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A depth-suitable and water-stable trap for CO₂ capture†

Zhaofu Zhang, ^a Shuaishuai Liu, ^{ab} Jun Ma ^a and Tianbin Wu ^a

In terms of CO₂ capture and storage (CCS), it is highly desired to substitute of high efficiency process for the applied one which is far from the ideal one. Physical processes cannot capture CO₂ effectively, meanwhile CO₂ desorption is energy-intensive in chemical processes. Herein, a depth-suitable and water-stable trap for CO₂ capture was discovered. Carboxylates can react with polybasic acid roots by forming united hydrogen bonds. Carboxylate ionic liquid (IL) aqueous solutions can absorb one equimolar CO₂ chemically under ambient pressure, and its CO₂ desorption is easy, similar to that in physical absorption/desorption processes. When used as aqueous solutions, carboxylate ILs can replace alkanolamines directly in the applied CCS process, and the efficiency is enhanced significantly due to the low regenerating temperature. CO₂ (or polybasic acids) can be used as a polarity switch for ILs and surfactants. A new method for producing carboxylate ILs is also proposed.

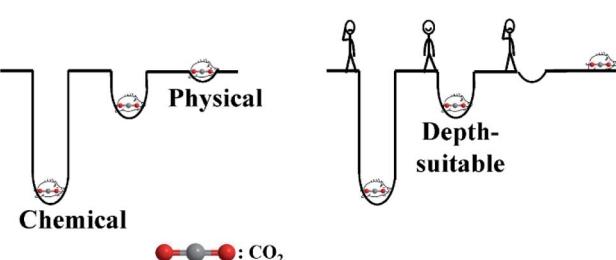
Being the main greenhouse gas, CO₂ capture and storage (CCS) is indispensable for achieving carbon neutrality, and it has been a hot topic for many years.¹ Besides CO₂ generated from the energy demand of human being's daily activities, energy requirement in CCS also produces more CO₂, which comes from fuel consumption, and this will lead to an increase in electricity prices.^{2,3} So, the enhancement of energy efficiency in CCS is highly desired. Alkanolamines are the main absorbents applied for CCS in industry, and their regeneration processes are energy intensive, as shown in Scheme 1 (chemical trap). There are more inherent shortages, such as amine degradation and volatilize, and hence, the CCS process applied in this study is far from the ideal one.

Having many unique features, such as extremely low vapor pressure, ionic liquids (ILs) have aroused the interest of many scientists,^{4–6} including their ability to absorb CO₂ physically.⁷ Physical absorption is conducted under high pressure and anhydrous conditions. There are several shortcomings as follows: the sorption capacity is limited at low pressure, water is invariably present in almost all ILs,⁸ CO₂ and water are the two main exhaust products in fossil fuel burning. It is difficult to get satisfactory results in physical absorption, as shown in Scheme 1. Functional ILs have also been tested for absorbing CO₂ (ref. 9 and 10) and SO₂ (ref. 11 and 12) chemically, and some authors claimed that the products obtained are carbamic acids or amides while absorbing CO₂. Recently, Dupont *et al.* considered that carbonates/

bicarbonates are generated because water is inevitable in most cases,⁸ and this is similar to the alkanolamine aqueous solution in the applied CCS process. The regeneration of those ILs is energy intensive, and the stronger the functional ILs used for absorbing CO₂, the more energy is needed in the regeneration process. The high viscosity of ILs is also unfavourable for capturing CO₂ effectively. Finding a depth-suitable trap (as shown in Scheme 1) with low viscosity and water-stability for CO₂ capture is highly desirable.

Various chemical reactions are going on at this moment in nature and our bodies, and many of them have been discovered and explained clearly.¹³ Most of them form new chemical bonds, including covalent bonds, ionic bonds, and metal bonds.¹⁴ In comparison, hydrogen bonding is a weak interaction that has been known for a century¹⁵ and has been redefined recently.¹⁶ Although weak, hydrogen bonds are vital for water keeping its state as we know generally¹⁷ and for life passing on its genetic code.^{18,19}

Herein, a depth-suitable and water-stable trap for CO₂ capture was discovered. Carboxylate roots can react with polybasic acid roots by forming united hydrogen bonds, and this



Scheme 1 Schematic diagram of a depth-suitable trap for CO₂ capture.

^aBeijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid and Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: zhangzf@iccas.ac.cn

^bSchool of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

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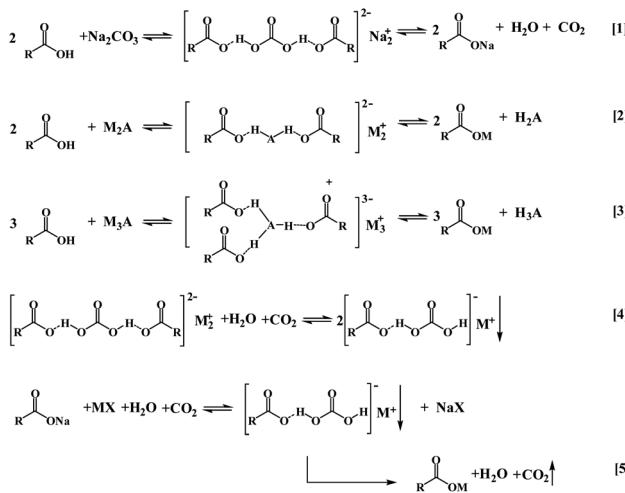


lower energy of the products make them more stable even in water. Carboxylate IL aqueous solutions can replace alkanol-amine aqueous solutions directly in the applied CCS process, and the efficiency is enhanced significantly, which comes from the low regenerating temperature. CO_2 (or polybasic acids) can be used as a polarity switch for ILs and surfactants. A new way for producing carboxylate ILs is also proposed.

Finding the trap

Strong acids reacting with weak acid salts to produce weak acids are classic reactions that are widely applied in industry. Most carboxylic acids, such as formic acid and acetic acid, are stronger than carbonic acid, and can react with carbonates to form carboxylates, CO_2 , and water. On the contrary, some carboxylates can absorb CO_2 under certain conditions.²⁰⁻²⁶ So, there must be an intermediate in this reaction, which is relatively stable under certain conditions. Bicarbonate is a reasonable explanation, and Yasaka *et al.* considered that bicarbonate is stabilized by a hydrogen bond with a carboxylic acid.²⁵ However, those systems are viscous and not stable in water, and the CO_2 sorption shrinks down sharply with an increase in water concentration.

In this study, 1 mole of sodium 2,2-dimethylbutyrate with 0.5 mol water could absorb 0.5 mol CO_2 under ambient conditions in one bottle. In another bottle, 2,2-dimethylbutyric acid and sodium carbonate (molar ratio of 2 : 1) were added and stirred, and there was no CO_2 bubbling out as the bottle was covered with a cap. Proportions of the 2,2-dimethylbutyrate root, sodium ion, and carbonic acid (CO_2 plus H_2O) in the two bottles are the same, so it is reasonable to consider that the structure of the products from the left and right sides of eqn (1) (in Scheme 2) are the same, and the product has a lower energy level than the reactants of two sides of the reaction under certain conditions. It is an equilibrium reaction, and the equilibrium will shift to the right side by moving CO_2 out or adding water. The stability of the intermediate varies with carboxylate anions. As the caps of the bottles are opened, the CO_2 release



Scheme 2 Reactions between carboxylates and polybasic acid roots. M represents inorganic or organic cation.

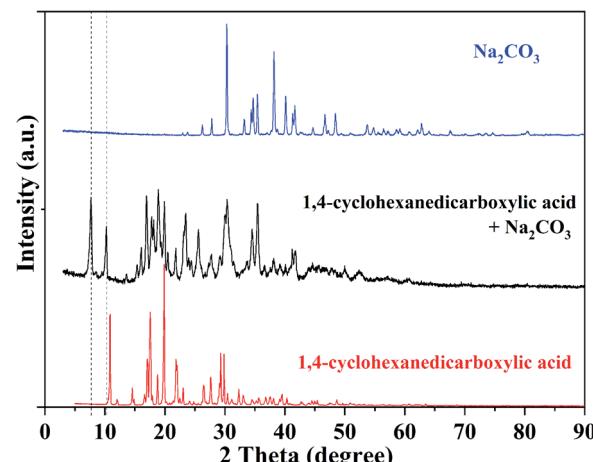


Fig. 1 Powder XRD patterns of 1,4-cyclohexanedicarboxylic acid + Na_2CO_3

rate from formic acid and sodium carbonate is faster than that from acetic acid and sodium carbonate. X-ray diffraction (XRD) and infrared radiation (IR) analysis results of the product of sodium carbonate reacting with 1,4-cyclohexanedicarboxylic acid are shown in Fig. 1 and S1a,[†] respectively. The results show that the product is different from both the reactants. The new peaks at 7.7° and 10.3° in XRD indicate that an ordered structure is formed between the two reactants.

The stability of the intermediates also varies with different cations, including inorganic and organic cations. Tributylhexylphosphonium 2-ethylhexanoate (**1**) is a hydrophilic IL and miscible with water. When **1** is selected as the carboxylate in eqn (1), the product after the absorption of CO₂ is stable in water, and the sorption remains constant with water being added. When the aqueous solution (50 wt%) is exposed to the CO₂ atmosphere, a new liquid phase appears during the absorption of CO₂, as shown in Fig. 2, and the sorption is 0.49 mol CO₂ per mol IL under ambient temperature. This suggests that the sorption of CO₂ changes the polarity of the reaction system and induces product separation from water.

With the above understanding, we proposed that there are two hydrogen bonds in the intermediates of eqn (1), and the two united hydrogen bonds tie two carboxylate roots and one carbonate root together, as shown in the spatial conformation

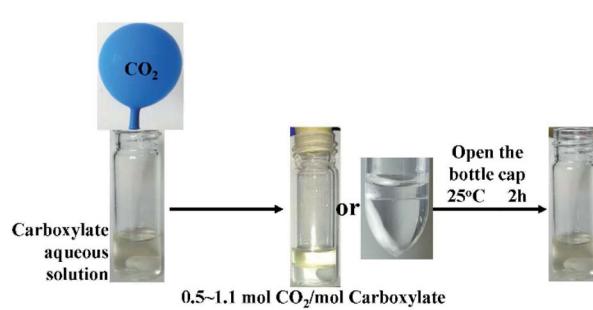


Fig. 2 Phase behaviour of some carboxylate IL aqueous solutions with or without CO_2 .

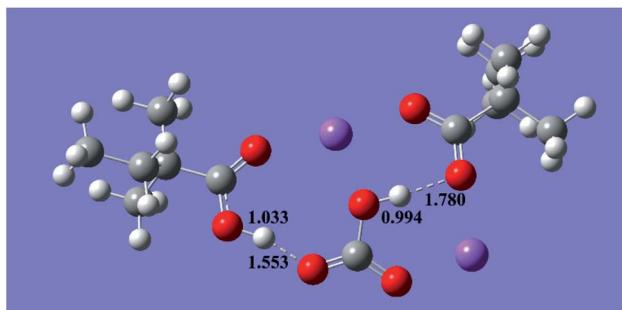


Fig. 3 Spatial conformation of the product from 2,2-dimethylbutyric acid + Na_2CO_3 obtained from DFT calculation.

obtained from DFT calculation (see Fig. 3 and S2a, b[†]). The united hydrogen bonds lower the energy of the products and enhance their stabilities even in an aqueous solution. The united hydrogen bonds also change the polarity of the product and cause its separation from water.

Reaction of carboxylates with other polybasic acid roots

This reaction is also tested with sulfur dioxide (SO_2), hydrogen sulfide (H_2S), and phosphoric acid, and they can all react with an aqueous solution of **1** and form two liquid phases. The top phase of aqueous solution **1** absorbing SO_2 was tested with ^1H NMR spectroscopy (Fig. S3[†]), and the results show that tributylhexylphosphonium ions and 2-ethylhexanoate ions in the top phase are equimolar. This implies that the top organic phase separating from the aqueous solution is not 2-ethylhexanoic acid, which may come from 2-ethylhexanoate ions reacting with sulfite acid. Some products of 1,4-cyclohexanedicarboxylic acid and 1,3,5-benzenetricarboxylic acid reacting with sodium sulfite and dipotassium hydrogen phosphate were tested with XRD (Fig. S4a-c[†]), IR spectroscopy (Fig. S1b and c[†]), and scanning electron microscopy (SEM, Fig. S5a-d[†]). XRD and IR analysis of the products indicate that the products are different from the raw reactants, and new ordered structures are generated. The SEM images show the shapes of those products, and there is one kind of substance in each photo, while not mixture of two reactants. This represents the reactants reacting with each other and forming new products. The products from 1,3,5-benzenetricarboxylic acid + K_2HPO_4 (Fig. S5a[†]) and 1,3,5-benzenetricarboxylic acid + Na_2SO_3 (Fig. S5d[†]) are sheets, and this implies that the united hydrogen bond products from 1,3,5-benzenetricarboxylic acid are ready to form a sheet. The shapes of products from 1,4-cyclohexanedicarboxylic acid + K_2HPO_4 (Fig. S5c[†]) and 1,4-cyclohexanedicarboxylic acid + Na_2SO_3 (Fig. S5b[†]) are different. It is seen from the four images that the shape varies with the type of carboxylate acids and salts. The spatial conformations of sulfite acid and H_2S reacting with **1** from DFT calculation (Fig. S2c and d[†]) show that there are two hydrogen bonds in both of their products.

The product of tripotassium phosphate reacting with 1,4-cyclohexanedicarboxylic acid was tested with XRD (Fig. S4d[†])

and SEM (Fig. S5e[†]). The product of tripotassium phosphate reacting with 1,3,5-benzenetricarboxylic acid was tested using IR spectroscopy (Fig. S1d[†]). The results demonstrate that the product is different from that of dipotassium hydrogen phosphate plus carboxylate acid. This means that carboxylate roots can react with phosphate root in two ways. One is two carboxylate ions combining with one hydrogen phosphate ion, and forming two hydrogen bonds (Fig. S2e[†]). The other is three carboxylate ions combining with one phosphate ion, and forming three hydrogen bonds (Fig. S2f[†]).

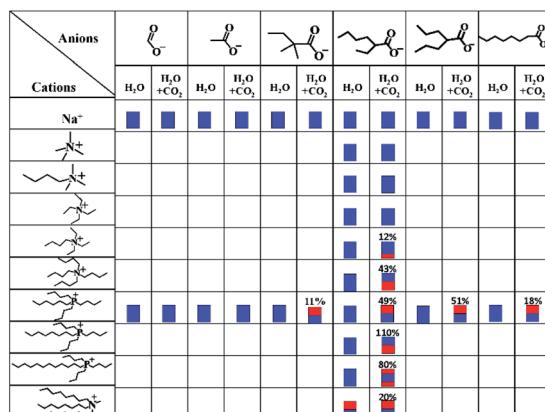
In order to show the reaction clearly, the general equations are given as eqn (2) and (3). The united hydrogen bonds enhance the stability of the products as in DNA,¹⁹ and some of them are stable in water. The united hydrogen bonds tie two or three carboxylate ions together, and this induces different polarities of the products with reactants.

Influence of different anions and cations

The influence of different anions and cations on the system of carboxylates absorbing CO_2 in water was studied and listed in Table 1. When the salts are strongly hydrophilic, such as sodium carboxylates, they are soluble in water, and there is no change in the phase behaviour of their aqueous solutions with the addition of CO_2 . When the carboxylate ILs have suitable hydrophilicity, they are miscible with water, and new phases appear in their aqueous solutions with the addition of CO_2 . Some of them form new liquid phases, and some others form solid phases, as shown in the table. CO_2 sorption in the systems forming two phases was measured and marked in the table. For tributylhexylphosphonium aqueous solutions, there are four anions that can form a new liquid phase with the addition of CO_2 . For **1** and tributylhexylphosphonium 2-propylpentanoate, CO_2 sorption is about 0.5 mole per mol IL, and this implies that these two ILs can form stable, united hydrogen bonds in water. For tributylhexylphosphonium 2,2-dimethylbutyrate and tributylhexylphosphonium *n*-octanoate, the sorptions are 0.11 and 0.18 mol CO_2 per mol IL, respectively. This indicates that the united hydrogen bonds in their products are not stable, resulting from the strong hydrophilicity of anions.

When the anion of ILs are selected as 2-ethylhexylate, several IL aqueous solutions form solids with the addition of CO_2 , and there are great differences in CO_2 sorption. For tributyl-*n*-octylphosphonium-2-ethylhexylate (**2**), the sorption of CO_2 can get to 1.1 mole per mol **2**. During CO_2 absorption by the aqueous solution of **2**, a state of liquid–liquid–solid was found, as shown in Fig. 2. The three-phase state was also found in the CO_2 release of **2** + H_2O + CO_2 system. A liquid–liquid state was found in this system, absorbing CO_2 at 80 °C. All these findings suggest that the united hydrogen bond product shown in eqn (1) is an intermediate, and it reacts with CO_2 and water further and generates the solid as shown in eqn (4). The solid is the crystallization of the product with some more carbonic acid. The solid has lower energy than the liquid united hydrogen bond product shown in eqn (1) and can tie more CO_2 . The



Table 1 Phase behaviour of carboxylate aqueous solutions with/without CO_2 ^a

^a For sodium carboxylate aqueous solutions, the concentrations are 10 wt%; for carboxylate ILs, weight ratios of IL: water are 1 : 1. Blue represents the water phase, and red represents the organic phase. The organic phase below water represents the solid depositing out. Numbers present CO_2 sorption (on carboxylates) under ambient pressure and temperature.

energy change may come from crystallization, which forms new hydrogen bonds.²⁵ So, this reaction step is a part of the united hydrogen bond reaction. For tributyl-*n*-dodecylphosphonium-2-ethylhexylate (**3**) aqueous solution, after it reacts with CO_2 for 12 h, beside the solid, there is also a little organic liquid phase in the system (liquid–liquid–solid state), and this shows that the solid of **3** + CO_2 + H_2O is not as stable as the solid of **2** + CO_2 + H_2O . For aqueous solutions of triethyl-*n*-butylammonium-2-ethylhexylate and tetrabutylammonium-2-ethylhexylate, there is no liquid–liquid–solid state observed during the absorption of CO_2 . It means that the united hydrogen bond products formed from the reaction between these two ILs and carbonic acid do not have enough hydrophobicity to separate from water, but further react with carbonic acid and form solids. Yet, they are more hydrophilic than **2**, so only a part of them is deposited.

When ILs are strongly hydrophobic, such as methyl-trioctylammonium 2-ethylhexanoate (**4**), it is immiscible with water at room temperature. Two liquid phases appeared as **4** is mixed with the same weight of water, and there is no change in the phase behaviour of its water mixture with or without CO_2 . The CO_2 sorption is 0.2 mole per mol of **4**. The sorption of CO_2

in **4** with equimolar water is 0.52 mole per mol IL, as determined in this work. The difference may come from the ability of **4** combining more water than equimolar, and the combined water influences the stability of the united hydrogen bonds, so its CO_2 sorption declines with the addition of water.

Utilization of the united hydrogen bond reaction

As mentioned above, aqueous solutions of carboxylate IL can be used for CO_2 absorption with relatively low viscosity. For IL **1** and **2**, their aqueous solution (50 wt%) can absorb 0.49 and 1.1 mol CO_2 per mol IL, respectively, under CO_2 atmosphere. High temperature is unfavorable for CO_2 sorption. When the temperature rises to 80 °C, the sorption of atmospheric CO_2 with an aqueous solution of **1** and **2** can obtain 0.31 and 0.30 mole per mol IL, respectively. For real flue gas, CO_2 may be diluted by nitrogen gas, and its partial pressure will be lower than 1 bar. In this work, we test the CO_2 absorption of simulated flue gas with CO_2 partial pressure 0.1 bar, and the sorption for aqueous solutions of **1** and **2** (50 wt%) are 0.20 and 0.25 mol CO_2 per mol IL, respectively.

The regeneration of IL solution only requires opening the bottle cap at room temperature for 2 h, as shown in Fig. 2. The CO_2 absorbed in the IL aqueous solutions is tied only by two united hydrogen bonds, and the trap of united hydrogen bonds is depth-suitable for CO_2 capture, as shown in Scheme 1. On the one hand, it has enough power to capture CO_2 effectively under relatively high temperature and low pressure in an aqueous solution. On the other hand, its CO_2 -desorption process is easy, similar to that in physical-absorption processes. The comparison of the CO_2 capture efficiency between carboxylate ionic liquid in this work and monoethanolamine (MEA) applied in industry are shown in Table 2. It can be seen that the CO_2 capture efficiency is significantly enhanced. When used as an aqueous solution, carboxylates can replace alkanolamines directly in the CCS process.

The united hydrogen bond reaction can also be used to absorb SO_2 and H_2S , as aforementioned. Many previous works on absorbing CO_2 and SO_2 with carboxylates need to take this united hydrogen bond reaction mechanism into consideration.

Jessop *et al.* have reported a kind of CO_2 switchable ILs and surfactants.^{27,28} In their works, CO_2 reacts with organic bases

Table 2 Comparison of the CO_2 capture efficiency between carboxylate ionic liquid in this work and MEA

	Carboxylates	MEA ²³
Content in water	50 w%	30 w%
CO_2 absorption	1 bar: ~1.1 mol L^{-1} , 0.1 bar: ~0.25 mol L^{-1}	3.5 mol L^{-1}
Regenerating temperature	Room temperature	120 °C
Chemical structure to be broken in regeneration	Two hydrogen bonds	$[\text{HOCH}_2\text{CH}_2\text{NH}_3]^+\text{HCO}_3^-$ to $\text{HOCH}_2\text{CH}_2\text{NH}_2 + \text{CO}_2 + \text{H}_2\text{O}$
Need of extra energy for water evaporation	No	Yes
Volatile, decompose	No	Yes



generating carbonates and dicarbonates, and the organic solvents transform from nonpolar to polar. In this work, the united hydrogen bond reaction could change the polarity of carboxylate systems, and they can be used as switchable solvents and surfactants. A series of carboxylate ILs were found that can be separated from water and form a new liquid phase with the addition of CO_2 or other polybasic acids ($\text{SO}_2 + \text{H}_2\text{O}$, H_3PO_4 , etc.). CO_2 can be released at room temperature in a short time, and it will be miscible with water again. Selecting long-chain tetraalkylammonium carboxylates and tetraalkylphosphonium carboxylates as surfactants and switching their polarities by CO_2 may realize the separation of surfactants from water or other solvents. For tributylhexadecylphosphonium ion, it can be separated out with 2-ethylhexanoate root from aqueous solution by dissolving tributylhexadecylphosphonium bromide and sodium 2-ethylhexanoate, even at a concentration of 1 wt%, in several minutes with CO_2 bubbling (Fig. S6†). The separation process is reversible. The mixtures are miscible again and become clear in three minutes as they are exposed to air. This process can separate tetraalkylphosphonium (tetraalkylammonium or other ions) carboxylates from water (solid or a new liquid phase) and leave the corresponding ions in water as shown in eqn (5), and so it provides a new way for producing carboxylate ILs.

Conclusions

In summary, we discovered a depth-suitable and water-stable trap for CO_2 capture that can replace the one currently in use, and the efficiency is significantly enhanced. Carboxylates can react with polybasic acid roots by forming united hydrogen bonds, and the united hydrogen bonds enhance the stability of the products even in aqueous solution. Some united hydrogen bond carbonates can interact with CO_2 and water further and form water-stable solids. It can be used to capture acidic gases (CO_2 , SO_2 , and H_2S) chemically. The CO_2 sorption can exceed one equimolar for carboxylates under ambient pressure. Having suitable heats of absorption, carboxylates can absorb CO_2 chemically, and its CO_2 -desorption process is easy, almost like that in physical absorption/desorption processes. CO_2 (or other polybasic acids) can be used as a polarity switch for carboxylate ionic liquids and surfactants. This reaction also provides a new method for producing carboxylate ILs.

Author contributions

Z. Z. proposed the idea, performed most experiments and wrote the manuscript. S. L. and T. W. performed the characterization. J. M. conducted DFT calculations.

Conflicts of interest

There are no conflicts to declare.

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