processes

Review

Capture of Acidic Gases from Flue Gas by Deep Eutectic Solvents

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Abstract: Up to now, many kinds of deep eutectic solvents (DESs) were investigated for the capture of acidic gases from flue gases. In this review, non-functionalized and functionalized DESs, including binary and ternary DESs, for SO_2, CO_2 and NO capture, are summarized based on the mechanism of absorption, physical interaction or chemical reaction. New strategies for improving the absorption capacity are introduced in this review. For example, a third component can be introduced to form a ternary DES to suppress the increase in viscosity and improve the CO_2 absorption capacity. DESs, synthesized with halogen salt hydrogen bond acceptors (HBAs) and functionalized hydrogen bond donors (HBDs), can be used for the absorption of SO_2 and NO with high absorption capacities and low viscosities after absorption, due to physicochemical interaction between gases and DESs. Emphasis is given to introducing the absorption capacities of acidic gases in these DESs, the mechanism of the absorption, and the ways to enhance the absorption capacity.

Keywords: deep eutectic solvents; capture; sulfur dioxide; carbon dioxide; nitric oxide

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1. Introduction

Acidic gases, such as sulfur dioxide (SO_2), nitric oxide (NO) and carbon dioxide (CO_2), are the main pollutants of fuel gases, which are mainly released from the combustion of fossil fuels (coal, oil, and natural gas), posing a significant threat to the environment by forming acid rain, ozone destruction, global warming and so on. Due to the high hazards of these acidic gases, various methods have been developed to reduce their emissions, such as lime−limestone flue gas desulfurization process for SO_2 capture [1], carbon dioxide capture and sequestration process for CO_2 capture [2], selective catalytic reduction, and selective non-catalytic reduction for NO conversion [3,4]. Nevertheless, the drawbacks of them are obvious, such as volatility of absorbents, catalyst poisoning, substantial energy consumption and corrosiveness, the generation of huge amounts of byproduct and wastewater, which may generate secondary pollution to the environment if not properly treated. Therefore, it is necessary to capture the acidic gases with high efficiency, low cost, no by-products and high sustainability. Some work has been focused on the solutions to the above problems, among them one of the most effective and feasible ways is to develop novel recyclable green absorbents with high absorption efficiency and low desorption energy consumption.

Over the past two decades, ionic liquids (ILs) have received the most extensive attention in the field of gas absorption, owing to their unique characteristics. The promising advantages of ILs that can be used for gas capture are their negligible vapor pressures and their design ability by changing the structures of their cations and anions to meet different needs. The lower vapor pressure cannot only ensure no contamination of the gas stream but also lower the energy consumption and solvent regeneration. Hence, considerable efforts have been made to design novel ILs able to solubilize acidic gases physically and/or chemically [5–7]. For non-functionalized ILs that are able to dissolve acidic gases physically, the solubility of gases is proportional to its partial pressure, which has the advantage of absorbing high-pressure gases, and follows Henry's Law. For functionalized ILs, the gas solubility follows the chemical equilibrium and pressure is not significantly effective, so it can be used to absorb low-concentration gases. Although it is reported that ILs with halogen anions or halogen-containing anions can effectively absorb SO_2 through charge transfer interactions, the analysis confirmed that it was a physical absorption [8–11]. The solubility of gases in ILs driven by a physical absorption at low partial pressures is too low to develop a practical separation process. To obtain a higher absorptive capacity, ILs with functionalized groups such as carboxylate, azolate, amine, and acylamido were developed for acidic gas chemisorption [12–17]. Generally, compared to the traditional solvents, ILs have made great improvement in gas absorption; however, the high cost, complicated synthesizing and high viscosity impede its development in gas absorption, which inspire people to seek novel and efficient solvents [18,19].

Deep eutectic solvents (DESs), as IL analogs, have been developed on the basis of IL research, which share many of the same general characteristics. In addition to low vapor pressure, relatively wider liquid range and equivalent absorption capacity, DESs also have the advantages of low cost, low viscosity, convenient synthesis and easy achievement of dual functions compared to ILs. Therefore, DESs are considered to be promising alternatives to ILs. DESs with high purity can be easily prepared by mixing hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs), which may contain two or more constituents, and does not require further purification, therefore simplifying the processes. The interactions between the constituents can be hydrogen bonds, halogen bonds, or Pi-Pi interactions that cause the melting point of synthesized DES to be significantly reduced and lower than any of the individual component [20–22]. Abbott et al. [23] reported the first example of DES through mixing choline chloride (ChCl) with urea (UE), and then Zhu et al. [24] reported that ChCl:UE DES can effectively catalyze the reactions of CO_2 and epoxides. After that a significant number of studies were conducted on the capacity of the multifarious DESs for acidic gases absorption.

Recently, several reviews focusing on DESs were published. For instance, Hansen et al. reviewed various applications, physicochemical properties, and characterization techniques applicable to DESs [25]. Ji et al. [26] reviewed IL/DES-based absorbents for CO_2 capture, together with COSMO-RS models. Wu et al. [27] reviewed general trends in the development of DESs for the separation of mixtures. Chen et al. [28] gave a comprehensive summary of toxic gases capture by DESs, and reviewed the effects of HBD and HBA, temperature, their molar ratio, water content and gas flow rate on the absorption capacity. Generally, the factors that affect the gases capture capability of DESs can be divided into two categories: internal factors (e.g., structure of HBA and HBD, and molar ratio) and external factors (e.g., temperature, pressure, time, gas flow rate, and water content). To the best of our knowledge, almost all DESs follow the law that the absorption capacity decreases with the increase of temperature. The influence of water content (<8%) on the absorption of DESs is uncertain but generally slight. Gas flow rate only influences absorption/desorption rate and the time to reach absorption equilibrium. The gas solubility is proportional to its partial pressure for non-functionalized DESs. The saturated capacity of functionalized DESs increases with the increase of gas partial pressure. Therefore, the influence of external factors on absorption capacity will not be discussed here. In this review, we mainly focus on the influence of the nature and molar ratio of HBAs/HBDs on gas capture capacity and desorption rate. The functionalized and non-functionalized DESs were reviewed, according to whether chemical reactions occurred to form new substances or not, for SO_2, CO_2 and NO capture, respectively. This perspective includes the following sections: (1) non-functionalized DESs for SO_2 capture, (2) functionalized DESs for SO_2 capture, (3) non-functionalized DESs for CO_2 capture, (4) functionalized DESs for CO_2 capture, (5) functionalized DESs for NO capture, (6) conclusions and outlooks.

2. Non-Functionalized DESs for SO_2 Capture

The S atom in SO_2 is sp2 hybridized to form two σ bonds with two O atoms, which is a V-shaped geometric structure. The uneven distribution of positive and negative charges between the sulfur atom and the two oxygen atoms resulting in a great net dipole, which means that its dipole-dipole interaction is very strong. According to the "law of similarity and intermiscibility" principle, SO_2 can be easy absorbed by polar solvents through physical interaction. Thus, selecting polar organics as HBDs or HBAs is one way to improve the absorption capacity of DESs.

2.1. Caprolactam-Based DESs

In 2010, Duan et al. [29] synthesized a series of DESs by mixing caprolactam (CPL) and tetrabutyl ammonium bromide (TBAB) with different molar ratios. The solubility of SO_2 in CPL:TBAB DES (1:1) is about 0.1 g SO_2/g DES at 298.2 K and 101 kPa. They found the solubility of SO_2 decreased as both temperature and the molar ratio of CPL to TBAB increased, due to CPL is a weakly polar molecule. Then, Liu et al. [30] investigated a series of CPL-based DES with more polar organic acids and bases, such as acetamide (AA), furoic acid, benzoic acid, o-toluic acid. CPL: AA DES with a molar ratio of 1:1 presents the highest SO_2 solubility of 0.497 g SO_2/g DES at 303.15 K and 101 kPa. ^1H NMR analysis confirmed that CPL: AA DES absorbed SO_2 through physical interaction. The SO_2 absorption capacity of CPL:AA DES is higher than that of CPL:organic acids DESs. After that, they developed an inorganic thiocyanate-based DESs paired with organic bases to improve the SO_2 absorption capacity [31], based on the report that thiocynate and dicyanide anions in ILs play an important role in the physical capture of SO_2 [32,33]. CPL:KSCN DES (3:1) possessed SO_2 solubility of 0.607 g SO_2/g DES at 293.15 K and 101 kPa. The DESs could be easily regenerated under vacuum at 343.15 K and recycled for five times without an apparent decline of the absorption efficiency.

2.2. DESs Containing Halogen Anion

Simulating works were conducted to find a criterion that can explain the solubility order of SO_2 at 101 kPa in ILs. Elliott et al. [34] suggested an SO_2 affinity order of $Br^- \approx [NO_3]^- > [NTf_2]^- > [BF_4]^- > [PF_6]^-$ with a cation of $[C_4C_1im]^+$. On the basis of the solvation free energy and binding energies of SO_2 in ILs, Mondal et al. [35] inferred the SO_2 solubility order as $Cl^- > [BF_4]^- > [NO_3]^- > [PF_6]^- > [NTf_2]^-$. Notably, simulation results suggested that halogen anions have stronger potential to physically capture SO_2 than any other anions.

Han et al. [36] investigated the SO_2 absorption capacities of ChCl:glycerol(Gly) DESs with different molar ratios (from 1:1 to 1:4). The absorption amount is decreased with the increase of the molar ratio of Gly to ChCl, which implies that ChCl is a major component of absorption. For example, the solubility of SO_2 in ChCl:Gly DES (1:1) is 0.678 g SO_2/g DES, which is much higher than that of ChCl:Gly DES (1:2, 0.482 g SO_2/g DES), at 293.15 K and 101 kPa. The entire absorption process was completed in 10 min and the absorbed SO_2 could be easily released at a relatively low temperature of 323.15 K within 20 min. ^1H and ^{13}C NMR analyses were conducted to investigate the mechanism of absorption. The investigation concluded that ChCl: Gly DESs interacted with SO_2 physically, as there is no new peak and no significant peak shift after SO_2 capture. However, it still retained the absorptive capacity of 0.153 g SO_2/g DES at 10 kPa, which is much better than that of most physical absorption DESs and attracted extensive attention.

Ab initio molecular dynamics (AIMD) and density functional theory (DFT) have been used to investigate the interaction between SO_2 molecules and ChCl:Gly DESs [37,38]. A strong interaction between Cl^- and SO_2 was observed by different methods. The results showed that an electron is transferred from ChCl: Gly DES to SO_2 during the direct interaction between S and Cl atoms, and accompanied a disruption of the anion-OH network and nonpolar-nonpolar network, which can explain the dramatic drop in viscosity. Charge transfer interaction is believed to play an important role in SO_2 absorption. The interaction energies were calculated by the different models and the value ranged from −28.45 to −60.25 kJ/mol, which is a moderate interaction for SO_2 absorption. It means that the interactions are very sensitive to the solvent structure and easy to regenerate, which is consistent with the low regeneration temperature and high desorption rate in Han's work [36].

Due to the excellent property and high capacity of SO_2, more and more DESs containing halogen anions were designed and synthesized. Wei et al. [39] determined the absorption capacities of SO_2 in four kinds of ChCl-based DESs, including ChCl: ethylene glycol (EG) DES (1:2), ChCl:malonic acid (MA) DES (1:1), ChCl:UE DES (1:2), and ChCl:thiourea DES (1:1) at different temperatures and SO_2 partial pressures. The SO_2 absorption capacities of these DESs at 293K and 101 kPa followed the order of ChCl:thiourea (1:1, 2.96 mol SO_2/mol DES) > ChCl:EG (1:2, 2.88 mol SO_2/mol DES) > ChCl:MA (1:1, 1.88 mol SO_2/mol DES) > ChCl:UE (1:2, 1.41 mol SO_2/mol DES). At atmospheric pressure, the gravimetric capacity of ChCl:EG (1:2, 0.70 g SO_2/g DES) was comparable to that of ChCl:Gly (1:1, 0.678 g SO_2/g DES), but lower than that of ChCl:thiourea (1:1, 0.88 g SO_2/g DES). However, this order would be totally different at 20 kPa, i.e., ChCl:EG (1:2, 0.65 mol SO_2/mol DES) > ChCl:UE (1:2, 0.56 mol SO_2/mol DES) > ChCl:thiourea (1:1, 0.30 mol SO_2/mol DES) > ChCl:MA (1:1, 0.28 mol SO_2/mol DES). The mole absorptive capacity of ChCl:EG DES (1:2) was more than two times higher than that of ChCl:thiourea DES (1:1), which means that hydroxyl functional groups are more conducive to absorbing SO_2 under a low pressure. Deng et al. [40] further improved the absorption capacity of DESs by selecting a more polar organic acid levulinic acid (LA) as HBD compared to polyols, paired with a variety of HBAs. Such as choline acetyl chloride (ChAC), tetraethylammoniumchloride (TEAC), tetrabutylammonium chloride (TBAC), 1-ethyl-3-methylimidazolium chloride (EmimCl). The effect of these HBAs on absorption capacity was ordered as TEAC > ChAC > ChCl > TBAC.

2.3. Imidazolium-Based DESs

It is reported that imidazolium-based ILs exhibited considerable SO_2 absorption capacity. Therefore, Yang et al. [41–43] designed a series of EmimCl-based DESs, including EmimCl:EG DES (1:1), EmimCl:triethylene glycol(TEG) DES (1:1), and EmimCl:succinonitrile (SN) DES (1:1), for efficient SO_2 capture and obtained the corresponding absorption capacity of 1.03, 0.91, and 1.13 g SO_2/g DES, respectively, at 293.15 K and 101 kPa. It showed that the efficiency of imidazolium cation is better than that of ammonium. This can be interpreted as the $\pi \cdots \pi$ interaction between SO_2 and imidazole ring. The effect of HBD in DESs for SO_2 capture was ordered as succinonitrile > EG > TEG. The SO_2 solubility in EmimCl:TEG DESs with different molar ratios (from 6:1 to 1:1) were determined, as shown in Figure 1. The SO_2 uptake in EmimCl:TEG DESs increased by ~24% from 1:1 to 4:1, whereas only 4% increment was observed at a 6:1 ratio. When the molar ratio is larger than 1:4, the absorption capacity remains almost unchanged. It was demonstrated that there is a limit to increase the absorptive capacity by the increase of the molar ratio of effective absorption components. Considering the cost and absorptive capacity, there is an optimal molar ratio. With the optimal molar ratio, the absorption capacities of EmimCl:EG DES (1:2) and EmimCl:TEG DES (1:4) were 1.03 and 1.20 g SO_2/g DES, respectively, at 293.15 K and 101 kPa. It is especially noted that EmimCl:SN DES (1:1) can capture 0.120 g SO_2/g DES at 2000 ppm, while EmimCl:EG DES (1:1) can only absorb 0.047 g SO_2/g DES at the same conditions. Furthermore, all the SO_2 captured by EmimCl:EG DES (1:2) can be desorbed at 313.15 K within 50 min, which is lower than the desorption temperature of EmimCl:SN DES (353.15 K) and EmimCl:TEG (373.15 K).

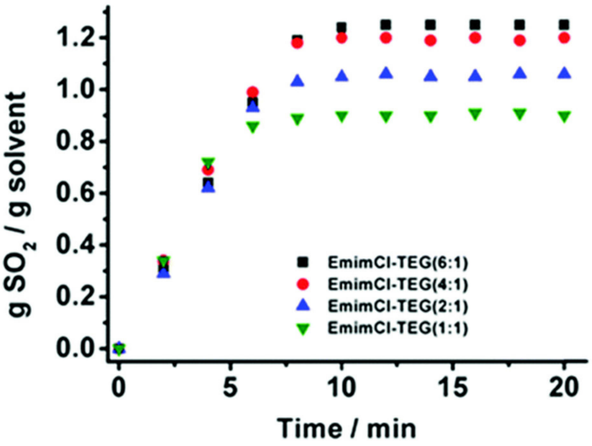


Figure 1. Comparison of SO_2 absorption by EmimCl:TEG DESs with different molar ratios as a function of time at 293.15 K and 101 kPa (Reprinted with permission from Ref[42]. Copyright (2018) The Royal Society of Chemistry).

The effect of HBAs and HBDs in DESs was further investigated by Tantai et al [44]. As shown in Figure 2, the gravimetric SO_2 absorption capacities of ethylenurea (EU) and 1,3-dimethylurea (DMU)-based DESs with various HBAs displayed the same trend: EmimCl > BmimCl > BmimBr > TBAC~P_{4444}Cl. Among them, the DESs with imidazolium salts as HBAs exhibited lower viscosities than those containing TBAC or P_{4444}Cl. After SO_2 absorption, the viscosities of all DESs (188~389 mPa·s) decreased significantly to below 8 mPa·s, which can be attributed to the disruption of the anion-OH network and nonpolar-nonpolar network by the strong interaction between SO_2 and Cl^-. Moreover, it was also noted that when the SO_2 partial pressure decreased to 2 kPa at 298.15 K, the SO_2 absorption capacities of EU:BmimCl DES (1:2) could still be retained at 0.25 g SO_2/g DES. Using the unit of mol SO_2/mol DES, some intrinsic conclusions could be drawn. For instance, the gravimetric absorption capacities of SO_2 in EU-based DESs increased, following the order of EU:BmimCl (1:2) > EU:BmimCl (1:1) > EU:BmimCl (2:1) with the values of 1.18, 1.07, and 0.94 g SO_2/g DESs, respectively, while the molar capacities of SO_2 in EU:BmimCl DES (1:2), EU:BmimCl DES (1:1), and EU:BmimCl DES (2:1) were 8.03, 4.38, and 5.10 mol SO_2/mol DESs, respectively. It could be concluded that both HBDs and HBAs took an active part in SO_2 capture.

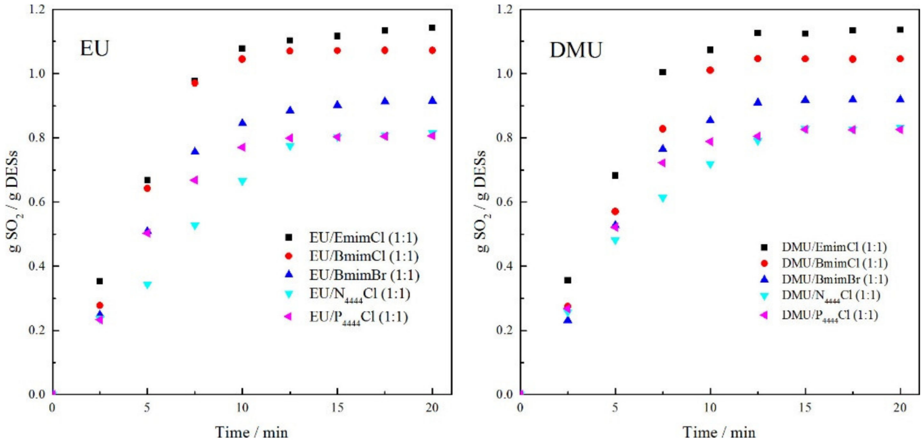


Figure 2. SO_2 absorption by DESs with different HBAs at 293.15 K and 101 kPa (Reprinted with permission from Ref. [44]. Copyright (2019) American Chemical Society).

The effect of the alkyl chain length of imidazole-based DESs on SO_2 absorption capacity was investigated by Hu et al. [45]. The result showed that the absorption capacity of SO_2 in a mass unit decreased with the increase of alkyl chain length, which may be due to the increase of molecular weight. However, this order would be totally different if the unit was changed into mol SO_2/mol DES, i.e., EmimCl: AA > BmimCl:AA > HmimCl:AA with the values of 1.25, 1.17, and 1.02 g SO_2/g DESs, corresponding to 4.01, 4.28, 4.16 mol SO_2/mol DES. EmimCl:AA performed the highest gravimetric absorption capacity and BmimCl:AA performed the highest molar absorption capacity. However, the effect of alkyl chain length on absorptive capacity became a minor factor with the decrease of SO_2 partial pressure. The absorptive capacities of SO_2 in EmimCl:AA DES (1:1), BmimCl:AA DES (1:1), and HmimCl:AA DES (1:1) were 0.46 (1.48), 0.44 (1.61), 0.38 (1.55) g SO_2/g DESs (mol SO_2/mol DES) at 101 kPa. A series of DESs paired EmimCl with different HDBs was investigated [46,47], including EmimCl:DMU, EmimCl:N-methylurea (MU), EmimCl:thioacetamide(TAA), EmimCl:CPL, and EmimCl:N-Formylmorpholine (NFM). The absorption properties of SO_2 in terms of gravimetric absorption are very close in those DESs, distributed from 0.36 to 0.45 g SO_2/g DES at 10 kPa and from 1.09 to 1.26 g SO_2/g DES at 101 kPa, 293.15 K, as shown in Table 1. In general, HBAs of EmimCl-based DESs have a much stronger influence on the solubility of SO_2 than the HBDs, which played a vital role in absorption and leaded to the similar absorption capacity of EmimCl-based DESs.

Table 1. SO_2 solubility in non-functionalized DESs.

DESs	Molar Ratio	*T*/K	Capacity at 101 kPa (g SO_2/g DES)	Capacity at 10 kPa (g SO_2/g DES)	Capacity at ~2000 ppm (g SO_2/g DES)	Ref.
ACC:LA	1:1	293.15	0.567			[40]
AA:KSCN	3:1	293.15	0.588			[31]
AA:NH_4SCN	3:1	293.15	0.579			[31]
BmimBr:DMU	1:1	293.15	0.92			[44]
BmimBr:EU	1:1	293.15	0.91			[44]
BmimCl:AA	1:1	293.15	1.17 (4.28) ^{1}	0.44 (1.61) ^{1}		[45]
BmimCl:DMU	2:1	293.15	1.14	0.42	0.26 ^{3}	[44]
BmimCl:DMU	1:1	293.15	1.14			[44]
BmimCl:EU	2:1	293.15	1.18	0.42	0.25 ^{3}	[44]
BmimCl:EU	1:1	293.15	1.07			[44]
BmimCl:EU	1:2	293.15	0.94			[44]
ChCl:EG	1:2	293.15	0.7(2.88) ^{1}	(0.65) ^{2}		[39]
ChCl:MA	1:1	293.15	(1.88) ^{1}	(0.28) ^{2}		[39]
ChCl:UE	1:2	293.15	(1.41) ^{1}	(0.56) ^{2}		[39]
ChCl:Gly	1:1	293.15	0.678	0.153		[36]
ChCl:Gly	1:2	293.15	0.482	0.077		[36]
ChCl:Gly	1:3	293.15	0.38	0.053		[36]
ChCl:Gly	1:4	293.15	0.32	0.046		[36]
ChCl: LA	1:1	293.15	0.557			[40]
ChCl:thiourea	1:1	293.15	0.88 (2.96) ^{1}	(0.3) ^{2}		[39]
CPL:AA	1:1	303.15	0.497			[29]
CPL:KSCN	3:1	293.15	0.607			[31]
CPL:NH_4SCN	3:1	293.15	0.595			[31]
CPL:TBAB	1:1	298.2	0.099			[29]
EmimCl:AA	2:1	293.15	1.39 (7.63) ^{1}	0.49 (2.70) ^{1}		[45]
EmimCl:AA	1:1	293.15	1.25 (4.01) ^{1}	0.46 (1.48) ^{1}		[45]
EmimCl:AA	1:2	293.15	1.13 (4.69) ^{1}	0.27 (1.12) ^{1}		[45]
EmimCl:CLAA	2:1	293.15	1.26 (8.00) ^{1}	0.45 (2.86) ^{1}		[47]
EmimCl:DMU	1:1	293.15	1.04			[44]

Table 1. *Cont.*

DESs	Molar Ratio	*T*/K	Capacity at 101 kPa (g SO_2/g DES)	Capacity at 10 kPa (g SO_2/g DES)	Capacity at ~2000 ppm (g SO_2/g DES)	Ref.
EmimCl:DMU	2:1	293.15	1.22 (7.26) [1]	0.43 (2.50) [1]		[47]
EmimCl:EG	2:1	293.15	1.15	0.42		[41]
EmimCl:EG	1:1	293.15	1.03	0.31		[41]
EmimCl:EG	1:2	293.15	0.82	0.22		[41]
EmimCl:EPyBr	3:1	293.15	1.395	0.698	0.17	[46]
EmimCl:EPyBr	2:1	293.15	1.336	0.662	0.162	[46]
EmimCl:EPyBr	1:1	293.15	1.286	0.627	0.155	[46]
EmimCl:EU	1:1	293.15	1.14			[44]
EmimCl:MU	2:1	293.15	1.09 (6.25) [1]	0.36 (2.06) [1]		[47]
EmimCl:SAA	2:1	293.15	1.18 (6.79) [1]	0.37 (2.13) [1]		[47]
EmimCl:SN	1:1	293.15	1.13		0.12	[43]
EmimCl:SN	1:2	293.15	0.96		0.085	[43]
EmimCl:SN	1:4	293.15	0.79		0.047	[43]
EmimCl:TEG	6:1	293.15	1.25	0.54		[42]
EmimCl:TEG	4:1	293.15	1.2	0.5		[42]
EmimCl:TEG	2:1	293.15	1.06	0.38		[42]
EmimCl:TEG	1:1	293.15	0.91	0.31		[42]
EmimCl:NFM	1:1	293.15		0.429		[46]
HmimCl:AA	1:1	293.15	1.02 (4.16) [1]	0.38 (1.55) [1]		[45]
TBAC:DMU	1:1	293.15	0.83			[44]
TBAC:EU	1:1	293.15	0.81			[44]
P_{4444}Cl:DMU	1:1	293.15	0.83			[44]
P_{4444}Cl:EU	1:1	293.15	0.81			[44]
TBAB:LA	1:1	293.15	0.547			[40]
TBAC: LA	1:1	293.15	0.541			[40]
TEAB: LA	1:1	293.15	0.622			[40]
TEAC: LA	1:1	293.15	0.625			[40]
Urea:NH_4SCN	3:1	303.15	0.372			[31]

[1] Data in brackets are the molar fraction. [2] At 20 kPa. [3] At 2 kPa.

Kang et al. [48] developed a new type of DES formed by EmimCl and N-ethylpyridinium bromide (EPyBr), in which halogen anions were introduced into both HBA and HBD. Although the viscosity of EmimCl:EPyBr was 2260 mPa·s before absorption, the viscosity dropped rapidly from 2260 to 6 mPa·s with the dissolution of SO_2, owing to the strong charge transfer interactions between SO_2 and the anions Cl^- and Br^-. The SO_2 absorption capacity of EmimCl:EPyBr with a molar ratio of 3:1 was 0.698 g SO_2/g DES at 293.15 K and 10 kPa, which was higher than the results of most DESs and ILs reported previously. Moreover, it could still absorb 0.170 g SO_2/g DES at 293.15 K and an SO_2 concentration of 2000 ppm and the regeneration of EmimCl:EPyBr could be achieved at 363.15 K within 45 min by blowing N_2.

3. Functionalized DESs for SO_2 Capture

There are two methods to obtain functionalized DESs for SO_2 capture. Due to the strong acidity of SO_2, it is expected to reach a high capacity by selecting organic compounds with alkaline functional groups as HBA or HBD, such as alcohol amines, polyamines, and azoles. Using conjugate bases of weak acids as HBAs, such as carboxylated and phenolated ones, is another way to enhance SO_2 solubility. Basicity is significant during the structure property designing of DESs for enhancing SO_2 solubility. It is reported that SO_2 capture by DESs could be tuned by the basicity of components. Recently, by mixing the halogen salt HBAs which can efficiently absorb SO_2 through physical interaction mentioned above and functionalized HBDs can achieve higher absorption capacity and desorption rate than DESs, which relies mainly on physical or chemical absorption. The reported functionalized DESs for SO_2 capture and their SO_2 capacities at different conditions are included in Table 2.

3.1. Azole-Based Functionalized DESs

Azoles, such as imidazole (Im), triazole (Tri), tetrazole (Tetz), are definitely able to interact with SO_2 based on Lewis acid-base reaction in a form of N··S bonding. Due to the excellent property and high capacity of SO_2 capture, numerous azole-based functionalized DESs were designed and synthesized. In 2013, Liu et al. [29] reported CPL:Im DES (1:1). The solubility of SO_2 in CPL:Im DES (1:1) is 0.624 g SO_2/g DES at 303.15 K and 101 kPa. During the absorption process, the transplant and colorless CPL:Im DES (1:1) turned to a yellowish paste, which can be interpreted by the chemical reaction between imidazole and SO_2. Deng et al. [49] synthesized the azole-based DES with acetyl choline chloride (ACC) as HBA. The results showed that the structure of azole has evident influence on the SO_2 absorption capacity. As shown in Table 2, ACC:Im DES possessed higher absorption capacity of SO_2 than ACC:Tri DES, which is related to the higher basicity of the imidazole than that of 1,2,4-triazole. ACC:Im DES with molar ratio of 1:3 exhibited the highest absorption capacity of 0.383 g SO_2/g DES at 0.1 bar and 303.15 K. The higher absorption capacity of ACC:Im than that of Im:Gly [50] could be attributed to the stronger physical absorption of chloride anion. However, the two DES performed differently in desorption experiments. For the DES of ACC:Tri (1:1), the absorbed SO_2 could be completely stripped out by bubbling N_2 at 363.15 K, while there was approximately 0.025 g SO_2/g DES still remained after regeneration for ACC:Im DES (1:2).

The effect of substituents on imidazole ring was studied by Wu et al. [50]. They designed Im:Gly, 2-methylimidazole (2-Me):Gly, 2-ethylimidazole (2-Et):Gly and 2-propylimidazole (2-Pr):Gly for efficient SO_2 capture at 313.15 K, 2 kPa and obtained the corresponding absorption capacity of 0.253, 0.246, 0.241, 0.225 g SO_2/g DES. The result demonstrated that the alkyl connected to the N(3) atom has almost no effect on the molar absorption capacities which reach 1:1 stoichiometry. However, with the increase of the molecular weight of HBAs, the mass absorption decreased. The SO_2 absorption mechanism was proposed after the saturated system was characterized by ^{1}H NMR and FTIR, the acidic SO_2 reacted with the basic N atom in Im through strong acid–base reaction, which leaded to an increase in viscosity from 149 mPa·s to 470 mPa·s for Im:Gly DES (1:2) at 313.15 K and incomplete desorption. Considering that flue gas contains a large amount of water (e.g., 8 vol %), which does not just act as a hydrogen bond donor such as Gly, but also can increase the absorption capacity per mass unit and significantly reduce the viscosity due to its low molecular weight, Wu et al. [51] mixed 2-Me:Gly, 2-Et:Gly and 2-Pr with H_2O to synthesize three kinds of cheap and low viscosity functional DESs. The absorption results showed that the mole absorption capacities of three DESs were all about 1 mol SO_2/mol HBA at 313 K and 2 kPa. Im:H_2O DES (1:4) showed a mass absorption capacity of 0.331 g SO_2/g DES, which is higher than that of most DESs reported in the literature.

Inspired by previous reports, BmimCl-based DESs and azole-based DESs could efficiently absorb SO_2 through physisorption and chemisorption. A series of imidazole derivatives were selected as HBDs, including imidazole, 4-methylimidazole ($4CH_3$-Im), pyrazole (Pyr), tetrazole, and benzimidazole (Ben-Im), paired with four different types of salts containing halogen anions to synthesize DESs by Tantai et al. [52]. SO_2 absorption capacities of TBAC with different HBDs at 293.2 K and 101.3 kPa were ordered as TBAC:$4CH_3$-Im (1:2) > TBAC:Im (1:2) > TBAC:Ben-Im (1:2) > TBAC:Pyr (1:2) > TBAC:Tetz (1:2), corresponding with the basicity of HBDs. For $4CH_3$-Im-based DESs, the effect of HBAs on absorption capacity was ordered as BmimCl:$4CH_3$-Im (1:2) > P_{4444}Cl:$4CH_3$-Im (1:2)~ TBAC:$4CH_3$-Im (1:2) > TBAC:Im (1:2) > TBAB:Im (1:2). The investigation concluded that SO_2 capacity could be tuned by different substituents on the imidazole ring (high basicity > low basicity), the types of cations (e.g., imidazolium > TBA ≈ TBP) and anions (e.g., Cl^- > Br^-). BmimCl:$4CH_3$-Im DES (1:2) exhibited a better absorption performance compared to P_{4444}Cl:$4CH_3$-Im DES (1:2), which indicated that imidazole ring also participated in SO_2 absorption. As shown in Figure 3, the effect of SO_2 partial pressure on the absorption capacity was dramatical, the SO_2 absorption capacity of BmimCl:$4CH_3$-Im DES (1:2) increased sharply from 2 to 10 kPa with the value increased from 0.244 to 0.613 g SO_2/g

DES and then increased linearly with the pressure from 10 to 101.3 kPa (1.42 g SO_2/g DES), which implied that the chemical absorption is efficient for the SO_2 capture at low partial pressures (2~10 kPa) and then the physical absorption played a dominant role as the pressure increases (10~101.3 kPa). An interesting phenomenon accompanied by the absorption process is that the colorless solvent gradually turned to brown in CPL:Im DES (1:1), which was also observed by Liu et al. [29]. Based on previous research, Tantai et al. put forward a novel strategy to prepare ternary functionalized DESs capable of chemically binding ultralow concentration (2000 ppm) SO_2 in the flue gas, by mixing low-cost azole derivatives with ternary EU:BmimCl DESs [53]. By comparing the absorption capacity of ternary EU:4-CH_3-Im:BmimCl DESs (1:1:1, 2:1:1, 1:2:1, and 1:1:2) with binary DESs, including EU:BmimCl DES (1:1), CH_3-Im:BmimCl DES (1:1) and 4-CH_3-Im:BmimCl DES (2:1), as shown in Table 2. Several conclusions can be drawn: (1) The introduction of 4-CH_3-Im or Im as secondary HBDs could effectively increase the absorption capacity, which was little affected by introducing pyrazole, triazole and tetrazole. (2) EU also participated in the absorption process as an active component, as the molar absorption capacity of EU:4-CH_3-Im:BmimCl DES (1:1:1) were higher than that of CH_3-Im:BmimCl DES (1:1). (3) EU could remarkably regulate the interaction between SO_2 and ternary DESs. 4-CH_3-Im:BmimCl DES (1:1) turned into a gel during the SO_2 absorption, while EU:4-CH_3-Im:BmimCl DES (1:1:1) could still be liquid after absorption. The gravimetric absorption capacities of ternary EU:4-CH_3-Im:BmimCl DESs (1:1:1, 1:2:1, and 1:1:2) reached 0.294, 0.347, and 0.255 g SO_2/g DES, respectively, at 298 K and 2000 ppm of SO_2, corresponding to 1.58, 2.29, and 2.07 mol SO_2/mol DES.

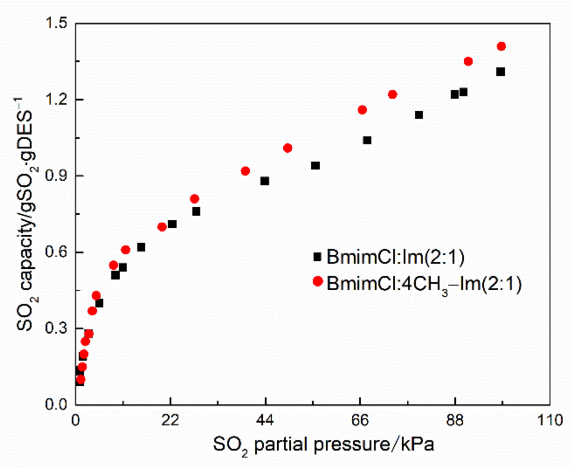


Figure 3. Effect of SO_2 partial pressure on the SO_2 capture at 293.2 K (Reprinted with permission from Ref. [52]. Copyright (2018) American Chemical Society).

3.2. Other Kinds of Functionalized DESs

Cui et al. [54] designed a series of functionalized DESs based on piperazinium cation, which were prepared by mixing 1-hydroxyethyl-1,4-dimethyl-piperazinium bromide (PPZBr) with Gly at different molar ratios. The absorption capacities of PPZBr:Gly with different molar ratios were ranged from 0.08 to 0.1 g SO_2/g DES at 293.15 K and 1 kPa, corresponding to 0.96~0.99 mol SO_2/mol DES, which indicated that the molar ratio did not significantly affect the adsorption capacity under low SO_2 partial pressures. The change of viscosity along with the absorption of SO_2 under atmospheric conditions was investigated, as shown in Figure 4. It can be seen that the viscosity of each PPZBr:Gly DES dramatically increased in first 5 min and then decreased sharply with a further increase of SO_2 dissolution. This phenomenon is similar to the finding of Wu et al. [55] and Zhang et al. [56] on SO_2 absorption by ILs. The results of viscosity experiments proved that PPZBr:Gly efficiently absorbed SO_2 through a combination of chemical and physical interactions.

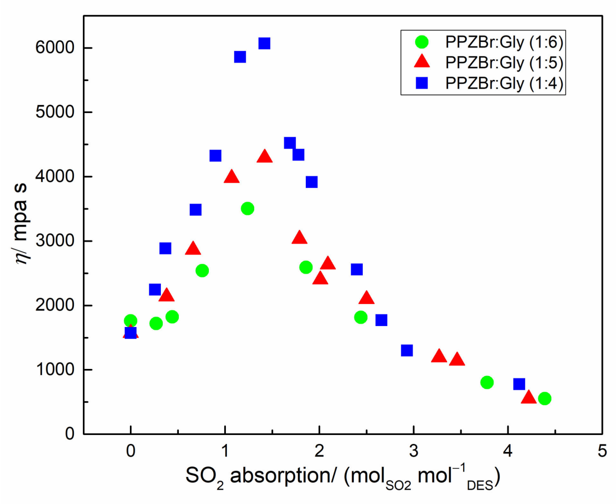


Figure 4. Viscosity of DESs as a function of the absorption amount of SO_2. (Reprinted with permission from Ref. [54]. Copyright (2019) American Chemical Society).

Wu et al. [57] reported a new type of internal salt type DES based on betaine (Bet) or L-carnitine (L-car), with the ability to chemically absorb SO_2 by strong acid–base reactions between the acidic SO_2 and Lewis–based COO^-. The absorption capacity of L-car:EG with a molar ratio of 1:3 was 0.151 g SO_2/g DES at 2 kPa, 313.15 K. However, due to the strong acid–base reactions between the acidic SO_2 and Lewis–based COO^-, the absorbed SO_2 cannot be completely released.

Table 2. SO_2 solubility in functionalized DESs.

DESs	Molar Ratio	*T*/K	Capacity at 101 kPa g SO_2/g DES	Capacity at 10 kPa g SO_2/g DES	Capacity at 2 kPa g SO_2/g DES	Capacity at ~2000 ppm g SO_2/g DES	Ref.
ACC:Im	1:2	303.15	0.989	0.381			[49]
ACC:Im	1:3	303.15		0.383			[49]
ACC:Tri	1:1	303.15		0.227			[49]
Bet:EG	1:3	313.15	0.366 (1.735) [1]		0.0701 (0.332) [1]		[57]
BmimCl:4-CH_3-Im	1:2	293.2	1.42	0.613		0.244	[52]
BmimCl:4-CH_3-Im	1:1	293.2	1.31				[52]
BmimCl:4-CH_3-Im	1:1	293.15			0.354 (1.42) [1]		[53]
BmimCl:4-CH_3-Im	2:1	293.15			0.258 (1.37) [1]		[53]
BmimCl:Im	2:1	293.2	1.32	0.564		0.225	[52]
BmimCl:Im	1:1	293.2	1.29				[52]
BmimCl:Im	1:2	293.2	1.24				[52]
CPL:Im	1:1	303.15	0.624				[29]
2-Et:Gly	1:2	313.15			0.241		[50]
EU:4-CH_3-Im:BmimCl	1:1:1	293.15			0.294 (1.58) [1]		[53]
EU:4-CH_3-Im:BmimCl	2:1:1	293.15			0.232 (1.54) [1]		[53]
EU:4-CH_3-Im:BmimCl	1:2:1	293.15			0.347 (2.29) [1]		[53]
EU:4-CH_3-Im:BmimCl	1:1:2	293.15			0.255 (2.07) [1]		[53]
Im:Gly	1:2	313.15			0.253	0.211	[50]
Im:H_2O	1:4	313.15	0.369 (1.208) [1]		0.331 (1.083) [1]	0.267 (0.873) [1]	[51]

Table 2. *Cont.*

DESs	Molar Ratio	*T*/K	Capacity at 101 kPa g SO_2/g DES	Capacity at 10 kPa g SO_2/g DES	Capacity at 2 kPa g SO_2/g DES	Capacity at ~2000 ppm g SO_2/g DES	Ref.
L-car:EG	1:3	313.15	0.365 (1.979) [1]		0.151 (0.819) [1]		[57]
2-Me:Gly	1:2	313.15			0.246		[50]
TBAC:4-CH_3-Im	1:2	293.2	1.04				[52]
TBAC:Im	1:2	293.2	0.96				[52]
2-Pr:Gly	1:2	313.15			0.225		[50]
PPZBr:Gly	1:4	298.15	0.42 (3.97) [1]	0.15 (1.47) [1]	0.10 (0.98) [2]		[54]
PPZBr:Gly	1:6	298.15	0.35 (4.28) [1]	0.13 (1.55) [1]	0.08 (0.99) [2]		[54]
PPZBr:Gly	1:5	298.15	0.38 (4.10) [1]	0.13 (1.43) [1]	0.09 (0.96) [2]		[54]

[1] Data in brackets are the molar fraction. [2] At 1 kPa.

4. Non-Functionalized DESs for CO_2 Capture

In 2006, Zhu et al. [24] reported that ChCl:urea DES supported on molecular sieves could effectively catalyze the reactions of CO2 and epoxides. After that a significant number of studies were conducted on the capacity of the choline chloride-based DES for CO_2 capture [58–60]. Lu et al. [61] reviewed the choline-based DESs for CO_2 separation recently. Thus, CO_2 capture by choline chloride-based DESs is not included in this review. Since CO_2 is a linear non-polar molecule, it is difficult for CO_2 to dissolve in DESs at atmospheric pressure. According to the reported results, high capacity of CO_2 physical absorption in non-functionalized DESs is favored with lower temperatures and higher pressures. Later, different combinations of HBDs and HBAs components were tried to optimize the CO_2 uptake capacity in DESs but the capacities of all the tested DESs remained in the range of 0.009–0.85 mol CO_2/kg DES.

Ali et al. [62] studied 17 different types of DESs based on different ammonium and phosphonium salts with five different HBDs, namely EG, Gly, diethanolamine (DEA), triethanolamine (TEA), and monoethanolamine (MEA), for CO_2 capture. The solubility values for CO_2 in DESs at 298.15 K and pressures up to 1.0 MPa remained in the range of 0.013–0.0749 g CO_2/g DES and 0.0211–0.1441 mol CO_2/mol DES, as shown in Table 3. The experimental results demonstrated that the DESs have intricate physical behaviors compared to pure HBA or HBD. Thus, the absorption capacity cannot be simply predicted by considering the contribution effect of its components. For instance, ChCl:EG DESs had lower CO_2 solubility compared to pure EG, while the CO_2 solubility in glycerol-based DESs was found to be higher than that in pure glycerol. For ChCl:MEA DES (1:6), the solubility was 0.1096 mol CO_2/mol DES, which was nearly two times higher than that in a 30 wt% MEA aqueous solution at 298.15 K and 1 MPa. However, the gravimetric absorption of DES was 0.0749 g CO_2/g DES, which was much lower than 0.62 g CO_2/g DES in the 30 wt% MEA aqueous solution. Moreover, high-performance liquid chromatography (HPLC) analysis results showed that only 10% of amine reacted with CO_2 while for the aqueous solution of MEA, all of amine reacted with CO_2. This means that the strong intermolecular hydrogen bonding was formed between Cl anions and MEA, which may hinder MEA from reacting with CO_2.

Sarmad et al. [63] synthesized 35 DESs, in order to understand how HBD, HBA and other factors affect the properties of DESs at 298.15 K and pressures of up to 2 MPa, as shown in Table 3. For all DESs, the solubility increased with the increase of pressure, as is typically expected for the physical solubility of gases in liquids, i.e., the CO_2 solubility is proportional to its partial pressure. The effect of different types of HBD with hydroxyl group or carboxylic group on the CO_2 solubility was ordered as: [TEMA]Cl:EG > [TEMA]Cl:Ac > [TEMA]Cl:LV > [TEMA]Cl:LA > [TEMA]Cl:GLY at the molar ratio of 1:2. The different types of HBA also had effect on the CO_2 solubility. The CO_2 solubilities in TPAC:MEA, TBAB:MEA and ChCl:MEA DESs under 298.15 K and 2 MPa of CO_2 were 3.525, 3.009 and 3.584 mol CO_2/kg DESs, respectively, and they followed the trend: TBAB:MEA >

TPAC:MEA > ChCl:MEA. Additionally, increasing the alkyl chain length of HBA or HBD could lead to an increase of CO_2 solubility. For example, the solubilities of CO_2 in TEAC:AC DES (1:2) and TBAC:AC DES (1:2) were 1.177 and 1.411 mol CO_2/kg DESs, which increased as the alkyl chain length increased from ethyl to butyl. By increasing the alkyl chain length from acetic acid (AC) to octanoic acid (OCT) in TEAC:AC DES and TEAC:OCT DES, the solubility of CO_2 increased from 1.230 to 1.390 mol CO_2/kg DESs. It is plausible that the length of the alkyl chain had a significant effect on the free volume within the DESs.

Zubeir et al. [64] investigated the CO_2 solubility and Henry's constants in six hydrophobic DESs, which were prepared by combining decanoic acid (DecA) with five quaternary ammonium salts. The results show that the effect of the halide anions chloride and bromide of the quaternary ammonium salts on the CO_2 solubility is negligible. The effect of alkyl chain length is consistent with the research by Sarmad [60]. Among the DESs, TBAC:DecA DES (1:2) shows the highest CO_2 solubility of 1.52 mol CO_2/kg DESs at 298.15 K and 1990 kPa.

Table 3. CO_2 solubility and Henry's constant in physical-based DESs.

DESs	Molar Ratio	*T*/K	*P*/kPa	CO_2 Solubility(mol/kg)	Henry's Constant(MPa)	Ref.
BHDE:AC	1:2	298.15	210–2026	0.064–0.84		[63]
BHDE:LA	1:2	298.15	283–2086	0.016–0.50		[63]
BTEA:AC	1:2	298.15	325–2054	0.13–0.97		[63]
BTMA:AC	1:2	298.15	219–2037	0.078–1.45		[63]
BTMA:GLY	1:2	298.15	394–2026	0.037–0.26		[63]
[BTPP]Br:EG	1:12	298.15	1000	0.6		[62]
[BTPP]Cl:GLY	1:12	298.15	1000	0.47		[62]
ChCl:MEA	1:7	298.15	182–2035	0.78–3.58		[63]
Gua:MEA	1:2	298.15	226–2025	0.31–1.66		[63]
MTPP:1,2-Pro	1:4	298.15	220–2026	0.022–0.55		[63]
MTPP:AC	1:4	298.15	173–2014	0.073–3.02		[63]
MTPP:EG	1:3	298.15	192–2018	0.045–0.35		[63]
MTPP:GLY	1:4	298.15	161–2026	0.009–0.29		[63]
MTPP:LV	1:3	298.15	301–2068	0.024–0.69		[63]
MTPP:MEA	1:6	298.15	1000	1.63		[62]
MTPP:MEA	1:7	298.15	1000	1.46		[62]
MTPP:MEA	1:8	298.15	1000	1.44		[62]
TBAC:DecA	1:2	298.15–323.15	90–1990	0.042–1.52	7.55–10.71	[64]
$[N_{8881}]$Br:DecA	1:2	298.15–323.15	90–1990	0.041–1.31	7.15–9.43	[64]
$[N_{8881}]$Cl:DecA	1:2	298.15–308.15	90–1990	0.045–1.35	7.18–8.27	[64]
$[N_{8888}]$Br:DecA	1:2	298.15–323.15	90–1990	0.039–1.33	6.26–8.49	[64]
$[N_{8888}]$Cl:DecA	1:1.5	298.15–323.15	90–1990	0.041–1.41	5.90–7.70	[64]
$[N_{8888}]$Cl:DecA	1:2	298.15–323.15	90–1990	0.042–1.41	6.17–8.42	[64]
TBAB:AC	1:2	298.15	388–2011	0.14–1.13		[63]
TBAB:DEA	1:6	298.15	1000	0.85		[62]
TBAB:MEA	1:6	298.15	1000	1.34		[62]
TBAB:MEA	1:6	298.15	351–2021	0.44–2.78		[63]
TBAB:MEA	1:7	298.15	381–2040	0.53–3.01		[63]
TBAB:TEA	1:3	298.15	1000	0.47		[62]
TBAC:AC	1:2	298.15	348–2002	0.18–1.41		[63]
TEAC:AC	1:2	298.15	281–2018	0.14–1.18		[63]
TEAC:AC	1:3	298.15	397–2016	0.13–1.23		[63]
TEAC:OCT	1:3	298.15	353–2018	0.16–1.39		[63]
TEMA:AC	1:2	298.15	198–1837	0.081–1.18		[63]
TEMA:EG	1:2	298.15	138–1345	0.062–0.63		[63]
TEMA:GLY	1:2	298.15	150–1648	0.017–0.43		[63]
TEMA:LA	1:2	298.15	143–1863	0.047–0.53		[63]
TEMA:LV	1:2	298.15	136–1617	0.057–0.61		[63]
TMAC:AC	1:4	298.15	294–2096	0.12–1.56		[63]
TPAC:AC	1:6	298.15	350–2030	0.25–1.72		[63]
TPAC:MEA	1:4	298.15	481–2009	0.34–1.43		[63]
TPAC:MEA	1:7	298.15	357–2019	1.71–3.53		[63]

5. Functionalized DESs for CO_2 Capture

5.1. Amino-Based Functionalized DESs

Amines are commonly used for the chemical absorption of CO_2. Generally, two equivalents of amine can react with one equivalent of CO_2 to form one equivalent of carbamate under anhydrous conditions, whereas an increase in viscosity is usually accompanied by the absorption process. MEA aqueous solution is widely used in industry for CO_2 absorption. However, the solvent degradation and evaporation, corrosive to equipment limited the application of MEA. Zhang et al. [65] synthesized several BmimCl-based DESs with MEA as HBD. The CO_2 uptake of BmimCl:MEA increased from 8.4% to 21.4% with the increase of the molar ratio of MEA from 1:1 to 1:4 at 298.15 K and 101 kPa, which was much higher than ChCl:MEA DES (1:6) (7.49%) at 298.15 K and 1 MPa. The different performance of ChCl:MEA and BmimCl:MEA can be attributed to the ability of cations to form hydrogen bonding with Cl^-. According to the results of ^1H NMR, the C2 hydrogen in the DESs shifted to downfield as the composition changed with the addition of MEA, which implied that both of them formed hydrogen bonds with HBA as hydrogen bond donors. The acidic C2 hydrogen of imidazolium can formed a strong localized and highly directional hydrogen bond, which weakens the hydrogen bond between MEA and Cl^-, resulting in an increase in absorption capacity.

Choi et al. [66] synthesized four dual amino-functionalized DESs by reacting various amino compounds, such as MEA, TEA, UE, TAA, ethylendiamine (EDA) with HCl, and then mixed with EDA. The CO_2 uptake capacity was ordered as: MEAC:EDA > TEAC:EDA > UEC:EDA > TAAC:EDA. The gravimetric uptake of MEAC:EDA DES with a molar ratio of 1:3 is 31.5 wt% correspond to 0.502 mol CO_2/mol DES for 3h, while the viscosity increased sharply from 21.6 mPa·s to 3995 mPa·s after 2.5 min of CO_2 absorption. Excessive viscosity hindered the mass transfer process of CO_2 in DES and is not conducive to the progress of absorption. To facilitate atmospheric regeneration and avoid high viscosity, MEAC:EDA DES (1:3) was diluted to be 30 wt% in EG. The CO_2 desorption was achieved by heating the solution at 373.15K for 2.5 h. After that Shukla et al. [67] studied different types of polyamines and alcohol amines DESs formed between HBAs such as MEAC, HmimCl and TBAB and HBDs such as EDA, diethylenetriamine (DETA), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), 3-amino-1-propanol (AP) and aminomethoxypropanol (AMP). The results showed that the increase of the number of secondary amines in the molecule can hardly help to increase the mole absorption capacity of DES, but it will significantly reduce the mass absorption of DES, as shown in Table 4. For example, the CO_2 uptakes by four MEA-based DESs could be ordered as MEAC:EDA (39.0 wt%) > MEAC:DETA (25.5 wt%) > MEAC:TEPA (16.6 wt%) > MEAC:PEHA (12.7 wt%), corresponding to 0.57, 0.57, 0.63, 0.59 mol CO_2/mol DES, respectively,. The effect of HBAs at a 1:4 molar ratio are following the order MEAC:AP > HmimCl:AP > TBAB:AP > TBAB:AMP. The CO_2 absorption capacities of TBAB:AP DES (1:4) and TBAB:AMP DES (1:4) were 0.51 and 0.38 mol CO_2/mol DES, respectively, which implies that steric hindrance cannot improve the absorption capacity of MEA-based DESs.

Wu et al. [68] Designed a new class of functionalized DESs based on ammonium salts obtained from triethylenetetramine (TETA) and HCl at different molar ratios as HBA and EG and diethylene glycol (DG) as HBD. The results demonstrated that three aminos in [TETA]Cl can be activated by EG or DG. For example, the CO_2 absorption capacities in [TETA]Cl and EG are 0.625 mol CO_2/mol [TETA]Cl and 0.0132 mol CO_2/mol EG at 313.15 K, 101 kPa, while the mole absorption capacity of [TETA]Cl:EG DES (1:3) was 1.465 mol CO_2/mol [TETA]Cl, corresponding to 0.175 g CO_2/g DES at the same condition. The effect of chloride ion was also studied and the result showed that CO_2 absorption capacity decreased with the increase of the number of chloride ion. For instance, CO_2 absorption capacity is 1.456 mol CO_2/mol [TETA]Cl for [TETA]Cl:EG DES, 0.986 mol CO_2/mol [TETA]Cl_2 for [TETA]Cl_2:EG DES, and 0.6 mol CO_2/mol [TETA]Cl_3 for [TETA]Cl_3:EG DES. As we know, there is always an amount of water in flue gas which can be absorbed by DESs during the absorption process. Although water content has a slight effect on absorptive capacity, it may increase the energy cost during the desorption process. Wu et al. [69] synthesized a new kind of hydrophobic functionalized DES formed by polyamine hydrochloride and thymol, which is hydrophobic before and after CO_2 absorption. The absorption capacity of [TETA]Cl:thymol DES (1:3) was 0.09 g CO_2/g DES at 313.15 K and ambient pressure, corresponding to 1.298 mol CO_2/mol DES, which indicated that thymol could not enhance the capacity of CO_2 in DESs.

Li et al. [70] synthesized a series of DESs based on ethanolamine and quaternary ammonium salt. From the results, the gravimetric absorption capacities vary with the length of the alkyl chain of the quaternary ammonium salt as follows: ChCl ≈ TMAC >TEAC > TEAB > TBAC > TBAB. The effect of alcohol amine HBD with different numbers of substituents on absorption was ordered as: MEA > DEA > MDEA > TEA. ChCl:MEA DES (1:5) exhibited the best performance with the capacities of 0.2523 g CO_2/g DESs. Considering the cost and absorptive capacity, there is an optimal molar ratio of 1:5. The desorption experiment requires higher temperatures (373.15–413.15 K) and longer time (5~6 h) due to high viscosity and strong interaction between DES and CO_2.

5.2. Azole-Based Functionalized DESs

Azole-based functionalized DESs are another kind of functionalized DESs used for the capture of CO_2. Yang et al. [71] reported a new class of DESs made up of solid azole-based ILs and EG. It was found that [P_{2222}][Triz]:EG DES, [P_{2222}][Im]:EG DES, [N_{2222}][Triz]:EG DES and [N_{2222}][Im]:EG DES had almost the same amounts of absorption. The CO_2 absorption capacities of four different DESs with a molar ratio of 1:2 were 0.118, 0.118, 0.125, 0.129 g CO_2/g DES at 298.15 K and 101 kPa, corresponding to 0.91, 0.91, 0.92 and 0.94 mol CO_2/mol DES, which implied the absorption mechanism of azolide anions in DES is different from ILs [72,73]. The results of NMR and FTIR indicated that CO_2 did not directly interact with the azolide anions to form a carbamate species but reacted with EG that was deprotonated by [Triz] anion to form carbonate. CO_2 absorbed by the solvent can be completely released at 343.15 K under N_2 flow. Gurkan et al. [74] reported a new reactive DES formed by 1-ethyl-3-methylimidazolium 2-cyanopyrrolide ([Emim][2-CNpyr]) and EG. [Emim][2-CNpyr]:EG DES (1:2) formed is thermally stable and has low viscosity DES, which shows absorption capacities of 10.3 and 11.4 wt% at 0.005 bar and 1 bar of CO_2, respectively, at 298.15 K. The absorbed CO_2 at 298.15 K can easily be released under N_2 at 313.15 K. Multiple species were found in the product of CO_2 absorption. On the basis of NMR and FTIR analysis, they proposed four possible routes, as shown in Figure 5. Route 1 is the complexation of CO_2 with the pyrrolide anion that forms carbamate (N−COO). Route 2 is the deprotonation of the imidazolium cation by the anion that forms a carbene zwitterion, which then binds with CO_2 to form carboxylate (−C−COO). Route 3 is the protonation of the anion by EG, resulting in deprotonated EG that subsequently reacts with CO_2 to form carbonate(−O−COO). In the presence of water, bicarbonate (HO-COO) also forms via Route 4.

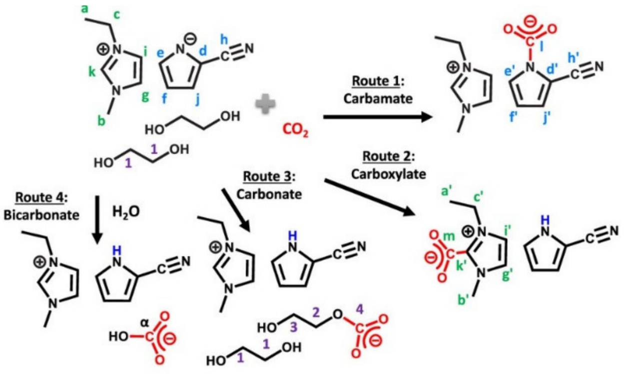


Figure 5. Proposed reaction network with NMR labeling of the reactants and CO_2 bound products. (Reprinted with permission from Ref. [74]. Copyright (2021) American Chemical Society).

5.3. Super Base Functionalized DESs

Another covalent strategy for reversible CO_2 capture is to combine organic compounds containing alcohol functionalized groups with superbases. Superbases (SBs), neutral organic bases with proton affinities so high that their protonated conjugate acids (BH^+) cannot be deprotonated by the hydroxide ion, play a key role as proton acceptors in the preparation of supported protic ionic liquids (PILs) with exceptional thermal stability [75,76]. Due to the many similarities between DESs and ILs, Baker et al. [77] for the first time added super base into ChCl:Gly DES to form ternary DESs. The structures of DES components and various superbases are shown in Figure 6A. The result demonstrated the addition of super base enabled ChCl:Gly DES to chemically absorb CO_2 by deprotonating the hydroxyl group in choline chloride or glycerol to form the negative oxygen which acted as chemical absorption site to react with CO_2 and generate carbonate under ambient conditions (Figure 6B). The effect of three different types of SBs on CO_2 absorption capacity was investigated under ambient conditions, and obtained the corresponding absorption capacity of 0.103, 0.100, 0.035 g CO_2/g DES for ChCl:Gly:1,5-diazabicyclo[4.3.0]-non-5-ene (DBN) DES (1:2:6), ChCl:Gly:7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) DES (1:2:6), ChCl:Gly:1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) DES (1:2:6), respectively. DBN leaded to optimal CO_2 capture, due to its higher basicity and less steric hindrance. As a result of chemical absorption, the viscosity of all ternary DES systems increased with the increase of absorbed amount. After absorption, ChCl:Gly:DBN DES (1:2:6) showed a viscosity ranged from 5450 to 34,613 mPa·s that is 1 to 2 orders of magnitude higher than traditional ILs and separated into two phases. Such a viscosity increase negatively affects mass transfer and capture kinetics, hindering further CO_2 capture. However, the absorbed CO_2 could be released completely within 35 min at 333.15 K, while a noticeable capacity decreased can be observed after three cycles during the cycling experiments due to slight evaporative losses of the superbase component.

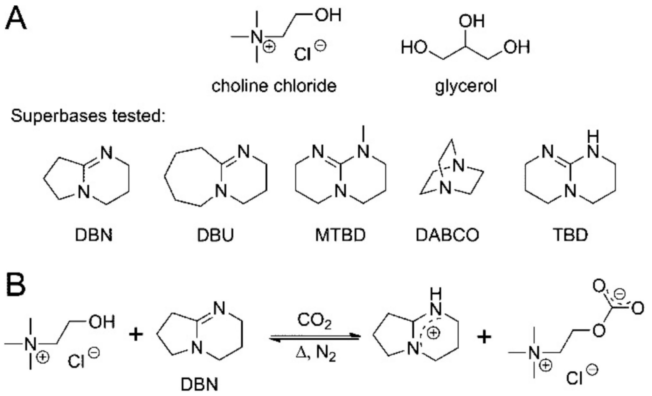


Figure 6. (**A**) Structures of the DES components: choline chloride, glycerol, and various superbases. (**B**) Proposed reaction scheme for superbase-promoted CO_2 capture using a task-specific DES. In this scheme, choline chloride and the superbase DBN are shown for illustration; however, a similar reaction is believed to be operative for the other superbases as well as for CO_2 binding to the multiple alcohol functionalities of glycerol (Reprinted with permission from Ref. [77]. Copyright (2014) American Chemical Society).

Afterward, Zhang et al. [78] paired DBN with EU, 1,3-dimethylurea (DMU), and dimethylolurea (DMLU) to synthesize a series of novel superbase/acylamido-based DESs with low viscosity. Most of these DESs with the viscosity no more than 12 mPa·s exhibited excellent gravimetric absorption capacity. For example, the CO_2 gravimetric absorption capacities of DBN:EU DES (2:1), DBN:DMU DES (2:1), and DBN:DMLU DES (2:1) were 23.02, 17.34, and 4.27 wt%, respectively. Even though it is inevitable that the viscosity increases with the increase of the amount of CO_2 absorbed. Owing to the coaction of reaction dynamics and reaction thermodynamics, the absorption capacity and the rate of the DBN:EU DES (2:1) increased with the increase in temperature from 298.15 K to 318.15 K, after that the CO_2 uptake decreased from 318.15 K to 338.15 K. So that it can be regenerated at 353.15 K, with the desorption ratio in the range of 86–87%. The results of NMR and FTIR indicated that DBN deprotonated the –NH in EU, and a new N−C bond was formed after capturing CO_2. Then they prepared ternary DESs by mixing DBN with BmimCl:Im for CO_2 absorption [79]. The experimental results of DBN:BmimCl:Im DES (1:1:1) and DBNH:Im DES (1:1) indicated that these two absorbents exhibited different absorption behavior. For instance, the viscosity of [DBNH][Im] increased rapidly with

CO_2 absorption and became solid after absorption, while DBN:BmimCl:Im DESs with different molar ratios were all clear liquids after absorbing CO_2, and the time consumption of reaching the adsorption balance was much shorter than that of [DBNH][Im]. The CO_2 uptake of DBN:BmimCl:Im DES (1:2:1), exhibited the highest absorption capacity of 1.07 mol CO_2/mol DES. On the basis of NMR and FTIR analysis, CO_2 was reacted with nitrogen atom on imidazole which was deprotonated by DBN to form $[Im\text{-}COO]^-$ and then a strong intermolecular hydrogen bond was formed between $[Im\text{-}COO^-]$ and $[DBNH]^+$ in DBNH:Im DES. For ternary DESs, CO_2 was reacted with C2 hydrogen on the $[Bmim]^+$ and then $[Bmim^+\text{-}COO^-]$ formed a hydrogen bond with $[DBNH]^+$.

Zeng et al. [80] prepared three superbase ILs, [HDBU][Im], [HDBU][Ind], and [HDBU][Triz] and further combined with EG to from IL-based DESs for an efficient and reversible capture of CO_2. The amount of CO_2 absorbed by IL-based DESs followed the order of [HDBU][Im]:EG (0.141 g CO_2/g DES) > [HDBU][Ind]:EG (0.117 g CO_2/g DES) > [HDBU][Triz]:EG (0.108 g CO_2/g DES) with a mass ratio of 7:3 at 313.15 K and 100 kPa, which is consistent with the basic order of DESs. The viscosities of all three DESs after absorbing CO_2 increase slightly, while the three pure ILs after CO_2 absorption become a gelatinous state. The absorbed CO_2 could be completely released under 343.15 K with N_2 purging, and CO_2 absorption capacity remained nearly unchanged. Two kinds of possible mechanism of [HDBU][Im]:EG DES for CO_2 absorption were proposed. One pathway was that the H atom on EG transfers to the electronegative N of the IL to obtain the final product of carbonate, and the other was that IL reacts with CO_2 directly to generate carbonate. Therefore, the process of IL-based DES for CO_2 absorption was proved to be the synergistic interaction between EG, IL, and CO_2, resulting in the mixed product of carbamate and carbonate.

Table 4. CO_2 solubility in functionalized DESs.

DESs	Molar Ratio	*T*/K	Capacity at 101 kPa/wt%	Viscosity of Pure DESs/mPa·s	Viscosity of DESs after CO_2 Uptake/mPa·s	Ref.
BmimCl: MEA	1:1	298	8.4			[65]
BmimCl: MEA	1:2	298	17.9			[65]
BmimCl: MEA	1:4	298	21.4			[65]
ChCl:Gly:DBN	1:2:3	RT	9.6			[77]
ChCl:Gly:DBN	1:2:6	RT	10.3			[77]
ChCl:Gly:DBN	1:2:7	RT	10.5			[77]
ChCl:Gly:DBN	1:2:8	RT	10.3			[77]
ChCl:Gly:DBN	1:3:10	RT	10.4			[77]
ChCl:Gly:DBU	1:2:6	RT	3.55			[77]
ChCl:Gly:MTBD	1:2:6	RT	10			[77]
ChCl:MEA	1:5	303.15	25.23			[70]
DBN:BmimCl:Im	1:1:1	298.15	(1.02) [1]			[79]
DBN:BmimCl:Im	1:1:2	298.15	(0.97) [1]			[79]
DBN:BmimCl:Im	1:2:1	298.15	(1.07) [1]			[79]
DBN:DMLU	2:1	318.15	4.27; 2.47 [2]	>1000	>10000	[78]
DBN:DMU	2:1	318.15	17.34; 16.8 [2]	2.52 ± 0.05	>3000	[78]
DBN:EU	2:1	318.15	23.02; 19.98 [2]	11.85 ± 0.10	>3000	[78]

Table 4. *Cont.*

DESs	Molar Ratio	T/K	Capacity at 101 kPa/wt%	Viscosity of Pure DESs/mPa·s	Viscosity of DESs after CO$_2$ Uptake/mPa·s	Ref.
DBN:EU	3:1	318.15	19.31; 17.33 [2]	7.56 ± 0.03		[78]
[Emim][2-CNpyr]:EG	1:2	298.15	11.4, 10.3 [3]			[74]
[HDBU][Im]:EG	7:3	313.15	0.141			[80]
[HDBU][Ind]:EG	7:3	313.15	0.117			[80]
[HDBU][Triz]:EG	7:3	313.15	0.108			[80]
HmimCl:AP	1:1	RT	2.0 (0.04) [1]	130.6		[67]
HmimCl:AP	1:2	RT	9.5 (0.21) [1]	57		[67]
HmimCl:AP	1:3	RT	13.9 (0.30) [1]	49.9		[67]
HmimCl:AP	1:4	RT	19.4 (0.37) [1]	39		[67]
HmimCl:PEHA	1:4	RT	8.4 (0.4) [1]	213		[67]
HmimCl:DETA	1:4	RT	22.8 (0.55) [1]	17.3		[67]
HmimCl:EDA	1:1	RT	9.0 (0.19) [1]	80		[67]
HmimCl:EDA	1:2	RT	25.0 (0.45) [1]	14.1		[67]
HmimCl:EDA	1:3	RT	26.7 (0.45) [1]	7.7		[67]
HmimCl:EDA	1:4	RT	30.8 (0.50) [1]	5.8		[67]
HmimCl:TEPA	1:4	RT	9.9 (0.39) [1]	100.5		[67]
MEAC:AP	1:1	RT	15.8 (0.28) [1]	126.7		[67]
MEAC:AP	1:2	RT	21 (0.37) [1]	67		[67]
MEAC:AP	1:3	RT	24.3 (0.42) [1]	64		[67]
MEAC:AP	1:4	RT	26.3 (0.46) [1]	55		[67]
MEAC:DETA	1:4	RT	25.5 (0.57) [1]	19.2		[67]
MEAC:EDA	1:1	RT	23.5 (0.38) [1]	128		[67]
MEAC:EDA	1:2	RT	30.9 (0.47) [1]	17.3		[67]
MEAC:EDA	1:3	RT	36.5 (0.54) [1]	9.6		[67]
MEAC:EDA	1:3	303.15	33.7	21.6	3995	[66]
MEAC:EDA	1:4	RT	39.0 (0.57) [1]	7		[67]
MEAC:PEHA	1:4	RT	12.7 (0.59) [1]	222		[67]
MEAC:TEPA	1:4	RT	16.6 (0.63) [1]	109.4		[67]
[N$_{2222}$][Im]:EG	1:2	298.15	12.9 (0.94) [1]			[71]
[N$_{2222}$][Triz]:EG	1:2	298.15	12.5 (0.92) [1]			[71]
[P$_{2222}$][Im]:EG	1:2	298.15	11.8 (0.91) [1]			[71]
[P$_{2222}$][Triz]:EG	1:2	298.15	11.8 (0.91) [1]			[71]
TAEC:EDA	1:3	303.15	14.6	30.7	748.8	[66]
TBAB:AMP	1:3	RT	10.5 (0.35) [1]	199.7		[67]
TBAB:AMP	1:4	RT	12.2 (0.38) [1]	252.263		[67]
TBAB:AP	1:2	RT	11.1 (0.43) [1]	243		[67]
TBAB:AP	1:3	RT	15.6 (0.49) [1]	51.2		[67]
TBAB:AP	1:4	RT	18.1 (0.51) [1]	38.4		[67]
TEAC:EDA	1:3	303.15	24.2	52.4	3343	[66]
[TETA]Cl:DG	1:2	313.15	0.159			[68]
[TEPA]Cl:thymol	1:3	313.15	0.088 (1.355) [1]	295.7	16,800	[69]
[TETA]Cl:EG	1:3	313.15	0.175			[68]
[TETA]Cl:thymol	1:3	313.15	0.09 (1.298) [1]	205.1	6770	[69]
UEC:EDA	1:3	303.15	17.8	29.5	3011	[66]

[1] Data in brackets are the molar fraction. [2] The CO$_2$ concentration was 14%. [3] The CO$_2$ concentration was 0.5%.

6. Non-Functionalized DESs for NO Capture

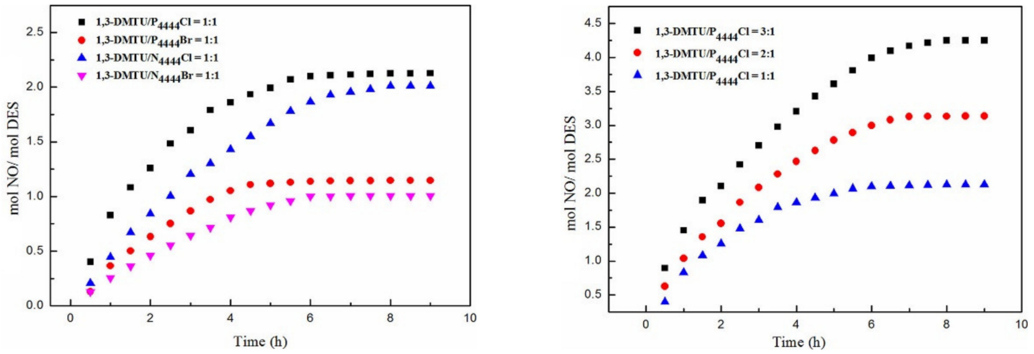
In 2011, Duan et al. [81] synthesized three kinds of DESs using CPL as HBD and tetrabutylamine halide as HBAs to absorbed NO. The solubility of NO with various halide anions displayed the following trend: F$^-$ > Br$^-$ > Cl$^-$, which means that halogen anions play an important role in the absorption process. It can be seen that the solubility of NO in the DESs increased as the temperature increased from 308.15 to 363.15 K and molar ratio affected the absorption rate. The solubility of NO in CPL:TBAB DESs (4:1 and 6:1) increased sharply with an increase in temperature. The highest mole fraction solubility of NO was 0.170 mol NO/mol DES with a molar ratio of 4:1 at 353.15 K. The results of ^{1}H NMR spectra showed that NO was physically absorbed by DESs. It is worth noting that the colorless TBAB:CPL DES changed to pale yellow after absorbing NO. It is well-known that the appearance of a yellowish to orange color in the sulfur dioxide solvates of halides and pseudohalides are assigned to a charge transfer interaction, where SO_2 acts as an electron acceptor species [82,83]. It is reported that NO can also act as an electron acceptor [84,85]. Therefore, the color change of TBAB:CPL DES may be due to the charge transfer between Br^- and NO.

7. Functionalized DESs for NO Capture

In recent years, considerable efforts have focused on the experimental and theoretical studies in the field of acidic gas separation and absorption by ILs. However, it was difficult for NO to form the hydrogen bonding with ILs, owing to its weak chemical polarity. Therefore, DESs, with chemical absorption capacity, are highly desirable. In 1960, Drago et al. [84] for the first time reported that NO could reacted with secondary amines to form the product $Et_2NH_2{}^+Et_2N_2O_2{}^-$. However, the mechanism of whether the nitric oxide molecule dimer added base or whether nitric oxide added base and then reacted with another nitric oxide molecule have not been clarified. Until 2008, Laali et al. [83] explored the kinetics and mechanism of the reaction between secondary amines and NO. The mechanism is interpreted in terms of competitive addition of amine to either NO or its dimer. The NO solubility with the scale of mol mol^{-1} for the studied DESs are given in Table 5.

Amino-Functionalized DES

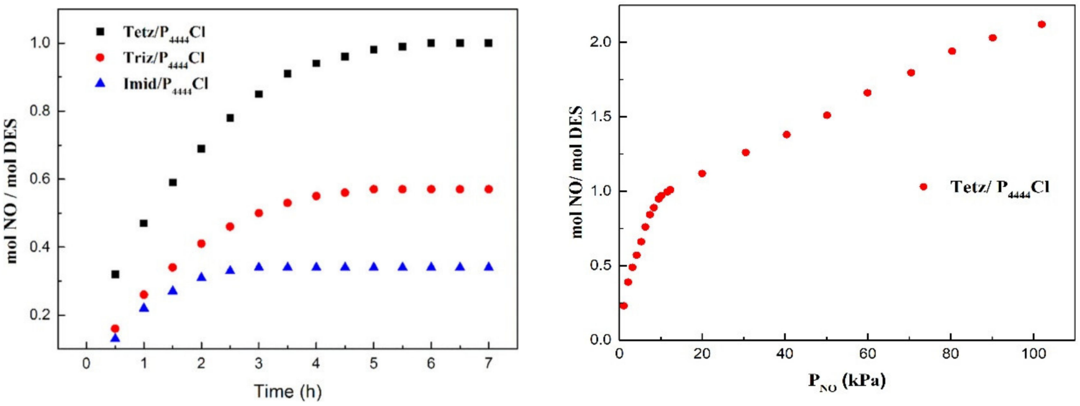
Tantai et al. [86,87] synthesized a series of DMU and 1,3-dimethylthiourea (1,3-DMTU)-based DESs, paired with tetrabutylphosphine halides and tetrabutylamine halides, such as P_{4444}Cl, P_{4444}Br, TBAC, and TBAB. The result showed that the DESs containing chlorine salts as HBAs performed much better absorption capacity than those containing bromine salts, which is consistent with previous reports, as shown in Figure 7a. Moreover, the NO absorption capacity increased with the increase of the molar ratio of 1,3-DMTU in the DESs (Figure 7b), which indicated that the primary amine of 1,3-DMTU is the main site for chemical absorption of NO. For example, the absorption capacity of P_{4444}Cl:DMTU increased from 2.10 to 4.25 mol NO/mol DES at 303.15 K and 101.3 kPa, as the molar ratio increased from 1:1 to 3:1. Additionally, 1,3-DMTU exhibits better performance than DUM as HBA in absorption capacity. The solubility of NO in P_{4444}Cl:1,3-DMTU DES (1:1) is 1.13 mol NO/mol DES at 303.15 K and 101.3 kPa, which is much higher than 0.663 mol NO/mol DES in P_{4444}Cl:DMTU DES (1:1). The results can be interpreted as sulfur atom is more electronegative than oxygen atom, so more of the charge from nitrogen is transferred to sulfur atoms, resulting in a drop in the electron cloud density of a nitrogen atom. As a consequence, the amino groups on 1,3-DMTU are prone to deprotonated than the amino groups on DMU, which is more conducive to the progress of the reaction. Nevertheless, the desorption residue P_{4444}Cl:1,3-DMTU DES (1:3) was about 1.3 mol NO/mol DES, while the absorbed NO by P_{4444}Br: DMU DES (1:3) can be completely desorbed, due to the stronger interaction between NO and 1,3-DMTU.



(**a**) (**b**)

Figure 7. (**a**) NO absorption by DESs with different HBAs at 303.15 K; (**b**) NO absorption by DESs with different molar ratios of 1,3-DMTU to P_{4444}Cl at 303.15 K (Reprinted with permission from Ref. [87]. Copyright (2017) American Chemical Society).

Considering the effect of deprotonation on absorptive capacity, they chose azole-derived as HBDs paired with P_{4444}Cl as HBA to synthesize DESs for further research [88]. The absorption capacity with different azole-derived HBDs was ordered as Tetz:P_{4444}Cl > Triz:P_{4444}Cl > Im:P_{4444}Cl, and the same trend was observed in ChCl-based DESs (Figure 8a). Please note that this order was opposite to the basic order of azole derivatives. As shown in Figure 8b, the effect of NO partial pressure on the NO absorption capacity of Tetz:P_{4444}Cl was studied. Notably, under low partial pressures ranging from 2 to 12 kPa, the NO absorption capacities increased sharply from 0.39 to 1.01 mol NO/mol DES, which confirmed the efficient chemical absorption of NO under low partial pressures. After that it increased linearly to 2.10 mol NO/mol DES when the partial pressure of NO increased from 12 to 101 kPa at 303.15 K, which was a physical absorption process. The experiment corroborated that Cl^- can significantly absorb NO through physical interaction. The highest absorption capacity of Tetz:P_{4444}Cl is equivalent to that of 1,3-DMTU:P_{4444}Cl under the same conditions. Although Tetz:P_{4444}Cl possessed desirable reusability for NO absorption and could maintain high NO absorption after recycling five times. About 0.72 mol NO/mol DES remained after desorption, indicating a desorption rate of nearly 66%.



(**a**) (**b**)

Figure 8. (**a**) NO absorption by P_{4444}Cl-based DESs at 343.15 K and 101.3 kPa; (**b**) Effect of NO partial pressure on the NO capture of Tetz/P_{4444}Cl DES at 303.15 K (Reprinted with permission from Ref. [88]. Copyright (2019) American Chemical Society).

However, the DESs mentioned above were only performed to capture pure NO. In the light of the reaction of NO with the primary amine of dipropylamine (DPA) to form dipropyldiazeniumdiolate [83], Wu et al. [89] synthesized a series of polyamine-based DES and successfully used them for the absorption of low concentrations. Triethylenetetramine chloride([TETA]Cl) and tetraethylenepentamine chloride ([TEPA]Cl) were chosen as HBAs and 1,3-propanediol (1,3-PDO), Gly, polyethylene glycol (PEG), and EG were chosen as HBDs. [TEPA]Cl:EG DES with 1:3 molar ratio exhibited the best performance with the capacity of 4.52 mol NO/mol DES (0.33 g NO/g DES) at 303 K and 101 kPa. It is worth noting that even though EG is not the main absorption component, increasing the molar ratio of EG can still increase the gravimetric absorption capacity, which demonstrated that EG can promote the absorption process enhancing the basicity of [TEPA]Cl though hydrogen bonding interactions.

Table 5. NO solubility in functionalized DESs.

DESs	Molar Ratio	*T*/K	Capacity at 101 kPa g NO/g DES	Capacity at 10 kPa mol NO/mol DES	Viscosity of Pure DESs/mPa·s	Viscosity of DESs after NO Uptake/mPa·s	Ref.
[TEPA]Cl:1,3-PDO	1:1	303.15		(3.25) [1]			[89]
[TEPA]Cl:EG	1:1	303.15		(3.10) [1]			[89]
[TEPA]Cl:EG	1:3	303.15		(4.52) [1]			[89]
[TEPA]Cl:Gy	1:1	303.15		(3.35) [1]			[89]
[TEPA]Cl:PEG	1:1	303.15		(3.45) [1]			[89]
[TETA]Cl:EG	1:1	303.15		(2.49) [1]			[89]
CPL:TBAB	4:1	353.15	(0.17) [1]				[81]
TBAB:1,3-DMTU	1:1	303.15	(1.00) [1]		1123		[87]
TBAB:Tetz	1:1	303.15	0.024 (0.32) [1]		279.15	26.32	[88]
TBAC:1,3-DMTU	1:1	303.15	(2.05) [1]		512		[89]
TBAC:Tetz	1:1	303.15	0.126 (1.46) [1]		87.88	9.85	[88]
P_{4444}Br:1,3-DMTU	1:1	303.15	(1.13) [1]		245		[87]
P_{4444}Br:DMU	1:1	303.15	(0.66) [1]				[86]
P_{4444}Br:DMU	1:2	303.15	(0.92) [1]				[86]
P_{4444}Br:DMU	1:3	303.15	(1.17) [1]				[87]
P_{4444}Br:Tetz	1:1	303.15	0.035 (0.48) [1]		68.26	5.63	[88]
P_{4444}Cl:1,3-DMTU	1:3	303.15	(4.25) [1]		286		[87]
P_{4444}Cl:1,3-DMTU	1:2	303.15	(3.18) [1]		173		[87]
P_{4444}Cl:1,3-DMTU	1:1	303.15	(2.13) [1]		105		[87]
P_{4444}Cl:Imid	1:1	303.15	0.013 (0.16) [1]		52.34	5.16	[88]
P_{4444}Cl:Tetz	1:1	303.15	0.173(2.100) [1];(0.231) [2]		40.22	3.15	[88]
P_{4444}Cl:Triz	1:1	303.15	0.059 (0.71) [1]		67.23	7.13	[88]

[1] Data in brackets are the molar fraction. [2] At 1 kPa.

8. Regeneration

The regeneration of absorbents is an important property that determines the production cost and the sustainability of equipment investment in industrial processes. Experimentally, the regeneration of an absorbent was conducted by bubbling N_2 at a high flow rate into the saturated absorbent to sweep out the absorbed gas or reducing the pressure of absorbents at a desired temperature until the weight of the absorbent maintains constant. The whole process of absorption and desorption is repeated at least five times to verify the reusability of DESs.

The strength of the interaction between an acidic gas and a DES determines the conditions required for desorption. Weak interaction between the gas and the non-functionalized DES makes the desorption process easy and fast. For example, SO_2 absorbed by ChCl:Gly

DES (1:1) could be completely released by bubbling N_2 at 60 mL min^{-1} and 323.15 K within 20 min [36]. For other non-functionalized DESs with ChCl as an HBA, such as ChCl:EG (1:2), ChCl:MA (1:1), ChCl:UE (1:2), and ChCl:thiourea (1:1), absorbed SO_2 could be completely released at 250 mL min^{-1} and 353.15 K with 20 min [39]. Yang et al. [41] reported that the molar ratio of HBA to HBD could also affect the desorption behavior. About 96% SO_2 captured by EmimCl:EG DES (2:1) can be released at 353.15 K within 50 min. For EmimCl:EG DES (1:1), captured SO_2 can be released completely at the same condition. While all SO_2 captured by EmimCl:EG DES (1:2) can be desorbed at 333.15 K within 50 min. The different desorption behaviors are mainly because the increase in EmimCl/EG molar ratio can reduce the interaction between EmimCl and SO_2, which is favorable for the desorption process. Compared with functionalized DESs, non-functionalized DESs have a weaker interaction with acidic gases. Thus, it can achieve a higher desorption rate (90~100%) at lower temperatures (323.15~353.15 K).

For functionalized DESs, the stronger interaction between DESs and gases would make regeneration harder. For instance, due to the strong interaction between NO and DESs, the desorption rates of NO in Tetz:P_{4444}Cl DES (1:1) [89], P_{4444}Cl:1,3-DMTU DES (1:3) [87], [TEPA]Cl:EG DES(1:3) [89] are 66%, 70% and 70%, respectively, at 353.15 K for 60 min. The desorption rates of SO_2 (2 vol %) in L-car:EG DES (1:3) [57] and Im:Gly DES (1:2) are about 70% and 80% at 363.15 K and 373.15 K, respectively. As the partial pressure of an acidic gas increases, the saturated absorption capacity increases, which leads to an increase in the desorption rate. The desorption rate of EU:4-CH_3-Im:BmimCl (1:2:1) and EU:4-CH_3-Im:BmimCl (1:1:1) for 0.2 vol % SO_2 could reach 74.6% and 72.1%, respectively, at 100 mL/min and 353.15 K, while the desorption rates were calculated to be 92.1% and 92.7%, respectively, based on the saturated absorption capacity of pure SO_2 at the same conditions [53]. Deng et al. [49] reported that the different desorption behaviors of ACC:Im DES (1:2) and ACC:Tri DES (1:1) were related to the basicity of DESs. For ACC:Tri DES (1:1), absorbed SO_2 could be completely stripped out by bubbling N_2 at 363.15 K. However, approximately 6% SO_2 still remained after regeneration in ACC:Im DES (1:2) at the same condition. The residue of desorption was attributed to different basicity of DES. It is well-known that the pK_a values of Im and Tri are 18.6 and 14.8, respectively. Thus, the basicity of the former is stronger than that of the latter. The interaction between ACC:Im DES (1:2) and SO_2 is stronger than that between ACC:Tri DES (1:1) and SO_2, which make the desorption harder.

9. Conclusions and Outlook

In summary, DESs can effectively absorb SO_2, CO_2 and NO of low concentrations in flue gas, and generally have lower viscosity before absorption compared to ILs. Especially for DESs used for SO_2 capture, the absorption capacity of non-functionalized DESs with BmimCl as HBA can be comparable to that of functionalized DESs at low pressures ($\leq$ 10 kPa), but the DESs with BmimCl as HBA shows fast desorption rate, low desorption temperature and no desorption residual problem. The synthesis process of DESs is simple and does not require further purification. The absorption capacity and viscosity can be adjusted by changing the molar ratio of HBD to HBA, which makes a great room for cost adjustment. However, the study on the capture of acidic gases from flue gas by DESs still has a lot of challenges in the near future. First, although DESs used for the absorption of SO_2 and NO can inhibit the significant increase in the viscosity during the absorption process by introducing halogen anions, the significant increase in viscosity caused by the chemical interaction between CO_2 and DESs is still remains a challenge. This may limit the application of functionalized DESs in industrial scale. Second, the density, viscosity, solubility enthalpy, heat capacity, toxicity and the long-time stability (> 6 months) are important for applications, but they are seldom reported in the literature. Third, because of the limitation of the difficult complete desorption of functionalized DESs, except for changing the type of HBD or HBA, there is no effective method to remove residual gas. The interaction mechanism between residual gas and DESs remains to be studied. Fourth, the molar ratio of HBA to HBD is a very important factor for DESs. In general, HBA and HBD can form a DES at molar ratios from 1:1 to 1:7, and the absorption capacity and viscosity can be tuned by changing the molar ratio. Generally, for DESs with chloride salt as an HBA paired with different types of HBDs, the highest mass absorption occurs between the molar ratios of 1:3 to 1:5 (HBD:HBA). However, considering the cost and absorptive capacity, the optimal molar ratio is usually different from that at the highest mass absorption. The influence of molar ratio on absorptive capacity has been widely discussed in previous reports, but it is too dispersed to be studied systematically and lacks in-depth studies. More importantly, the flue gas is made of a variety of gases, and hence it is necessary to study the effects of mixed gases on absorption and regeneration performance. DESs containing polyamine, imidazole and triazole can absorb SO_2, CO_2 and NO simultaneously by the free amino groups in DESs with similar mechanism. The competitive absorption between acidic gases and the competitive desorption of the acidic gases are inevitable problems in industrial applications, but no research in this area has been published. Although there are above challenges, functionalized DESs, especially functionalized DESs with strong physical absorption, show enormous potentials for gases capture with easy preparation, low cost, biodegradability, and nontoxicity.

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Abbreviations

A	
AA	acetamide
AC	acetic acid
ACC	acetyl choline chloride
AIMD	ab initio molecular dynamics
AP	3-amino-1-propanol
AMP	aminomethoxypropanol
B	
Ben-Im	benzimidazole
BmimCl	1-Butyl-3-methylimidazolium chloride
BmimBr	1-Butyl-3-methylimidazolium bromide
[BTPP]	butyltriphenylphosphonium
BHDE	*N*-Benzyl-2-hydroxy-*N*,*N*-dimethyl ethanaminium chloride
BTEA	benzyltriethylammonium chloride
BTMA	benzyltrimethylammonium chloride
C	

ChCl	choline chloride
ChAC	choline acetyl chloride
4CH$_3$-Im	4-methylimidazole
CPL	caprolactam
D	
DBN	1,5-diazabicyclo[4.3.0]-non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DEA	diethanolamine
DecA	decanoic acid
DES	deep eutectic solvent
DETA	diethylenetriamine
DFT	density functional theory
DG	diethylene glycol
DMU	1,3-dimethylurea
DMLU	dimethylolurea
1,3-DMTU	1,3-dimethylthiourea
DPA	dipropylamine
E	
EDA	ethylendiamine
EG	ethylene glycol
2-Et	2-ethylimidazole
EmimCl	1-ethyl-3-methylimidazolium chloride
[Emim][2-CNpyr]	1-ethyl-3-methylimidazolium 2-cyanopyrrolide
EU	ethylenurea
G	
Gly	glycerol
Gua	guanidinium hydrochloride
H	
HBAs	hydrogen bond acceptors
HBDs	hydrogen bond donors
HmimCl	1-hexyl-3-methylimidazolium chloride
HPLC	high-performance liquid chromatography
I	
ILs	ionic liquids
Im	imidazole
L	
LA	lactic acid
LV	levulinic acid
M	
MA	malonic acid
MDEA	methyl diethanolamine
MEA	monoethanolamine
MEAC	monoethanolamine hydrochloride
2-Me	2-methylimidazole
MTBD	7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene
MTPP	methyltriphenyl phosphonium bromide
MU	N-methylurea
MU	N-methylurea
N	
[N$_{2222}$][Im]	Tetraethylammonium imidazolium
[N$_{2222}$][Triz]	tetraethylammonium
[N$_{8881}$]Cl	methyl trioctyl ammonium chloride
[N$_{8888}$]Br	tetraoctylammonium bromide
[N$_{8888}$]Cl	tetraoctylammonium chloride
NFM	N-Formylmorpholine
O	
OCT	octanoic acid

P	
$[P_{2222}]$[Im]	tetraethylammonium imidazolium
$[P_{2222}]$[Triz]	tetraethylammonium 1,2,4-triazolium
$P_{4444}Cl$	tetrabutylphosphonium chloride
$P_{4444}Br$	tetrabutylphosphonium bromide
1,3-PDO	1,3-propanediol
PEHA	pentaethylenehexamine
PEG	polyethylene glycol
PILs	protic ionic liquids
2-Pr	2-propylimidazole
PPZBr	1-hydroxyethyl-1,4-dimethyl-piperazinium bromide
Pyr	pyrazole
S	
TAC	thioacetamide
SBs	Superbases
SN	succinonitrile
T	
TAA	thioacetamide
TAAC	thioacetamide hydrochloride
TBAB	tetrabutylammonium bromide
TBAC	tetrabutylammonium chloride
TEA	triethanolamine
TEAB	tetraethylammonium bromide
TEAC	triethanolamine hydrochloride
TEAC	tetraethylammonium chloride
TEG	triethylene glycol
TEMA	triethylmethylammonium chloride
TEPA	tetra-ethylenepentamine
[TEPA]Cl	tetraethylenepentamine chloride
TETA	triethylenetetramine
[TETA]Cl	triethylenetetramine chloride
Tetz	tetrazole
TMAC	tetramethylammonium chloride
TPAC	tetrapropylammonium chloride
Tri	1,2,4-triazole
U	
UE	urea
UEC	urea hydrochloride

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