Liquid amine–solid carbamic acid phase-separation system for direct capture of CO_2 from air

Corresponding author

Prof. Seiji Yamazoe

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

E–mail address: yamazoe@tmu.ac.jp

List of authors

Soichi Kikkawa[a,b,c], Kazushi Amamoto[a], Yu Fujiki[a], Jun Hirayama[a,b], Gen Kato[d], Hiroki Miura[b,c,d], Tetsuya Shishido[b,c,d], and Seiji Yamazoe[a,b,c,e*]

Affiliations and full postal addresses

a. Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo, 192−0397, Japan
b. Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto, 615−8245, Japan
c. Research Center for Hydrogen Energy-Based Society, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192−0397, Japan
d. Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo, 192−0397, Japan
e. Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8, Honcho, Kawaguchi-shi, Saitama 332-0012, Japan

Abstract

The phase separation between a liquid amine and the solid carbamic acid exhibited >99% CO_2 removal efficiency under a large-scale gas stream of 400 ppm CO_2. Isophorone diamine [IPDA; 3-(aminomethyl)-3,5,5-trimethylcyclohexylamine] reacted with CO_2 in the CO_2/IPDA molar ratio of ≥ 1 even in H_2O as a solvent. The captured CO_2 was completely desorbed at 333 K because the disolved carbamate ion releases CO_2 at low temperature. The reusability of IPDA under CO_2 adsorption-and-desorption cycles without degradation, the >95% efficinecy kept for 100 hours under direct air capture condition, and high CO_2 capture rate (214 mmol/h for 1 mol amine) suggest that the phase separation system using IPDA is robust and durable for practical use.

Introduction

Reducing the concentration of carbon dioxide (CO_2) in the atmosphere is becoming essential for building a sustainable society because an increase in the atmospheric concentration of CO_2 is closely linked to global warming and climate change.[1] Reduction of atmospheric CO_2 levels will require a concerted effort to both limit future emissions of CO_2 and to implement strategies for decreasing the existing atmospheric concentration of CO_2. Artificial storage of CO_2 through direct injection into underground strata or the oceans is relatively well established and has attained plant-level operation;[2, 3] however, such carbon capture and storage techniques involve the risk of subsequent CO_2 leakage. On the other hand, the utilization of CO_2 as a value-added product by carbon capture and storage (CCS) is expected to provide a potential strategy for maintaining net CO_2 emissions at zero.[4-7] However, the existing CCS technology

requires further development to improve the CO_2 absorption/desorption efficiency of sorbents and to establish methods for subsequent conversion of captured CO_2.

Among CCS techniques, the sorbents for capturing atmospheric <500 ppm of CO_2 without any condensation and separation, known as direct air capture (DAC), is a promising technology and desired to operate under a large stream of ambient or low-pressure compressed gas.[7-9] The challenges in the sorbents for DAC techniques is high absorption efficiency of low-concentration CO_2, because the existing CCS techniques have insufficient absorption efficiency to perfectly remove the low-concentration CO_2. In addition, the desorption of the adsorbed CO_2 should require as little energy as possible; currently, the most-well-established sorbent, 2-aminoethanol (monoethanolamine; MEA), requires a temperature of >473 K for efficient desorption.[6, 10-12] Finally, the reusability and durability of the sorbents for use in CO_2 capture-and-desorption cycles is required to reduce the frequency of their regeneration and/or replacement. An ideal sorbent should be easily separated and collected from the absorption apparatus for subsequent regeneration.

To satisfy these demands, a number of solid amine-based sorbents[13-19] and CO_2-absorption systems that utilize phase separation[20-27] have been developed. The ability of homogeneous liquid-phase systems to absorb CO_2 has been improved by modifying the structures of the amine sorbents. For example, Inagaki *et al.* reported that the introduction of the hydrophobic phenyl group into alkylamines enhances their CO_2-absorption ability through the formation of a liquid bilayer structure.[28] Hanusch *et al.* discovered that pyrrolizidine-based diamines showed more-efficient CO_2 capture than does conventional MEA (**Fig. 1A-a**).[29] Although these are promising sorbents for CO_2 capture and desorption, further improvements in the rate of CO_2 absorption and more efficient

absorption at low CO_2 concentrations are required. Liquid–liquid phase-separation of amine–H_2O mixtures with lower critical solution temperatures have recently been developed to reduce the costs of regenerating the sorbent (**Fig. 1A-b**).[23, 30, 31] After CO_2 absorption, the organic and aqueous phases in these phase-change systems are immiscible, of which CO_2-rich aqueous phase are suitable to concentrate CO_2 by heating.[23] Such systems have achieved higher CO_2 capacities and lower costs compared with those of conventional MEA sorbent-based systems.[30] However, the solvents used in the phase-change systems are volatile and corrosive, limiting their range of operating conditions. Actually, the abovementioned systems were evaluated in static systems under ambient or high-pressure CO_2. To establish an efficient system for the large-scale streams of low-concentration CO_2, new concepts for sorbents are required.

According to the proposed carbamate mechanism of MEA [$2R^1R^2NH(l) + CO_2(g) \rightarrow R^1R^2NCOO^-(l) + R^1R^2NH_2^+(l)$], the produced carbamate ion inhibits the forward reaction.[32] Liquid–solid phase separation provides a possible way of overcoming the equilibrium limitations that inhibits the efficient CO_2 absorption. If the products from the absorption of CO_2 are solids, their equilibrium concentration in the liquid phase will remain low, thus leading high absorption rate of CO_2 into the liquid phase. Moreover, as another benefit, liquid sorbents contact dissolved CO_2 much more efficiently than do solid sorbents, which allow efficient absorption of low-concentration CO_2 from large-scale gas streams. Same liquid–solid phase separation systems have been reported up to now under high concentrated CO_2 conditions using potassium prolinate,[26] bis(iminoguanidine),[24] and triethylenetetramine with polyethylene glycol.[22] A DAC system using liquid–solid phase separation with an iminoguanidine-based sorbent for CO_2 has recently been reported (**Fig. 1A-c**).[25] Although CO_2 desorption from the CO_2-incorporated crystal
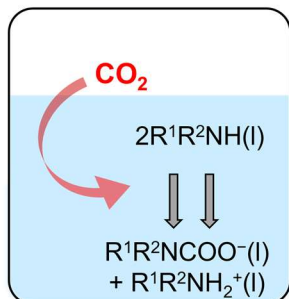
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began at 333 K, complete CO_2 release required high temperatures above 393 K. In addition, this system requires a large amount of solvent because of low solubility of the sorbent. Custelcean *et al*. recently developed DAC system using amino acid potassium solution followed by the reaction with guanidine compound resulting in crystallization of insoluble carbonate salt.[20, 21] These systems could remove CO_2 from air, but the system requires sequential CO_2 transfer system. Further research is therefore required to develop a versatile and simple solid–liquid separation system that are suitable for ambient CO_2 absorption and that lead efficient CO_2 desorption at low temperatures.

Here, we focus on carbamic acids that exist as a minor-route intermediates $[R^1R^2NH (l) + CO_2(g) \rightarrow R^1R^2NCOOH(l)]$.[32, 33] Especially, the carbamic acids that have low solubility compared with corresponding liquid amines are promising to solidification. If a liquid amine forms a solid carbamic acid by reaction with CO_2 $[R^1R^2NH(l) + CO_2(g) \rightarrow R^1R^2NCOOH(s)]$, an efficient CO_2 absorption system might be established due to the liquid–solid phase separation and the high amine-utilization efficiency (a 1:1 CO_2-to-amine ratio) (**Fig. 1A-d**). Especially, this liquid–solid phase change with carbamic acid formation would lead high absorption rate of CO_2 even at a low CO_2 concentration and large stream, which could not be achieved by using the existing CO_2 absorption systems. Furthermore, in the desorption system under heating, the increase in solubility of solid carbamic acids would aid the efficient desorption of CO_2.
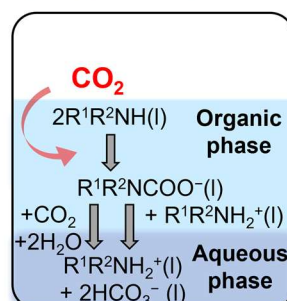
We investigated a number of amine compounds to prove our hypothesis. First, we evaluated their CO_2 removal efficiency in a flow system under a large stream of ambient CO_2 (**Fig. 1B**). We found that cyclohexyldiamines showed the best properties as liquid–solid phase-separation sorbents. In particular, isophorone diamine [IPDA; 3-(aminomethyl)-3,5,5-trimethylcyclohexylamine] exhibited a superior CO_2 absorption

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efficiency under a wide range of CO_2 concentrations (400 ppm to 30%) in a N_2 stream, with solidification of the corresponding carbamic acid. The highly efficient CO_2 removal liquid–solid phase-separation phenomenon was observed in various solvents including H_2O. Moreover, this carbamic acid discharged CO_2 at a lower temperature than a conventional MEA-based system and it exhibited remarkable reusability. This benchmark study is the first demonstration of a potential large-stream DAC system with >90% CO_2 removal efficiency and reusability that is based on the phase separation between a liquid amine sorbent and a solid carbamic acid.
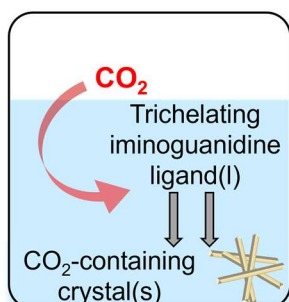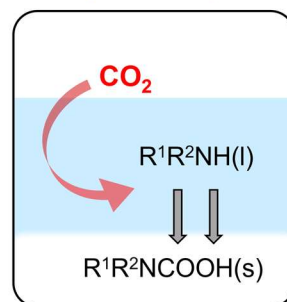
(A-a)
A typical carbamate mechanism (single phase)

CO_2

$2R^1R^2NH(l)$

$R^1R^2NCOO^-(l)$
$+ R^1R^2NH_2^+(l)$

(A-b)
Immiscible organic–aqueous liquid-phase separation

CO_2

$2R^1R^2NH(l)$ **Organic phase**

$R^1R^2NCOO^-(l)$
$+CO_2$ $+ R^1R^2NH_2^+(l)$
$+2H_2O$
$R^1R^2NH_2^+(l)$ **Aqueous phase**
$+ 2HCO_3^-(l)$

(A-c)
Phase separation between liquid amine and CO_2-containing crystal

CO_2
Trichelating iminoguanidine ligand(l)

CO_2-containing crystal(s)

(A-d)
Phase separation between liquid amine and solid carbamic acid (This work)

CO_2

$R^1R^2NH(l)$

$R^1R^2NCOOH(s)$

(B)

Online FT/IR analyzer

Mass flow controller

Low-concentration CO_2 (400ppm)

Amine + DMSO

IR beam   Detector
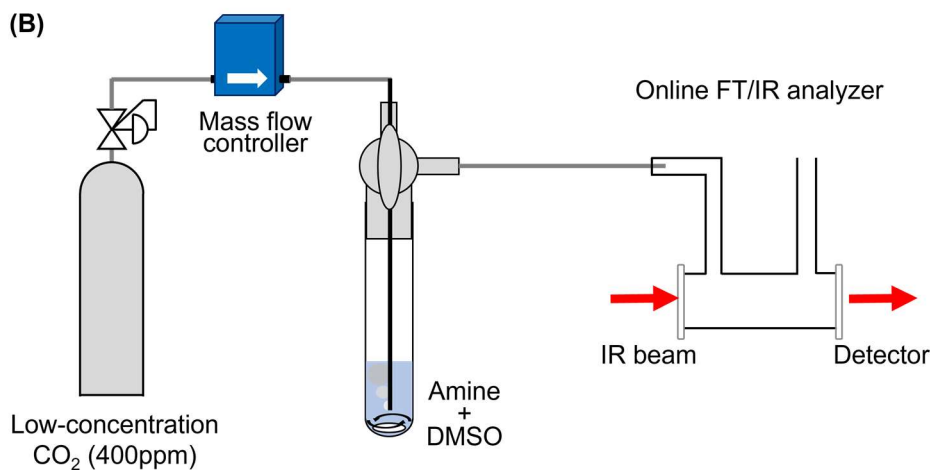
Fig. 1(A) CO_2 absorption/desorption system using phase separation. (a) a typical carbamate mechanism (Ref. 32). (b) Liquid–liquid phase-change solvents (Ref. 23). (c) Liquid–solid phase separation with an iminoguanidine-based sorbent (Ref. 25). (d) Liquid–solid phase separation with solid carbamate acid formation (This work). **(B)** An ambient-flow-type reactor equipped with online FT/IR analyzer for direct air capture system.
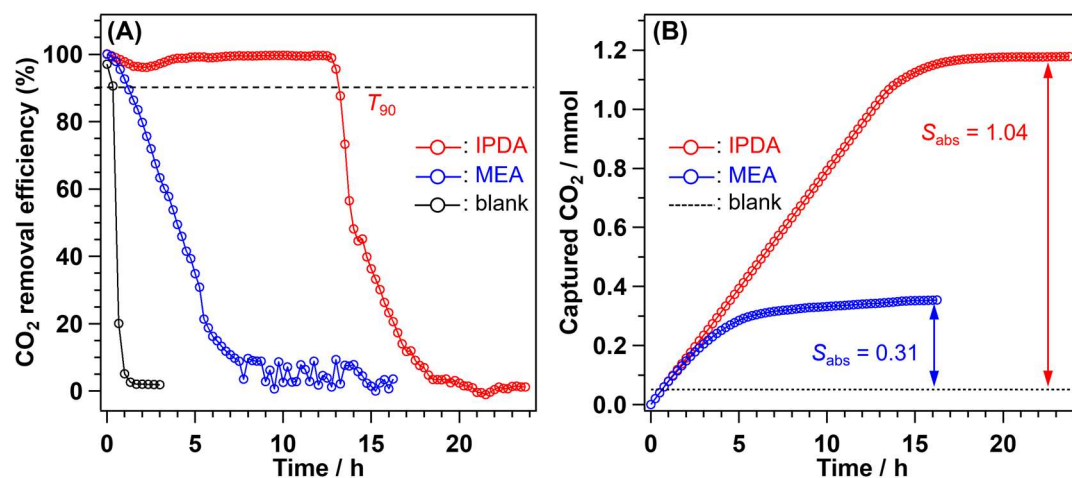
Fig. 2.(A) CO_2 removal efficiency over IPDA (red circles) and MEA (blue circles). Black circles represent the downstream CO_2 concentration w/o amine. **(B)** Total amounts of captured CO_2 over IPDA (red circles) and MEA (blue circles). Dashed line represents the amount of captured CO_2 in DMSO. 400ppm CO_2–N_2 at a flow rate of 75 mL min^{-1}. Amines: 1 mmol, DMSO: 1 mL.

Fig. 2A shows the efficiency of removal of 400 ppm of CO_2 from a flowing CO_2–N_2 mixture for amine-based sorbents in dimethyl sulfoxide (DMSO) solution, respectively. IPDA maintained almost a 100% efficiency (CO_2 absorption rate: 80 mmol h^{-1} for 1 mol amine) for CO_2 removal over 12 hours; its efficiency then suddenly decreased, reaching 0% after 21 hours. The total amount of captured CO_2 (S_{abs}) by IPDA reached 1.04 mmol (**Fig. 2B** and **Supplementary Table 1**). **Fig. 3** and **Supporting Information Video S1** show the changes that occurred during the CO_2 absorption process of **Fig. 2**. A white solid formed after a reaction time of 2.5 hours, and the viscosity of IPDA solution gradually increased as the formation of the precipitate. MEA, a typical amine-based sorbent, showed a lower efficiency of CO_2 removal than IPDA under the same conditions (**Fig. 2A**). After 10 hours, the removal efficiency of MEA reached 0% with a S_{abs} of 0.31 mmol. ^{13}C NMR spectroscopy revealed that the precipitate consisted

of [3-(aminomethyl)-3,5,5-trimethylcyclohexyl]carbamic acid (**CA1**) (**Supplementary Fig. 1A**). Hanusch *et al.* reported that the solid carbamic acids from aminopyrrolidines (the structures of which were established by means of single-crystal X-ray diffraction) formed through intramolecular or intermolecular cooperative activation of their primary and tertiary amino groups.[29] IPDA also formed **CA1** by interaction of its amino groups with CO_2.
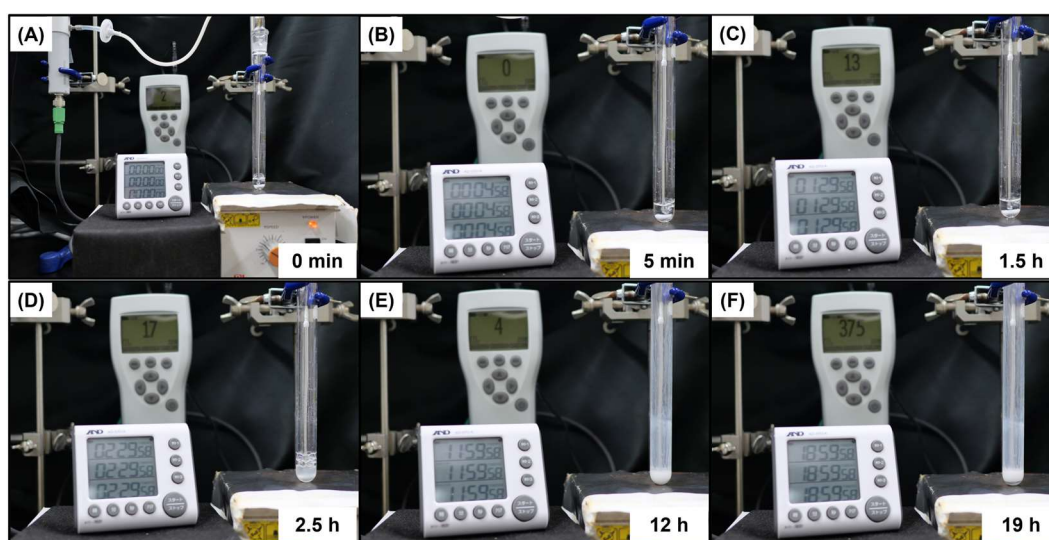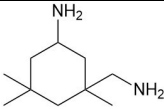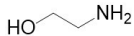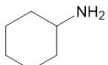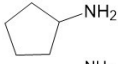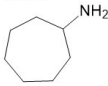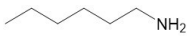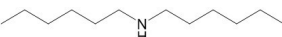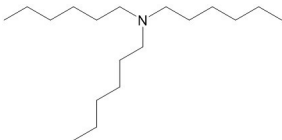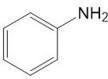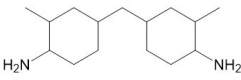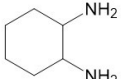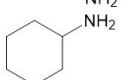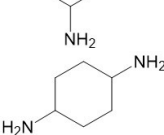

Fig. 3. Photographs of a DMSO solution of IPDA under a 400 ppm CO_2–N_2 flow. (**A**) 0 min, (**B**) 5 min, (**C**) 1.5 h, (**D**) 2.5 h, (**E**) 12 h, and (**F**) 19 h. The downstream concentration CO_2 was monitored by using a nondispersive infrared CO_2 meter (GMP252, Vaisala GmbH).

The IPDA also showed higher CO_2 removal efficiencies even under the 1% and 30% CO_2 conditions than MEA as shown in **Supplementary Fig. 2**. In the case of 30% CO_2, the CO_2-removal efficiency over IPDA remained above 90% over 24 min with a S_{abs} of 6.21 mmol. MEA showed a slightly lower durability and capacity ($S_{abs} = 4.46$ mmol). The S_{abs}/amine molecule ratios ($R_{CO2/molecule}$) for IPDA hardly depended on the CO_2 concentration, whereas those for MEA drastically decreased when using a low

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concentration CO_2 (**Supplementary Table 1**). Thus, IPDA is a superior sorbent to MEA over a wide range of CO_2 concentrations.

Next, amine scope has been carried out to determine the suitable amine compound for this liquid–solid phase-separation system. **Table 1** and **Supplementary Fig. 3** summarize the CO_2-absorption capacities of various amines under a 1% CO_2–N_2 flow. IPDA exhibited a superior CO_2 absorption durability even to that of equimolar-amine-containing MEA (Table 1, entries 1–3). $R_{CO2/molecule}$ for cycloalkyl amines (entries 4–6) was <0.6, which was *ca.* half of that of IPDA (entry 1). In addition, the T_{90} of these amines (entries 4–6) were shorter than that of IPDA (entry 1). Primary amines showed superior amine efficiencies to those of secondary and tertiary amines, probably due to steric hindrance (entries 7–9). In addition, aniline, in which the primary amine group is attached to a phenyl group, absorbed hardly any CO_2 (entry 10). Cycloalkyl diamines (entries 1 and 11–14) formed precipitates and showed relatively high T_{90} values. For all the diamines investigated in this study, $R_{CO2/molecule} \approx 1.0$. In addition, IPDA exhibited a CO_2-removal efficiency over a long time (T_{90} = 121 min). Among the regioisomeric cyclohexyldiamines (entries 12–14), cyclohexane-1,2-diamine, with a low T_{90} value of 36 min, afforded a less-viscous solution. These results show that the polarity of the carbamic acid is essential for efficient CO_2 removal and that differences in the absorption efficiency arise from the rate of formation and the solubility of precipitates from CO_2-absorption reactions.

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Table 1. CO_2 absorption capacities of various amines[a]

Entry	Amine	Precipitate	T_{90} / min	$R_{CO2/molecule}$
1	IPDA	formed	121	1.08
2	MEA	n.d.	43	0.62
3	MEA[b]	n.d.	68	0.60
4	cyclohexylamine	n.d.	27	0.56
5	cyclopentylamine	n.d.	23	0.49
6	cycloheptylamine	n.d.	28	0.53
7	hexylamine	n.d.	55	0.76
8	dihexylamine	n.d.	9	0.23
9	trihexylamine	n.d.	6	n.d.
10	aniline	n.d.	2	n.d.
11	4,4'-methylenebis-(2-methylcyclohexylamine)	formed	61	1.02
12	cyclohexane-1,2-diamine	partially formed	36	0.92
13	cyclohexane-1,3-diamine	formed	104	1.04
14	cyclohexane-1,4-diamine	formed	64	0.98

[a] CO_2 absorption capability was evaluated under 1% CO_2–N_2 flow. Flow rate: 20 mL min^{-1}, Amines: 1 mmol, DMSO: 5 mL.

[b] 2 mmol of MEA was applied, which contains equimolar of amino groups to 1 mmol of IPDA.
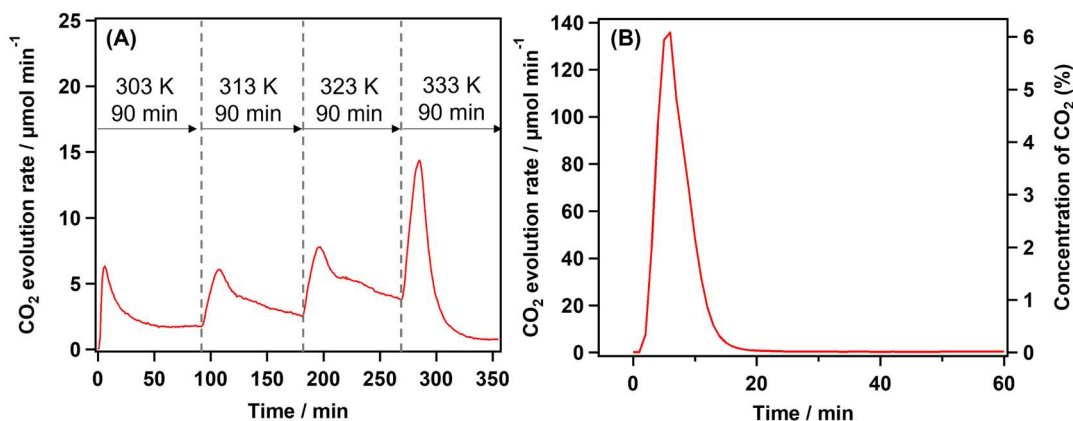
Fig. 4. The desorption profile of CO_2 over 1 mmol of **CA1** in 15 mL of DMSO under N_2 flow (50 mL min^{-1}). **(A)** The solution temperature raised at a range of 303–333 K step-by-step with a 90-min interval. **(B)** The solution was heated at 373 K.

The CO_2-desorption properties of **CA1** were also investigated. **Fig. 4A** shows the desorption rate of CO_2 at various temperatures. CO_2 desorption was first observed at 303 K. Further desorption occurred on increasing the temperature, and the CO_2 was completely desorbed at 333 K. As desorption occurred, the precipitate gradually vanished. **Fig. 4B** shows the desorption profile of CO_2 at 373 K. CO_2 desorption was finished within 20 minutes, and the maximum CO_2-desorption rate was 134 µmol min^{-1}. This indicates the low-concentration CO_2 as ambient air could be condensed to 6% CO_2.

The reusability of IPDA as a sorbent was also examined (**Fig. 5**). The > 90% CO_2-capture efficiency was kept for 120 min and, after switching the gas to N_2 and ramping the temperature to 333 K, the captured CO_2 was perfectly released into the inert gas. The absorption-and-desorption profile is therefore repeatable at least five times without degradation. Note that the desorption temperature was 333 K, which is lower than that for the conventional desorption system with MEA.[10-12] We therefore consider that

IPDA has the potential to replace the existing sorbent in absorption/desorption systems with MEA, requires a temperature of >473 K.[6, 10-12]
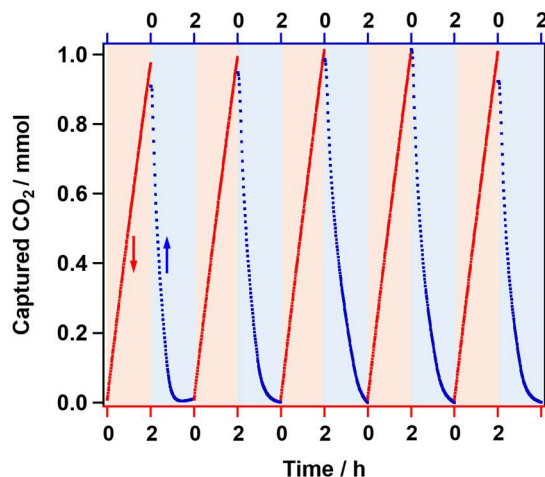

Fig. 5. The repetition profile of CO_2 absorption/desorption over 1 mmol IPDA in 15 mL of DMSO. The absorption capability test under 1% CO_2–N_2 flow (20 mL min^{-1}, 298 K, red line) and desorption of CO_2 under N_2 flow (50 mL min^{-1}, 333 K, blue line) were switched for 5 times with a 120-min interval. The left axis represents the total amounts of captured CO_2.

In this study, we found that IPDA efficiently absorbed CO_2 over a wide range of concentrations ranging from 400 ppm to 30% with >90% CO_2 removal efficiency in a flow system and the formation of precipitates of a carbamic acid product. This performance is superior to that of a comparable conventional CO_2-absorption system using MEA. The IPDA-based liquid–solid phase separation system has two advantages. The first is its high $R_{CO2/molecule}$ ratio. The $R_{CO2/molecule}$ ratio for a typical CO_2-absorption system involving a carbamate mechanism is about 0.5 [$2R^1R^2NH + CO_2 \leftrightarrow R^1R^2NCOO^-\cdots R^1R^2NH_2^+$],[32] whereas the $R_{CO2/molecule}$ ratio for the IPDA-based carbamic acid system was near 1.0 [$R^1R^2NH(l) + CO_2(g) \leftrightarrow R^1R^2NCOOH(s)$]. The second advantage is the high CO_2 removal efficiency (T_{90} value) of the liquid–solid phase

separation system, which is achieved as follows. The IPDA reacts with CO_2 to form the corresponding carbamic acid in the liquid phase. Initially, the concentrations of carbamic acid in the solution increase to maintain the equilibrium with carbamate ion $[R^1R^2NCOO^-\cdots R^1R^2NH_2^+(l) \leftrightarrow R^1R^2NH(l) + R^1R^2NCOOH(l)]$.[32] When its concentration is saturated, the carbamic acid precipitates from the solution $[R^1R^2NCOOH(l) \leftrightarrow R^1R^2NCOOH(s)]$. In fact, the white carbamate-acid precipitate formed after a reaction time of 1.5 hours, as shown in **Fig. 3** and **Supporting Information Video 1**. In addition, the T_{90} strongly depended on the amine concentration and a highly concentrated solution of IPDA showed a high T_{90} value with a high space velocity (SV; flow rate/volume of solution) of $240 \ h^{-1}$ (see **Supplementary Fig. 4A** and **Supplementary Table 2**). The high CO_2 removal efficiency was also achieved at high IPDA concentration condition (1 mmol IPDA/1 mL DMSO, **Fig. 2A**) at SV of $4500 \ h^{-1}$. In the case of cyclohexylamine which does not form a carbamic acid precipitate, the CO_2 absorption behaviour was independent of the amine concentration (DMSO: 5–15 mL, SV = 80–240 h^{-1}) whereas 1 mmol cyclohexylamine in 1 mL of DMSO showed 90% CO_2 removal efficiency under 1% CO_2 condition with the formation of precipitate, which was confirmed by ^{13}C NMR spectroscopy (**Supplementary Fig. 1B** and **Supplementary Fig. 4B**). These results indicate that a high concentration of IPDA favours CO_2 absorption and the maintenance of a high absorption rate due to the ease with which solution becomes saturated with liquid carbamic acid, resulting in continuous formation of the carbamic acid precipitate (**Fig. 6A**). The phase-separation system therefore overcomes the limitations imposed by the carbamate-ion concentration and the $R_{CO2/molecule}$ ratio. Inagaki *et al*. reported that phenyl group-containing alkylamines, such as 1,3-phenylenedimethanamine and phenylmethanamine exhibited efficient CO_2 capacity for DAC system.[28] We also tested

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those amines and found 1,3-phenylenedimethanamine showed a comparable CO_2 removal efficiency (T_{90}) and CO_2 absorption capacity to IPDA (**Supplementary Fig. 5**). This diamine formed precipitates when absorbing CO_2, whereas phenylmethanamine maintained the liquid form with showing low CO_2 removal efficiency. We conclude that phase separation between the liquid amine and the solid carbamic acid allows a high amine-utilization efficiency and a high CO_2-removal efficiency compared with conventional MEA solution, even at ambient CO_2 concentrations.

(A) CO_2 absorption

(B) CO_2 desorption

Low-concentration CO_2 (400ppm)

Concentrated CO_2

Liquid ⇵ Solid **CA1**

Liquid ⇵ Solid **CA1**

T < 353 K

Direct air capture / low-energy CO_2 desorption by phase separation between liquid amine sorbent and solid carbamic acid
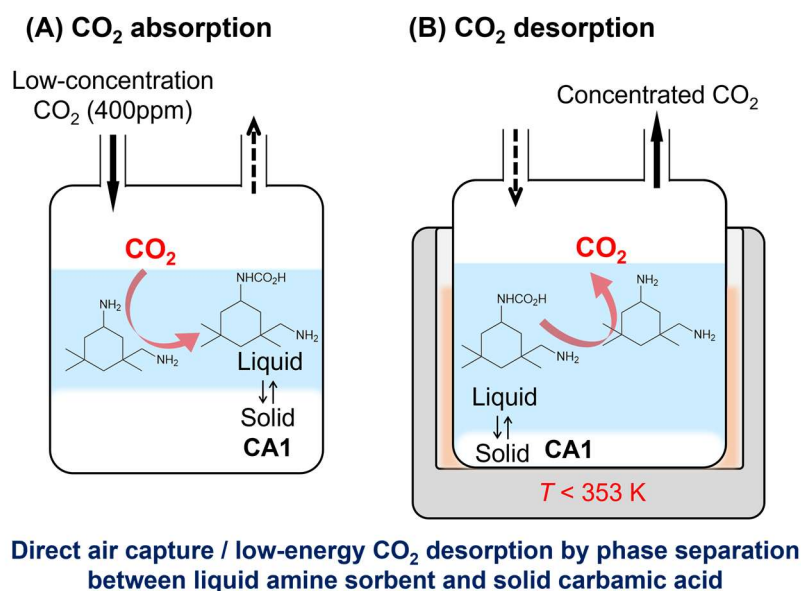
Fig. 6. Schematic image of CO_2 **(A)** absorption and **(B)** desorption system using phase separation between liquid IPDA and solid **CA1**.

We also found that CO_2 evolution from the CO_2-absorbed solution containing solid **CA1** began to occur at 303 K under a gas flow and that 6% concentration of CO_2 was achieved at 373 K. Thermogravimetry/mass (TG-MS) profile of the solid **CA1** showed two steps of weight losses (**Supplementary Fig. 6**); the first step, which occurred above 333 K, was accompanied with the desorption of CO_2 ($m/z = 44$), and the second

step, above 383 K, was attributed to volatilization of IPDA, as its fragmentation patterns appeared in the mass spectrum. Therefore, **CA1** should desorb CO_2 without volatilization in the temperature range 333–383 K. However, the desorption of CO_2 from the CO_2-absorbed solution occurred at a lower temperature than that required for solid **CA1**. This suggests that a part of carbamic acid is dissolved in solution and the carbamic ion, which is formed from carbamic acid in solution, desorb CO_2 at a low temperature. In addition, the concentration of liquid carbamic acid and carbamate ion increased on heating the solution because the solubility of **CA1** increases with increasing temperature (**Fig. 6B**). The liquid–solid phase-separation system is therefore also suitable for the CO_2-desorption process.
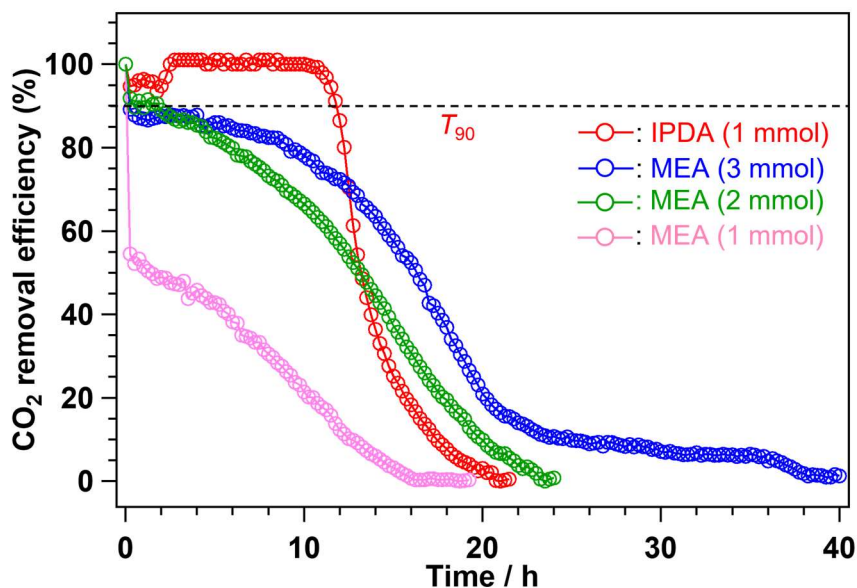

Fig. 7. CO_2 removal efficiency over 1 mmol of IPDA (red circles) and MEA (3 mmol, blue circles; 2 mmol; green circles, 1mmol; pink circles). 400ppm CO_2–N_2 at a flow rate of 75 mL min^{-1}. H_2O: 1 mL.
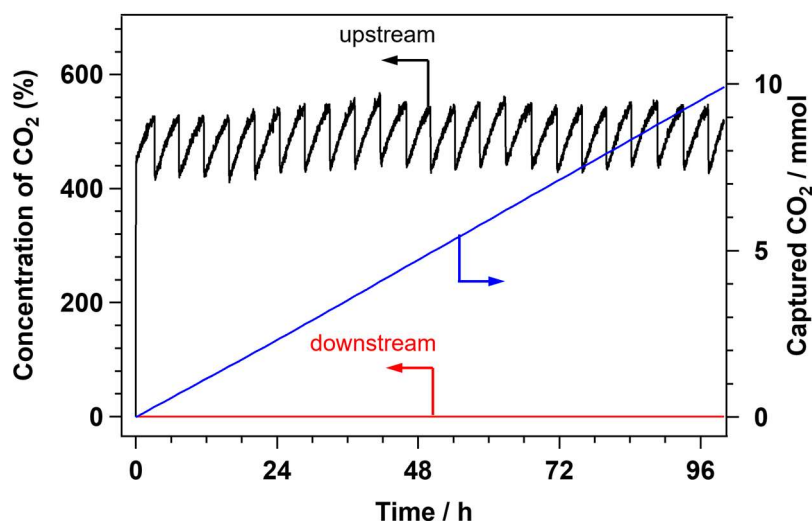
Fig. 8. CO_2 concentration at a downstream (red line) and upstream (black line) of the reactor under a compressed ambient air. Total amount of absorbed CO_2 is represented in a right axis. IPDA: 20 mmol, H_2O: 50 mL, gas flow rate: 75 mL min^{-1}. The CO_2 concentration was monitored by using a nondispersive infrared CO_2 meter (GMP252, Vaisala GmbH).

Among the diamine-based sorbents tested in this study, IPDA exhibited the best performance that would be relating to the solubility and thermal stability of solid carbamic acid (**Supplementary Table 3**). Carbamic acids from aminopyrrolidines have been reported as being formed by cooperative activation of their primary and tertiary amino groups, either intramolecularly or intermolecularly.[29] The intramolecular arrangement of the amino groups of IPDA should result in efficiency in both the formation of the solid precipitate and the reverse reaction. Compared with the reported liquid–solid pair of insoluble carbonate crystals,[25] the high solubility of IPDA in DMSO leads a higher density of captured CO_2 than that of chelate-ligating iminoguanidine, which has a low solubility. Moreover, the strong hydrogen-bonding network between the iminoguanidinium cation and the bicarbonate anion required a desorption energy of 81 kJ mol_{CO2}^{-1} and heating to >393 K.[25] The Gibbs free energy for the carbamation reaction

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has been reported to be >40 kJ mol_{CO2}^{-1} for a series of primary and secondary amines,[34-36] which is close to that of the present system. Consequently, CO_2 desorption in the liquid amine–solid carbamic acid phase-separation system proceeds at a low temperature.

Finally, to prove the general versatility of this liquid–solid phase-separation system, solvent effect on the CO_2 removal efficiency was tested as shown in **Supplementary Fig. 7**. The precipitate formed when either DMSO, *N,N*-dimethylformamide (DMF), H_2O, or toluene was used as the solvent at an amine-to-solvent ratio of 1 mmol per 5 mL, whereas the liquid form was maintained for a long time when using methanol as a solvent, suggesting that the production of a precipitate upon CO_2 storage is governed by the solubility of the carbamic acid in each solvent (**Supplementary Table 3**). The IPDA exhibited higher absorption efficiency as compared to MEA with equivalent molar amount (1 mmol MEA), amino groups (2 mmol MEA) and weight (3 mmol MEA) in H_2O solvent (**Fig. 7**). Moreover, CO_2 absorption rate increased after 3 h accompanied with the formation of solid **CA1**. Even at high space velocity, CO_2 absorption rate was enhanced after the **CA1** formation, achieving 214 mmol h^{-1} for 1 mol amine with >90% CO_2 removal efficiency at SV = 6000 h^{-1} (**Supplementary Fig. 8**) Moreover, IPDA maintained the >99% removal efficiency of ambient CO_2 from air for 100 hours with the wide-range supply rate of CO_2 (83–114 μmol h^{-1}) (**Fig. 8**). Recently, some efficient amines for DAC, such as 1,3-phenylenedimethanamine (CO_2 absorption rate: 32 mmol h^{-1} for 1 mol amine)[28] and pyrrolizidine (CO_2 absorption rate: 5.0 mmol h^{-1} for 1 mol amine)[29] were reported (**Supplementary Table 4**). In the DAC system using amino acid potassium and guanidine, the CO_2 absorption rate was reported to be *ca* 95 mmol h^{-1} for 1 mol amine.[20, 21] The DAC system using alkaline base solution has been established in a plant-level operation with

the CO_2 absorption rate of 16 mmol h^{-1} for 1 mol $NaOH^{37}$ and 13 mmol h^{-1} for 1 mol KOH,[38] however, the CO_2 desorption temperature is 1173 K,[7, 38-41] which is extremely higher than the CO_2 desorption temperature of the present system (333 K). Those results suggest that IPDA, which absorbs CO_2 with sufficient rapidity (CO_2 absorption rate: 214 mmol h^{-1} for 1 mol amine, SV: 6000 h^{-1}, **Supplementary Fig. 8**), might be a potential candidate for use as an amine-based sorbent for low concentrations of CO_2 and should be suitable for use in a DAC system. In addition, the system works well in H_2O solvent, promising to steam condense the absorbed CO_2 using steam-assisted temperature vacuum-swing adsorption technique.[42, 43] Those features realize high CO_2 absorption and desorption abilities, and our study has demonstrated the possibility of practical applications in low-energy DAC and CO_2-desorption systems.

Conclusion

In this study, we have developed a system for capturing CO_2 directly from air by using the phase separation between a liquid amine and the solid carbamic acid formed through the absorption of CO_2 by the amine. IPDA exhibited a CO_2 removal efficiency superior to that of conventional MEA for a wide range of CO_2 concentrations (400 ppm to 30%). Remarkably, under a large-scale gas stream containing 400 ppm of CO_2, IPDA reacted with CO_2 in the CO_2/IPDA molar ratio of ≥ 1 and exhibited >99% CO_2 removal over 12 hours, even in H_2O as a solvent, suggesting that it is a suitable sorbent for use in a direct air capture system. The IPDA system began to desorb CO_2 at ≥ 303 K and CO_2 was completely desorbed at 333 K under N_2 flow condition. The CO_2 capture-and-desorption cycle could be repeated at least five times without degradation, proving that IPDA is sufficiently robust and durable for practical use. The removal of IPDA-derived

carbamic acid from the liquid phase as solid during CO_2 absorption realizes high CO_2 removal efficiency even at the large-scale gas stream (space velocity: 6000 h^{-1} and CO_2 supply rate: 214 mmol h^{-1} for 1 mol IPDA) at low CO_2 condition (400 ppm). Moreover, the partially-dissolved IPDA-derived carbamic acid easily releases CO_2 in the liquid phase at low temperature during the CO_2 desorption process. This phase separation system between a liquid amine and the solid carbamic acid formed through absorption/desorption of CO_2 is available for other amines which form solid carbamic acid by CO_2 absorption. Therefore, the solidification of the sorbent should aid in efficient CO_2 absorption compared with the typical carbamate-based mechanism of the conventional MEA-based system.

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Author contributions

S.K. and S.Y. designed this study. K.A. and Y.F. contributed to all experimental works and data analysis. S.K. and J.H. conducted experimental setup and data analysis. G.K., H.M. and T.S. characterized the carbamic acids. S.K. and S.Y. proposed the mechanism with the help of H.M. and T.S. S.Y. supervised this study. All authors took part in the writing of this manuscript.

Competing interests

The authors declare no competing interests.