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Review

Tuning ionic liquid-based functional deep eutectic solvents and other functional mixtures for CO_2 capture

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ABSTRACT

Ionic liquids (ILs) have several unique properties, including low vapor pressure, high thermal and chemical stability, high solubility, tunable structures and properties, *etc*. As carbon capture, utilization, and separation (CCUS) is one of the main strategies to reduce carbon emissions and deal with global climate change, IL-based functional deep eutectic solvents (DESs) and other mixtures with functional CO_2-philic groups have been developed for efficient capture of CO_2. This paper focuses on the research progress in the past five years (2017 ~ 2022). The main contents include functional DESs based on IL salts (conventional IL salt + amine, conventional IL salt + HBD + superbase, functional IL salt + alcohol, functional IL salt + amine), and other functional mixtures based on ILs (conventional IL + amine, conventional IL + superbase, conventional IL-based ternary mixtures, functional IL + alcohol, functional IL + amine, functional IL + water, functional IL + alcohol + water, functional IL + amine + water, functional IL + amine + alcohol, functional IL + conventional IL). The absorption mechanisms of single or multiple carbamate and carbonate are discussed systematically. Finally, future directions and prospects for IL-based functional DESs and mixtures in CCUS are discussed. This review is benefit for researchers to obtain an overall understanding of CO_2-philic functionalized DESs and other functional mixtures.

1. Introduction

With the development of economy, the consumption of fossil energy is increasing rapidly, although people can obtain energy from solar, wind, and water sources. Thus, the concentration of CO_2 in the atmosphere increased from 278 ppm in 1750 (represent pre-industrial conditions) to 413.2 ± 0.2 ppm in 2020 and could reach or exceed 414 ppm in 2021, according to the recent report "*State of the Global Climate 2021*" from the World Meteorological Organization (WMO)[1]. As the increasing concentration of CO_2 leads to the greenhouse effect and global climate change, carbon capture, utilization, and separation (CCUS) has been developed to reduce carbon emissions [2]. Kinds of CCUS technologies have been developed, which can be divided into three categories: post-combustion carbon capture, pre-combustion carbon capture, and oxy-fuel combustion systems [3]. Among these strategies, post-combustion carbon capture is the most commonly used, and monoethanolamine (MEA) has been used in industrial processes for chemical post-combustion CO_2 capture during these decades because of its high reactivity with CO_2 [4]. However, this sorbent also has the drawbacks of volatility and serious equipment corrosion. Thus, green solvents as alternative sorbents should be developed for CO_2 capture.

During the past few decades, ionic liquids (ILs), especially task-specific ILs, are developed as a kind of green solvents, catalysts, and building blocks for dissolution, delivery, and synthesis in many fields including capture and separation,[5,6] energy and environment,[7–9] catalyst and synthesis,[10–12] pharmaceutics and medicine,[13–15] due to their attractive properties such as non-flammability, negligible vapor pressure, high thermal and chemical stability, wide liquid temperature range, and tunable structures and properties [16,17]. More recently, Cui and Wang reported imide-based anion-functionalized ILs for efficient and reversible capture of low-concentration CO_2 with high weight capacity up to 22 wt% [18]. However, the ILs with functional CO_2-philic active sites are high viscosity fluids and always difficult to prepare. Thus, other sustainable green solvents are encouraged to be

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developed.

In recent years, deep eutectic solvents (DESs) have been developed as a kind of novel green solvent with unique properties like ILs, such as high stability, low vapor pressure, low cost, high biodegradability, and tunable structures and properties. DESs are mixtures and usually synthesized from a halide salt as a hydrogen bond acceptor (HBA) mixing with a hydrogen bond donor (HBD) [19]. These halide salts are ionic compounds, here we focus on the salts based on organic cations named IL salts. The different between ILs and IL salts is their melting points. ILs are normally defined as compounds completely composed of ions with melting points below 100 °C, the boiling point of water [20,21]. This temperature ceiling distinguishes ILs from the high-temperature inorganic molten salts. For organic salts with melting points above 100 °C, they can be classified as IL salts. With the additional HBDs, DESs with melting points below 100 °C could be obtained from IL salts as HBAs. Thus, DESs is a kind of sustainable solvents analogous to ILs, and also named deep eutectic ILs. Due to the easy synthesis and tunable properties, DESs could be used in the fields of gas capture,[22,23] extraction, [24,25] analysis, energy,[26], environment,[25,27] pharmaceutics and medicine [28]. The first study of CO_2 capture by DESs was reported by Han *et al.* using a cholinium chloride ([Ch][Cl]) + urea eutectic mixture [29]. However, the low capacities were obtained because of the weak physical interactions between conventional DESs and CO_2 [29,30]. Compared with conventional DESs, functionalized DESs have the advantages of fast absorption, high capture capacity, good stability and recyclability in the CO_2 capture process. Baker *et al.* [31] reported the first task-specific ternary DES containing [Ch][Cl], glycerol (Gly), and a superbase for CO_2 capture with high capacity *via* chemical binding mechanism. Subsequently, many kinds of functionalized DESs were developed.

Several review articles have been published for CO_2 capture by DESs. For example, Zhang and Lu *et al.* [32] reviewed and thermodynamic analyzed the cholinium-based DESs for CO_2 separation. Paul *et al.* [33] focused on the ILs and DES for CO_2 conversion technologies. Recently, Ren and Wu *et al.* [34] reviewed the capture of acidic gases from flue gas by DESs, including some DESs for CO_2 capture. However, with the development of functionalized ILs and the increasing attention on DESs, it is crucial to review this field from a viewpoint of functionalization.

In this critical review, we focus our attention not only on the recent advances of IL-based functional DESs for CO_2 capture but also on the recent advances of IL-based other mixtures for CO_2 capture in the past five years (2017 ~ 2022). The main contents include (1) the classification of IL-based CO_2-philic green solvents, (2) the CO_2 absorption mechanisms of CO_2-philic sites, (3) systematically discussed kinds of functional DESs and other functional mixtures for CO_2 capture, (4) key factors effect on CO_2 capture, and (5) future directions and prospects for IL-based functional DESs and functional mixtures for CO_2 capture (Fig. 1). For facilitate reading, an abbreviation list with full names of phrases and organics in this work are collected in Table 1. Additionally, the abbreviation and full names of mentioned ILs are also collected in Table S1. Moreover, two units of CO_2 capacity, including weight capacity in g CO_2 g^{-1} solvent (or wt%, wt% = g g^{-1} × 100%) and molar capacity in mol CO_2 mol^{-1} solvent, are both used in this work, in order to discuss and compare the capacity efficiency of different functional mixtures from both industrial application and mechanism viewpoints. This review is benefit for researchers to obtain an overall understanding of CO_2-philic functional DESs and other functional mixtures.

2. Classification of IL-based CO_2-philic green solvents

It is known that DESs are prepared from salts as the HBAs mixing with the HBDs, and their melting points lower than those of their components. Thus, kinds of solid ionic salts based on the designing of ILs are used to prepare IL-based DESs, especially functional DESs, for CO_2 capture. Some mixed solvents which are prepared from ILs and water or organics are also used for CO_2 capture. It is known that, according to the active sites on ILs or not, IL are mainly classified into two categories: conventional ILs and functional ILs. Here, according to the definitions of IL, DES, and mixture, and the mechanisms of CO_2 absorption, IL-based CO_2-philic green solvents are classified into two categories (Fig. 2):

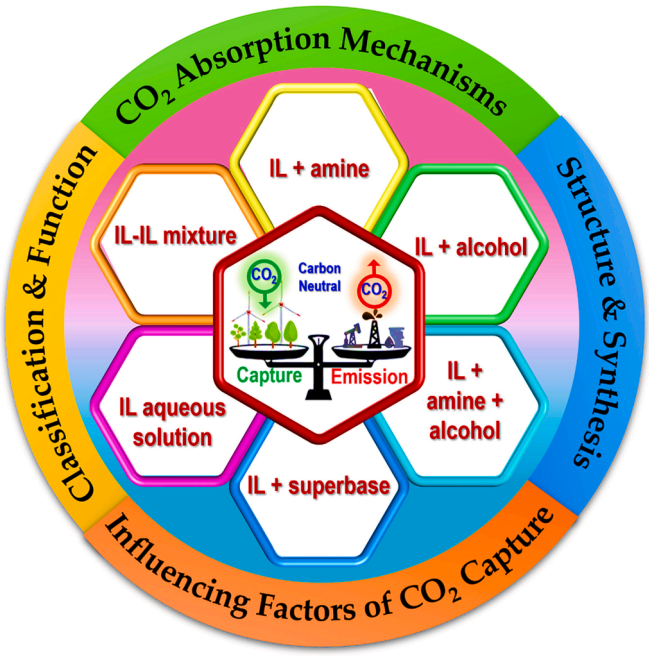


Fig. 1. A summary on IL-based functional eutectics and other solvents for CO_2 capture.

(1) Functional DESs based on IL salts, including conventional IL salt + amine, conventional IL salt + HBD + superbase, functional IL salt + alcohol, functional IL salt + amine.

(2) Other functional mixtures based on ILs, including conventional IL + amine, conventional IL + superbase, conventional IL-based ternary mixtures, functional IL + alcohol, functional IL + amine, functional IL + water, functional IL + alcohol + water, functional IL + amine + water, functional IL + amine + alcohol, functional IL + conventional IL.

3. Synthesis and general CO_2 absorption mechanisms

The efficiency of CO_2 capture is related to the active sites on the components of IL-based CO_2-philic green solvents. On one hand, from the type of sites, these active sites are amino-based sites and non-amino sites. On the other hand, from the number of sites and absorption mechanism, the mechanisms of functional DESs and other functional mixtures could be classified into typical equimolar mechanisms and typical multiple-molar mechanisms.

3.1. Synthesis IL-based functional DESs and other functional mixtures

3.1.1. Amino-containing functional mixtures

Amino-containing functional mixtures are mixtures containing amino-functional cations, amino-functional anions, or amino-containing nonionic components. Amino-based functional ILs include amino-cation functional ILs and amino-anion functional ILs. Amino-based cation-functional ILs could be obtained from (a) direct acid-base neutralization reactions between polyamines and acids (hydrochloric acid, nitric acid, *etc.*), or (b) indirect quaternization-dehydrogenation using protic halogenated amines as the raw reaction components. Amino-based anion-functional ILs could be obtained from dehydrogenated amino acids as the anions through multiple steps including quaternization, anion exchange, and acid-base neutralization reactions. The structure of amines and polyamines could be found in Fig. 3a. General synthesis steps of

Table 1
Abbreviations and full names of nomenclature and organics in this work.

Abbreviation	Full name
CCUS	carbon capture, utilization, and separation
DES	deep eutectic solvent
HBA	hydrogen bond acceptor
HBD	hydrogen bond donor
MEA	monoethanolamine
DEA	diethanolamine
MDEA	methyldiethanolamine
TEA	triethanolamine
AEEA	aminoethylethanolamine
MAPA	N-methyl-1,3-propanediamine
BDA	1,4-butanediamine
3-AP	3-amino-1-propanol
EDA	ethylenediamine
DETA	diethylenetriamine
TETA	triethylenetetramine
TEPA	tetraethylenepentamine
PEHA	pentaethylenehexamine
HMDA	hexamethylenediamine
PMDETA	N,N,N′,N″,N″-pentamethyldiethylenetriamine
Pz	piperazine
AEP	1-(2-aminoethyl)piperazine
EG	ethylene glycol
DEG	diethylene glycol
TEG	triethylene glycol
TTEG	tetraethylene glycol
PEG_{200}	polyethylene glycol with molecular weight of ~ 200 g mol^{-1}
Gly	glycerol
Car	carvacrol
Thy	thymol
UE	urea
MLU	methyl urea
DMU	1,3-dimethyl urea
MTU	N-methylthiourea
DTU	1,3-dimethylthiourea
TAE	thioacetamide
TMG	1,1,3,3-tetramethylguanidine
DBN	1,5-diazabicyclo[4.3.0]-non5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DABCO	1,4-diazabicyclo[2.2.2]octane
TBD	1,5,7-triazabicyclo[4.4.0]-dec-5-ene
MTBD	7-methyl-1,5,7-triazabicyclo[4.4.0]-dec-5-ene
BEMP	2-*tert*-butylamino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine
EtP_2	ethyl-2,2,4,4,4-pentakis-(dimethylamino)-2λ^5,4λ^5-catenadi (phosphazene)

amino-containing IL-based functional DESs and other functional mixtures could be found in Fig. 3b.

Besides, amino-based nonionic components, for example, MEA, could be used directly as another kind of amino-source. Based on the synthesis of amino-functional ILs and the utility of amino-based nonionic components, functional DESs and other functional mixtures based on amino active sites could be prepared for CO_2 capture *via* a simple mixing process at desired temperature. Generally, these functional DESs and other functional mixtures include conventional IL salt + amine, conventional IL + amine + water, amino-functional IL + amine, amino-functional IL + alcohol, amino-functional IL + water, amino-functional IL + amine + water, amino-functional IL + alcohol + water, amino-functional IL + amine + alcohol, amino-functional IL + conventional IL.

3.1.2. Amino-free functional mixtures

There are many kinds of IL-based functional DESs and other functional mixtures without amino groups have been developed during these years. The key point is to design amino-free ILs with functional anions. These functional anions could be obtained from proton donors with weak acidity or basicity *via* acid-base neutralization reactions with superbases or hydroxide anion ([OH]) solutions. The typical anions are phenols, azoles, imides, and partially fluorinated alcohols. These anions in ILs could react with CO_2 directly due to their basicity. Amino-free functional DESs and other functional mixtures based on these ILs could be prepared for CO_2 capture *via* a simple mixing with water and/or alcohol at desired temperature.

Besides, based on Jessop's switchable solvents,[35] other kinds of functional mixtures containing ILs and superbases were designed and prepared for CO_2 capture. Superbases, including DBN, DBU, TMG, *etc*., could directly react with CO_2 or combine with HBDs such as alcohols to form switchable solvents or CO_2-binding organic liquids for chemical 1:1 binding CO_2 *via* proton transfer. The structure of superbases could be found in Fig. 4a. Thus, these functional DESs and other functional mixtures are conventional IL + superbase, conventional IL + superbase + water, conventional IL + superbase + alcohol, amino-free functional IL + alcohol, amino-free functional IL + water, and amino-free functional IL + alcohol + water. General synthesis steps of IL-based amino-free functional DESs and other functional mixtures could be found in Fig. 4b.

3.2. General CO_2 absorption mechanisms

Compare with CO_2 capture by pure sorbents, such as amines and functional ILs, the mechanisms of CO_2 capture by IL-based functional DESs and other functional mixtures are more complex including several multiple reaction paths with multiple reaction steps. It is known that the mechanisms could be classified into two groups, single site mechanisms and multiple site mechanisms, according to the number of active sites. Here, we classified these absorption mechanisms into three groups, direct interaction with CO_2, cooperative interaction with CO_2, and chelative interaction with CO_2, according to the types of interactions with CO_2.

3.2.1. Direct interaction with CO_2

Direct interaction with CO_2 means that one kind of active site that can react with CO_2 without the assistance of other kinds of sites (Fig. 5).

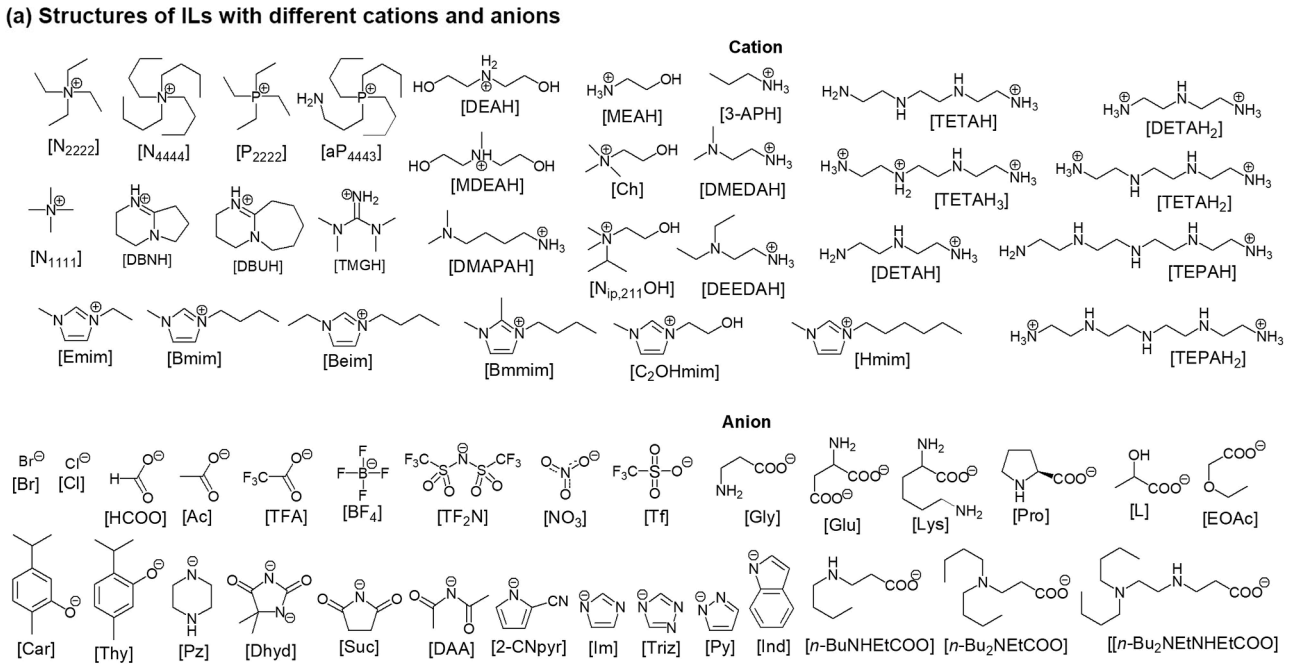
The typical active sites are amino groups, accurately primary amino and secondary amino groups. It is known that there are three kinds of amino groups, including primary amino, secondary amino, and tertiary amino. The structures of former two are nitrogen bonded with hydrogen (s), while that of tertiary amino is the nitrogen without bonded hydrogen(s). Thus, the different reaction pathways are followed by different amino groups for CO_2 capture. The mechanisms of primary and secondary amino-CO_2 reactions containing two steps *via* 1:1 or 2:1 (amino:CO_2) carbamate mechanism which could be expressed in Fig. 5a, even in the case of mixed solvents.

Besides, amino-free anion-functional basic ILs with phenolates, azolates, and fluorinated alcoholates anions could react with CO_2 directly through 1:1 carbonate or carbamate mechanisms, even when mixed with a small amount of other solvents (Fig. 5b). Based on the same absorption mechanisms like aforementioned mechanisms of single active site, multiple "equimolar" absorption could be obtained *via* simple adding strategies of same or different kinds of active sites. For example, the multi-molar CO_2 absorption capacities could be obtained by ILs with polyamine-based cations *via* multiple 2:1 carbamate mechanism. Another example is CO_2 capture by azolate anion-functional IL + amine mixture, where azolate-CO_2 and amine-CO_2 could be formed simultaneous during the absorption.

3.2.2. Cooperative interaction with CO_2

Clearly, cooperative interaction with CO_2 requires at least two active sites in the IL-based functional DESs and other functional mixtures, resulting 1:1 or 1:2 stoichiometric CO_2 absorption capacity (system: CO_2). These active sites can be classified into two groups according to the different absorption mechanism, (a) proton transfer to form an alternative active site for CO_2 absorption, and (b) an active site stimulates another site to form two active sites for CO_2 absorption (Fig. 6).

Cooperative interaction with CO_2 by many systems could be



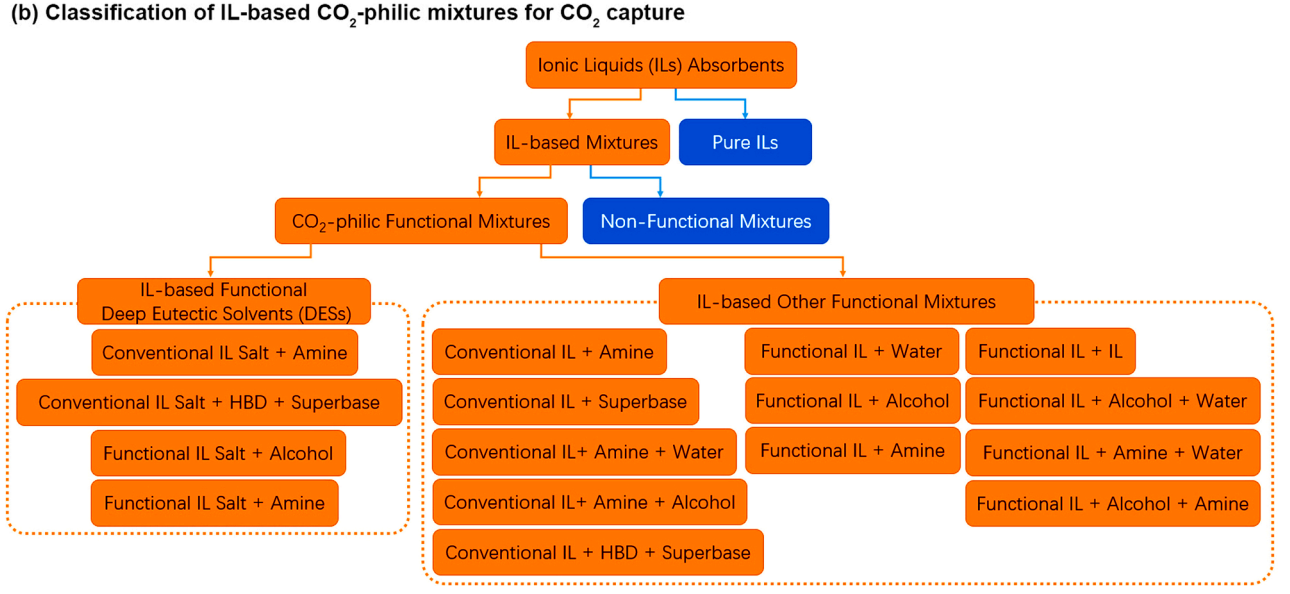


Fig. 2. (a) The structures of ILs with different cations and anions, and (b) the classification of IL-based CO_2-philic mixtures for CO_2 capture.

occurred through proton transfer. A typical active site is tertiary amino group, which is considered unreactive with CO_2 under anhydrous conditions. When a tertiary amino group and an active hydrogen of HBD like water or alcohols in a system, the lone pair electrons on the tertiary amino group will attack and remove the hydrogen atom and form an oxygen anion (HO^- or RO^-), which subsequently react with CO_2 to form carbonates. Actually, not only tertiary amino groups, but also other non-amino basic anions and superbases follow the similar cooperative interaction with CO_2 *via* proton transfer and carbonate mechanisms. These basic anions include phenolates, azolates, and fluorinated alkoxides anions, while the superbases include DBN, DBU, TMG, *etc*.

Another kind of cooperative interaction with CO_2 obtained via an active site stimulates another site to form two active sites for CO_2 absorption. For pure ILs, pyridine-phenolate anion-functional ILs could capture more than 1 (up to 1.65) mol CO_2 mol^{-1} IL due to the cooperative N-CO_2 and O-CO_2 interactions, compared with low CO_2 capacities of neutral pyridine and phenolate anion [36]. Amino-dicarboxylate anion-functional ILs with a −2 valent could capture 1.69 mol CO_2 mol^{-1} IL through amino-CO_2 and carboxylate-CO_2 interactions, compared with low CO_2 capacities of amino and carboxylate anion [37].

3.2.3. *Chelative interaction with CO_2*

Chelative interaction with CO_2 also requires at least two active sites, and two sites in a small substructure (*e.g.* anion) could interact with one CO_2 molecule through chelation (Fig. 7). The typical anions are kinds of imide anions, containing one nitrogen atom and two C = O oxygen atoms. The reported imide anions were $[P_{4442}][Suc]$, $[P_{4442}][DAA]$, and $[P_{4442}][Ph\text{-}Suc]$ [18,38]. Other functional IL with hydantoin anion, $[P_{4442}][1\text{-}MHy]$, was also reported for CO_2 absorption *via* chelation [39]. For some mixtures of $[P_{4442}][Suc]$ with different concentration of water, the absorption mechanism remained steady under low concentration of water, while the mechanism changed to cooperative interaction under high concentration of water [40].

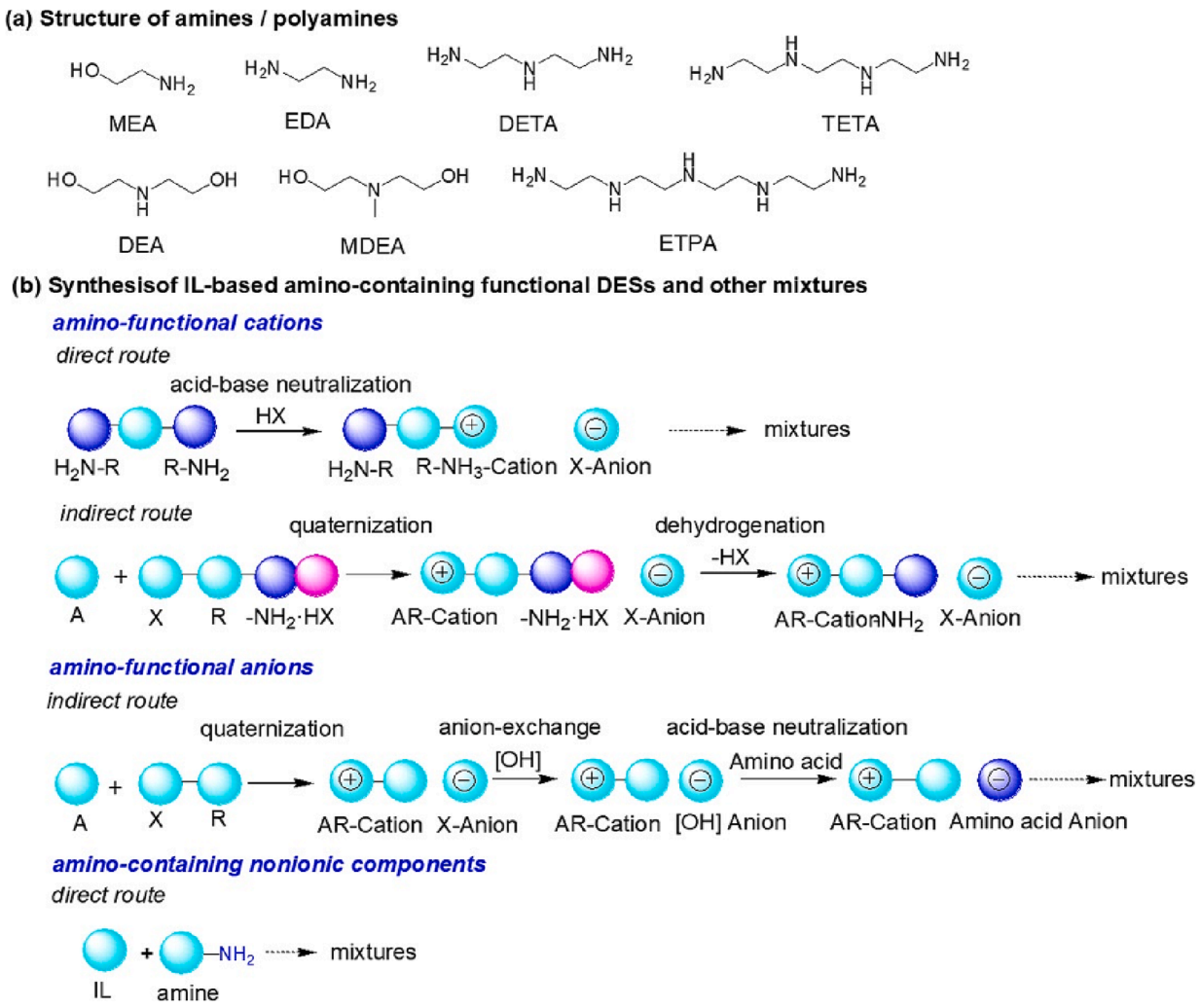


Fig. 3. (a) The structure of amines / polyamines, and (b) general synthesis steps of IL-based amino-containing functional DESs and other functional mixtures.

4. Functional DESs based on IL salts

4.1. Functional DESs based on conventional IL salts

4.1.1. Conventional IL salt + amine

(1) Alkanolamine.

Zhang *et al.* [41] synthesized a series of alkanolamine-based functionalized DESs with [Bmim][Cl] as a HBA and MEA as a HBD (molar ratios of [Bmim][Cl] to MEA were 1:1, 1:2 and 1:4) for CO_2 capture *via* carbamate mechanism. The results showed that CO_2 uptake in [Bmim][Cl]:MEA (1:1, 1:2, and 1:4) at 25 °C and 1 bar were 8.4, 17.9, and 21.4 wt%, respectively, indicating the influence of molar ratio of HBA:HBD on CO_2 capture. Alnashef *et al.* [42,43] reported that amine-based DESs with [Ch][Cl] as a HBA and three different amines as HBDs, including MEA, DEA, and MDEA, with HBA:HBD = 1:6, 1:8 and 1:10. The selected amines represent the primary, secondary and tertiary amines. The determined solubilities of CO_2 in 30 wt% amines were ~ 0.12, ~0.95, and ~ 0.86 g CO_2 per g amine for 30 wt% MEA, DEA, and MDEA, respectively. Their results showed that CO_2 capacities of [Ch][Cl]:MEA (1:8), [Ch][Cl]:DEA (1:8), and [Ch][Cl]:MDEA (1:8) were 265, 163, 16% of the CO_2 capacities of aqueous solutions of 30% weight MEA, DEA, and MDEA, respectively. This means that in the first two cases there is an increment in capacity compared with aqueous amine solutions, while in the last case there is a decrement in capacity. The reason for former cases is that water is not required for the reaction of MEA (primary amine) and DEA (secondary amine) with CO_2, and the addition of IL and the increase concentration of amine in DESs could increase the absorption capacity. For the latter case, the reaction of CO_2 and MDEA (tertiary amine) would not proceed in the absence of water. Recently, Li *et al.* [44] reported that CO_2 capture capacities of [Ch][Cl]:MEA (1:5), [Ch][Cl]:DEA (1:6), and [Ch][Cl]:MDEA (1:7) were 0.2715, 0.1713, and 0.0611 g g^{-1}. Wibowo *et al.* [45] investigated [Ch][Cl]:MEA DES for CO_2 capture in biogas operation conditions (40 vol% CO_2 + 60 vol% CH_4). Their results showed that the CO_2 absorption capacity of [Ch][Cl]:MEA (1:5) was ~ 0.25 mol CO_2 per mol DES at 20 °C and 10 bar. Kumar *et al.* [46] investigated 15 different types of amine- and glycol-based DESs for CO_2 absorption. It indicated that amine-based DESs showed higher CO_2 absorption capacity than glycol-based DESs. For example, 0.29 mol CO_2 mol solvent could be captured by $[N_{4444}][Br]$:MDEA (1:4) at 30 °C and 10 bar. Li and Shen *et al.* [47] synthesized several amine-functionalized DESs, using [Ch][Cl], $[N_{1111}][Cl]$, $[N_{2222}][Cl]$, $[N_{2222}][Br]$, $[N_{4444}][Cl]$, and $[N_{4444}][Br]$ as HBAs and MEA, DEA, MDEA, and TEA as HBDs. The results showed that the order of IL on CO_2 capacity was [Ch][Cl] ≈ $[N_{1111}][Cl]$ > $[N_{2222}][Cl]$ > $[N_{2222}][Br]$, $[N_{4444}][Cl]$ > $[N_{4444}][Br]$, while the order of HBD was MEA > DEA > MDEA > TEA. Thus, CO_2 capacity of 0.2523 g CO_2 per g DESs (25.23 wt%) could be obtained by [Ch][Cl]:MEA (1:5) at 30 °C and 1 bar. Xu *et al.* [48] reported a special synthesis of [MEAH][Cl]:MEA *via* mixing $[NH_4][Cl]$ and MEA at 30 °C for 30 min. CO_2 uptake capacity increased with MEA contents, reaching to around 0.25 g per g at the ratio of 1:4 at 20 °C and 1 bar. Cichowska-Kopczyńska *et al.* [49] investigated the solubility of CO_2 in DESs with AP as the HBD and $[N_{4444}][Br]$, $[N_{4444}][Cl]$, and $[N_{2222}][Cl]$ as the HBAs at

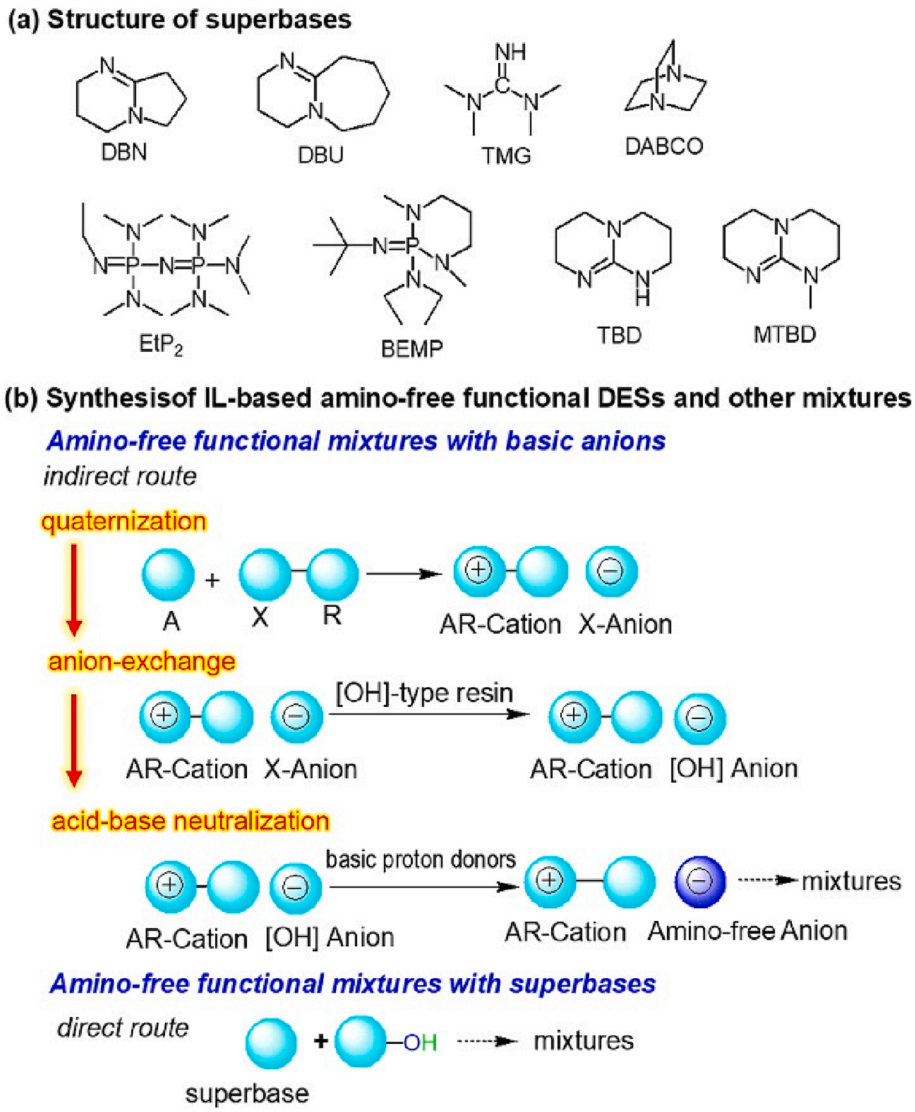


Fig. 4. (a) The structure of superbases, and (b) general synthesis steps of IL-based amino-free functional DESs and other functional mixtures.

the molar ratios of 1:4, 1:6 and 1:8 in the temperature range from 293.15 to 318.15 K at low pressures of CO_2. Recently, Jahanbakhsh-Bonab *et al.* [50] reported that the pressure effects on the amine-based DES [Ch][Cl]:MDEA (1:6) performance in the natural gas sweetening *via* molecular dynamics simulation.

(2) Dual amines.

Sarmad *et al.* [51] investigated CO_2 capture by several amine-based DESs. Based on the obtained solubility data, the absorption capacity followed [Ch][Cl]:MEA:Pz (1:7:1) > [Ch][Cl]:MEA:AEP (1:7:1) > [Ch][Cl]:MEA:MDEA (1:7:1) > [Ch][Cl]:MEA:DEA (1:7:1).

(3) Diamine.

Choi *et al.* [52] reported a series of DES employed [MEAH][Cl], [TEAH][Cl], [UEH][Cl], and [TAEH][Cl] as HBAs with ethylenediamine (EDA) as a HBD in molar ratios from 1:1 to 1:4. Their results indicated that these functionalized DESs capture CO_2 *via* carbamate mechanism of amine-CO_2, reaching a gravimetric CO_2 uptake above 30 wt%. Su *et al.* [53] reported CO_2 absorption with diamine-functionalized DESs, [Ch][Cl]:EG:diamine (1:4:1), where diamines were HMDA, AEEA, MAPA, EDA, and BDA. The results showed that [Ch][Cl]:EG:MAPA could reach 0.78 mol CO_2 per mol diamine at 40 °C and 1 bar.

(4) Multi-amine.

Shukla and Mikkola *et al.* [54] reported a series of amine-based functionalized DESs with [MEAH][Cl] and [Hmim][Cl] as HBAs and EDA, 3-AP, DETA, TEPA, and PEHA as HBDs. Their results showed that CO_2 capture capacity increased with the increasing molar ratio of HBA:HBD (from 1:1 to 1:4). The CO_2 capacity of [MEAH][Cl]:EDA (1:4) was ~36 wt% at 55 °C and ambient pressure, whereas ~34 wt% for [Hmim][Cl]:EDA (1:4). These DESs capture CO_2 also *via* carbamate mechanisms. Subsequently, they synthesized another kind of amine-based DESs by complexing [MEAH][Cl], $[N_{4444}][Br]$, and $[DETAH_3][Cl]_3$ with moderate to high basicity HBDs such as MEA, DEA, TEA, EDA, AP, and TEPA. The results indicated that strong "synergistic interactions" between donor and acceptor moieties satisfactorily relate to the w/w% of CO_2 in DESs. [55] Murshid *et al.* [56,57] prepared amine-based DESs by complexing [MEAH][Cl] salt as a HBA to EDA, MEA, TEPA, TETA and DETA as HBDs with mol $_{HBA}$: mol $_{HBD}$ = 1:1, 1:3, 1:6 and 1:9. The results showed that [MEAH][Cl]:DETA (1:9), [MEAH][Cl]:TETA (1:9) and [MEAH][Cl]:TEPA (1:9]) achieved the CO_2 solubility of 0.6611, 0.6572 and 0.7017 mol CO_2 per mole DES, respectively, *via* the carbamate formation in DES-CO_2 mixtures. The results indicated that the solubility increases with increasing the number of amino groups.

4.1.2. *Conventional IL salt + HBD + superbase*

Baker *et al.* [31] reported first superbase-containing functional ternary DESs for CO_2 capture. These DESs were prepared from [Ch][Cl], Gly, and one of three different superbases at different molar ratios.

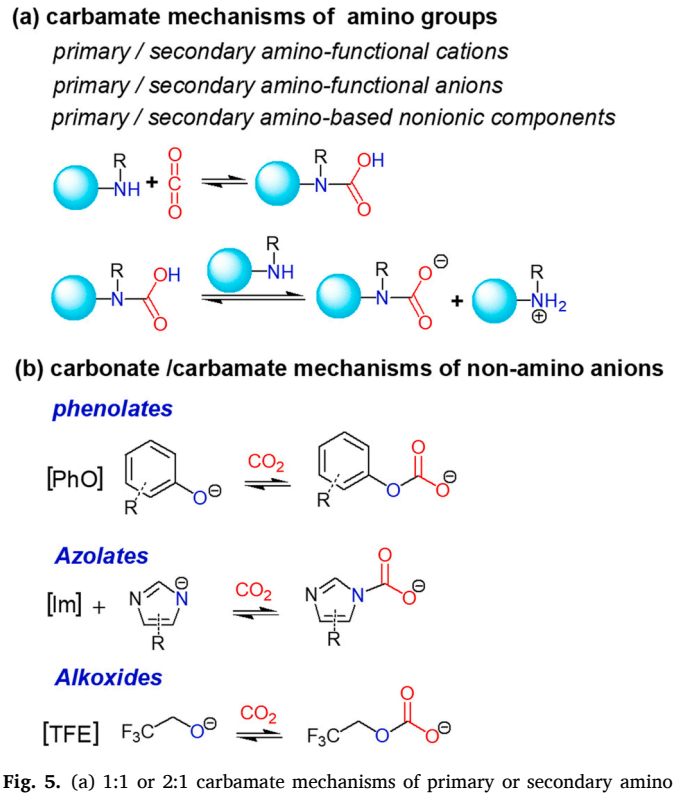


Fig. 5. (a) 1:1 or 2:1 carbamate mechanisms of primary or secondary amino groups; (b) 1:1 carbonate or carbamate mechanisms of non-amino anion-CO_2 reactions.

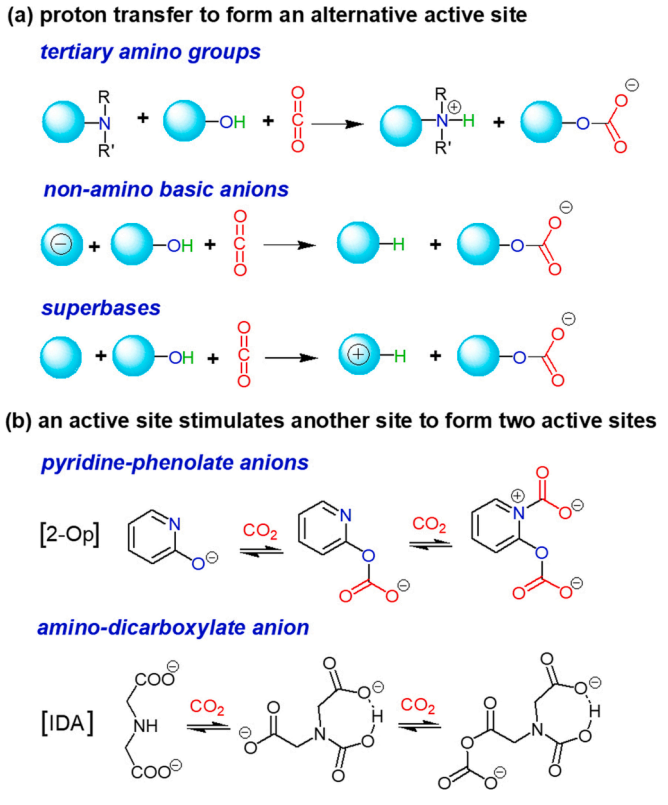


Fig. 6. (a) Proton transfer to form an alternative active site for CO_2 absorption; (b) an active site stimulates another site to form two active sites for CO_2 absorption.

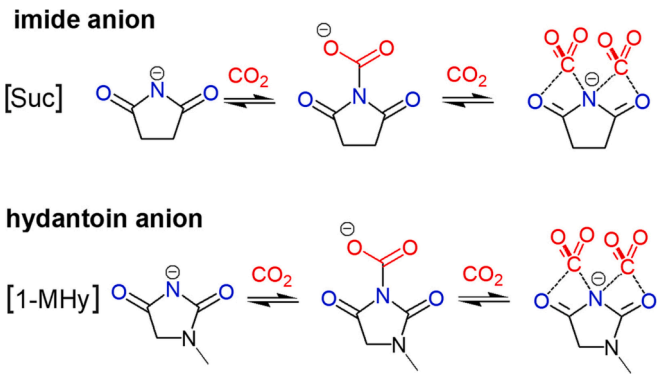


Fig. 7. Anion-CO_2 reaction mechanisms of imide anions and hydantoin anions.

These superbases included DBN, DBU, TBD, MTBD, and DABCO. The results showed that tup to a capacity of ~10% by weight, equivalent to 2.3 ~ 2.4 mmol CO_2 captured per g DES sorbent. Zhang *et al.* [58] reported ternary functional DESs with imidazole (Im) as HBD. These DESs, DBN:[Bmim][Cl]:Im (1:1:1), DBN:[Bmim][Cl]:Im (1:2:1), and DBN:[Bmim][Cl]:Im (1:1:2) exhibited excellent CO_2 absorption capacity up to 1 mol CO_2 per mol DES *via* deprotonation of C-2 proton in the imidazolium cation by superbase and forming the liquid amidinium carboxylate salt. Khan *et al.* [59] prepared a kind of task-specific ternary DES of [Ch][Cl]: Urea: DBU (1:2:4) for CO_2 capture *via* the CO_2 insertion reactions into O-H or N-H with the dehydrogenation by DBU. Kuperkar *et al.* [60] reported several ternary betaine hydrochloride ([BHC])-DESs with two HBDs, Urea and diols, including EG, DEG, TEG, and Gly, with the optimized molar ratio (1: 4: 2.5). Their results showed that ternary DES alone was not able to bind CO_2 covalently, while DBN could promote CO_2 capture *via* forming alkylcarbamate and alkylcarbonate.

4.2. Functional DESs based on functional IL salts

4.2.1. Functional IL salt + alcohol

(1) Amino-based cation-functional IL salts.

Ren and Wu *et al.* [61] reported a series of functional DESs with EG and DEG as HBDs and ammonium salts obtained from TETA and HCl at different mole ratios as HBAs. For [TETAH][Cl]:EG DES, the mole absorption capacity increases from 0.748 mol CO_2 per mol [TETAH][Cl]:EG (1:1) to 1.456 mol CO_2 per mol [TETAH][Cl]: EG (1:3) at 40 °C and 1 bar *via* activating − NH or − NH_2 on [TETAH][Cl] by EG or DEG in DESs. Subsequently, Ren *et al.* [62] reported two hydrophobic DESs based on [TETAH][Cl] and [TEPAH][Cl] as HBAs and thymol (Thy) as HBD at the molar ratios of HBA:HBD = 1:3, 1:5, and 1:7. Their results showed that the CO_2 capacities of [TETAH][Cl]:Thy (1:3) and [TEPAH][Cl]:Thy (1:3) were 1.298 and 1.355 mol mol^{-1}, respectivley, at 40 °C and 1 bar. In addition, these DESs were always hydrophobic during CO_2 absorption. Furthermore, the addition of Thy in DESs played a negative role on the absorption capacity of CO_2, compared with EG as HBD. Mukesh and Mikkola *et al.* [63] reported several functional DESs containing polyamine based dications (diprotic DETA and diprotic TEPA), imidazolate anion ([Im]), and EG. The prepared DESs, $[DETAH_2][Im]_2$:EG (1:2) and $[TEPAH_2][Im]_2$:EG (1:4), showed high CO_2 capacities of 22.35 and 17.36 wt%, respectively, at 25 °C and 1 bar *via* the carbamate mechanism.

(2) Amino acid-based anion-functional IL salts.

Duan *et al.* [64] synthesized a series of hydrophilic DES (L-Arg:Gly, at mole ratios of 1:4, 1:5, 1:6, 1:7, 1:8). The results showed that 0.403, 0.457, 0.451 mol CO_2 per mol DES could be achieved by L-Arg:Gly DESs (1:5, 1:6, 1:7), respectively, at 80 °C under atmospheric pressure.

(3) Phenolate-based anion-functional IL salts.

Yang *et al.* reported several DESs prepared from the mixing of $[N_{2222}]$-derived IL salts [65] or DBU-derived IL salts [66] as HBAs and

EG or 4-methylimidazole as HBDs at different molar ratios of HBA:HBD. The anions of these IL salts were based on carvacrol (Car) and Thy. The capacities of these DESs were all around 1 mol CO_2 per mol DES at 25 °C and atmospheric pressure. Their results indicated that the EG could be dehydrogenated by phenolate anion and then reacted with CO_2 forming a carbonate species, while 4-methylimidazole could not.

(4) Azolate-based anion-functional IL salts.

Yang *et al.* [67–69] reported that several functional DESs based on azolate IL salts and EG at the molar ratio 1:2 or 1:3. These azolate IL salts contained [P_{2222}], [N_{2222}] or protic [MEAH] as the cations with [Im] and [Triz] as the anions. Their results showed that the nearly equimolar absorption capacities could be obtained by these DESs at 25 °C and 1 bar, and the corresponding mass absorption capacities were about 11 wt %. Spectroscopy analysis results indicated that EG could be dehydrogenated by azolate anions and then reacted with CO_2 forming a carbonate species. Zeng *et al.* [70] reported that superbase IL-based DESs for CO_2 absorption. These DESs were formed from protic DBU [DBUH]-based ILs ([DBUH][Im], [DBUH][Ind], [DBUH][Triz]) and EG. CO_2 mass capacity up to 0.141 g CO_2 per g DES under 40 °C and 1 bar could be achieved by [DBUH][Im]:EG (7:3). Gurkan *et al.* [71] prepared a series of DESs from [Emim][2-CNpyr] and EG with the molar ratios: 1:0.5, 1:1, 1:2, 1:3, 1:4, 1:5, and 1:10. The results showed that [Emim][2-CNpyr]:EG (1:2) formed a thermally stable and low viscosity DES with an absorption capacity of 10.3 and 11.4 wt% at 0.005 bar and 1 bar of CO_2, respectively. Three reversible routes were found that yield carbonate (major product), carboxylate (moderate), and carbamate (minor) species (Fig. 8). Fu *et al.* [72,73] reported several functional DESs based on superbase-derived ILs. These ILs were composed of protic DBU ([DBUH]) and protic DBN ([DBNH]) as cations and dehydrogenated ureas as anions, such as MLU, DMU, MTU, and DTU. The reported DESs had the ability to absorb CO_2 *via* the coordinated absorption by imino and hydroxyl groups.

4.2.2. Functional IL salt + amine

DESs containing functional IL salts and amines are dual-functional DESs. Xu *et al.* [74] prepared several binary DESs by mixing [MEAH][Cl], [DEAH][Cl], [MDEAH][Cl] as HBAs with MDEA as HBD at the molar ratio of 1:3. Their results indicated that the CO_2 absorption performance was dependent on the HBA type, in the order: [MEAH][Cl]:MDEA > [DEAH][Cl]:MDEA > [MDEAH][Cl]:MDEA, around 0.1158, 0.1082, and 0.0594 g CO_2 per g DES, respectively, at 25 °C and 1 bar.

4.3. Summary of CO_2 capacities of IL-based functional DESs

There are kinds of IL-based functional DESs reported for CO_2 capture as aforementioned. The proportions of the mixtures were different in different literatures, and the performances of CO_2 absorption were tested under different conditions, as well as the units of absorption capacities were not uniform. Nevertheless, it is still helpful to compare most of the absorption capacity data in order to develop novel IL-based CO_2-philic DESs. Table 2 shows the CO_2 capacities of IL-based functional DESs.

5. Other functional mixtures based on ILs

5.1. Other functional mixtures based on conventional ILs

5.1.1. Conventional IL + amine

Liu and Liang *et al.* [75] reported a series of nonaqueous binary absorbents by mixing conventional ILs ([Bmim][BF_4], [Beim][BF_4], [Bpim][BF_4], [Bbim][BF_4]) and amines (MEA, MDEA) for CO_2 capture. The results showed that the CO_2 capacities of [Bmim][BF_4] + MEA, [Beim][BF_4] + MEA, [Bmim][BF_4] + MDEA, and [Beim][BF_4] + MDEA with mass ratio of IL:amine = 7:3 were 0.1198, 0.1193, 0.0526, and 0.0517 g CO_2 per g absorbent, respectively, at 25 °C and 1 bar. As the maximum CO_2 capacities of [Bmim][BF_4] and [Beim][BF_4] were reported to be 0.0168 and 0.0174 g CO_2 g^{-1} IL, respectively, at 25 °C and 1 bar, the CO_2 capacities of pure MEA and MDEA were calculated to be 0.3586 and 0.1339 g CO_2 g^{-1} amine, respectively. As there was no chemical reaction between the pure ILs and CO_2, the additional amines greatly improved solvents for CO_2 absorption. Hu and Huang *et al.* [76] studied the CO_2 capture by ILs [3-APH][TFA] and [MDEAH][TFA] blended with MEA improved the absorption capacity up to 0.50 mol CO_2 per mol absorbent at 20 °C and 1 bar.

5.1.2. Conventional IL + superbase

Dai *et al.* [77] synthesized a series of mixtures *via* molar ratio 1:1 mixing a hydroxyl functionalized IL and one of superbases, including DBU, MTBD, and BEMP. Their results showed that the CO_2 absorption capacities of [$Im_{21}OH$][Tf_2N] + DBU, [$Im_{21}OH$][Tf_2N] + MTBD, [$Im_{21}OH$][Tf_2N] + BEMP, and [$N_{ip,211}OH$][Tf_2N] + DBU were 1.04, 1.02, 0.81 and 1.02 mol CO_2 per mol IL, respectively. Subsequently, Wang and Dai *et al.* [78] reported that the another mixture systems of imidazolium-based ILs with superbases such as DBU, MTBD, TMG, and

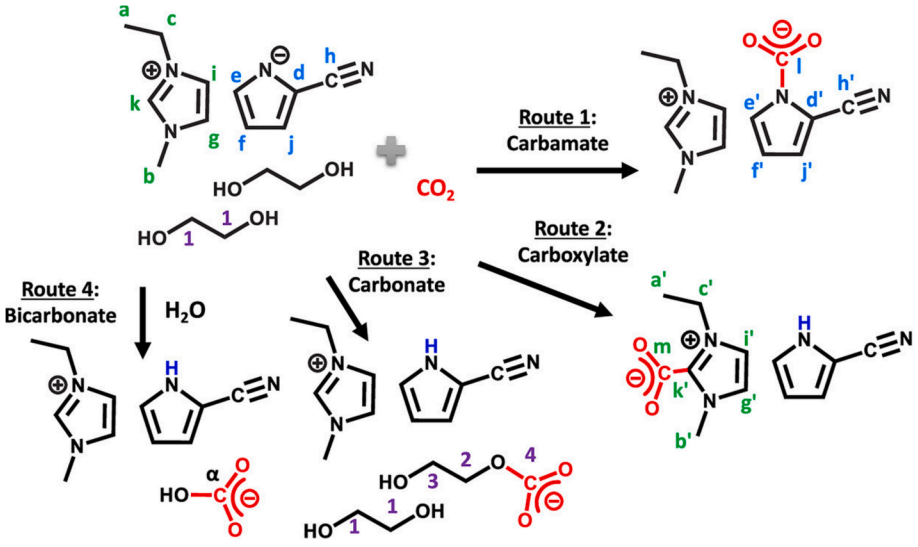


Fig. 8. Proposed reaction network with NMR labeling of the reactants and CO_2 bound products. (Reprinted with permission from Ref. [71]. Copyright 2021 American Chemical Society.

Table 2
CO_2 capacities of IL-based functional DESs.

DES	Molar ratio (n_{HBA}:n_{HBD})	M (g mol^{-1})[a]	T (°C)	P (bar)	CO_2 Capacity (g g^{-1})	CO_2 Capacity (mol mol^{-1})	Ref.
[Bmim][Cl]:MEA	1:1	235.75	25	1	0.084	0.45	[41]
[Bmim][Cl]:MEA	1:2	296.84	25	1	0.179	1.21	[41]
[Bmim][Cl]:MEA	1:4	419	25	1	0.214	2.04	[41]
[Ch][Cl]:MEA	1:5	445.04	—	1	0.2715	2.75	[44]
[Ch][Cl]:DEA	1:6	770.44	—	1	0.1713	3.00	[44]
[Ch][Cl]:MDEA	1:7	973.76	—	1	0.0611	1.35	[44]
[Ch][Cl]:MEA	1:5	76.4[b]	20	0.4	0.144	0.25	[45]
[Ch][Cl]:MDEA	1:6	122.086[b]	30	11	0.0649	0.18	[46]
[Ch][Cl]:MDEA	1:7	121.720[b]	30	10	0.0896	0.248	[46]
[Ch][Cl]:DEA	1:6	110.066[b]	30	10	0.0400	0.1	[46]
[N_{4444}][Br]:MDEA	1:3	169.965[b]	30	10	0.0663	0.256	[46]
[N_{4444}][Br]:MDEA	1:4	159.804[b]	30	10	0.0798	0.29	[46]
[N_{4444}][Br]:DEA	1:6	136.173[b]	30	10	0.0365	0.113	[46]
[Ch][Cl]:MEA	1:5	445.04	30	1	0.2523	2.55	[47]
[MEAH][Cl]:MEA	1:4	341.88	20	1	0.25	1.94	[48]
[Ch][Cl]:EG:MAPA	1:4:1	476.05	40	0.1	0.07	0.78	[53]
[MEAH][Cl]:EDA	1:4	337.94	55	1	0.36	2.76	[54]
[Hmim][Cl]:EDA	1:4	443.12	55	1	0.34	3.42	[54]
[MEAH][Cl]:DETA	1:9	1026.04	40	8	0.0284	0.6611	[56]
[MEAH][Cl]:TETA	1:9	1413.65	40	8	0.0205	0.6572	[56]
[MEAH][Cl]:TEPA	1:9	1801.26	40	8	0.0171	0.7017	[56]
DBN:[Bmim][Cl]:Im	1:1:1	366.93	25	1	0.1223	1.02	[58]
DBN:[Bmim][Cl]:Im	1:2:1	541.6	25	1	0.0788	0.97	[58]
DBN:[Bmim][Cl]:Im	1:1:2	435.01	25	1	0.1082	1.07	[58]
[TETAH][Cl]:EG	1:1	244.76	40	1	0.1345	0.748	[61]
[TETAH][Cl]:EG	1:3	368.9	40	1	0.175	1.456	[61]
[$TETAH_2$][Cl]$_2$:EG	1:4	467.43	40	1	0.0928	0.986	[61]
[$TETAH_3$][Cl]$_3$:EG	1:10	876.3	40	1	0.0301	0.6	[61]
[TETAH][Cl]:thymol	1:3	633.35	40	1	0.09	1.298	[62]
[TETAH][Cl]:thymol	1:3	633.35	40	0.1	0.0411	0.592	[62]
[TEPAH][Cl]:thymol	1:3	676.42	40	1	0.088	1.355	[62]
[$DETAH_2$][Im]$_2$:EG	1:2	363.46	25	1	0.2235	1.85	[63]
[$TEPAH_2$][Im]$_2$:EG	1:4	573.73	25	1	0.1736	2.26	[63]
[N_{2222}][Thy]:EG	1:2	403.6	25	1	0.0981	0.90	[65]
[N_{2222}][Car]:EG	1:2	403.6	25	1	0.0948	0.87	[65]
[N_{2222}][Thy]:4-CH_3Im	1:2	443.67	25	1	0.0893	0.90	[65]
[N_{2222}][Car]:4-CH_3Im	1:2	443.67	25	1	0.0873	0.88	[65]
[DBUH][Car]:EG	1:2	426.59	25	1	0.1000	0.97	[66]
[DBUH][Car]:EG	1:3	488.66	25	1	0.0891	0.99	[66]
[DBUH][Car]:EG	1:4	550.73	25	1	0.0791	0.99	[66]
[DBUH][Thy]:EG	1:2	426.59	25	1	0.1000	0.97	[66]
[DBUH][Thy]:EG	1:3	488.66	25	1	0.0891	0.99	[66]
[DBUH][Thy]:EG	1:4	550.73	25	1	0.0799	1.00	[66]
[P_{2222}][Triz]:EG	1:2	339.41	25	1	0.118	0.91	[67]
[P_{2222}][Im]:EG	1:2	338.42	25	1	0.118	0.91	[67]
[N_{2222}][Triz]:EG	1:2	322.44	25	1	0.125	0.92	[67]
[N_{2222}][Im]:EG	1:2	321.46	25	1	0.129	0.94	[67]
[Emim][2-CNpyr]:EG	1:2	326.39	25	1	0.856	0.114	[71]
[Emim][2-CNpyr]:EG	1:2	326.39	25	0.005	0.777	0.103	[71]
[MEAH][Cl]:MDEA	1:3	455.03	25	1	0.1158	1.20	[74]
[DEAH][Cl]:MDEA	1:3	499.08	25	1	0.1082	1.23	[74]
[MDEAH][Cl]:MDEA	1:3	513.11	25	1	0.0594	0.69	[74]

[a] Molecular weight, $M = n_{HBA}M_{HBA} + n_{HBD}M_{HBD}$; [b] $M=(X_{HBA}M_{HBA} + X_{HBD}M_{HBD})/(X_{HBA} + X_{HBD})$, and $X_{HBA} = n_{HBA}/(n_{HBA} + n_{HBD})$ while $X_{HBD} = n_{HBD}/(n_{HBA} + n_{HBD})$.

EtP_2. Their results indicated that equimolar absorption capacity could be obtained by these systems *via* deprotonation of C-2 proton in the imidazolium cation by superbase and forming the liquid amidinium carboxylate salt.

5.1.3. Conventional IL-based ternary mixtures

(1) Conventional IL + amine (superbase) + water.

Different from CO_2 capture by amines, CO_2 absorption capacity in pure water was very low, only 0.033 mol kg^{-1}, at 25 °C under 1 bar [79]. However, on one hand, the presence of water had a beneficial effect for the mass transfer and diffusion of CO_2. On the other hand, water could react with CO_2 forming the HCO_3^-/CO_3^{2-} and affect the absorption mechanism. Yan *et al.* [80] and Wibowo *et al.* [45] showed that the water addition had a positive effect on CO_2 solubility of [Ch][Cl]:MEA DES. For example, the CO_2 absorption capacity of 0.608 mol CO_2 per mol [Ch][Cl]:MEA (1:5) with 75% vol water content could be captured at 20 °C and 1.5 MPa under 40 vol% CO_2 + 60 vol% CH_4. Li *et al.* [44] studied the effect of additional water on the CO_2 capture by different types of amines. Their results indicated that the addition of water destroyed the hydrogen bond network and reduced the concentration of amino groups, leading to the inhibited CO_2 absorption by primary amine and secondary amine in [Ch][Cl]:MEA and [Ch][Cl]:DEA, while increased the absorption of CO_2 by tertiary amine in the [Ch][Cl]:MDEA because the reaction between the tertiary amine and CO_2 requires the participation of water. Yusoff *et al.* [81] measured the CO_2 absorption capacities of aqueous mixtures of MDEA and [gua][FAP] at 40, 60, 80 °C and at partial pressures 0.5 ~ 3 MPa. Hu and Huang *et al.* [76] studied the CO_2 capture by aqueous mixtures from trifluoroacetate-based ILs, [3-APH][TFA] and [MDEAH][TFA], blending with MDEA. The mass ratios of IL:MDEA were 2:1, 1:1, 1:2, 1:4 and 1:6, and the weight of IL + MDEA and water were 20 % and 80 % of total weight of the absorbent. Their results showed that the CO_2 capacities of [3-APH][TFA] + MDEA (mass ratio 1:6) and [MDEAH][TFA] + MDEA (mass ratio 1:4) were 0.91 and 0.93 mol CO_2 per mol IL at 20 °C and 1 bar. The results indicated that the reaction of MDEA with CO_2 in water was considered to be a catalyzed hydrolysis and the carbamate and the bicarbonate were produced.

(2) Conventional IL + amine + alcohol.

Xu *et al.* [48] determined the CO_2 capture capacities of [MEAH][Cl] + MEA + Gly and [MEAH][Cl] + MEA + EG mixtures. Gly and EG in these mixtures only served as solvent to improve thermal stability of [MEAH][Cl] + MEA. The molar ratio of [MEAH][Cl]:MEA was 1:4, and the mass ratios of Gly and EG in the mixtures were 30 wt% and 10 wt%, respectively. Their results showed that the CO_2 capacities of these mixtures were 0.16 g g^{-1} and 0.225 g g^{-1} for [MEAH][Cl] + MEA + Gly and [MEAH][Cl] + MEA + EG, respectively.

(3) Conventional IL salt + HBD + superbase.

Pandey *et al.* [82] studied CO_2 capture by three binary DESs, reline ([Ch][Cl]:urea), ethaline ([Ch][Cl]: EG), and MEACC ([Ch][Cl]:MEA) at different molar ratios in the absence or presence of three superbases (DBN, DBU, TBD). The results showed that the addition of superbase was found to significantly increase the CO_2 capture ability of reline and ethaline; for the MEACC, the CO_2 capture ability was not changed much as MEA and MEACC on their own exhibit appreciable CO_2 capture efficiency. Thus, dehydrogenation of –NH or –OH by superbase was the key for improving CO_2 capacity. It is found that DBN (as compared to DBU and TBD) was the most effective in increasing CO_2 capture ability of a DES.

5.2. Other functional mixtures based on functional ILs

5.2.1. Functional IL + water

(1) Cation-functional ILs.

MacFarlane *et al.* [83] reported CO_2 capture by a series of mixtures from water and ILs with N,N- [DMEDAH] cation with [Cl], [Ac] or [Tf] anions. Their results showed that the CO_2 absorption of [DMEDAH][Cl] + water (molar ratio 1:1), [DMEDAH][Ac] + water (molar ratio 1:1), and [DMEDAH][Tf] + water (mass ratio of water 20 wt%), were 0.27, 0.48, and 0.35 mol CO_2 per mol IL, respectively, at 20 °C and 1 bar. Meng *et al.* [84] reported the absorption of CO_2 in aqueous solutions of amine-based ILs. The cations were obtained from TETA, EDA, triethylamine, propylamine, diethylamine, and anions were obtained from fluoroboric acid (HBF_4) nitric acid (HNO_3) and sulfuric acid (H_2SO_4). Their results showed that the CO_2 molar capacity of ILs followed [NO_3] > [BF_4] > [SO_4] or [HSO_4], attributing to the strength of the interaction between anions and CO_2. Besides, with the same anion, CO_2 capacities of

ILs followed multiple amine cation > diamine cation > monoamine cation. Thus, 40 wt% [TETAH][NO_3] in water showed the capacity of 1.49 mol CO_2 per mol IL at 15 °C and 1 bar for CO_2 absorption *via* carbamate – bicarbonate mechanism. Hu *et al.* [85] showed that CO_2 absorption capacity of [DETAH][Br] in water (mass ratio 1:4) was 0.868 mol per mol IL at 20 °C and 1 bar. Vijayaraghavan *et al.* [86] reported that diamino protic IL [DMAPAH][HCOO] plus water mixtures for CO_2 capture. Different [DMAPAH][octanoate] ILs were synthesized from different molar ratios of amine to acid. Their results indicated that the CO_2 absorption mass capacities of these mixtures increased with the increasing mass ratio of water in the mixtures (0 ~ 20 wt%), attributing to the simultaneous formation of carbamate and bicarbonate species. Then the capacity decreased at higher water concentrations because the active absorber became more dilute. Chen and Xu *et al.* [87] reported the solubility of CO_2 in the three aqueous ethoxyacetate anion-based protic ILs (90 wt% IL + 10 wt% H_2O) at 30 ~ 60 °C and 0 ~ 1.2 bar. Their results showed that the solubilities of CO_2 in aqueous [DMAPAH][EOAc], [DEEDAH][EOAc], and [DMEDAH][EOAc] were 2.44, 1.28, and 2.32 mol kg^{-1} at 30 °C and 1 bar, respectively. The mechanisms of aqueous ILs with secondary amino group and tertiary amino group were different, due to the indirect reaction of tertiary amino group and CO_2.

(2) Anion-functional ILs.

ILs with amino acid anions. Jing *et al.* [88] reported the kinetics of CO_2 absorption into aqueous [Hmim][Gly] solution. Their results showed that the absorption capacity reached about 0.45 mol CO_2 per mol of [Hmim][Gly] at 30 °C and 15 vol% CO_2. They showed that CO_2 reacted with the [Hmim][Gly] *via* the formation of a zwitterion, subsequently deprotonated by a base present in solution, where the bases were H_2O, [OH] and [Hmim][Gly], and the deprotonation played a leading role. Luo *et al.* [89,90] reported the kinetics of CO_2 absorption into aqueous solution of [Emim][Gly] or [Emim]$_2$[Glu]. Yang *et al.* [91] studied the thermodynamic property of CO_2 absorption in aqueous solutions of five cholinium-based amino acid ILs ([Ch][AA]). Based on the zwitterion mechanism, the solubility of CO_2 in aqueous [Ch][AA] solutions could be correlated with a reaction equilibrium thermodynamic model.

ILs with amino-free anions. Brennecke *et al.* [92] reported that the solubility of CO_2 in [P_{66614}][2-CNPyr] increased slightly in the presence of water (<5 wt%). Dupont *et al.* [93] reported the CO_2 capture by mixtures of [Bmmim][Im] and water with different molar ratios of 1:2, 1:10, 1:100, and 1:1000 at 25 °C and 20 bar. The results showed that bicarbonate formation increased from 0.33 to 1.96 mol CO_2 per mol IL with the molar ratio of water increased from 1:2 to 1:1000. As the physisorbed CO_2 was 8.15 mol CO_2 per mol IL in IL:H_2O (1:1000), more than 10.1 mol CO_2 per mol IL could be estimated from NMR *via* physical and chemical interaction. Cui and Wang *et al.* [18,40] reported the CO_2 capture by the mixtures of [P_{4442}][Suc] and water with the mass ratios of water were 3.3, 8.8, and 17.6 wt%. The results showed that the molar ratios of the absorbed CO_2 to [P_{4442}][Suc] at 20 °C and 1 bar were 1.87, 1.90, 1.19, and 0.92 for pure IL, IL + 3.3 wt% H_2O, IL + 8.8 wt% H_2O, and IL + 17.6 wt%H_2O, respectively. Their results indicated that the CO_2 absorption capacity of ILs in the mixtures first increased and then decreased with the increasing mass ratio of water in the mixtures (Fig. 9).

(3) Dual-functional ILs.

Amino-cation and amino-anion. Guo *et al.* [94] investigated the CO_2 absorption by amino-cation and amino-anion dual functional IL [aP_{4443}][Gly] in water (w_{H2O} = 0.599) by experiments and models. Their results indicated that CO_2 uptake of HCO_3^- by carbonation was dominant in the chemical absorption of CO_2, compared with the reactions of CO_2 with amino-cation and amino-anion. Wu and Hu *et al.* [95] prepared aqueous solutions based on dual-functional IL [DMAPAH][Ac] with the concentrations of 60, 70, 80 and 90 wt%. For example, the CO_2 capacity of [DMAPAH][Ac] (70 wt%) was 2.32 mol kg^{-1} at 25 °C and 1 bar. Their results also showed that in the low-pressure region (<0.7 bar), the chemical reaction dominated the absorption, while in the high-pressure region (greater than 0.7 bar), the physical absorption played the main role due to most of the absorbent completely reacted with CO_2.

Amino-cation and azolate-anion. Lv *et al.* [96] studied the CO_2 capture by aqueous dual-functional ILs (0.5 mol L^{-1}) with the combination of ammonium cation ([DETAH]) and aprotic heterocyclic anions ([AHA]), such as [Im], Py], and [Triz]. Their results showed that CO_2 absorption loadings of [DETAH][Im], [DETAH][Py], and [DETAH][Triz] were 11.91, 11.39, and 10.10 mol CO_2 per kg IL, respectively, at 40 °C and 1 bar *via* the reactions of [DETAH] cation and [AHA] anion with CO_2 to produce carbamates. The [AHA] – CO_2 subsequently hydrolyzed into HCO_3^-/CO_3^{2-} by water, which would promote the CO_2 absorption. Subsequently, Jing *et al.* [97] reported the kinetic and heat duty study of aqueous [AHA]-based dual functionalized ILs, [DETAH][Im] and [DETAH][Triz], for CO_2 capture. Pant and Upadhyayula *et al.* [98] investigated the CO_2 absorption in aqueous four dual functional ILs (0.5 mol L^{-1}), containing [TETAH] cation and anions such as [Pz], [Im], [Py], and [Triz]. The results showed that CO_2 loadings in mol of CO_2 per mol IL of these aqueous ILs were 2.05, 1.81, 1.73 and 1.50, respectively, at 27 °C and ambient pressure, *via* the carbamate mechanism. Their results also showed that the absorption was an exothermic process and the formation of carbamates decreases with increasing temperature.

5.2.2. *Functional IL + alcohol*

(1) Cation-functional ILs.

Clyburne *et al.* [99] investigated the CO_2 capture from ambient air (~400 ppm) by [DETAH][NO_3] in polyethylene glycol with molecular

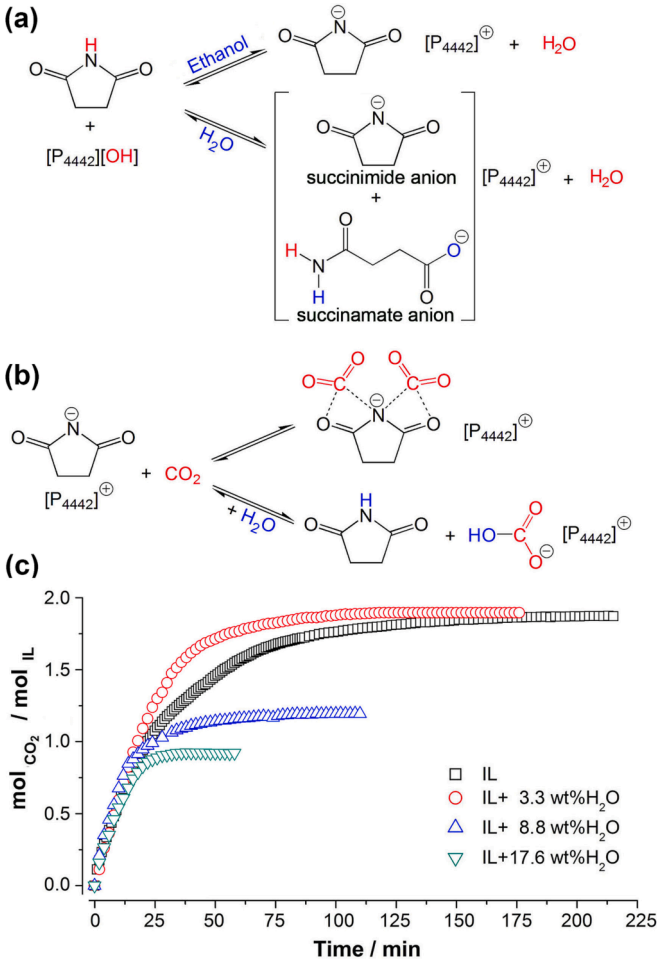


Fig. 9. Effect of water on the preparation of [P_{4442}][Suc], the absorption mechanism, and the CO_2 absorption capacity at 20 °C and 1 bar. Reprinted with permission from Ref. [40]. Copyright 2019 Wiley-VCH.

weight of ~ 200 g mol^{-1} (PEG_{200}) at v/v % concentrations of 0, 5, 10, 15 and 20%. PEG_{200} was chosen as the solvent because of its nonreactivity toward the sorbent and CO_2 as well as its low volatility and toxicity. The solubility of CO_2 in PEG_{200} at ambient pressure is very small [100]. The results showed that the concentration of CO_2 decreased from 405.03 to 343.91 ppm after 10 min CO_2 capture by 5% [DETAH][NO_3] in PEG_{200}. Hu *et al.* [85] investigated the CO_2 capture by two kinds of polyamine-based cation-functional ILs ([DETAH][Br] and [TETAH][HCOO]) in PEGs (PEG_{200}, PEG_{300}, and PEG_{400}) at the mass ratio was 1:4, and phase change was observed. The results showed that the CO_2 capacity decreased from 1.184 to 0.324 mol CO_2 per mol IL with the molecular weight of PEG increased from 200 to 400 at 20 °C and 1 bar. Furthermore, the mechanism of biphase formation in CO_2 capture systems was studied. During the chemical reaction of amine and CO_2 on polyamine-based cation, more and more amine groups being transformed into charged ammonium and carbamate groups, leading to the unstable cationic and anionic centers in PEG. Thus, the mixture changed from gel to aggregation. Subsequently, Hu and Huang *et al.* [101] studied the CO_2 capture by [TETAH][HCOO] + PEG_{200} mixed system. As the mass concentration of [TETAH][HCOO] increased from 20 % to 60 % in the [TETAH][HCOO]-PEG_{200} mixed system, the CO_2 absorption capacity decreased from 1.340 to 0.8226 mol CO_2 per mol IL at 25 °C and 1 bar *via* carbamate mechanism.

(2) Anion-functional ILs.

Amino-based anion-functional ILs. Han *et al.* [102] studied CO_2 capture by [Ch][Pro] in PEG_{200} with [Ch][Pro] to PEG_{200} weight ratios of 1:0, 1:1, 1:2, and 1:3. The results showed that the capacities of [Ch][Pro] + PEG_{200} with weight ratios of 1:1, 1:2, and 1:3 were all 0.59 mol CO_2 per mol IL at 50 °C and 1 bar, indicating that the gas was mainly absorbed by the IL *via* the strong 2: 1 (amine: CO_2) stoichiometry mechanism of reaction between the basic group in [Ch][Pro] and CO_2. However, the absorption and desorption rates increased with increasing content of PEG_{200} the in absorbent even at lower temperature. Different CO_2 absorption mechanism was reported by Cheong and Kim *et al.* [103], using tetramethylammonium ([N_{1111}]) salts bearing a *β*-amino acid anions in water, methanol, or EG (30 wt% IL). Their results showed that the absorption capacities of 0.97, 1.01 and 1.02 mol of CO_2 per mole of IL were obtained, respectively, at 40 °C and 1 bar, for [N_{1111}][*n*-BuNHEtCOO], [N_{1111}][*n*-Bu_2NEtCOO] and [N_{1111}][*n*-Bu_2NEtNHEtCOO] in methanol *via* the formation of methylcarbonate species in a 1:1 mechanism.

Amino-free anion-functional ILs. Zeng and Zhang *et al.* [104] reported the CO_2 chemisorption by dianionic-functionalized IL in EG with the mass ratios of 3:7, 4:6, 5:5, 6:4, and 7:3. The used dianionic-functionalized IL was [DBUH]$_2$[Dhyd]). Their results showed that the capacity of CO_2 increased from 0.07 to 0.11 g CO_2 per g absorbent with the [DBUH]$_2$[Dhyd]/EG mass ratios of 3:7 to 7:3 at 40 °C and 1 bar. However, increased content of EG could improve the CO_2 absorption rate. The results indicated that the CO_2 capacity may be attributed to the simultaneous reaction of CO_2 with both the $[Dhyd]^{2-}$ anion and deprotonated EG.

5.2.3. Functional IL + amine

Zhao and Liu *et al.* [105] reported four protic IL-amine blends for CO_2 capture, where [DMAPAH][Ac] and [DMAPAH][L] were selected ILs while EDA and DETA were selected amines. They found that [DMAPAH][Ac] + EDA mixture shows the CO_2 uptake of 0.260 and 0.295 g CO_2 per g absorbent under 1 bar and at 30 °C or 50 °C, respectively, *via* carbamate mechanism. In addition, the absorption rate also increased gradually with increasing temperature. The results indicated that the influence of mass transfer was larger than the temperature during CO_2 absorption.

5.2.4. Functional IL + alcohol + water

Hu *et al.* [85] showed that the CO_2 absorption capacity of [DETAH][Br] in PEG_{200} increased from 1.046 to 1.184 mol CO_2 per mol IL as the water content increased from 1.3 wt% to 4.7 wt% at 20 °C and 1 bar. Then the capacity slightly decreased when the water content increased to 6.5 wt%. The results indicated that water disrupted the anion-cation interaction and increased cation-CO_2 interaction, as well as the water content could change the hydrogen bond network in the mixture. Jing *et al.* [106] reported the dissolved dual-functional [TETAH][Lys] in ethanol:water solvent at different volume ratios to form a biphasic solvent for CO_2 capture. When the concentration of [TETAH][Lys] was 0.5 mol L^{-1} and the volume ratio of ethanol:water solvent was 4:6, the [TETAH][Lys] solution separated into two phases after CO_2 absorption, and the loading of the CO_2-rich phase was 2.0 mol CO_2 per mol ILs, which devoted about 93% of the total loading of the solution. The absorption mechanisms were CO_2 absorption into [TETAH][Lys] firstly formed carbamate, further hydrolyzed to HCO_3^-/CO_3^{2-}, and reacted with ethanol and formed the ethyl carbonate. Lv *et al.* [107] investigated another dual-functional IL [DETAH][Triz] which dissolved into a 1-propanol:water solvent to form a novel biphasic solvent for CO_2 capture. The rich phase kept 96% of the total CO_2 loading (1.713 mol mol^{-1}). The results indicated that the high CO_2 loading was originated from the multiple amino groups into [DETAH] cation and the equimolar reaction of [Triz] anion. 1-propanol and water ensured the high regeneration efficiency of the rich solution by enhancing the hydrolysis of $RNCOO^-$ to form HCO_3^-/CO_3^{2-} and propyl carbonate.

5.2.5. Functional IL + amine + water

(1) Cation-functional ILs.

Vijayaraghavan *et al.* [86] studied the CO_2 capture by the mixtures of protic IL + aqueous 30 wt% MEA, where ILs were [DMAPAH][HCOO] and [DMAPAH][octanoate] at different molar ratios of amine to acid. There results indicated the absorption capacity of [DMAPAH][HCOO] + 30 wt% MEA first increased and then decreased with the molar ratio of amine:acid increased while [DMAPAH][octanoate] + 30 wt% MEA increased with the molar ratio of amine:acid increased, may be due to the more polar nature of the [HCOO] anion to octanoate. Wu and Hu *et al.* [95] investigated the [DMAPAH][Ac] + MDEA + water mixture for the capture of CO_2. The results showed that CO_2 capacities of [DMAPAH][Ac] + MDEA + water with 70 wt% [DMAPAH][Ac] + MDEA were 2.50 and 2.74 mol kg^{-1} for different MDEA:IL molar ratios of 2 and 4, respectively, at 25 °C and 1 bar. The mechanism included intramolecular hydrolysis and intermolecular hydrolysis of MDEA with CO_2. Subsequently, Zhao and Liu *et al.* [105] reported that when adding water with a mass fraction of 20% in [DMAPAH][Ac] + EDA mixture, CO_2 uptake of 0.299 g CO_2 per g absorbent could be obtained at 50 °C and 1 bar. The mechanism study showed that bicarbonate formed after capturing CO_2 with [DMAPAH][Ac] + EDA + H_2O (20 wt%). Chen and Yu *et al.* [108] reported the CO_2 capture by a series of functional solutions based on [TETAH]-based ILs, [TETAH][Br], [TETAH][BF_4] and [TETAH][NO_3]. In their study, with PMDETA as a solute, CO_2 capacity of [TETAH][Br] + PMDETA + water system was 2.631 mol L^{-1} at 30 °C and 1 bar when the mole ratio of [TETAH][Br]:PMDETA was 3:7, and the concentration of IL + PMDETA was 4 mol L^{-1}. The improvement was due to the four amino groups in [TETAH][Br] and the promotion of tertiary amines in PMDETA.

(2) Anion-functional ILs.

Li *et al.* [109] synthesized four amino acid-based ILs, [N_{1111}][Gly], [N_{2222}][Gly], [N_{1111}][Lys] and [N_{2222}][Lys], then mixed with MDEA and water to form aqueous solutions for CO_2 capture. The results indicated that IL enhanced the absorption and increased the absorption rate of CO_2 in MDEA aqueous solutions. Higher absorption rate and larger uptake of CO_2 could be obtained by 15% IL and 15%, compared with other IL + MDEA solutions of 30% total amines. Li *et al.* [110] reported an aqueous blend of MEA and a hydrophilic amino acid IL [C_2OHmim][Gly]. The mole ratios of MEA to [C_2OHmim][Gly] in water were 1:0, 9:1, 8:2, 7:3, 6:4, 5:5, 3:7 and 0:1, respectively, and the optimum proportion of the blend was chosen as 0.7 mol L^{-1} MEA and 0.3 mol L^{-1} [C_2OHmim][Gly]. The results showed that the absorption capacities of

MEA solution and mixed solution was 0.430 and 0.534 mol CO_2 per mol absorbent, indicating that IL was utilized to enhance MEA process for CO_2 capture. Fu *et al.* [111] reported the absorption performance of (CO_2 + N_2) gas mixtures in amino acid ILs ([Bmim][Lys], [N_{1111}][Gly] and [Bmim][Gly]) promoted MDEA aqueous solutions with different concentrations. Their results showed that in the case of w_{MDEA} = 0.400 and $w_{[Bmim][Lys]}$ = 0.050, CO_2 capacity increased from 6.28 to 9.61 g CO_2 per 100 g aqueous solution at 40 °C when CO_2 partial pressure increased from 0.2 to 1 bar, indicating the mass of the absorbed CO_2 increased with increasing CO_2 partial pressure. Krawczyk *et al.* [112] reported several ternary IL-amines-water systems for CO_2 capture. Two ILs ([Bmim][Ac] and [Emim][$OcSO_4$]) and five amines (TMG, DBU, DABCO, triethylamine, and DEA) were used for preparing ternary sorbents. The sorption mechanisms were analyzed by NMR and included carbamate, imidazolium C2-CO_2, bicarbonate pathways.

5.2.6. Functional IL + amine + alcohol

Orhan *et al.* [113] reported that non-aqueous MEA (4 mol L^{-1}) + [Bmim][Ac] (1 mol L^{-1}) + hexanol blend exhibited higher absorption and desorption activities than MEA (5 mol L^{-1}) + hexanol. Their results showed that the absorption capacities of MEA + [Bmim][Ac] + hexanol and MEA + hexanol were 0.51 and 0.46 mol CO_2 per mol amine, respectively, at 30 °C and 2 bar, indicating the addition of the IL significantly improved the CO_2 absorption activity in the non-aqueous MEA solution. Additionally, the desorption results indicated that zeolite catalysts (HZSM-5, MOR, and FER) could enhanced the CO_2 desorption rate and reduced the desorption time.

5.2.7. Functional IL + IL mixtures

Due to the increased viscosity of neat functional ILs during the CO_2 capture and the non-volatile nature of ILs, mixed ILs prepared from a functional IL with CO_2-philic site and a conventional IL with low viscosity are investigated for CO_2 capture. Huang and Tao *et al.* [114] investigated the CO_2 capture by mixtures of amino acid-based IL ([Emim][Gly] or [Emim][Ala]) + [Emim][Ac] at the molar ratio 1:1. These ILs were both reported to absorb CO_2 *via* chemical interaction. However, the viscosity of former IL increased dramatically after absorption while that of latter IL with low viscosity did not increase dramatically. Thus, [Emim][Ac] as a diluent of amino acid IL in the mixture, leading to enhanced kinetics for CO_2 absorption. Their results showed that the CO_2 absorption capacity of [Emim][Gly] + [Emim][Ac] at 0.15 bar decreases from 2.05 to 1.30 mol kg^{-1} with the temperature increased from 25 to 80 °C. Wang *et al.* [115] reported the capture of CO_2 from flue gas (10 vol%) at high temperature by polyamine-based hybrid ILs, where functional ILs were [Li(DETA)][Tf_2N], [Li(TETA)][Tf_2N], and [Li(TEPA)][Tf_2N] while conventional ILs were [Li(TEG)][Tf_2N] and [Li(TTEG)][Tf_2N]. Their results showed that compared with the CO_2 capacity of neat [Li(TEPA)][Tf_2N] (0.72 mol mol^{-1}), the mole ratio of CO_2 to [Li(TEPA)][Tf_2N] was 1.95 when the weight ratio of [Li(TEPA)][Tf_2N] to [Li(TEG)][Tf_2N] reached 1:2 at 80 °C and 0.1 bar *via* carbamate mechanism (CO_2:amino = 1:2).

5.3. Summary of CO_2 capacities of IL-based other functional mixtures

Many kinds of IL-based other functional mixtures have been reported for CO_2 capture, and the capacities of CO_2 absorption were measured under different conditions. Table 3 shows the summarized CO_2 capacities of IL-based other functional mixtures in g CO_2 g^{-1} mixture, which is helpful to compare most of the absorption capacity data in order to develop novel IL-based CO_2-philic mixtures.

6. Key factors affecting CO_2 capture

The key factors that affect the efficiency of CO_2 capture by IL-based functional DESs and other mixtures can be classified into two groups: internal factors (functional groups and ratio of mixture ratios) and external factors (absorption temperature and CO_2 partial pressure).

6.1. Functional groups

Compared with conventional organic solvents, ethanolamine aqueous solutions and IL-based functional DESs or other functional mixtures, one can safely concluded that (1) functional groups with active CO_2-philic sites are most important for CO_2 capture with high efficiency, and (2) solvents containing ILs will result in high stability. The CO_2-philic sites are mainly N-sites from amino groups and azolate anions, O-sites from dehydrogenated water or alcohols and phenolate anions, and C-sites from carbenes. These active sites are mainly tethered on the anions, except amino groups, which could be tethered both on cations and anions. The interactions between these active sites and CO_2 are mainly direct interactions, cooperative interactions, and chelate interactions.

6.2. Mixture ratios

IL-based functional DESs and other functional mixtures are developed to overcome the high viscosity of pure ILs, especially functional ones. Compared with different CO_2 absorption performance of different IL-based functional DESs or other functional mixtures, the molar ratios of components in the mixture will affect the absorption capacity, and increase the components with active sites or cooperative sites will increase the absorption capacity. However, for functional aqueous solutions, the CO_2 capacity will first increase and then decrease with the increasing concentration of water. Thus, the mixture ratios should be optimized to not only increase the mass transfer of CO_2 but also maintain the concentration of the CO_2-philic sites in a reasonable range.

6.3. Absorption temperature and CO_2 partial pressure

Absorption temperature and partial pressure are two key factors that affect the gas sorption efficiency. From a thermodynamic point of view and based on the le Chatelier's principle and the Henry's law, low absorption temperature and high CO_2 partial pressure are most helpful for CO_2 absorption by IL-based functional DESs and other functional mixtures through chemical interaction and physical interaction, because the reaction between functional groups and CO_2 are exothermic. Generally, the temperature and CO_2 partial pressure in the flue gas from power plants after combustion, desulfurization, and heat transfer processes are 40 ~ 50 °C and 0.1 ~ 0.15 bar, respectively. Thus, efficient CO_2 capture under high temperature and low CO_2 partial pressure should be encouraged to develop.

6.4. Weight capacity vs. Molar capacity

Generally, there are two quantification methods used in different research studies to describe the capture efficiency, weight capacity and molar capacity. In order to identify which method is the main method used in literatures, the references in Table 2 and Table 3 have been checked. Although some of publications prefer to use weight capacity in g CO_2 g^{-1} solvent rather than molar capacity, most of research publications prefer to use molar capacity rather than weight capacity, because of two reasons, (1) the need for absorption mechanism study, and (2) considering the effect of inefficient ingredients in absorbents on weight capacity.

7. Conclusions and outlook

IL-based functional DESs and other functional mixtures for CO_2 capture in recent years have been systematically reviewed. Functional DESs based on IL salts include conventional IL salt + amine, conventional IL salt + HBD + superbase, functional IL salt + alcohol and functional IL salt + amine, while other functional mixtures based on ILs

Table 3
CO_2 capacities of IL-based other functional mixtures.

Absorbent	Composition	T (°C)	P (bar)	CO_2 Capacity (g CO_2 g^{-1} mixture)	Ref.
[Ch][Cl] + MEA + H_2O	molar ratio of IL:MEA = 1:5, 75% vol H_2O	20	0.6	0.608 [a]	[45]
[MEAH][Cl] + MEA + Gly	molar ratio of IL:MEA = 1:4, 30 wt% Gly	20	1	0.16	[48]
[MEAH][Cl] + MEA + EG	molar ratio of IL:MEA = 1:4, 10 wt% EG	20	1	0.225	[48]
[Bmim][BF_4] + MEA	mass ratio 7:3	25	1	0.1198	[75]
[Beim][BF_4] + MEA	mass ratio 7:3	25	1	0.1193	[75]
[Bmim][BF_4] + MDEA	mass ratio 7:3	25	1	0.0526	[75]
[Beim][BF_4] + MDEA	mass ratio 7:3	25	1	0.0517	[75]
[3-APH][TFA] + MDEA + H_2O	mass ratio 1:6:28	20	1	0.91[b]	[76]
[MDEAH][TFA] + MDEA + H_2O	mass ratio 1:4:20	20	1	0.93[b]	[76]
[C_2OHmim][Tf_2N] + DBU	molar ratio 1:1	20	1	1.04[b]	[77]
[C_2OHmim][Tf_2N] + MTBD	molar ratio 1:1	20	1	1.02[b]	[77]
[C_2OHmim][Tf_2N] + BEMP	molar ratio 1:1	20	1	0.81[b]	[77]
[$N_{ip,211}$OH][Tf_2N] + DBU	molar ratio 1:1	20	1	1.02[b]	[77]
[DMEDAH][Cl] + H_2O	molar ratio 1:1	20	1	0.27[b]	[83]
[DMEDAH][Ac] + H_2O	molar ratio 1:1	20	1	0.48[b]	[83]
[DMEDAH][Tf] + H_2O	mass ratio 4:1	20	1	0.35[b]	[83]
[TETAH][NO_3] + H_2O	mass ratio 2:3	15	1	1.49[b]	[84]
[TETAH][NO_3] + H_2O	mass ratio 6:4	15	1	1.05[b]	[84]
[DETAH][Br] + H_2O	mass ratio 1:4	20	1	0.868[b]	[85]
[DETAH][Br] + PEG_{200}	mass ratio 1:4	20	1	1.184[b]	[85]
[DETAH][Br] + PEG_{300}	mass ratio 1:4	20	1	0.868[b]	[85]
[DETAH][Br] + PEG_{400}	mass ratio 1:4	20	1	0.324[b]	[85]
[DETAH][Br] + PEG_{200}	mass ratio 98.7:1.3	20	1	1.046[b]	[85]
[DETAH][Br] + PEG_{200}	mass ratio 95.3:4.7	20	1	1.184[b]	[85]
[DMAPAH][EOAc] + H_2O	mass ratio 9:1	30	1	0.107	[87]
[DEEDAH][EOAc] + H_2O	mass ratio 9:1	30	1	0.056	[87]
[DMEDAH][EOAc] + H_2O	mass ratio 9:1	30	1	0.102	[87]
[Hmim][Gly] + H_2O	IL: 1 mol/L	30	0.15	0.45[b]	[88]
[Bmmim][Im] + H_2O	molar ratio 1:2	25	20	0.33[b]	[93]
[Bmmim][Im] + H_2O	molar ratio 1:10	25	20	0.92[b]	[93]
[Bmmim][Im] + H_2O	molar ratio 1:100	25	20	1.32[b]	[93]
[Bmmim][Im] + H_2O	molar ratio 1:1000	25	20	1.96[b]	[93]
[P_{4442}][Suc] + H_2O	mass ratio 96.7:3.3	20	1	1.90[b]	[40]
[P_{4442}][Suc] + H_2O	mass ratio 91.2:8.8	20	1	1.19[b]	[40]
[P_{4442}][Suc] + H_2O	mass ratio 82.4:17.6	20	1	0.92[b]	[40]
[DMAPAH][Ac] + H_2O	mass ratio 7:3	25	1	0.102	[95]
[DMAPAH][Ac] + MDEA + H_2O	n_{IL}:n_{MDEA} = 1:2, 30 wt% H_2O	25	1	0.11	[95]
[DMAPAH][Ac] + MDEA + H_2O	n_{IL}:n_{MDEA} = 1:4, 30 wt% H_2O	25	1	0.12	[95]
[TETAH][Pz] + H_2O	IL:0.5 mol/L	27	1	2.05[b]	[98]
[TETAH][Im] + H_2O	IL:0.5 mol/L	27	1	1.81[b]	[98]
[TETAH][Py] + H_2O	IL:0.5 mol/L	27	1	1.73[b]	[98]
[TETAH][Triz] + H_2O	IL:0.5 mol/L	27	1	1.50[b]	[98]
[TETAH][HCOO] + PEG_{200}	mass ratio 1:4	25	1	1.340[b]	[101]
[TETAH][HCOO] + PEG_{200}	mass ratio 3:2	25	1	0.8226[b]	[101]
[Ch][Pro] + PEG_{200}	mass ratio 1:1	50	1	0.59[b]	[102]
[Ch][Pro] + PEG_{200}	mass ratio 1:2	50	1	0.59[b]	[102]
[Ch][Pro] + PEG_{200}	mass ratio 1:3	50	1	0.59[b]	[102]
[N_{1111}][*n*-BuNHEtCOO] + H_2O	mass ratio 3:7	40	1	0.94[b]	[103]
[N_{1111}][*n*-Bu_2NEtCOO] + H_2O	mass ratio 3:7	40	1	0.95[b]	[103]
[N_{1111}][*n*-Bu_2NEtNHEtCOO] + H_2O	mass ratio 3:7	40	1	1.01[b]	[103]
[N_{1111}][*n*-BuNHEtCOO] + methanol	mass ratio 3:7	40	1	0.97[b]	[103]
[N_{1111}][*n*-Bu_2NEtCOO] + methanol	mass ratio 3:7	40	1	1.01[b]	[103]
[N_{1111}][*n*-Bu_2NEtNHEtCOO] + methanol	mass ratio 3:7	40	1	1.02[b]	[103]
[N_{1111}][*n*-BuNHEtCOO] + EG	mass ratio 3:7	40	1	0.96[b]	[103]
[N_{1111}][*n*-Bu_2NEtCOO] + EG	mass ratio 3:7	40	1	0.98[b]	[103]
[N_{1111}][*n*-Bu_2NEtNHEtCOO] + EG	mass ratio 3:7	40	1	1.03[b]	[103]
[DBUH]$_2$[Dhyd] + EG	mass ratio: 3:7	40	1	0.07	[104]
[DBUH]$_2$[Dhyd] + EG	mass ratio: 5:5	40	1	0.10	[104]
[DBUH]$_2$[Dhyd] + EG	mass ratio 7:3	40	1	0.11	[104]
[DMAPAH][Ac] + EDA	mass ratio 1:1	30	1	0.260	[105]
[DMAPAH][Ac] + EDA	mass ratio 0.5:1	30	1	~0.33	[105]
[DMAPAH][Ac] + EDA	mass ratio 1:0.5	30	1	~0.2	[105]
[DMAPAH][Ac] + EDA	mass ratio 1:1	30	0.1	0.207	[105]
[DMAPAH][Ac] + DETA	mass ratio 1:1	30	1	0.188	[105]
[DMAPAH][L] + EDA	mass ratio 1:1	30	1	0.233	[105]
[DMAPAH][L] + DETA	mass ratio 1:1	30	1	0.156	[105]
[DMAPAH][Ac] + EDA	mass ratio 1:1	50	1	0.295	[105]
[DMAPAH][Ac] + EDA + H_2O	mass ratio 2:2:1	50	1	0.299	[105]
[TETAH][Br] + PMDETA + H_2O	n_{IL}:n_{PMDETA} = 3:7, IL + amine: 4 mol L^{-1}	30	1	2.631[c]	[108]
[C_2OHmim][Gly] + MEA + H_2O	IL: 0.3 mol L^{-1} MEA: 0.7 mol L^{-1}	30	0.15	0.534 [a]	[110]
[Bmim][Gly] + MEA + H_2O	mass ratio: 0.05:0.4:0.55	40	0.2	0.0628	[111]
[Bmim][Gly] + MEA + H_2O	mass ratio: 0.05:0.4:0.55	40	1	0.0961	[111]
[Bmim][Ac] + MEA + hexanol	IL: 1 mol L^{-1} MEA: 4 mol L^{-1}	30	2	0.51 [d]	[113]
[Emim][Gly] + [Emim][Ac]	molar ratio 1:1	25	0.15	0.09	[114]
[Emim][Gly] + [Emim][Ac]	molar ratio 1:1	25	1	0.13	[114]
[Emim][Gly] + [Emim][Ac]	molar ratio 1:1	80	0.15	0.06	[114]
[Emim][Gly] + [Emim][Ac]	molar ratio 1:1	80	1	0.09	[114]
[Li(TEPA)][Tf_2N] + [Li(TEG)][Tf_2N]	mass ratio: 1:2	80	0.1	1.95[b]	[115]
[Li(TEPA)][Tf_2N] + [Li(TEG)][Tf_2N]	mass ratio: 1:2	80	1	2.05[b]	[115]
[Li(TEPA)][Tf_2N] + [Li(TEG)][Tf_2N]	mass ratio: 1:2	80	0.5	1.29[b]	[115]
[Li(TEPA)][Tf_2N] + [Li(TEG)][Tf_2N]	mass ratio: 1:2	80	0.038	0.83[b]	[115]

[a] mol CO_2 mol^{-1} (IL + MEA); [b] mol CO_2 mol^{-1} IL; [c] mol L^{-1}; [d] mol CO_2 mol^{-1} MEA.

include conventional IL + amine, conventional IL + superbase, conventional IL-based ternary mixtures, functional IL + alcohol, functional IL + amine, functional IL + water, functional IL + alcohol + water, functional IL + amine + water, functional IL + amine + alcohol, and functional IL + conventional IL. The classification is based on the reaction mechanism of active sites and CO_2. The absorption mechanisms of single or multiple carbamate and carbonate are discussed systematically in this critical review. The typical equimolar mechanisms include direct interaction with CO_2 and cooperative with CO_2, while typical multiple-molar mechanisms include multiple "equimolar", multiple "cooperative sites", and multiple "chelating sites". Through tuning the structures of functionalized ILs and the molar ratios of components in the DESs and other mixtures, regulating the interactions between active sites and CO_2 could be realized, and the efficient absorption of CO_2 with a high capacity, low energy consumption, and high reversibility could be reached. This review is benefit for researchers to obtain an overall

understanding of CO_2-philic functionalized DESs and other functional mixtures.

CCUS based on pure IL-technology is far from large-scale industrial application due to the high viscosity, low mass transfer, and high cost of pure ILs. Here, technologies using IL-based functional DESs and mixtures as sorbents will open a door to use ILs in large-scale industrial application for CO_2 capture. The following issues should be considered in the future investigations.

(1) Although complex mechanisms can also be present in pure ILs, such as physisorption and chemisorption with carbamate and carbonate species, the modulation of these mechanisms are maybe more complex in DESs or other mixtures due to the presence of more players.

(2) The CO_2 absorption capacity in mass ratio is better than that in molar ratio. Different from CO_2 capture by pure ILs, various components in IL-based functional DESs and mixtures all contribute to the absorption capacity. There by, using mol CO_2 per mol IL expression cannot accurately express the absorption mechanism, and it will also lead to confusion. It is important to investigate capture efficiency in mass absorption capacity or gravimetric capacity in order to better comparison and realize the competitive absorbents.

(3) Adhere to problem orientation, and combine theory with practice. It is well known that the conditions of CO_2 absorption from flue gas are harsh as the composition of flue gas is very complex. Except the high temperature and low CO_2 partial pressure, other compositions are SO_2, NO_x, water, ash, *etc*. There is still a big gap between laboratory research and industrial application. Thus, novel strategy and efficient CO_2 absorbents should be developed based on the real flue gas conditions. For example, a strategy for CO_2 absorption with high selectivity by IL-based mixtures is designing an IL-based bi-absorbent system, one absorbent with weak basicity for selective SO_2 removal while another one with strong basicity for selective CO_2 removal.

(4) Give equal attention to absorption and desorption. The regeneration of the IL-based functional DESs and functional mixtures is important and related to energetic consume and the absorption cost. Besides, compared to absorption capacity, the available absorption capacity or working absorption capacity is important. For example, the available capacity for aqueous 30 wt% MEA solution is only 0.3 mol CO_2 per mol MEA, while the theoretical absorption is 0.5 mol CO_2 per mol MEA [116].

Thus, continuously developing novel IL-based functional DESs and functional mixtures and systematically investigating the reaction mechanisms of CO_2 with active sites under real flue gas conditions are the main concerns of IL-based alternative CCUS technologies in order to realize large-scale application of ILs as well as economical and reversible absorption of CO_2.

CRediT authorship contribution statement

Yisha Xu: Data curation, Visualization. **Ruina Zhang:** Data curation, Visualization. **Ying Zhou:** Resources, Supervision. **Daqing Hu:** Formal analysis. **Chunliang Ge:** Resources, Formal analysis. **Wenyang Fan:** Formal analysis. **Biao Chen:** Validation. **Yaoji Chen:** Validation. **Wei Zhang:** Resources, Validation. **Huayan Liu:** Methodology, Formal analysis. **Guokai Cui:** Supervision, Conceptualization, Project administration, Funding acquisition, Investigation, Writing – original draft, Writing – review & editing. **Hanfeng Lu:** Resources, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

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