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$^{13}$C-NMR study of acid dissociation constant (pKa) effects on the CO$_2$ absorption and regeneration of aqueous tertiary alkanolamines

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Abstract

We have studied the formation rates of chemical species such as CO$_3^{2-}$/HCO$_3^-$, amine/protonated amine, and carbonate/protonated carbonate in the course of CO$_2$ absorption at room temperature and concentration changes after CO$_2$ release upon heating at 93 °C for 30 min for aqueous solutions of 12 kinds of tertiary alkanolamines using $^{13}$C-NMR spectroscopy. A positive linear correlation was found between the CO$_2$ capture rates of alkanolamines having a normal hydroxyalkyl group and their pKa values. The CO$_2$ capture rates of alkanolamines having a branched hydroxyalkyl group were lower than those in this relationship. The CO$_2$ release amount of each tertiary amine increased with decreasing pKa, as a general trend. N-ethyldiethanolamine (EDEA) showed the largest CO$_2$ release amount and a moderately high rate of CO$_2$ absorption.

Keywords: $^{13}$C-NMR; tertiary amine; acid dissociation constant; CCS.

1. Introduction

Carbon dioxide (CO$_2$) is a greenhouse gas that contributes to global warming and climate change problems. Aqueous solutions of amines are used as absorbents for removing CO$_2$ from flue gas of fossil fueled power plants [1]. An amine absorbent absorbs CO$_2$ at room temperature and releases CO$_2$ at high temperature; the separated CO$_2$ will be buried underground. This is called carbon dioxide capture and storage (CCS). One of key parameters for CCS is
to use a high performance absorbent: rapid CO₂ absorption; large CO₂ release; small heat for CO₂ release. Since a single amine absorbent did not show high performance, a blend of two amines, for example, a tertiary alkanolamine N-methyldiethanolamine (MDEA) and piperazine (PZ) (see Fig. 1) [2], was used as an absorbent. The kinetics of the reaction of CO₂ with aqueous solutions of alkanolamines was reviewed [3]. The CO₂ absorption rate of an aqueous solution of MDEA is slow, whereas the CO₂ release amount is large and the heat of CO₂ release is small. The rate can be enhanced by the addition of PZ, whereas the CO₂ release amount is maintained to be large. ¹³C-NMR spectroscopy is a powerful tool for qualitative and quantitative analyses of chemical species formed in CO₂-absorbed aqueous solutions of amines [4−13]. It has been elucidated that in a CO₂-absorbed aqueous amine there exist bicarbonate ion (HCO₃⁻), carbonate ion (CO₃²⁻), amines, protonated amines, amine carbamates, and amine carbonates, etc. It is not possible to distinguish the signals originating from an amine and its protonated species, HCO₃⁻ and CO₃²⁻, etc. using ¹³C-NMR spectroscopy, because of rapid proton exchanges. A tertiary alkanolamine does not make its carbamate. Most of aqueous solutions of tertiary alkanolamines emit low heat when the solutions absorb CO₂. The pKa dependence of CO₂ absorption and release is useful in evaluating the performance of amine absorbents [14, 15], because pKa can be used as a measure of proton acceptor. Research on the pKa dependence of CO₂ absorption/regeneration of aqueous tertiary alkanolamines is useful in selecting a tertiary alkanolamine as an amine blended with PZ instead of MDEA.

In this paper, we will present ¹³C-NMR study on the formation rates of chemical species (HCO₃⁻/CO₃²⁻, amine/protonated amine, carbonate/protonated carbonate, etc.) in the course of CO₂ absorption and concentration changes of these species after CO₂ release upon heating at 93 °C for 30 min for aqueous solutions of tertiary alkanolamines shown in Fig. 1: 2-dimethylamino-1-ethanol (DMAE), 3-dimethylamino-1-propanol (DMAP), 1-dimethylethanolamine-2-propanol (DMA2P), 4-dimethylethanol-1-butanol (DMAB), 2-diethylethanolamine-1-ethanol (DEAE), 3-diethylethanolamine-1-propanol (DEAP), 1-diethylethanolamine-2-propanol (DEA2P), 4-diethylethanolamine-2-butanol (DEA2B), 1-(2-hydroxyethyl)piperidine (1-HE-PP), 1-(2-hydroxyethyl)pyrrolidine (1-HE-PRL), MDEA, and EDEA. On the basis of the ¹³C-NMR results, we will investigate the pKa effects on the absorption rate and the loading change after CO₂ release upon heating.

![Chemical structures of tertiary amines](image)

Fig. 1. Chemical structures of tertiary amines: (a) DMAE; (b) DMAP; (c) DMA2P; (d) DMAB; (e) DEAE; (f) DEAP; (g) DEA2P; (h) DEA2B; (i) 1-HE-PP; (j) 1-HE-PRL; (k) MDEA; (l) EDEA.

2. Experimental

The sample of DEA2B was synthesized according to the previous method [15]; DMAP and 1-HE-PP were purchased from Sigma-Aldrich; other tertiary amines were purchased from Tokyo Chemical Industry. In the experiments of CO₂ absorption kinetics, gaseous CO₂ was bubbled through a D₂O solution of an amine at a rate of 150 mL/min at room temperature in a flask. The concentration of the aqueous solution of a tertiary amine was 20 wt%. The volume of the solution was about 50 mL. In the absorption–regeneration experiments, a D₂O solution (50 mL) of the amine (20 wt%) bubbled with CO₂ gas at a rate of 150 mL/min for 60 min at room temperature was heated at 93 °C for 30 min. ¹³C-NMR spectra were measured at room temperature on a JEOL JNM-500ECX 500 MHz NMR spectrometer using the inverse gated proton decoupling method. Because of a long spin–lattice relaxation time, the holding time between scans was set at 1 min. The data of 64 scans were accumulated for each spectrum. As the standard of chemical shifts, 1,4-dioxane-d₆ (D, 99%) (chemical shift, 67.4 ppm [16]) was added into the sample. The pKa value of each amine was measured at room temperature using the potentiometric titration
method [17]. The pH values were measured on a Horiba F-51 pH meter. A 2.0×10^{-4} \text{ mol/L} amine aqueous solution was titrated with the 0.5 \text{ mol/L} HCl aqueous solution. This measurement was performed three times for each amine; the average of the measurements was used as pK\text{a} of the amine.

3. Results and discussion

3.1. Absorption of CO\textsubscript{2}

The $^{13}$C-NMR spectrum of an aqueous solution of EDEA (20 wt\%) and that after 30-min bubbling of gaseous CO\textsubscript{2} are shown in Fig. 2a and 2b, respectively. The observed $^{13}$C-NMR spectra were assigned on the basis of the data in the literature [4–13]. The assignments of the observed bands are listed in Table 1. The observed $^{13}$C-NMR spectra of the other amines were also assigned. No signals of carbamates and CO\textsubscript{2} (125.3 ppm [7]) were observed. No signals of carbonates were observed for DMA2P, DEA2P, and DEA2B; a small amount of carbonate was observed for the other alkanolamines. The concentrations of the amine/protonated amine, the carbonate/protonated carbonate, and the CO\textsubscript{3}^{2−}/HCO\textsubscript{3}− species were calculated using the band at 50–70 ppm of the N-bonded carbon atom of the hydroxyalkyl chain, the band at ~160 ppm of CO\textsubscript{2}− of the amine carbonate, and the band at ~163 ppm of CO\textsubscript{3}^{2−}/HCO\textsubscript{3}−, respectively.

Fig. 2. $^{13}$C-NMR spectra of (a) an aqueous solution of EDEA (20 wt\%) and (b) after 30-min CO\textsubscript{2} bubbling.
Table 1. Assignments of observed bands

| Chemical shift / ppm | Species | Carbon numbering a) |
|---------------------|---------|---------------------|
| 11.5–10.2           | EDEA carbonate and its protonated species | 5 |
| 12.1–9.8            | EDEA and its protonated species | 1 |
| 50.6–49.8           | EDEA and its protonated species | 2 |
| 54.1–53.3           | EDEA carbonate and its protonated species | 6 |
| 56.3–55.8           | EDEA and its protonated species | 4 |
| 56.3–56.1           | EDEA carbonate and its protonated species | 8 |
| 59.5–57.5           | EDEA carbonate and its protonated species | 7 |
| 60.6–57.2           | EDEA and its protonated species | 3 |
| 63.4–62.4           | EDEA carbonate and its protonated species | 10 |
| 160.6–160.0         | EDEA carbonate and its protonated species | 11 |
| 163.4–162.1         | $\text{CO}_3^{2-}/\text{HCO}_3^-$ | – |

a) The numbering of carbon atoms is shown in the chemical structures below.

Temporal concentration changes of $\text{CO}_3^{2-}/\text{HCO}_3^-$, amine/protonated amine, carbonate/protonated carbonate for the aqueous solution of EDEA in the course of CO$_2$ absorption are shown in Fig. 3. The sum of the concentrations of $\text{CO}_3^{2-}/\text{HCO}_3^-$ and carbonate/protonated carbonate is equal to the amount of CO$_2$ capture; the temporal concentration change of the sum is also shown in Fig. 3. Thus, most of CO$_2$ is captured as $\text{CO}_3^{2-}/\text{HCO}_3^-$ in the absorbent. In the other tertiary alkanolamine solutions, most of CO$_2$ is captured as $\text{CO}_3^{2-}/\text{HCO}_3^-$, because the tertiary alkanolamines make no carbamates and small amount of carbonates.

Fig. 3. Concentration changes of $\text{CO}_3^{2-}/\text{HCO}_3^-$ (●), EDEA (■), carbonate (●), total CO$_2$ capture (●), and pH (○) for the aqueous solution of EDEA as a function of CO$_2$ bubbling time.

The initial rate of CO$_2$ capture was calculated from the data between 0 and 5 or 10 min. The obtained initial rates of CO$_2$ capture for aqueous tertiary alkanolamines were plotted against p$K_a$ values in Fig. 4; the observed p$K_a$ values of DMAE, DMAP, DMA2P, DMAB, DEAE, DEAP, DEA2P, DEA2B, 1-HE-PP, 1-HE-PRL, MDEA, and EDEA were 9.34, 9.57, 9.55, 9.79, 9.94, 10.17, 10.14, 10.25, 9.56, 9.73, 8.60, and 9.08, respectively. Since the rate of CO$_2$ absorption for aqueous PZ is fast, its rate obtained in this study is also shown as a reference in Fig. 4. Among alkanolamines having a normal hydroxyalkyl chain (DEAE, DEAP, DMAE, DMAP, DMAB, 1-HE-PP, 1-HE-PRL, MDEA, and EDEA), a positive linear tendency is found between the CO$_2$ absorption rates and the p$K_a$ values. However, this relationship does not hold for the CO$_2$ absorption rates for DMA2P, DEA2P, and DEA2B having a branched hydroxyalkyl group. The CO$_2$ capture originates mainly from $\text{CO}_3^{2-}/\text{HCO}_3^-$, because no
carbamates and a small amount of carbonates of the tertiary alkanolamines were formed. Accordingly, the rates of \( \text{CO}_3^{2-}/\text{HCO}_3^- \) formation and CO\(_2\) capture is sensitive to the chemical structure of tertiary amines. On the other hand, the CO\(_2\) absorption rates of MDEA aqueous solutions in the concentration range between 20 and 1 wt\% showed almost the same values. These results suggest that the tertiary alkanolamine plays a role like a catalyst in the reaction of HCO\(_3^-\) formation [3], and the transition state of this reaction contains the tertiary alkanolamine molecule.

![Fig. 4. Initial rates of CO\(_2\) capture versus pKa values for aqueous tertiary alkanolamines (20 wt\%). The dashed line is an eye guide.](image)

### 3.2. Release of CO\(_2\)

The CO\(_2\) loading, mol-CO\(_2\)/mol-amine, can be obtained from dividing the molar concentration of absorbed CO\(_2\) by the molar concentration of the amine. The maximum CO\(_2\) loadings for all the tertiary alkanolamine solutions ranged between 0.94 and 1.12. The CO\(_2\) loading of each alkanolamine decreased upon heating at 93 °C for 30 min. The change in CO\(_2\) loading upon heating is expressed by \( \Delta (\text{mol-CO}_2/\text{mol-amine}) \). The decrease in \( \Delta (\text{mol-CO}_2/\text{mol-amine}) \) upon heating means the release of CO\(_2\) from the solution. The \( \Delta (\text{mol-CO}_2/\text{mol-amine}) \) values were calculated from the \(^{13}\)C-NMR and are shown in Fig. 5. A positive linear tendency is found between the \( \Delta (\text{mol-CO}_2/\text{mol-amine}) \) values and the pKa values. Thus, the CO\(_2\) release upon heating increases with decreasing pKa. EDEA showed the highest value in CO\(_2\) release.

The rate of CO\(_2\) absorption increases and the amount of CO\(_2\) release decreases with increasing pKa value, as a general trend. Thus, there exists the best pKa value as an CO\(_2\) absorbent. Among the tertiary alkanolamines studied in this work, EDEA is promising.

![Fig. 5. \( \Delta (\text{mol-CO}_2/\text{mol-amine}) \)s versus pKa values for aqueous tertiary amines (20 wt\%). The dashed line is an eye guide.](image)
2. Conclusions

We have investigated the concentration changes of $\text{CO}_3^{2-}/\text{HCO}_3^-$, amine/protonated amine, and carbonate/protonated carbonate generated in the course of $\text{CO}_2$ absorption at room temperature and those after $\text{CO}_2$ release upon heating at $93\,^\circ\text{C}$ for 30 min for aqueous solutions of 12 tertiary alkanolamines using $^{13}\text{C}$-NMR spectroscopy. The $pK_a$ dependence of the initial rates of $\text{CO}_2$ capture and the $\text{CO}_2$ release amount were investigated. The $\text{CO}_2$ capture rate of each alkanolamine having a normal hydroxyalkyl chain increased with increasing $pK_a$ values of the amines. The $\text{CO}_2$ capture rates of alkanolamines having a branched hydroxyalkyl chain were lower than those in this relationship. The $\text{CO}_2$ release amount of each tertiary alkanolamine increased roughly with decreasing $pK_a$. EDEA showed the largest $\text{CO}_2$ release amount and a moderately high rate of $\text{CO}_2$ absorption.

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