Effect of alcohol chain length on carbon dioxide absorption into aqueous solutions of alkanolamines

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Abstract

To identify structural factors of alkanolamine molecule which influence the CO2 absorption properties, we systematically investigated the CO2 absorption into aqueous solutions of 2-(ethylamino)ethanol (EAE), 3-ethylamino-1-propanol (EAP), 4-ethylamino-1-butanol (EAB), 2-(propylamino)ethanol (PAE) and 2-(butylamino)ethanol (BAE). It was shown that the CO2 loading exhibited a clear dependence on the alcohol chain length by quantitative 13C nuclear magnetic resonance measurements. In contrast, it did not differ significantly among EAE, PAE and BAE. The results support the idea that the hydroxyl functional group of alkanolamine has a specific effect on the CO2 absorption reactions in the aqueous solutions by intramolecularly interacting with the central amino moiety.

Keywords: amine absorbent; CO2 loading; hydrogen bonding; NMR

1. Introduction

Alkanolamines are the most established absorbents used to remove CO2 from process gas streams. Therefore, the chemical reaction of CO2 with alkanolamines is of fundamental and practical importance [1].

In the aqueous alkanolamine solutions, CO2 is absorbed by the formation of carbamate or bicarbonate anions:

\[ 2R_1R_2NH + CO_2 \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \] (1)

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\[ R^1R^2R^3N + CO_2 + H_2O \leftrightarrow HCO_3^- + R^1R^2R^3NH^+ \]  
\[ 2R^1R^2NH + CO_2 \rightarrow R^1R^2NH^+COO^- \]  
\[ CO_2 + OH^- \rightarrow HCO_3^- \]

where \( R^1, R^2 \) and \( R^3 \) are substituents \([1-3]\). Note that equations (1) and (2) describe the overall reactions of \( CO_2 \) absorption in the solutions. Some elementary reactions have critical roles in providing the absorbent capability. Below are listed examples of the possible elementary steps:

The sterically hindered alkanolamines such as 2-amino-2-methyl-1-propanol (AMP) and 2-isopropylaminoethanol (IPAE) have been chosen as potential alternative absorbents for their high \( CO_2 \) loading capacities and regenerative capabilities \([4-7]\). The steric hindrance of the substituents adjacent to the amino group lowers the stabilities of the carbamate anion formed by reaction (1) and the zwitterion formed by reaction (3). Eventually, an aqueous solution of hindered amine reacts with \( CO_2 \) to form mostly bicarbonate ions and shows a high solubility of \( CO_2 \) \([8]\). This is a traditional explanation of the advantage of sterically hindered alkanolamines.

Recently we have reported based on quantum chemical calculations that the formation of the carbamate through a zwitterionic intermediate is kinetically favored over the bicarbonate formation even in the sterically hindered alkanolamine solutions \([5,6]\). We have also found that small but significant amounts of carbamate stably exist even in the \( CO_2 \) rich solutions of aqueous AMP and IPAE, which may explain the properties of these amines such as high absorption rates.

Our quantum chemical calculations for AMP and IPAE revealed the transition states and the reaction pathways along intrinsic reaction coordinates, using the density functional theory with the latest continuum solvation model (SMD/IEF-PCM) \([9]\). The results suggest that the hydroxyl group of alkanolamine is likely to interact intramolecularly with the amino group or the carbonyl group \([5]\). It should be noted that both AMP and IPAE have the molecular structure of N-C-C-OH, in which two carbon atoms exist between the amino and hydroxyl groups. This fact implies that such a structural factor of alkanolamine, which is different form the steric hindrance factor, influences the reaction mechanism and the absorbent properties.

In this work, we study the absorption into aqueous solutions of 2-(ethylamino)ethanol (EAE), 3-ethylamino-1-propanol (EAP), 4-ethylamino-1-butanol (EAB), 2-(propylamino)ethanol (PAE) and 2-(butylamino)ethanol (BAE) to systematically explore the above implication.

2. Methods

The molecular structures of the alkanolamines investigated in this work are shown in Figure 1. EAE (>98%, Aldrich), EAB (>98%, Tokyo Chemical Industry), PAE (98+%, Aldrich) and BAE (99%, Aldrich) were purchased from chemical companies and used without further purification.

EAP was prepared by the following synthetic procedures. Into 250 ml of 70wt % aqueous ethylamine solution, 138 g of \( K_2CO_3 \) was added dropwise stirring with 95 g of 3-chloro-l-propanol at 0°C. After the addition was completed, the cooling bath was removed and the solution was stirred at 50°C for 72 h. The reaction was monitored by liquid chromatography-mass spectrometry. After the reaction completion, the water and excess ethylamine were evaporated off. The residue was diluted with methanol and the
potassium salt was filtered. The obtained crude product was distilled under vacuum to give EAP as a colorless liquid (99% purity by gas chromatography).

Figure 1. Molecular structures of the investigated amines.

For a comparison of the alkanolamines, we used a gas composition of 20% CO$_2$ with the balance being N$_2$ and let it flow at a rate of 700 ml/min into 50 g of a 30wt% aqueous alkanolamine solution for 60 min. A glass scrubbing bottle was used as the vessel in a water bath controlled at 40°C. After that, the bottle was moved to another water bath that was controlled at 70°C. The outlet gas was monitored with a CO$_2$ analyzer (VA-3001, Horiba) [6].

The sample solutions thus prepared were analyzed with a NMR spectrometer (JNM-ECA400, JEOL). To improve the lock signal, 100 mL D$_2$O was added to 500 mL of each sample. Quantitative spectra were obtained at 100 MHz and 21–23°C using the inverse gated decoupling technique with a pulse angle of 30°, a delay time of 30 s and 400 scans. The CO$_2$ loadings were also quantified by a total organic carbon analyzer (TOC-VCSH, Shimadzu) [2].

Figure 2. $^{13}$C NMR spectrum of the CO$_2$ loaded aqueous PAE solution with relative peak areas.
3. Results and Discussion

All the prepared aqueous solutions of the alkanolamines in Figure 1 showed high CO₂ absorption rates, which were comparable with those of 30wt% aqueous monoethanolamine or IPA solutions, and well saturated with CO₂ within 60 min under the experimental conditions. In all the solutions, the amounts of desorbed CO₂ at 70°C for 60 min were in the range 12–15 g CO₂/kg solvent, which were less than half of that of the 30wt% aqueous IPA solution.

Figure 2 shows the ¹³C NMR spectrum of the CO₂ saturated aqueous PAE solution with the carbon peaks with their relative areas. The existence of CO₃²⁻ can be ignored, because the CO₂ saturated aqueous amine solutions are weakly basic. Jakobsen et al. [10] reported that the limiting shifts at 20°C in samples containing solely CO₃²⁻ or HCO₃⁻ were 168.9 and 161.4 ppm, respectively. Therefore, the peak at 161.2 ppm in Figure 2 is assigned to the carbon of HCO₃⁻. The peaks at 163.8 ppm and 56.6 ppm in Figure 2 represent the carbonyl carbon of carbamate (NCOO⁻) and the alpha carbon of the alcohol chain of neutral or protoned amine (CH₂OH), respectively.

Figure 3. ¹³C NMR spectrum of the CO₂ loaded aqueous EAP solution with relative peak areas.

Figure 3 shows the ¹³C NMR spectrum of the CO₂ saturated aqueous EAP solution with the carbon peaks with their relative areas. The peaks at 161.0 ppm, 163.2 ppm and 58.5 ppm represent the carbons of HCO₃⁻, NCOO⁻ and CH₂OH respectively. The CO₂ loading obtained from the areas of these peaks is 0.85 mol CO₂/mol amine, which is close to the value determined by the TOC analysis (0.80 mol CO₂/mol amine).

Surprisingly, we found that the relative peak areas of carbamate to bicarbonate significantly differed between PAE and EAP, despite the very similar molecular structures. The more significant difference was observed between BAE and EAB.

The results of the ¹³C NMR measurements are summarized in Table 1. The relative amounts of carbamate are markedly different among EAE, EAP and EAB. In contrast, they do not differ significantly among EAE, PAE and BAE. These results cannot be explained by the steric hindrance of alkanolamine,
and clearly demonstrate that the number of carbon atoms between the amino and hydroxyl groups is more critical for the carbamate yield.

Table 1. Chemical shift and the relative peak area for carbon of bicarbonate, carbonyl carbon of carbamate and $\alpha$ carbon of the alcohol chain of neutral or proposed amine in the $^{13}$C NMR spectra of the CO$_2$ loaded aqueous alkanolamine solutions at 21–23°C.

| amine | chemical shift [ppm] | relative area |
|-------|----------------------|--------------|
|       | HCO$_3^-$ | NCOO$^-$ | COH | HCO$_3^-$ | NCOO$^-$ | COH |
| EAE   | 162.3     | 163.5    | 56.7 | 0.49 | 0.24 | 1.0 |
| EAP   | 161.0     | 163.2    | 58.5 | 0.83 | 0.11 | 1.0 |
| EAB   | 160.7     | 163.2    | 60.6 | 0.93 | 0.05 | 1.0 |
| PAE   | 161.2     | 163.8    | 56.6 | 0.60 | 0.22 | 1.0 |
| BAE   | 161.1     | 163.8    | 56.7 | 0.61 | 0.23 | 1.0 |

The depression of the carbamate formation leads to increased CO$_2$ absorption capacity. The CO$_2$ loadings determined by the $^{13}$C NMR quantifications are compared among the alkanolamine in Figure 4. Apparently, the aminobutanol and the aminopropanol show better performances than the aminoethnols in terms of the CO$_2$ loading.

![Graph showing CO$_2$ loadings of 30wt% aqueous alkanolamine solutions equilibrated with 20% CO$_2$ gas at 40°C.](image)

Figure 4. CO$_2$ loadings of 30wt% aqueous alkanolamine solutions equilibrated with 20% CO$_2$ gas at 40°C.

4. Conclusions

The CO$_2$ loading and the chemical species distribution in the alkanolamine–H$_2$O–CO$_2$ system has been investigated by systematically varying the substituents of alkanolamines. The $^{13}$C NMR spectra of CO$_2$ loaded alkanolamine solutions have shown that the chemical species distributions are critically dependent on the alcohol chain length of alkanolamine. We conclude that the hydroxyl functional group of
alkanolamine can strongly influence the CO₂ absorption properties of the aqueous alkanolamine solution through the intramolecular interaction of the hydroxyl functional group with the amino moiety.

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