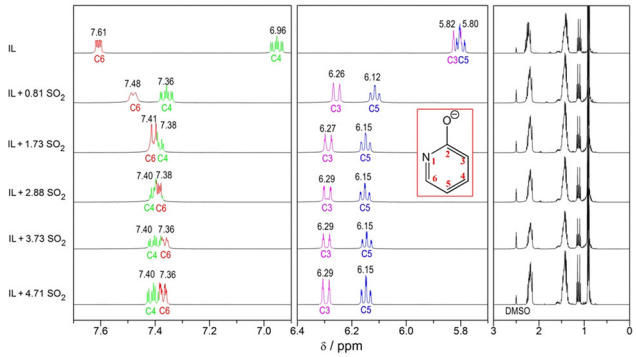

Fig. 11 Comparison of the ^{1}H NMR spectra of [P_{4442}][PyO] before and after the absorption of different amounts of SO_2 (in mol SO_2 mol^{-1} IL). Reprinted with permission from ref. 70. Copyright 2020, the American Chemical Society.

example, Cui *et al.*[70] employed the *in situ* NMR method to record the spectra of the IL + SO_2 system during absorption (Fig. 11). The original chemical shifts of C3–H, C4–H, C5–H, and C6–H for the fresh [P_{4442}][PyO] were located at 5.82, 6.96, 5.80, and 7.61 ppm, respectively. After the absorption of 1.73 mol mol^{-1} SO_2, they quickly shifted to 6.27, 7.38, 6.15, and 7.41 ppm, respectively. These shifts indicated the chemical interactions of O···SO_2 and N···SO_2. Additionally, during the absorption of 1.73–4.71 mol mol^{-1} SO_2, only a slight shift could be obtained, indicating the physisorption of SO_2. Thus, SO_2 capture originated from chemisorption and physisorption.

Recording fluorescence spectra before and after the absorption of SO_2 by ILs is another approach that can be employed to verify the adsorption sites. For example, Wang *et al.*[105] reported the synthesis of an anion-functionalized fluorescent IL, trihexyl(tetradecyl)phosphonium 2-(2′-hydroxyphenyl)benzoxazole ([P_{66614}][HBO]), as an efficient and reversible turn-off sensor for detecting SO_2. [P_{66614}][HBO] emitted blue fluorescence and its fluorescence was quenched completely after absorbing SO_2 (Fig. 12). However, through the combination of experimental absorption, spectroscopic investigation, and quantum chemical calculations, the results indicated that the quenching of the fluorescence originated from the physical absorption of SO_2, not chemical absorption, which permitted the quantification of its amount in the quenching process.

Factors influencing SO_2 sorption

Temperature and SO_2 partial pressure

Temperature and SO_2 partial pressure also play an important role in SO_2 capture and utilization. In the case of SO_2 absorption, low temperature or high partial pressure will result in high capacity, while high temperature or low partial pressure will result in low capacity, especially absorption through only physical interaction. In the case of chemisorption and quasi-chemisorption, the capacity under high temperature or low partial pressure id due to the active sites on the structure.[95] For example, multiple-site chemisorption will result in high

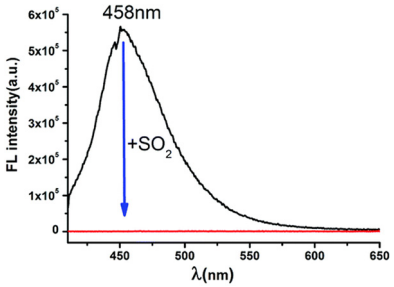

Fig. 12 Fluorescence spectra of pure $[P_{66614}][HBO]$ before and after exposure to gaseous SO_2 under a UV lamp (λ_{ex} = 400 nm). Reprinted with permission from ref. 105. Copyright 2017, the Royal Society of Chemistry.

absorption capacity.[60] Due to the low SO_2 partial pressure in flue gas, SO_2 capture should be performed efficiently at low partial pressures. Actually, the SO_2 content in flue gas is in the range of 1000 to 3000 ppm, and the average is 2000 ppm (0.002 bar). To improve the weight capacity, ILs with low molecular weights are encouraged to be developed. For example, Wang *et al.*[61] reported an IL, $[P_{4442}][Tetz]$, which showed the high absorption capacity of 0.18 g SO_2 per g IL and excellent reversibility for 2000 ppm SO_2 at 25 °C. Subsequently, Zhao *et al.*[83] showed that the SO_2 capacity of [TMEA][Im], which was directly prepared *via* the acid–base neutralization of equimolar TDA-1 and imidazole, could reach 0.321 g SO_2 per g IL at 25 °C under 2000 ppm. Thus, functional ILs with abundant active absorption sites (azole N, ether O, and tertiary amine N) are considered to be able to exhibit efficient SO_2 capture performances under flue gas conditions. In case conventional ILs, with a decrease in the absorption temperature or increase in SO_2 partial pressure, the absorption capacity will increase slightly following the Henry's law due to only physical interaction.

Potential sites and active sites

The active sites in the structures of ILs are crucial for SO_2 capture and utilization. Briefly, the potential sites are the sites that may interact with the absorbate efficiently, while the active sites are the sites that can interact with the absorbate efficiently. It is known that electron-negative O, N, and S atoms may increase the capacity for SO_2, especially when these atoms are on the anions. Thus, a strategy of "multiple sites" was developed for efficient SO_2 capture by ILs.[60] However, more potential sites do not mean more active sites. For example, conventional ILs with the [TFSI] anion, which contains four O atoms and one N atom, have low SO_2 capacity (about 1–1.5 mol mol^{-1}) at room temperature and 1 bar, indicating the weak interactions between the ILs and SO_2.[65] Another example was reported by Wang *et al.*,[54,60] where the SO_2 capacities of $[P_{66614}]$-based ILs with [Pyro] (one N atom), [Im] (two N atoms), and [Tetz] (four N atoms) anions were 2.52, 4.80 and 3.72 mol mol^{-1}, respectively. Because of the greater number of potential sites sharing one negative charge on the anion, the number of active sites is controlled by the amount of negative electric charges. Thereby, a strategy of "limited number of active sites" was reported by Cui *et al.*,[64] which means a small number of active sites can improve the solubility of SO_2 in ILs.

Basicity

The efficiency of SO_2 absorption is affected by the basicity of ILs. Because SO_2 is a type of acidic gas, basic ILs can efficiently uptake SO_2 through acid–base reaction. For example, imidazole (pK_a = 18.6 in DMSO) and pyrrole (pK_a = 23 in DMSO) are strong basic organic compounds, and they were found to show efficient SO_2 capture, especially under low concentration SO_2. The interaction enthalpies of the [Im] + SO_2 and [Pyro] + SO_2 complexes were calculated to be −124.6 and −139.2 kJ mol^{-1}, respectively, resulting in difficult desorption.[54,60] However, some types of acidic ILs can also efficiently uptake SO_2. For example, acetic acid (pK_a = 3.77 in H_2O) and benzoic acid (pK_a = 4.20 in H_2O) were also reported for efficient SO_2 capture.[48] Thus, the question arises, what are functional ILs for SO_2 capture?

Wu *et al.*[49] investigated the basicity of ILs for the chemisorption of SO_2. They found that pK_a could be used to differentiate functional ILs from normal ILs. They believed that the chemisorption of SO_2 by ILs occurred when pK_a of anion > pK_a of H_2SO_3. Wang *et al.*[54] showed that the quasi-chemisorption of SO_2 through $-CN\cdots SO_2$ interaction was affected by the basicity of ILs (Fig. 13). Anions with high basicity resulted in strong $CN\cdots S$ interactions. Their results showed that the incremental SO_2 sorption capacity increased linearly with the basicity of ILs.

Viscosity

Viscosity is an important physical property of absorbents. Due to the existence of various chemical bonds, such as ionic hydrogen bonds[106] and Z-bond,[107] the viscosity of ILs (10–10 000 cP) is generally higher than that of water (0.89 cp) and conventional solvents (0.1–100 cP). High viscosity usually imparts constraints on mass transport and reaction processes. It is known that increasing the temperature can reduce the viscosity. Besides, mixtures including deep eutectic solvent catalysts (DESs), IL–IL mixtures, and other IL-based solutions have been developed to decrease the viscosity of pure ILs. In the case of IL–IL mixtures, Chen *et al.*[108] and Brennecke *et al.*[109] investigated the viscosity of IL–IL mixtures based on common

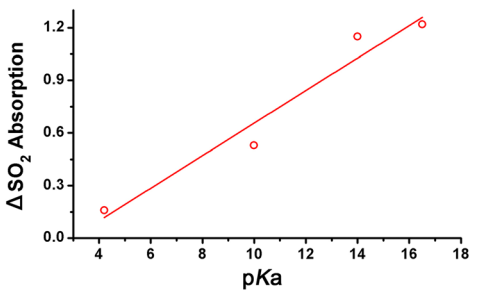

Fig. 13 Incremental SO_2 sorption capacity *vs.* pK_a value of cyano-free anions of ILs. Reprinted with permission from ref. 54. Copyright 2015, Wiley-VCH.

anions or functional anions, respectively. Robelin *et al.*[110] reviewed the viscosity models for ILs and their mixtures.

The viscosity of absorbents changes with the amount of SO_2 absorbed. The viscosity of the traditional ILs decreases with an increase in the SO_2 mole ratio, while the viscosity of task-specific ILs show a rising, and then falling trend during the absorption of SO_2 at room temperature and atmospheric pressure.[57,111] For example, the viscosity of [Bmim][BF_4] decreased from 38.6 to 9.5 mPa s at 45 °C after absorbing 0.71 mol mol^{-1} SO_2, while the viscosity of [TMG][L] increased from 418.0 to 794.5 mPa s at 45 °C after absorbing about 0.5 mol mol^{-1} SO_2, and then decreased to 78.0 mPa s after absorbing 1.57 mol mol^{-1} SO_2 at 1 bar.[112] The increase in viscosity is related to the amount of chemisorption of SO_2. Cui *et al.*[111] showed that the viscosity of each [PPZ][Br] mixed with different molar ratios of Gly dramatically increased after absorbing 1–1.5 mol SO_2 per mol anion, indicating the chemisorption of 1–1.5 mol SO_2 per mol anion (Fig. 14). Then, the viscosity decreased sharply during further SO_2 absorption, indicating the physisorption of more SO_2. Thus, the increase in viscosity is governed by chemisorption. It is safely concluded that in large-scale SO_2 capture from mixed gases or flue gases, the viscosity of the ILs increases greatly after chemically absorbing a large amount of SO_2, which may limit their eventual applications.

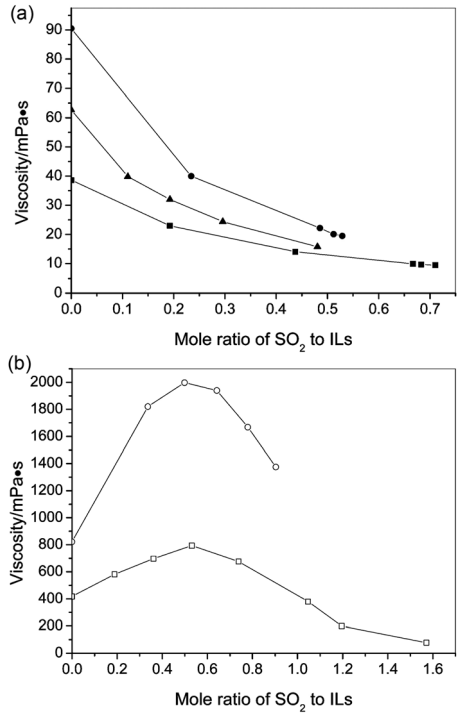

Fig. 14 (a) Effect of SO_2 on the viscosity of different normal ILs at 45 °C: ■, [BMIM][BF_4]; ●, [BMIM][PF_6]; ▲, [TMG][BF_4]. (b) Effect of SO_2 on the viscosity of task-specific ILs at 45 °C: □, [TMG]L; ○, [MEA]L. Reprinted with permission from ref. 112. Copyright 2010, the American Chemical Society.

Water (H_2O)

Coal-fired flue gases contain 10–15% water.[113,114] Thus, the influence of water on the physical properties, especially viscosity, of absorbents and their absorption mechanism should also be considered in the process of desulfurization. Water molecules cause a decrease in the viscosity of ILs. For example, Magee *et al.*[115] reported data for viscosity *vs.* water content for ILs. The results showed that the viscosity of the ILs decreased significantly as their water content increased. The decrease in the viscosity of ILs could improve the mass transfer during the absorption. However, Liu and Yu *et al.*[116] found that the viscosity of [Bmim][Ac] increased first, and then decreased with an increase in water content. This unique phenomenon could be attributed to the formation of a chainlike anion···water···anion cluster structure. A similar phenomenon was also found based on the viscosity data of the imidazolate-based ILs [HDBU][Im], [BDBU][Im], and [TMG][Im] with different water contents reported by Xu *et al.*[117,118]

Water affects the SO_2 absorption capacity because it possesses good affinity with most ILs, especially hydrophilic ILs.[119] The effects are different, including increasing absorption, decreasing absorption, and no change. For example, Wu *et al.*[120] found that the presence of water in simulated flue gas could decrease the viscosity of the IL greatly, and it had no effect on the absorption of 2% SO_2 by [TMG][L] with or without 7.3% water in the simulated flue gas at 40 °C. Wang *et al.* showed that the effect of different flue gas constituents (*e.g.*, water) on the capture of SO_2 by azolate-based ILs[60,65] or amide/imide-based ILs[66] was weak. For example, the SO_2 absorption capacity of [P_{66614}][BenIm] was 5.78 mol SO_2 per mol IL at 20 °C and 1 bar under 100% wet SO_2, compared with 5.75 mol SO_2 per mol IL under dry conditions. Besides, Cui *et al.*[64] showed that 4.43 mol SO_2 per mol IL could be captured by [P_{4442}][BTFA] under 100% humidity SO_2, whereas the dry SO_2 absorption capacity was 4.27 mol SO_2 per mol IL at 20 °C and 1 bar. However, some results indicated that the changes in the SO_2 capacities of different ILs were different under 100% wet SO_2.[25] Actually, this is because of (1) the competition behavior between water and SO_2 when interacting with absorbents, (2) water can absorb SO_2 to form sulfurous acid, and (3) multiple-site absorption by ILs changes to single-site absorption by water, and thus the effect of water on the absorption capacity is more complex.

The effect of water on the absorption mechanism is relatively clear. The mechanisms of SO_2 absorption by ILs with or without water are different. It is known that an alcohol will react with SO_2 upon dehydrogenation by an organic base to form an IL with the *O*-alkylsulfite anion.[121,122] Similarly, water can directly react with SO_2 to form sulfurous acid (H_2SO_3), which is subsequently converted to sulfite ($[HSO_3]^-$) through ionization by water or dehydrogenation by basic anions from anion-functionalized ILs.[36,66,123] Therefore, the following reactions are likely to take place in the presence of water when anion has high basicity:

$$SO_2(g) \rightleftharpoons SO_2(l) \quad (R1)$$

$$SO_2(l) + H_2O \rightleftharpoons H_2SO_3 \quad (R2)$$

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \quad (R3)$$

$$[Cation]^+[Anion]^- + H_2SO_3 \rightleftharpoons HAnion + [Cation]^+[HSO_3]^- \quad (R4)$$

$$[Cation]^+[Anion]^- + [Cation]^+[HSO_3]^- \rightleftharpoons HAnion + [Cation]_2^+[SO_3]^{2-} \quad (R5)$$

It is concluded that the basicity of the anions should be higher than H_2SO_3 to serve functional anions, which can react with H_2SO_3 to produce $[HSO_3]^-$ anion. In the case of the [Phth] anion, given that phthalimide (pK_a = 8.3) is a weaker acid than H_2SO_3 (pK_{a1} = 1.9, pK_{a2} = 7.21), $[HSO_3]^-$, $[SO_3]^{2-}$ and neutral phthalimide were obtained in the reaction solvent. In the case of conventional anions but with the active sites on the cations, reactions (R4) and (R5) are changed to: $[Cation]^+[Anion]^- + H_2SO_3 \rightleftharpoons [Anion]^- + H^+[Cation]^+ + [HSO_3]^-$ (R4) and $[Cation]^+[Anion]^- + [HSO_3]^- \rightleftharpoons HAnion + [Cation]^+ + [SO_3]$.

To increase the selectivity for SO_2/water, hydrophobic ILs are encouraged to be designed and developed. For example, ILs with fluorinated acetylacetonate anions such as [BTFA], [TTFA] and [HFA] were proven to be hydrophobic by Cui *et al.*[64] They showed that the solubilities of ILs in water for $[P_{4442}][TFSI]$, $[P_{4442}][BTFA]$, $[P_{4442}][TTFA]$ and $[P_{4442}][HFA]$ were measured to be 0.016, 1.14, 0.71, and 0.86 g IL/100 g H_2O, while the solubilities of water in these ILs were measured to be 0.05, 0.24, 0.07, and 0.12 g H_2O per g IL, respectively. Thus, these ILs functionalized with fluorinated acetylacetonate anions are alternative sorbents for the selective capture of SO_2 under high humidity conditions compared with the conventional ILs with [TFSI] anion.

Carbon dioxide (CO_2)

It is known that due to its acidity, CO_2 can affect the SO_2 capture performance of absorbents with high basicity. For example, Wu *et al.*[49] suggested that if the pK_a of an organic acid is larger than that of sulfurous acid (or carbonic acid), the ILs formed by the organic acid can be called functional ILs for SO_2 (or CO_2) capture, and they can have a high absorption capacity of SO_2 (or CO_2) with low SO_2 (or CO_2) concentrations. Here, the pK_a of acetic acid is 4.76, while that of sulfurous acid is 1.81 in water. Thus, generally, the ILs formed from anions with a pK_a in the range of 1.81–4.76 can efficiently capture SO_2 from CO_2 selectively. Wang *et al.* showed that $[P_{66614}][Tetz]$ with a tetrazolate anion (pK_a = 4.89 in water) could efficiently absorb SO_2 through multiple-site chemical reactions,[60] while low reaction with CO_2.[124] Cui *et al.*[62] reported the effect of different substituents in the [Im] anion on SO_2 absorption, and found that $[P_{66614}]$[4,5-CN-Im] with a 4,5-dicarbonitrileimdazolate anion (pK_a = 5.75 in water) showed high SO_2/CO_2 selectivity among the substituted imidazolate-based ILs due to its high absorption capacity for SO_2 but low absorption capacity for CO_2 (Fig. 15).

Besides, among the different kinds of amine groups, the tertiary amine group was found to efficient react with SO_2, but

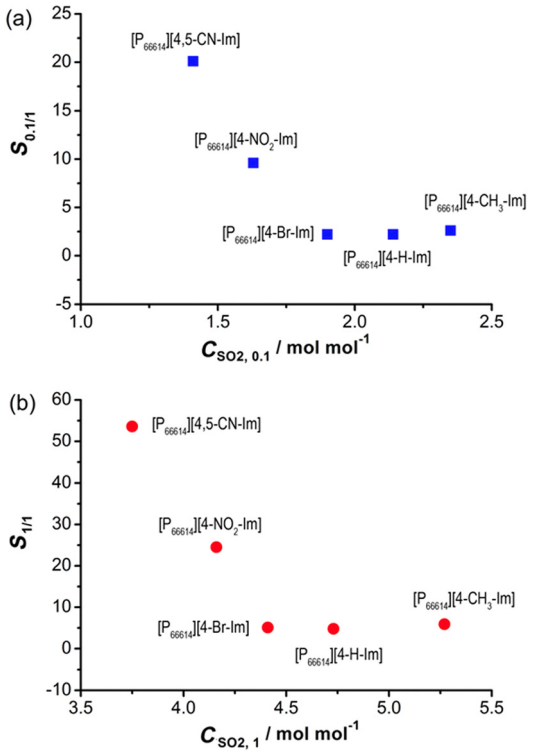

Fig. 15 $S_{0.1/1}$ *vs.* $C_{SO_2,1}$ (a) and $S_{1/1}$ *vs.* $C_{SO_2,1}$ (b) for different substituted imidazolate-based ILs. Reprinted with permission from ref. 62. Copyright 2017, Wiley-VCH.

cannot react directly with CO_2 in the absence of water. Cui *et al.*[25] reported that equimolar SO_2 could be captured by a metal chelate-based IL, [Li(TDA-1)][TFSI], under low concentration SO_2 through chemical interaction between the tertiary amine and SO_2. Subsequently, the same group found that deep eutectic solvents based on 1-hydroxyethyl-1,4-dimethylpiperazinium bromide [PPZ][Br] with tertiary amine functional groups showed high SO_2/CO_2 selectivities.[111] Recently, Wang *et al.*[125] reported that a protic IL, [THEEDH][Tetz], with a tertiary amine functional group and tetrazolate functional anion showed good selectivity of 80.6 (in molar capacity) or 120.4 (in weight capacity) under an atmosphere of 2000 ppm of SO_2 and 15% CO_2. Thus, tuning the basicity of ILs and using tertiary amine functional groups are two efficient strategies for designing functional ILs to increase the selectivity for SO_2/CO_2.

Design strategies

Design of active sites and groups on ILs

As mentioned above, active sites play a crucial role in SO_2 capture. Thus, for the design of cations of ILs, ether groups and tertiary amine groups are two types of efficient groups for their functionalization. Ether groups are efficient for the physisorption of SO_2, while tertiary amine groups are efficient for the chemisorption of SO_2. In addition, electron-negative O and N atoms on the anions are efficient for SO_2 chemisorption, especially at a high absorption temperature or low SO_2 partial

pressure due to the acid–base neutralization reaction between these anions and SO_2. The functional anions formed with these atoms are typically carboxylate anions, azolate anions, phenolate anions, amide anions, and imide anions. Furthermore, some groups on the anions can increase the capacity for SO_2 through additional quasi-chemisorption at low absorption temperature and high partial pressure, due to the moderate-strength quasi-chemical interactions. These groups include –C≡N, –C=O, and –X (halogen). Thereby, SO_2 absorption can be efficiently tuned through different active sites.

Design of IL-based solvents

To overcome the viscosity of ILs, IL-based solvents have been designed for efficient SO_2 capture. For example, Wu and Hu *et al.*[126] reported the preparation of two binary mixtures, [diglutarate]-based IL [N_{2222}][diglutarate]/sulfolane and [DMEA][diglutarate]/sulfolane, containing 40 wt.% ILs for SO_2 absorption. The binary mixtures could absorb 0.83–0.95 mol SO_2 per kg absorbent at 0.004 bar and 303.15 K, indicating the efficient chemisorption of SO_2. Yang *et al.*[127] showed that the IL-based mixtures [Emim][Cl]/[Emim][SCN] (1 : 1) and [Emim][Cl]/[Emim][SCN] (1 : 2) were efficient for SO_2 absorption due to the strong charge-transfer interaction between SO_2 and anions.

Adjusting the absorption conditions

Besides tuning the structures of ILs, increasing the activity of their sites and converting the potential sites into active sites can also be achieved by adjusting the absorption conditions, such as decreasing the absorption temperature and increasing the SO_2 partial pressure. For example, –C≡N is an electron-withdrawing group that can disperse the negative charge of the COO group on the anion and improve the stability of the [P_{66614}][4-CNPhCOO] IL (Fig. 16). Thus, the interaction between the COO group and SO_2 was weakened, and the absorption capacity decreased at a low partial pressure and high absorption temperature. Wang *et al.*[54] showed that the cyano group, which shared the Mulliken atomic charge, could be an additional site for interaction with SO_2 at a decreased absorption temperature or increased SO_2 partial pressure.

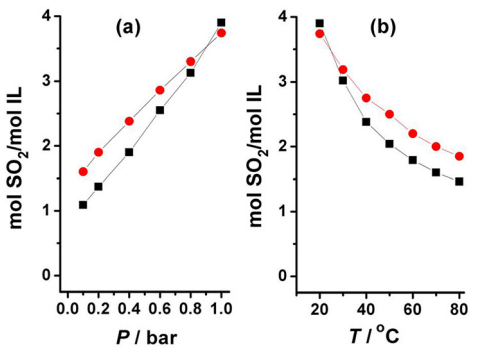

Fig. 16 Effect of pressure at 20 °C (a) and temperature at 1 bar (b) on SO_2 absorption using cyano-containing IL [P_{66614}][4-CNPhCOO] (■) and cyano-free IL [P_{66614}][PhCOO] (●). Reprinted with permission from ref. 54. Copyright 2015, Wiley-VCH.

SO_2 conversion by ILs

SO_2-philic ILs can not only absorb SO_2 as sorbents, but also convert the absorbed SO_2 to chemicals as catalysts. Additionally, SO_2-philic ILs can be used to design batteries and sensors.

Sulfur (S_8)

It is known according to the Claus reaction that SO_2 reacts with H_2S to form H_2O and solid sulfur, as follows:

$$16H_2S + 8SO_2 \rightarrow 3S_8 + 16H_2O$$

Low toxic polyethylene glycol ethers (PEGEs) have been applied as solvents and organic bases (*e.g.*, *N*,*N*-dimethylaniline) have been used as catalysts to accelerate this reaction for a long time. Considering the unique properties of ILs, Wu and Hu *et al.*[128] found that the reaction of SO_2 with H_2S proceeded in the [Hmim][Cl] IL to produce elemental sulfur. Subsequently, these authors reported SO_2 capture and conversion to sulfur in imidazolium-based DESs containing acetamide.[129] Other examples of SO_2 capture and conversion into sulfur were reported by Wu *et al.*[130] They showed that three lactate-based functional ILs, [MEA][Lac], [TMG][Lac], and [N_{2222}][Lac], could be used as absorbents and catalysts to absorb and convert low-concentration SO_2 to sulfur *via* the Claus reaction. Their results showed that the conversion of absorbed SO_2 was reduced with additional water in the ILs, while it increased with an increase in the acidity of the absorbents.

Cyclic sulfites

The first examples of SO_2 conversion into cyclic sulfites by ILs without any other organic solvents or additives were reported by He *et al.*,[30] as shown in Fig. 17. Their investigations showed that the ether-functionalized IL [E_3DABCO][TFSI] (DABCO = 1,4-diazabicyclo[2.2.2]octane) could activate SO_2 and convert it into cyclic sulfites.

Subsequently, Wu and Hu *et al.*[82] showed that dual ether-functionalized protic ILs, including [BDMAEEH][MOAc], [BDMAEEH][EOAc], [BDMAEEH][MEAAc], [DMDEEH][MOAc], [DMDEEH][EOAc], [DMDEEH][MEAAc], [EDBEAH][MOAc], and [TMPDAH][BAc], not only had high SO_2 absorption capacity but also served as catalysts for the cycloaddition of SO_2 with epoxides. Zhao and Liu *et al.*[131] prepared [Emim][Cl] mixed with azoles for the absorption and conversion of SO_2 to cyclic

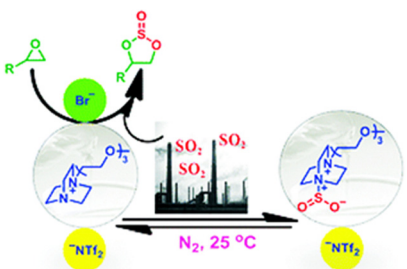

Fig. 17 Reactions of [E_3DABCO][TFSI] with SO_2 to form active SO_2, which subsequently reacts with epoxide to produce cyclic sulfites. Reprinted with permission from ref. 30. Copyright 2016, the Royal Society of Chemistry.

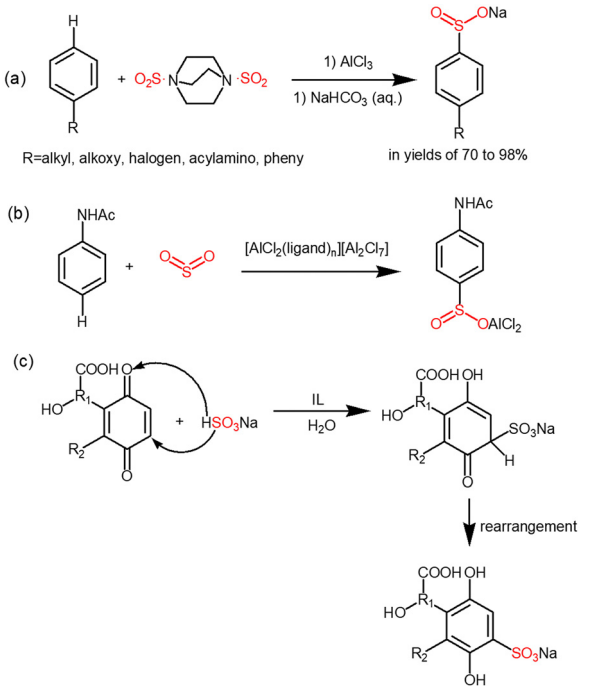

Fig. 18 (a) Reactions of arenes with DABSO as SO_2 surrogate, reprinted with permission from ref. 134, Copyright 2018, Elsevier B.V. (b) Sulfination of acetanilide using liquid coordination complexes as dual catalysts and solvents, reprinted with permission from ref. 135, Copyright 2018, Elsevier B.V. (c) Proposed mechanism of the sulfonation of HA, reprinted with permission from ref. 136, Copyright 2013, the Royal Society of Chemistry.

sulfites. Xu *et al.*[132] reported the preparation of several guanidinium-based ILs, [TMG][BF_4], [TMG][Ac], [TMG][MOAc], [TMG][EOAc], and found that [TMG][BF_4] was not a candidate for this type of reaction due to its lowest SO_2 absorption capacity among the four [TMG]-based ILs.

DABSO

DABSO is a complex of DABCO with two SO_2 (DABCO·2SO_2), namely, bis(sulfur dioxide)-1,4-diazabicyclo[2.2.2]octane, which is formed according to the equation: DABCO + 2SO_2 → DABSO. Liu *et al.*[133] showed that [Emim][Cl] with dimethylurea in a 2 : 1 molar ratio could achieve both high gravimetric (1.26 g per g of DES) and molar absorption capacity (8.00 mol per mol of DES) of SO_2 at 20 °C and 1.0 bar.

Benzenesulfinic acids

Sulfinic acids and their salts can be used as intermediates for the synthesis of various organic compounds with sulfonyl motifs (–SO_2–) (Fig. 18). Wang and Zhang *et al.*[134] reported that DABSO can be used as an "SO_2 surrogate" for the Friedel–Crafts sulfination reaction to synthesize aryl sulfinates in the presence of $AlCl_3$ (Fig. 18a). The same authors subsequently investigated the sulfination of acetanilide using liquid coordination complexes as dual catalysts and solvents for SO_2 and conversion (Fig. 18b).[135] Their results indicated that [Bmim][Cl]/$AlCl_3$ and [Et_3NH][Cl]/$AlCl_3$ could give 42.02% and 98.94% acetanilide conversion as well as 38.24% and 90.03% yield of the desired products, respectively. Hu *et al.*[136] applied [N_{4444}][Br] : CPL (1 : 1) as a sorbent and catalyst to absorb SO_2 and convert sodium humate solution to sulphonated humic acid (Fig. 18c).

Alternative ILs

Yasaka and Kimura *et al.*[137] reported that the absorption of equimolar SO_2 by [P_{4448}][HCO_3] resulted in the formation of the corresponding bisulfite IL [P_{4448}][HSO_3], accompanied by CO_2 release, with the suggested reaction: [P_{4448}][HCO_3] + SO_2 ⇄ [P_{4448}][HSO_3] + CO_2.

Conclusions and outlook

SO_2, emitted from the combustion of fossil fuels, leads to a series of environmental problems, including acid rain and haze. Conversely, it can be detected, captured, converted and utilized. ILs have been widely used in the areas of chemistry, chemical engineering, materials science, energy and the environment due to their outstanding properties, such as low melting point, low volatility and vapor pressure, high thermal stability, wide liquid range, high ionic conductivity, wide electrochemical window, designable structures and tunable properties. Thus, various types of ILs have been widely used in the capture of SO_2 and related applications.

In this critical review, we focused on the advances in SO_2 capture and conversion by different types of ILs. We showed that the presence of SO_2-philic active sites is essential for ILs to be used in the capture of SO_2 from post-combustion flue gas. However, it is difficult to judge which IL has realistic potential for SO_2 capture application. ILs with strong chemical sites result in difficult desorption and high energy consumption, while ILs with weak physical sites result in high reversibility and energy-saving. Besides, the interactions, sorption models, sorption mechanisms, and influencing factors were discussed systematically, and then several design strategies were proposed to design active sorbents for SO_2 capture. Based on the high solubility of SO_2 in physical or chemical ILs, absorbed SO_2 can be converted to various chemicals.

However, this field is still in its infancy. A number of issues need to be investigated and other applications, especially the synthesis of SO_2-based chemicals, need to be developed in the future. At least, the following points should be given more attention.

(1) Designing efficient SO_2-philic ILs and materials. Functionalized ILs containing active sites on their cations or anions are efficient for SO_2 capture. The active sites are mainly the negatively charged N atom and O atom. Besides, according to the size of the SO_2 molecule, IL-based materials with ultramicroporous (IUPs) hosting a high-density of basic $[Br]^-$ anions were reported for the efficient capture of low-concentration SO_2.[138] Thus, the direct capture of SO_2 from polluted air can be achieved by tuning the pore size and structure of ILs.

(2) Predicting SO_2 solubility in ILs using machine learning and computer-aided calculations. Machine learning, with various approaches, has been widely applied for the prediction of

the thermodynamic and physicochemical properties of ILs including solubility, density, viscosity, surface tension, and heat capacity.[139–141] However, compared with computer-aided calculations, machine learning used for the prediction of the solubility of SO_2 in ILs has hardly been reported. It is believed that with the large amount of SO_2 capacity data reported, different machine learning approaches will be applied in the near future for predicting SO_2-philic ILs.

(3) Synthesis of sulfonyl-containing compounds. Sulfonyl-containing compounds constitute an important class of therapeutical agents in medicinal chemistry, presumably because of the tense chemical structure and functionality of sulfonyl.[142] Besides, sulfonyl-containing COFs were reported for photocatalytic hydrogen evolution from water.[143] Because SO_2 is a useful sulfur resource to supply sulfonyl motifs (–SO_2–), SO_2 capture and conversion give an alternative opportunity to synthesize value-added sulfonyl-containing chemicals and functional materials. This is a great challenge but should be considered in the future.

(4) Electrochemical conversion of SO_2. The electrochemical conversion of SO_2 is another method for desulfurization, including electrochemical oxidation of SO_2 and electrochemical reduction of SO_2. It was reported that SO_2 could be electrochemically oxidized to H_2SO_4 or $NaHSO_4$,[144–147] while it could be electrochemically reduced to sulfur.[148,149] It is known that ILs have high ionic conductivity and wide electrochemical window. However, the use of ILs for the electrochemical conversion of SO_2 has hardly been reported, except for the development of electrochemical SO_2 sensors. It is believed that the simultaneous sorption and green electrochemical conversion of SO_2 to value-added chemicals is a new concept for desulfurization.

Author contributions

Ruina Zhang: data curation, formal analysis, investigation, methodology, validation, visualization, writing – original draft. Lina Tang: resources, formal analysis. Chunliang Ge: resources, formal analysis. Xiongfei Nie: formal analysis, validation, investigation. Limin Xu: formal analysis. Quanli Ke: formal analysis, Funding acquisition. Zekai Zhang: formal analysis. Ying Zhou: resources, formal analysis, funding acquisition. Xiaopo Niu: formal analysis. Huayan Liu: formal analysis. Hanfeng Lu: funding acquisition, supervision. Guokai Cui: conceptualization, project administration, funding acquisition, resources, writing – review & editing.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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