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Enhanced CO_2 absorption and desorption in a tertiary amine medium with a carbonic anhydrase mimic

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ABSTRACT

We report the effects of a series of carbonic anhydrase (CA) model complexes on CO_2 absorption and desorption in an aqueous tertiary amine medium. The CO_2 hydration efficiency was determined under basic conditions by using stopped-flow kinetics experiments. Catalyst **6** was found to exhibit the best CO_2 hydration efficiency ($3.130 \times 10^3\ M^{-1}\ s^{-1}$) in the tertiary amine medium. In a highly concentrated tertiary amine medium, catalyst **2** was found to enhance the absorption and regeneration efficiency of CO_2 by 10% and 24%, respectively. Our results for simple CA model complexes indicate that possible usage of synthesized complexes in post-combustion process.

Introduction

The industrial emission of carbon dioxide (CO_2) is a major contributor to the rise in CO_2 level in the atmosphere [1], which poses a serious threat to the Earth's ecosystems because of global warming and climate change [2]. To limit the undesirable effects of CO_2, many methods have been developed for the control of CO_2 emissions [3–9]. Using the CO_2 capture and sequestration technologies can reduce the CO_2 emissions significantly from existing and new power plants. Post-combustion capture is preferred for industrial CO_2 capture over other capture technologies such as pre-combustion, oxy-fuel combustion, and electrochemical process [10,11]. In the post-combustion processes, CO_2 has been chemically absorbed industrially by using alkanol amine liquid absorbents [12–14]. The alkanol amines that are used as a liquid absorbents in post-combustion processes, are primary, secondary and tertiary amines are commonly [15,16]. Although primary and secondary amines are superior to tertiary amines in effective absorption of CO_2, tertiary amines need less regeneration energy than that of primary and secondary amines [17,18]. Higher regeneration energy of primary and secondary alkanol amines due to the formation of stable carbamate increases the overall cost of CO_2 capture process [19]. Consequently, in CO_2 absorption process the tertiary amine methyldiethanolamine (MDEA) is preferred over primary and secondary amines. The low level of solvent degradation and the lower level of energy require to the stripper in post-combustion process to regenerate the absorbents are advantages of tertiary amines [20,21]. In addition, tertiary amine CO_2 loading capacity, mole of CO_2 per amine, is higher than the primary and secondary amines [20,21]. Furthermore, tertiary amines form an unstable carbamate which could be easily converted to bicarbonate. Despite many advantages, tertiary amine shows of slow CO_2 absorption in large-scale industrial absorption processes [22–24]. The biocatalyst bovine carbonic anhydrase (bCA) is combined with tertiary amines to enhance CO_2 absorption. Biological enzymes are the best catalysts with their precision, high selectivity and superior conversion rates. An approach of using an enzyme based model could be more relevant to enhance the of CO_2 absorption in tertiary amine medium. The overall conversion of CO_2 to bicarbonate in the presence of carbonic anhydrase(CA) enzyme is as follows

$$CO_2 + H_2O \overset{\text{CA enzyme}}{\rightleftharpoons} HCO_3^- + H^+$$

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CA is one of the fastest known enzymes for forward and back reaction of CO_2 to bicarbonate with catalytic efficiency as high as $10^6\,s^{-1}$ [22–24]. Although CA has the highest CO_2 hydration activity, CA is inappropriate to use in industrial conditions because of its high cost and poor stability. The CA-based model complexes that used in basic solution were (Zn(cyclen)(H_2O)){ClO_4] [25], which is the most studied active CA model complex [26–28], and salen-like ligands containing Zn complexes [29]. Recently, we have reported that the addition of CA model complexes to a tertiary amine medium enhances the CO_2 absorption [30]. The tridentate ligand based CA model complexes shown the CO_2 hydration efficiency of $2.860 \times 10^3\,M^{-1}\,s^{-1}$. However, the low absorption and desorption efficiency of CO_2 was observed for tridentate ligand based CA model complexes in the highly concentrated (30%) amine medium. Further, we studied the effects of adding an amine salt to a tertiary amine medium, which also enhanced the CO_2 absorption [31]. Problems associated with the addition of CA model complexes in highly concentrated amine solutions were the anion coordination to the metal center and weak dissociation of bicarbonate from the metal center [32]. We have designed and synthesized CA model complexes with tripodal, tris(2-aminoethyl)amine (tren), ligand derivatives that have hydrophilic groups as flexible pendant arm could support the enhanced dissociation of bicarbonate from metal center. The flexible pendant arm containing tripodal ligands could shield a cavity for a metal after binding to the four nitrogen atoms. More importantly, tripodal ligands further leave an additional coordination site for small exchangeable ligands such as H_2O and bicarbonate [33]. The flexible pendant arm containing tripodal metal complexes enhanced the CO_2 hydration rate and it also enhanced the dissociation of bicarbonate even in the highly concentrated amine medium. We discuss the development of this series of CA-based model complexes that enhance the absorption and desorption of CO_2 in a tertiary amine medium and the possible utilization of these new CA-based complexes in highly concentrated amine solutions for post-combustion processing.

Experimental

General consideration

All chemicals purchased were of analytical grade and used without further purification. FT-IR spectra were recorded using the ATR method with a Varian 640-IR FT-IR spectrometer. ^1H NMR and ^{13}C NMR were recorded on Varian 300 MHz and Varian 125 MHz instruments, respectively.

Stopped-flow kinetics measurements

Experimental catalytic rate constants for the CO_2 hydration reaction catalyzed by **1–7** were determined using stopped-flow spectrophotometry using methods similar to those previously described. Prior to the experiment, a solution of CO_2 saturated water was prepared by purging deionized water with 100% CO_2 gas at 25 °C for at least 60 min. Using Henry's constant, this solution was calculated to contain 33.8 mM [CO_2]. The catalyzed and uncatalyzed CO_2 hydration rates were found by rapidly mixing the dissolved CO_2 solution and the buffer solution 1:1 in an Applied Photophysics stopped-flow spectrophotometer while recording the time dependent absorbance at $\lambda = 596$ nm. For these studies, catalysts (0.25 mM), MDEA (30 mM) and Thymol Blue (25 μM) were used with minimum amount of DMSO(1.0 mL was added in 50 mL of above solution). The k_{cat} and K_m kinetic parameters were calculated using the Michaelis–Menten and Lineweaver–Burk equations. The ratio of k_{cat}/K_M is called catalytic efficiency and has the unit of 2nd order rate constant as the reaction depends on concentration of substrate and the concentration of enzyme.

CSTR absorption and desorption experiments

The CSTR experiments were carried out in MDEA (2.5 M, 30 wt %) with 2.0 mM of catalyst, the tertiary amine solution was prepared by mixing the amine and deionized water. In a stainless reactor, 500 g of fresh absorbent was used. To maintain constant temperature, silicon oil circulating bath was used. When the temperature in the reactor reached the experimental temperature, 15 mol% CO_2 containing N_2 was injected at a rate of 1 L/min. A mass flow controller (MFC) was used to maintain a certain flow rate during the injection of CO_2. Gas chromatography (GC) was used to analyze the concentration of CO_2 at the outlet of the reactor. A Porapak-Q column (0.32 m by 1.83 m, Supelco Inc.) and a TCD detector were installed in the GC. All the experiments were conducted over the temperature range 40 °C–90 °C and at atmospheric pressure (1 atm). The CO_2 loading and deloading was calculated by integrating differences between the concentrations of injected CO_2 and the concentrations of emitted CO_2. The amount of the CO_2 before injection into the reactor and the amount of CO_2 released after reactions were calculated by applying the ideal gas equation.

X-ray single crystal structural analysis

A single crystal was mounted at room temperature on the tips of quartz fibers, coated with Paratone-N oil, and cooled under a stream of cold nitrogen. Intensity data were collected on a Bruker CCD area diffractometer running the SMART software package with Mo Kα radiation ($\lambda = 0.71073$). The structure was solved by direct methods and refined on F^2 using the SHELXTL software package. The multi-scan absorption correction was applied with SADABS, which is part of the SHELXTL program package, and the structure was checked for higher symmetry by the program PLATON. All non-hydrogen atoms were refined anisotropically. In general, hydrogen atoms were assigned idealized positions and given thermal parameters equivalent to 1.2 times the thermal parameter of the carbon atom to which they were attached. Data collection and experimental details for the complex **7** (CCDC 1508511) is summarized in Supplementary Table S1, and bond angles and distance are summarized in Supplementary Table S2.

*Synthesis of catalysts **1–7***

*Synthesis of **2***

Synthesis of imine (A). To a solution of tris(2-aminoethyl)amine (0.500 g, 3.40 mmol) in EtOH (40 mL), 3-methoxybenzaldehyde (1.39 g, 10.25 mmol) was added and heated 70 °C for 12 h. After cooling to room temperature, light yellow solution was concentrated under reduced pressure. Resulting light yellow sticky mass was dried under high vacuum. Yield = 1.62 g, 85%.

Synthesis of amine (B). To a solution of imine (A) (1.70 g, 3.40 mmol) in THF (45 mL), $NaBH_4$ was added pinch by pinch. To this mixture, MeOH (10 mL) was added using syringe and heated to 40 °C for 6 h. After completion of reaction, monitored by TLC, the reaction mixture was diluted with DM water (100 mL) and extracted with DCM (80 mL). The layers were separated and organic layer was dried over Na_2SO_4 and concentrated. It afforded light yellow sticky mass. Yield = 1.68 g, 95%.

Methylation of amine (C). To a solution of amine (B) in CH_3CN and acetic acid, HCHO (1.65 ml) was added and stirred at room temperature for 3 h. Then the mixture was cooled to 0 °C and $NaBH_4$ was carefully added pinch by pinch. The reaction mixture temperature was slowly allowed to reach room temperature and at

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