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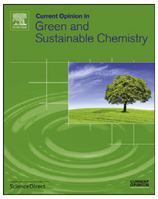

Review article

The development of carbon capture by functionalized ionic liquids

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A R T I C L E I N F O

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The CO_2 capture by functionalized ionic liquids developed in recent years was critically reviewed, where the relationship between the capacity and the enthalpy as well as that between the structure and the viscosity were discussed. This work reviews with special emphasis on tuning the basicity and designing the structure for improving absorption properties, such as adjusting the capacity and energy consumption, and decreasing the viscosity of ionic liquid. Subsequently, some unconventional absorption phenomenon was also set out detailed. Finally, the recent efforts in understanding CO_2 absorption and the future research directions were outlined.

1. Introduction

Up to now, energy conversion is based largely on the burning of fossil fuels—coal, oil, and natural gas. During these processes, carbon is released into the atmosphere in the form of gaseous carbon dioxide (CO_2), and 30 gigatons (Gt) of CO_2 is emitted per year as a result of the use of these fossil fuels at present [1,2]. As CO_2 is one of the most abundant greenhouse gas (GHG) [3], the emission of CO_2 has received worldwide attention because of its possible implications on environmental problems and pronounced ecosystem change [4]. Carbon dioxide capture and storage (CCS) is a technology aimed at reducing GHG emissions generated by the burning of fossil fuels during industrial and energy-related processes [5]. One of the most popular technologies for carbon capture is chemical absorption by aqueous solution of amine. In spite this absorption system has numerous advantages such as high reactivity, low cost and good absorption capacity, there are some serious inherent drawbacks including solvent loss, corrosion and high energy demand for regeneration when used.

Ionic liquid (IL) was born from the very fruitful activities in academic research field [6–20] and considered to be a promising alternative as absorbent attributing to their physical and chemical properties [21–31]. Davis [32] reported the first functionalized IL with amine group in cation for its affinity to CO_2. The results showed 0.5 mol CO_2 could be captured per mol of IL as two amines reacted with one CO_2 to form the carbamate and the ammonium. Later, Brennecke and her coworkers [33] reported the amine group in anion could react with CO_2 to produce the stable carbamic acid, and without the continued reaction with another amine group to carbamate salt. So, the capacity reach up to equimolar stoichiometry. There are lots of works about improving CO_2 absorption behavior [33–40], however, the chemisorption often has high capacity along with high absorption enthalpy, which means difficult desorption as well as extensive energy consumption for regeneration [41–45].

Furthermore, the applications of amine-based ILs were limited because of the dramatic increase in viscosity during CO_2 absorption [32,35,39,46,47]. Maginn [48] and Zhang [49] used a molecular dynamics simulation method and explained that the dramatic increase in viscosity was due to the formation of strong and dense hydrogen-bonded networks between the zwitterion and dication species during CO_2 capture by amino-tailored cation. The formation of density hydrogen-bond networks cause inconvenience for amino-based ILs as CO_2 absorbent because their viscosity would increase dramatically upon reaction with CO_2 and then transform into gel or solid-like substance, which restricts the mass transfer and limits their application in carbon capture. Goodrich [39] reported that the viscosity of amino-acid based ILs would increase by two orders of magnitude. In order to eliminate the problem on viscosity increase, some corresponding strategies were developed. Wu [50,51] designed phosphorous based ILs with very low viscosity through tuning the symmetry of ILs, however, the increase in

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viscosity was inevitable in CO_2 capture process. An efficient method for improving CO_2 capture was reported by non-amine functionalized ILs [44,45,52–54], whose viscosity were less affected upon the uptake of CO_2 because of the lacking formation of hydrogen bond whether before or after CO_2 capture. Wang [44,45,54] developed a series azole and phenolate based ILs with various basicity, it is interesting that the ILs' viscosities did not increase dramatically in the process of CO_2 absorption. Around the same time, Brennecke [52,53] reported the viscosities of ILs with substituted aprotic heterocyclic anions (AHAs) were insensitive to CO_2.

As mentioned above, mino- and non amino-based ILs were efficient functionalized absorbents for CO_2 capture, there were lots of strategies for improving their properties [18,55]. In this review, strategies developed to balance the capacity and energy consumption and the utilization of structure were reviewed. Tuning the basicity of ILs including enhancing the weaken interaction to increase capacity and weakening the strong interaction to decrease energy consumption, and designing the structures of functionalized moiety to improve the absorption behavior were reviewed particularly. (see Fig. 1)

2. Tuning the basicity

It can be seen from the Eq. (1) and (2) that Gibbs free energy is related to the equilibrium constant and the CO_2 capacity is according to the reaction enthalpy and entropy change during CO_2 capture process. Generally, the entropy change is regarded as a constant value of CO_2 from gas to fixed state, and the enthalpy change decides the CO_2 capacity.

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

$$\Delta G = -RT \ln K \tag{2}$$

ΔG: gibbs free energy, *ΔH*: reaction enthalpy, *T*: temperature used for CO_2 capture, *ΔS*: reaction entropy, *R*: perfect gas constant, *K*: reaction equilibrium constant.

2.1. Enhanced weak interaction

It is known that the proton in the C2 position (C2—H) on the imidazolium ring is acidic [42,56–59]. Therefore, CO_2 may be dissolved via forming hydrogen bonds at the C2 position [60–62]. However, the C2H containing ILs exhibit slightly higher solubilities of CO_2 at high pressure as above 70 bar because of the interaction between C2H and CO_2 is very weak [42,61–68]. In the case that the anion of imidazolium IL has the ability of catch hold of proton from C2-H, the imidazolium cation could form more basic carbene moiety from the delocalization of C2-H to anion [36–38,61,69,70]. However, the interaction between CO_2 and carbene is too strong to desorption, so more research about restraining carbene formation is needed.

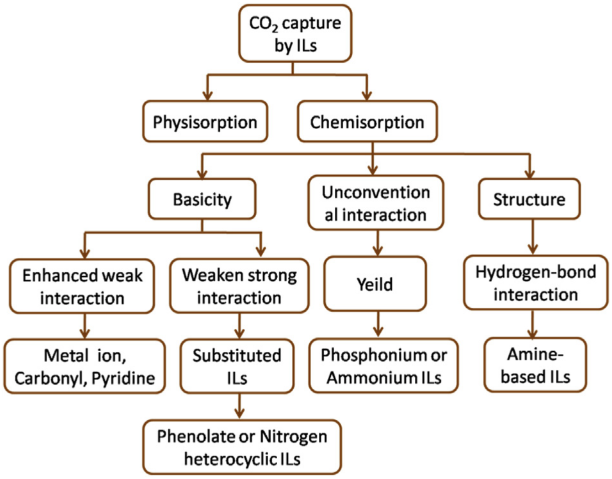

Fig. 1. Schematic representation of improving CO_2 capture by ILs through chemical property and structural design.

The anion of IL appears to be one of the major factors dominating CO_2 dissolution. Dynamic simulations and in-situ attenuated total reflection infrared spectroscopy study both demonstrate a Lewis acid-base interaction between CO_2 and the anion [71,72]. Therefore, enhancing the intermolecular interaction involving the fluorine atoms in the anion and CO_2 could improve CO_2 dissolution. Xing [73] proposed two effective ways to enhance the basicity of ILs such as weakening the cation-anion interaction strength and employing the anion-tethered strategy, which were instructive for improving the efficiency of CO_2 capture by acetate anion. The pyridine solvent can but dissolve 0.013 mol CO_2 per mol solvent [74] on account of the free volume, van de Waals forces, and the Lewis base-acid interaction between the N in pyridine and the O of CO_2. For the purpose of enhancing the interaction, our group [54] developed a strategy utilizing conjugation electric structure, such as 2-hydroxypyridine anion [2-Op], to increase the charge density of N as well as enhance the basicity of N by share the negative charge of oxygen. The results showed the N in [2-Op] anion, which paired with [P_{66614}] cation, had the ability capture CO_2 in the means of chemsorption due to the cooperation with phenolate anion. The [P_{66614}][2-Op] showed very high capacity as 1.58 mol/mol IL on the premise that phenolate anion kept its ability on CO_2 absorption. Although carboxylate anion can react with CO_2 efficiently, it would be deactivated by amino acids. Based on the dimemma of negative inductive effect of an amino group which reduces the alkalinity of carboxylate group, Dai [75] introduced electron-withdrawing sites to amino acid anion to activate carboxylate group. They used aminopolycarboxylate based amino acid IL with activated carboxylate group, the results demonstrated the [P_{4442}]$_2$[IDA] could capture CO_2 with an extremely high capacity as 1.69 mol/mol and with an additional benefit of little viscosity change because of non intermolecular hydrogen-bonded network formation.

2.2. Weaken chemisorption

One method to reduce the enthalpy of CO_2 absorption is tuning the basicity of the Lewis base, Wang [45] presented a strategy of tuning the enthalpy of CO_2 chemisorption by azole-based ILs. Their results showed a rough linear relationship between absorption enthalpy and the pKa value. The absorption enthalpies of [P_{66614}] Pyr] and [P_{66614}]Im] were as high as about −90 kJ/mol along with high capacities as about 1 mol CO_2 per mol IL, while the CO_2 capacity had a drop-off when absorption enthalpy at about −50 kJ/mol. Thus, the optimized CO_2 absolvent could select the one with lowest energy consumption from the candidates with high capacity. Tang [76] analyzed the reactivity of azole anions with CO_2 by DFT, the results demonstrated that adding the N or phenyl group in the anion could disperse the negative charge of N, which could mitigate the heat release of the reaction with CO_2. Jiang [43] evaluated CO_2 interaction with a series of oxygen-containing Lewis base anions such as cyclohexanolate and phenolate and their respective derivatives through computational analysis. The results showed the reactive properties can be tuned across a range from chemical to physical interactions along with the decrease of oxygen atom's charge, which was dominated by the substituent. Wang [44]