An Acid Dissociation Constant (pK_a)-based Screening of Chemical Absorbents that Preferably Capture and Release Pressurized Carbon Dioxide for Greenhouse Gas Control

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We describe an acid dissociation constant (pK_a)-based screening of chemical absorbents to treat a gas stream containing carbon dioxide (CO_2) in a wide range of partial pressures (0.1–4 MPa). The solubility differences of CO_2 in aqueous amine solutions at 40 and 70 °C plotted against pK_a revealed volcano-shaped profiles. The availability of amines with pK_a values suitable for capture/release cycles of CO_2 with targeted partial pressures shows that the pK_a-based screening method would be useful to develop advanced greenhouse gas control technologies.

In recent years, there have increased interests in developing potential methods of carbon dioxide (CO_2) capture and storage (CCS) from fossil fuel power plants to control greenhouse gas emission (Figure 1).[1,2] As one of the promising technologies for reducing CO_2 emission, a better choice would be the IGCC system (the integrated coal gasification cycle combined with the water–gas shift reaction, $CO + H_2O \rightarrow H_2 + CO_2$), which generates a pressurized gas stream ($\approx$5 MPa) containing a volume fraction of CO_2 ($\varphi \approx 40\%$).[3,4]

Recently, CO_2 absorption into a liquid agent is the most commonly used for the bulk removal of CO_2. At higher partial pressures of CO_2, physical absorption in polar organic solvents (i.e. polyethylene glycol derivatives) might be preferred.[5] However, reducing pressure is required to release CO_2 and regenerate the active solvents (pressure swing regeneration), causing loss of thermal efficiency for the power plants.

Meanwhile, a chemical absorption process, which preferably removes CO_2 (in partial pressures up to 0.7–1.4 MPa)[6] from a gas stream by reacting with amines to form carbamates and/or bicarbonate, does not require reducing pressure but elevating temperature to 120–140 °C for recycling the chemical solvents (temperature swing regeneration) is required.[7–12] Development of novel chemical absorbents that exhibit a great working capacity of CO_2 capture/release cycles even at high partial pressure conditions ($\geq$1 MPa) can reduce costs for compression of the separated CO_2 for subsequent pipeline transportation.

So far, aqueous solutions of bulky tertiary alkanolamines such as *N*-methyldiethanolamine (MDEA), triethanolamine (TEA), and triisopropanolamine (TIPA) have been studied to capture pressurized CO_2.[9,13,14] However, there remain some concerns connected with relatively large heat requirements to release CO_2 and/or small CO_2 solubilities per unit mass of the absorbents due to their greater molecular weight.

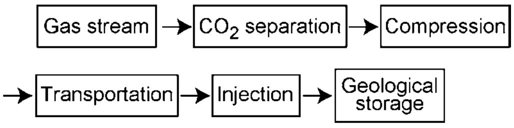

Figure 1. Illustration of the proposed CO_2 capture and storage (CCS) process.

In this paper, in order to extend the usability of the amine-based chemical absorption process to remove CO_2 in a wide range of partial pressures (0.1–4 MPa), we describe relationships between CO_2 partial pressures and differences in CO_2 solubilities in various aqueous amine solutions at temperatures for CO_2 capture (40 °C) and release (70 °C) cycles. We also propose that an acid dissociation constant (pK_a)-based chemical absorbent screening method is effective to develop an advanced chemical solvent system with features meeting a smaller sized absorbent molecule, a smaller heat requirement, and a greater working capacity at $\approx$4 MPa of CO_2 partial pressures.

First, we have selected seventeen amine derivatives with a variety of structural aspects and measured pK_a values of their conjugated acid forms in aqueous solution (initial amine concentration is 10 mM at 25–27 °C)[15] (see also Figure S1[16]). The pK_a values for representative amines increase in the following order: aminopyrazole < aminopyridines < Bis-Tris < imidazoles, 4-alkylmorpholines < trialkanolamines < 1-alkylpiperidines. Substitution of a ring-membered carbon atom in HEPD with an oxygen atom dramatically reduced its basicity (as for HEMO). Multiple hydroxylation of alkanolamines caused smaller pK_a values (in order of pK_a values: Bis-Tris < TEA = TIPA < MDEA = *n*BDEA; 3MO1,2Pdiol < HEMO < EMO; and 1HE4HPPD < HEPD). Methylation of imidazoles increased basicity (in order of pK_a values: 1MeIm = Im < 4MeIm < 2MeIm). Amination of pyridines also increased their basicity compared with the nonmodified form [in order of pK_a values: pyridine (5.20)[17] < 3APy < 2APy]. In diazaheterocycles, imidazoles were stronger bases than 3A5MPyzol, even though pyrazole was methylated and aminated. All of the amines examined were soluble in water at concentration $w = 30\%$. With amine derivatives in a wide range of pK_a in hand, we examined CO_2 solubility in aqueous amine solutions ($w = 30\%$) at 40 and 70 °C under the conditions of 0.1, 1, and 4 MPa of CO_2 partial pressures (see experimental section[16]).

CO_2 solubilities at 40 and 70 °C were shown in Figures S2–S18[16] and summarized in Figure S19.[16] Differences in CO_2 solubility at 40 and 70 °C (ΔC_{CO_2}) from data given in Figure S19[16] were plotted against pK_a values of the corresponding amines (Figure 2). From these results, the following points were found: (i) lowered temperature and/or elevated CO_2 partial pressure had CO_2 solubility increased; (ii) the ΔC_{CO_2} values plotted against pK_a were characterized with a volcano-shaped profile; (iii) strongly basic amines (pK_a > 8.5, i.e., MDEA) showed a large difference in CO_2 solubility at 40 and 70 °C (ΔC_{CO_2}) at 0.1 MPa of CO_2 partial pressure but small differences at higher pressures (1 and 4 MPa); (iv) moderately basic amines (p$K_a \approx 8$, i.e., TEA) showed great ΔC_{CO_2} values at 0.1 and

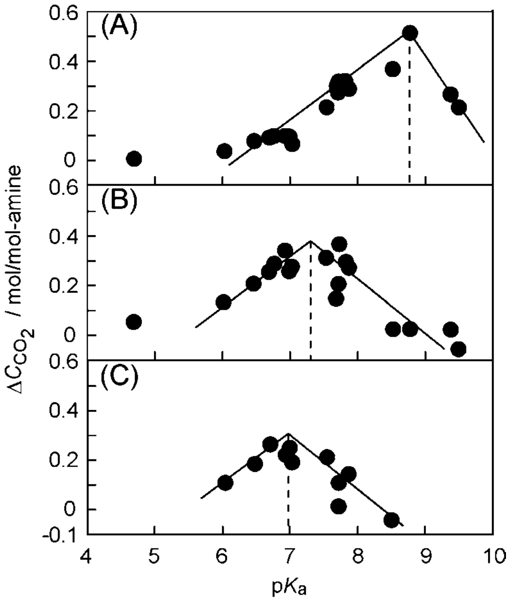

Figure 2. Differences in CO_2 solubility at 40 and 70 °C (working capacity for the CO_2 capture/release cycles: ΔC_{CO_2}) for aqueous amine solutions ($w = 30\%$) as a function of pK_a under the conditions of (A) 0.1, (B) 1, and (C) 4 MPa of CO_2 partial pressures.

1 MPa, but small at 4 MPa; (v) relatively weakly basic amines ($pK_a < 8$, i.e., Im) showed small ΔC_{CO_2} values at 0.1 MPa but great both at 1 and 4 MPa; (vi) totally, with increasing a CO_2 partial pressure, ΔC_{CO_2} values for amines with $pK_a = 6.5$–7.5 increased, oppositely decreased for those with pK_a values greater than 7.5, and no big differences for pK_a values smaller than 6.5.

The pK_a values affording the maximal ΔC_{CO_2} at each CO_2 partial pressure, pK_a(max)'s were determined to be approximately 8.7, 7.3, and 7.0 at 0.1, 1, and 4 MPa of CO_2 partial pressures, respectively. The pK_a(max) values shifted toward smaller pK_a with elevating CO_2 partial pressures, indicating that the availability of amines with pK_a values suitable for capture/release cycles of CO_2 with targeted partial pressures might play an important role for developing advanced greenhouse gas control technologies (Figure S20[16]).

Throughout this study, it was found that imidazole derivatives including Im, 1MeIm, 2MeIm, and 4MeIm had potential to capture and release CO_2 in the range of partial pressures from 1–4 MPa. Briefly, their larger differences in CO_2 solubility at 40 and 70 °C (ΔC_{CO_2}) at elevated pressures might reduce heat requirements to regenerate active absorbents compared to common MDEA which is too strong in basicity for operations under such conditions. Furthermore, smaller sized imidazoles also showed greater differences in CO_2 solubility per unit volume of the amine solutions ($w = 30\%$) at 4 MPa (Im: 50; 1MeIm: 31; 2MeIm: 23; and 4MeIm: 34 g/L-amine solution) relative to those for bulky alkanolamines such as MDEA (≈0) and TEA (1 g/L amine solution). Oppositely, weaker amines (pK_a values smaller than 6.5) do not exhibit working capacities enough to operate CO_2 capture/release cycles even at elevated CO_2 partial pressure conditions. Thus, imidazoles seem to be applicable to treat a CO_2-containing pressurized gas stream (generated from the IGCC process) with some improvements. Measurements of vapor–liquid equilibrium and absorption/desorption kinetics are now underway. The mechanism of absorption of pressurized CO_2 into aqueous solutions of imidazoles (having both secondary and tertiary amino groups within a molecule) also needs further clarification.

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