Direct Air Capture of CO₂ Using a Liquid Amine—Solid Carbamic Acid Phase-Separation System Using Diamines Bearing an Aminocyclohexyl Group

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ABSTRACT: The phase separation between a liquid amine and the solid carbamic acid exhibited >99% CO₂ removal efficiency under a 400 ppm CO₂ flow system using diamines bearing an aminocyclohexyl group. Among them, isophorone diamine [IPDA; 3-(aminomethyl)-3,5,5-trimethylcyclohexylamine] exhibited the highest CO₂ removal efficiency. IPDA reacted with CO₂ in a CO₂/IPDA molar ratio of ≥1 even in H₂O as a solvent. The captured CO₂ was completely desorbed at 333 K because the dissolved carbamate ion releases CO₂ at low temperatures. The reusability of IPDA under CO₂ adsorption-and-desorption cycles without degradation, the >99% efficiency kept for 100 h under direct air capture conditions, and the high CO₂ capture rate (201 mmol/h for 1 mol of amine) suggest that the phase separation system using IPDA is robust and durable for practical use.

KEYWORDS: direct air capture, amine method, aqueous amine sorbent, phase change sorbent, carbamic acid, isophorone diamine, aminocyclohexyl group

1. INTRODUCTION

Reducing the concentration of carbon dioxide (CO₂) in the atmosphere is becoming essential for building a sustainable society because an increase in the atmospheric concentration of CO₂ is closely linked to global warming and climate change.¹ Reduction of atmospheric CO₂ levels will require a concerted effort to both limit future emissions of CO₂ and to implement strategies for decreasing the existing atmospheric concentration of CO₂. Artificial storage of CO₂ 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 CO₂ leakage. On the other hand, the utilization of CO₂ as a value-added product by carbon capture and storage (CCS) is expected to provide a potential strategy for maintaining net CO₂ emissions at zero.⁴−⁷ However, the existing CCS technology requires further development to improve the CO₂ absorption/desorption efficiency of sorbents and to establish methods for subsequent conversion of captured CO₂.

Among CCS techniques, the use of sorbents for directly capturing CO₂ (<500 ppm) from the air, known as direct air capture (DAC), is a promising technology and desired to operate under a flow of ambient or low-pressure compressed gas.⁷−⁹ The challenge in the sorbents for DAC techniques is the high absorption efficiency of low-concentration CO₂ because the existing CCS techniques have insufficient absorption efficiency to perfectly remove the low-concentration CO₂. In addition, the CO₂-desorption temperature from the sorbent should be reduced; currently, the most-well-established sorbent, 2-aminoethanol (monoethanolamine; MEA), requires a temperature of >393 K for efficient CO₂ desorption.⁶,¹⁰−¹² Finally, the reusability and durability of the sorbents for use in CO₂ capture-and-desorption cycles are 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 sorbents¹³−²² and CO₂-absorption systems that utilize phase separation²³−³³ have been developed. The ability of homogeneous liquid-phase systems to absorb CO₂ has been improved by modifying the structures of the amine sorbents. Hanusch et al. discovered that pyrrolizidine-based diamines showed a more-efficient CO₂ capture than conventional MEA (Figure...
Although these are promising sorbents for CO$_2$ capture and desorption, further improvements in the rate of absorption of CO$_2$ are solids, their equilibrium concentration in the liquid phase will remain low, thus leading to a high absorption rate of CO$_2$ into the liquid phase. Moreover, as another benefit, liquid sorbents contact dissolved CO$_2$ much more efficiently than solid sorbents, which allows efficient absorption of low-concentration CO$_2$ from large-scale gas streams. The same liquid—solid phase separation systems have been reported up to now under high-concentration CO$_2$ conditions using triethylenetetramine with polyethylene glycol,\textsuperscript{14} bis(aminoguanidine),\textsuperscript{23,24,26,28,30} and potassium proline.\textsuperscript{15} Custelecan et al. recently developed a DAC system using liquid—solid phase separation over an amino acid potassium solution followed by the reaction with a guanidine compound, resulting in the crystallization of insoluble carbonate salt (Figure 1A-c).\textsuperscript{23,24} These systems could remove CO$_2$ from the air, but they require a sequential CO$_2$ transfer system. In another iminoguanidine-based sorbent reported by Cai et al.,\textsuperscript{37} CO$_2$ desorption from the CO$_2$-incorporated crystal began at 333 K and complete CO$_2$ release required high temperatures above 393 K.\textsuperscript{25,26} In addition, this system requires a large amount of solvent because of the low solubility of the sorbent. 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 to efficient CO$_2$ desorption at low temperatures.

CO$_2$ absorption and a more efficient absorption at low CO$_2$ concentrations are required. Liquid—liquid phase separation of amine—H$_2$O mixtures with lower critical solution temperatures has recently been developed to reduce the costs of regenerating the sorbent (Figure 1A-b).\textsuperscript{27,35,36} After CO$_2$ absorption, the organic and aqueous phases in these phase-change systems are immiscible, of which the CO$_2$-rich aqueous phases are suitable to concentrate CO$_2$ by heating.\textsuperscript{27,28} Such systems have achieved higher CO$_2$ capacities and lower costs compared with those of conventional MEA sorbent-based systems.\textsuperscript{35} 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 under a flow of low-concentration CO$_2$, new concepts for sorbents are required.

According to the proposed carbamate mechanism of MEA \[2R'RNH_2(l) + CO_2(g) \rightarrow R'RNH-+COO^-(l) + R'RNH_3^+(l)]\), the produced carbamate ion inhibits the forward reaction.\textsuperscript{37} Liquid—solid phase separation provides a possible way of overcoming the equilibrium limitations that inhibit the efficient CO$_2$ absorption. If the products from the

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**Figure 1.** (A) CO$_2$ absorption/desorption system using phase separation. (a) Typical carbamate mechanism (ref 37). (b) Liquid—liquid phase-change solvents (ref 27). (c) Liquid—solid phase separation with an iminoguanidine-based sorbent (refs 23 and 24). (d) Liquid—solid phase separation with solid carbamic acid formation (this work). (B) Ambient-flow-type reactor equipped with an online FT/IR analyzer for a direct air capture system.
reusability. This benchmark study is the first demonstration of a potential DAC system with >90% CO2 removal efficiency and reusability that is based on the phase separation between a liquid amine sorbent and a solid carbamic acid.

2. RESULTS AND DISCUSSION

Figure 2A shows the efficiency of removal of 400 ppm CO2 from a flowing CO2—N2 mixture for amine-based sorbents in dimethyl sulfoxide (DMSO) solution. IPDA maintained almost 100% efficiency (CO2 absorption rate: 80 mmol h⁻¹ for 1 mol of amine) for CO2 removal over 13 h; its efficiency then suddenly decreased, reaching 0% after 21 h. We defined the duration above >90% efficiency as T90, and IPDA showed T90 of 13 h. The total amount of captured CO2 (Sabs) by IPDA reached 1.04 mmol (Figure 2B and Table S1). Figure 3 and

![Image](Image)

**Figure 2.** (A) CO2 removal efficiency over IPDA (red circles) and MEA (blue circles) in DMSO and aqueous solution of 1 M KOH (green circles). Black circles represent the downstream CO2 concentration w/o sorbents in DMSO. (B) Total amounts of captured CO2 over IPDA (red circles) and MEA (blue circles) in DMSO and aqueous solution of 1 M KOH (green circles). The dashed line represents the amount of captured CO2 in DMSO. Reaction conditions: 400 ppm CO2 in a flow rate of 75 mL min⁻¹. Amines: 1 mmol, DMSO: 1 mL. KOH: 1 mmol, H2O: 1 mL.

Figure 3. Photographs of a DMSO solution of IPDA under a 400 ppm CO2—N2 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 CO2 was monitored by using a nondispersive infrared CO2 meter (GMP252, Vaisala GmbH).

Supporting Video S1 show the changes that occurred during the CO2 absorption process of Figure 2. A white solid formed after a reaction time of 2.5 h, and the viscosity of IPDA solution gradually increased as the precipitate formed. MEA, a typical amine-based sorbent, showed a lower efficiency of CO2 removal than IPDA under the same conditions (Figure 2A). After 10 h, the removal efficiency of MEA reached 0% with an Sabs of 0.31 mmol. The low CO2 removal efficiency was also obtained for the 1 M KOH aqueous solution, which is applied for the DAC system, as shown in Figure 2A,B.

The solid precipitate was analyzed by FT-IR and 13C and 1H NMR. The FT-IR spectrum of the precipitate (Figure S1) showed the absorption bands at 1600–1660 and 1500–1600 cm⁻¹, assigned to the carboxyl (−COOH) and amido groups (−NH−CO−), respectively, which are characteristics of carbamic acid. In addition, the absorption bands (3165, 3277, and 3346 cm⁻¹), which are characteristics of amine connected with the cyclohexyl group, disappeared, although the absorption bands of another amino group (the shoulder peak in Figure S1B at 1600 cm⁻¹ and the broad peak in Figure S1C at 3200–3400 cm⁻¹) remained in the precipitate. 13C NMR spectroscopy also indicated that the carbonyl species were incorporated into the precipitate (Figure S2). 1H NMR spectra showed a larger shift of the peak ascribed to a proton at the secondary carbon bearing an amino group than that ascribed to a proton at the primary aminomethyl group (Figure S3), which enables us to understand that CO2 preferentially bound to only −NH2 connected with a cyclohexyl group. From the reaction ratio of IPDA:CO2 = 1:1 and FT-IR and 13C and 1H NMR analyses, we concluded that the carbamic acid ([3-(aminomethyl)-3,5,5-trimethylcyclohexyl] carbamic acid, CA1) was formed by the following reaction (Scheme 1);

**Scheme 1. Formation of CA1 from IPDA**

![Image](Image)

IPDA also showed higher CO2 removal efficiencies even under the 1% and 30% CO2 conditions than MEA, as shown in Figure S4. In the case of 30% CO2, the CO2 removal efficiency over IPDA remained above 90% over 24 min with an Sabs of 6.21 mmol. MEA showed a slightly lower durability and capacity (Sabs = 4.46 mmol). The Sabs/amine molecule ratios (RCo2/amine) for IPDA hardly depended on the CO2 concentration, whereas those for MEA drastically decreased when using a low-concentration CO2 (Table S1). Thus, IPDA is a superior sorbent to MEA over a wide range of CO2 concentrations.

Next, the amine scope has been carried out to determine the suitable amine compound for this liquid–solid phase-separation system. Table 1 and Figure S5 summarize the CO2 absorption capacities of various amines under a 1% CO2—N2 flow. IPDA exhibited a superior CO2 absorption durability even to that of equimolar-amine-containing MEA (Table 1, entries 1–3). The RCo2/amine for cycloalkyl amines (entries 4–6) was <0.6, which was ca. half of that of IPDA (entry 1). In addition, the T90 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 CO2 (entry 10). Cycloalkyl diamines (entries 1 and 11–14) formed precipitates and showed relatively high T90 values. The diamines bearing an aminocyclohexyl group investigated in this study showed RCo2/amine ≈ 1.0, indicating that the one −NH2 connected with a cyclohexyl group in diamines preferentially reacted with CO2. In addition, IPDA exhibited a CO2-removal efficiency over a long time (T90 = 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 also 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.

The CO$_2$-desorption properties of CA1 were also investigated. Figure 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 CO$_2$ was completely desorbed at 333 K. As desorption occurred, the precipitate gradually vanished. Figure 4B shows the desorption profile of CO$_2$ at 373 K. CO$_2$ desorption was finished within 20 min, and the maximum CO$_2$-desorption rate was 134 μmol min$^{-1}$. This indicates that the low-concentration CO$_2$ as an ambient air could be condensed to 6% CO$_2$.

The reusability of IPDA as a sorbent was also examined (Figure 5). The >90% CO$_2$-capture efficiency was kept for 120

### Table 1. CO$_2$ Absorption Capacities of Various Amines$^a$

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

$^a$CO$_2$ absorption capability was evaluated under a 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.
IPDA reacts with CO₂ to form the corresponding carbamic solid phase separation system, which is achieved as follows. Repetition profile of CO₂ over 1 mmol of CA1 in 15 mL of DMSO under N₂ flow (50 mL min⁻¹). (A) The solution temperature was raised at a range of 303–333 K step by step with a 90 min interval. (B) The solution was heated at 373 K.

In this study, we found that IPDA efficiently absorbed CO₂ over a wide range of concentrations ranging from 400 ppm to 30% with >90% CO₂ 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 CO₂-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 CO₂-absorption system involving a carbamate mechanism is about 0.5 [2R’NH + CO₂ ↔ R’NCOO−···H₂N’−]. However, the R_{CO₂/molecule} ratio for the IPDA-based carbamic acid system was near 1.0 [NH₂−R−C₆H₄−NH(l) + CO₂(g) ↔ NH₂−R−C₆H₄−NH−COOH(s)]. The second advantage is the high CO₂ removal efficiency (T_{90}) value of the liquid–solid phase separation system, which is achieved as follows. IPDA reacts with CO₂ 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 the carbamate ion [NH₂−R−C₆H₄−NH−COO−···R−C₆H₄−NH−]. When its concentration is saturated, the carbamic acid precipitates from the solution [NH₂−R−C₆H₄−NH−COOH(s) ↔ NH₂−R−C₆H₄−NH−]. In fact, the white carbamate-acid precipitate formed after a reaction time of 1.5 h, as shown in Figure 3 and Supporting 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 Figure S6A and Table S2). The high CO₂ removal efficiency was also achieved under high IPDA concentration conditions (1 mmol of IPDA/1 mL of DMSO, Figure 2A) at an SV of 4500 h⁻¹. In the case of cyclohexylamine that does not form a carbamic acid precipitate under low concentration conditions, the CO₂ absorption behavior was independent of the amine concentration (DMSO: 5–15 mL; SV = 80–240 h⁻¹), whereas 1 mmol of cyclohexylamine in 1 mL of DMSO showed 90% CO₂ removal efficiency under 1% CO₂ conditions with the formation of precipitate, which was confirmed by ¹³C NMR spectroscopy (Figures S2B and S6B). These results indicate that a high concentration of IPDA favors CO₂ absorption and the maintenance of a high absorption rate due to the ease with which the solution becomes saturated with liquid carbamic acid, resulting in the continuous formation of the carbamic acid precipitate (Figure 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 CO₂ capacity for the DAC system. We also tested those amines and found that 1,3-phenylenedimethanamine and phenylmethanamine maintained the liquid form and showed low CO₂ 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 CO₂ removal efficiency compared with the conventional MEA solution, even at ambient CO₂ concentrations. We also found that CO₂ evolution from the CO₂-absorbed solution containing solid CA1 began to occur at 303 K under a gas flow and that 6% concentration of CO₂ was achieved at

![Figure 4. Desorption profile of CO₂ over 1 mmol of CA1 in 15 mL of DMSO under N₂ flow (50 mL min⁻¹). (A) The solution temperature was raised at a range of 303–333 K step by step with a 90 min interval. (B) The solution was heated at 373 K.](image-url)

![Figure 5. Repetition profile of CO₂ absorption/desorption over 1 mmol of IPDA in 15 mL of DMSO. The absorption capability test under 1% CO₂–N₂ flow (20 mL min⁻¹, 298 K, red line) and desorption of CO₂ under N₂ flow (50 mL min⁻¹, 333 K, blue line) were switched five times with a 120 min interval. The left axis represents the total amounts of captured CO₂.](image-url)

![Figure 6. Schematic image of a CO₂ (A) absorption and (B) desorption system using phase separation between liquid IPDA and solid CA1.](image-url)
373 K. The thermogravimetry/mass (TG-MS) profile of the solid CA1 showed two steps of weight losses (Figure S8); the first step, which occurred above 333 K, was accompanied with the desorption of CO₂ (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 CO₂ without volatilization in the temperature range 333–383 K. However, the desorption of CO₂ from the CO₂-absorbed solution occurred at a lower temperature than that required for solid CA1; the solid CA1 perfectly disappeared by heating at 333 K. This suggests that a part of carbamic acid is dissolved in solution and the carbamic ion, which is formed from carbamic acid in solution, desorbs CO₂ 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 (Figure 6B). The liquid–solid phase-separation system is therefore also suitable for the CO₂-desorption process.

Among the diamine-based sorbents tested in this study, IPDA exhibited the best performance that would be related to the solubility and thermal stability of solid carbamic acid (Table S3). Finally, to verify the general versatility of this liquid–solid phase-separation system, the solvent effect on the CO₂ removal efficiency was tested, as shown in Figure S9. The precipitate formed when either DMSO, N,N-dimethylformamide (DMF), H₂O, 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 methanol was used as a solvent, suggesting that the production of precipitate upon CO₂ storage is governed by the solubility of the carbamic acid in each solvent (Table S3). Remarkably, IPDA in H₂O exhibited the highest absorption property (T₉₀ and Rₐ₉₀ of CO₂/molecule ratio) among the solvents, suggesting its practical usefulness. The aqueous IPDA solution showed superior absorption efficiency to MEA with equivalent molar amount (1 mmol MEA), amino groups (2 mmol MEA), and weight (3 mmol MEA) in H₂O solvent and aqueous KOH solution (1 mmol) (Figure 7). In our flow-type system, 5 mmol of KOH (5 M) had a lower removal efficiency than 90% due to the equilibrium (Figure S10). In contrast, the CO₂ absorption rate of aqueous IPDA solution increased after 3 h accompanied with the formation of solid CA1 (Figure 7). After reaching the dissolution limit of liquid carbamic acid, the absorption proceeded accompanied with solid CA1 formation (Figure S11). Even at high space velocity, the CO₂ absorption rate was enhanced after the CA1 formation, achieving 201 mmol h⁻¹ for 1 mol of amine with >90% CO₂ removal efficiency at SV = 11,280 h⁻¹ (Figure S12). Moreover, IPDA maintained the >99% removal efficiency of ambient CO₂ from the air for 100 h with the wide-range supply rate of CO₂ (83–114 μmol h⁻¹) (Figure 8). Recently, some efficient amines for DAC, such as 1,3-phenylendimethanamine (CO₂ absorption rate: 32 mmol h⁻¹ for 1 mol of amine)²⁵ and pyrrolidine (CO₂ absorption rate: 5.0 mmol h⁻¹ for 1 mol of amine),³⁴ were reported (Table S4). In the DAC system using amino acid potassium and guanidine, the CO₂ absorption rate was reported to be ca. 95 mmol h⁻¹ for 1 mol of amine.²⁴,²⁶ The DAC system using alkaline base solution has been established in a plant-level operation with the CO₂ absorption rates of 13 mmol h⁻¹ for 1 mol of KOH⁴⁰ and 16 mmol h⁻¹ for 1 mol of NaOH.⁴² However, the CO₂ desorption temperature is 1173 K,⁷⁴,⁴³–⁴⁵ which is extremely higher than the CO₂ desorption temperature of the present system (333 K). Those results suggest that IPDA, which absorbs CO₂ with sufficient rapidity (CO₂ absorption rate: 201 mmol h⁻¹ for 1 mol amine, SV: 11280 h⁻¹, Figure S12), might be a potential candidate for use as an amine-based sorbent for low concentrations of CO₂ and should be suitable for use in a DAC system. In addition, the system works well in H₂O solvent. Therefore, the steam-assisted temperature vacuum-swing adsorption technique¹⁵,⁴⁶,⁴⁷ can be applied to our system. Those features realize high CO₂ absorption and desorption abilities, and our study has demonstrated the possibility of practical applications in low-energy DAC and CO₂-desorption systems.

3. CONCLUSIONS

In this study, we have developed a system for capturing CO₂ directly from the air by using the phase separation between a liquid amine and the solid carbamic acid formed through the absorption of CO₂ by the amine. IPDA exhibited a CO₂ removal efficiency superior to that of MEA with the typical carbamate-based mechanism for a wide range of CO₂ concentrations (400 ppm to 30%). Under 400 ppm CO₂, IPDA reacted with CO₂ in the CO₂/IPDA molar ratio of 1 and exhibited >99% CO₂ removal for more than 13 h. The IPDA system began to desorb CO₂ at ≥303 K and CO₂ was
completely desorbed at 333 K under N2 flow conditions. The CO2 capture-and-desorption cycle could be repeated at least five times without degradation. Remarkably, IPA in H2O as a solvent was applied to capturing CO2 from the air for 100 h with >99% efficiency. The removal of IPA-derived carbamic acid from the H2O solution as solid during CO2 absorption realizes high CO2 removal efficiency even at the high flow velocity of 400 ppm CO2 (space velocity: 11280 h−1 and CO2 supply rate: 201 mmol h−1 for 1 mol of IPA). Moreover, the partially dissolved IPA-derived carbamic acid easily releases CO2 in the liquid phase at low temperatures during the CO2 desorption process. This phase separation system between a liquid amine and the solid carbamic acid formed through absorption/desorption of CO2 was available for other amines, which form solid carbamic acid by CO2 absorption.

4. EXPERIMENTAL SECTION

4.1. Chemicals
All chemicals were used as received. Isophorone diamine [IPDA, 3-(aminomethyl)-3,5,5-trimethylcyclohexylamine; cis/trans mixture, >99.0%], 2-aminoethanol (MEA, monoethanolamine; >99.0%), cyclohexylamine (>99.0%), cyclohexylamine (>97.0%), cyclopentylamine (>98.0%), hexylamine (>99.0%), dihexylamine (>98.0%), trihexylamine (>98.0%), 4,4′-methylenebis(2-methylcyclohexylamine) (cis/trans mixture, >99.0%), cyclohexane-1,2-diamine (cis/trans mixture, >98.0%), cyclohexane-1,3-diamine (cis/trans mixture, >95.0%), cyclohexene-1,4-diamine (cis/trans mixture, >97.0%), 1,3-phenylene diamine (<99.0%), phenylethylamine (<99.0%), N,N-dimethylformamide (DMF; >99.0%), and dimethyl sulfoxide (DMSO; >99.0%) were purchased from Tokyo Chemical Industry Co., Ltd. Aniline (>99.0%) and KOH (>85.0%) were purchased from FUJIFILM Wako Pure Chemical Corp. Toluene (>99.5%), methanol (>99.0%), tricyclohexylamine (>98.0%), 4,4′-cyclohexylamine (>99.0%), cycloheptylamine (>97.0%), cyclopentylamine (>99.0%), 2-aminoethanol (MEA, monoethanolamine; >99.0%), and diethyl ether (>99.5%) were purchased from Kanto Co., Ltd. Aniline (>99.0%) and KOH (>85.0%) were purchased from FUJIFILM Wako Pure Chemical Corp. Toluene (>99.5%), methanol (99.8%), and diethyl ether (>99.5%) were purchased from Kanto Chemical Co., Inc.

4.2. CO2 Absorption
CO2 absorption was evaluated by using an ambient-flow-type reactor at room temperature (~303 K, uncontrolled) with monitoring by a downstream IR analyzer. Specific proportions of the amine or KOH substrates in DMSO or H2O were bubbled with a controlled flow of 400 ppm, 1%, or 30% CO2 in N2 with vigorous stirring. To suppress the decrease in solvent volume in the reactor due to volatilization, the CO2−N2 gas was through into a solvent at an upstream of the reactor. The concentration of CO2 in an optical cell downstream of the IR analyzer. The cell lengths and volumes were calculated as follows:

\[ S_{\text{obs}} \text{ (mmol)} = S_{\text{app}} - S_{\text{blank}} \]

where \( S_{\text{app}} \) and \( S_{\text{blank}} \) are the apparent amounts of CO2 adsorbed with and without the amine-based sorbent, respectively. The value of \( S_{\text{app}} \) was calculated as follows:

\[ S_{\text{app}} \text{ (mmol)} = \int_0^t C_{\text{CO2}}(t) \, dt \times F \]

where \( F \) is the flow rate of the dilute CO2 gas. A 4 day long-term durability test was carried out by using 20 mmol of IPDA dissolved in 50 mL of H2O solvent. Ambient room air compressed by using an oil-free air compressor (Bebicon, HITACHI Co. Ltd.) was supplied at a flow rate of 75 mL min−1. To suppress the decrease in H2O as a solvent, the humid gas was fed through H2O trap. The CO2 concentrations at up- and downstream of reactor were monitored by using nondispersive infrared CO2 meters (GMP252, Vaisala GmbH).

4.3. CO2 Desorption
The desorption of captured CO2 was evaluated by using the same flow reactor. After storing 1% CO2−N2, the gas flow was switched to pure N2 (50 mL min−1) while the temperature was ramped up to the operating temperature. The reactor temperature rapidly reached the set value within a few minutes. The solution temperature was raised in the range 303−333 K in a stepwise manner with 90 min intervals. The concentration of CO2 was monitored by using the same IR analyzer as discussed above. For the repeated CO2 absorption/desorption cycles, a 1% CO2−N2 flow at 298 K and a pure N2 flow at 333 K were switched five times at 120 min intervals.

4.4. Analysis
The CO2 desorption profile of the obtained solid material was measured by using a thermogravimetric analyzer (STA-2500 Regulus, Netzsch) equipped with a mass spectrometer (JMS-Q1500GC, JEOL). The temperature of the sample holder was ramped to 773 K at a rate of 10 K min−1 under flowing He. The sample was prepared by exposure of IPA to CO2 in diethyl ether. The precipitate was collected by centrifugation from diethyl ether, dried at room temperature, and subjected to analysis. Fourier-transform 100 MHz 13C NMR spectra were recorded on a JMN-ECS400 instrument (JEOL). Chemical shifts (δ) of the 13C{1H} NMR spectra were referenced to SiMe4. The samples were prepared by exposing the relevant amines to CO2 in toluene. Fourier-transform infrared spectra were recorded by a FT/IR-4X (JASCO) equipped with an attenuated total reflection unit.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenvironau.1c00065.

Supporting Video showing the solid formation during CO2 absorption (MP4)
Performances of reported CO2 sorbents, 13C and 1H NMR spectra and TG-DTA-MS profile of solid carbamic acid, and photograph of experimental setup (PDF)

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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 the 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.

Notes
The authors declare no competing financial interest.

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