Facile Determination of Dissolved Species in CO_2-Amine-H_2O System by NMR Spectroscopy

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In order to clarify the characteristic behavior of dissolved state of CO_2 in alkanolamine-H_2O system five different kinds of alkanolamines were examined spectroscopically under the following conditions: 40 °C for 30 min to 120 min. NMR analysis indicated the presence of five chemical species such as carbamate ion, free amine, bicarbonate, carbonate, and protonated amine. Based on proton NMR, distribution of the respective species against molar loading of CO_2 was successfully evaluated.

In the petroleum refining industry, CO_2-absorption technique by alkanolamine solvent is well known, and the detail has been studied in view of kinetics of gas-liquid reaction.[1-6] This technology is now accepting a lot of attention as a potential method to recover and utilize CO_2 from flue gas. As for the CO_2 recovery by alkanolamine, it is very important to reduce the energy required in this recovery as well as to enhance the CO_2 uptake even at low CO_2 partial pressures because of extremely large quantities of flue gas concerned. In this respect, kinetic study between CO_2 and alkanolamine seems to be the first step to propose more efficient CO_2 absorbents which lead to a lot of reduction in energy consumed.

We have been studying the absorption reaction of CO_2 by using primary, secondary, tertiary, and cyclic amines in the bench scale plant and the pilot plant, finding that secondary amine showed the specific behavior.

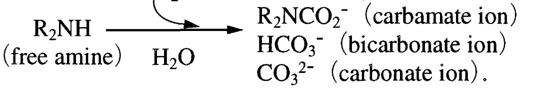
In the present study, the dissolved state of CO_2 in aqueous amine solution has been analyzed spectroscopically and the variation of dissolved species with a progress of CO_2 absorption has been examined quantitatively. The following amines are used; monoethanolamine (MEA), 2-(methylamino)ethanol (MAE), 2-(ethylamino)ethanol (EAE), 2-(buthylamino)ethanol (BEA), and N-methyl-2,2'-iminodiethanol (MDEA): the samples containing different amount of dissolved CO_2 in 30 wt% aqueous amine (mol of amine: 2.55 - 4.94 mol dm^{-3}) are prepared by changing the absorption time and partial pressure of CO_2 from 5 to 100% as are schematically shown in Figure 1. The amount of CO_2 absorbed in amine solution was determined by measuring the CO_2 gas evolved, with NDIR, after the injection of the sample into a reaction tube packed with phosphoric acid-mounted catalyst at 130 °C. ^1H- and ^{13}C-NMR spectra were obtained using a JNM-GX270 spectrometer with a capillary sealed TSP [sodium 3-(trimethylsilyl)propanate] as an external standard at 25 °C.

From the plots of molar loading of CO_2 per amine as a function of partial pressure of CO_2, it is clearly indicated that MAE, EAE, and BEA (secondary amines) have the highest ability to absorb CO_2 while MEA (primary amine) possesses molar loading around 0.5 which shows its less dependence on CO_2 partial pressure and MDEA (tertiary amine), on the other hand, shows the high pressure dependence.

In ^1H and ^{13}C NMR spectra of the aqueous alkanolamine samples appear the new peaks assigned to carbamate anion, the peak increasing with a progress of CO_2 absorption: much in primary amine, none in tertiary amine and intermediate (between those of primary and tertiary amines) in secondary amine. Beyond some CO_2 loading, however, these peaks decreased gradually, this suggesting the existence of a maximum peak height. The chemical shift of the carbamate formed by the interaction between alkanolamine and CO_2 in aqueous solution is assigned for the first time in this study, the representatives being as follows,

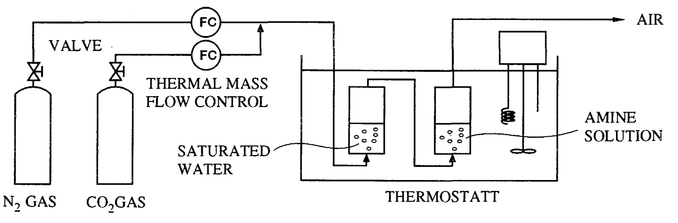
^{13}C-NMR δR-N-CO_2 (MEA, sec-Amine) 166-167 (166-167, Amide[7,8])
δC-N- (MEA) 46 (47, Carbamate of DGA[7])
^1H-NMR δN-C-H_3 (MAE) 2.87 (2.97, N-methylcarbamate[9])
δN-C-H2- (sec-Amine) 3.32 - 3.35 (3.37, sec-Amine[10])

Other species derived from the absorption of CO_2 are bicarbonate/ carbonate along with free amine/ protonated amine, the former being increased continuously and the latter shifted toward the protonated amine with a progress of CO_2 absorption. Therefore, the chemical species in the system with, for example, secondary amine are indicated as follows ;



$$\underset{\text{(free amine)}}{R_2NH} \xrightarrow[H_2O]{CO_2} \begin{array}{ll} R_2NH_2^+ & \text{(protonated amine)} \\ R_2NCO_2^- & \text{(carbamate ion)} \\ HCO_3^- & \text{(bicarbonate ion)} \\ CO_3^{2-} & \text{(carbonate ion)}. \end{array}$$

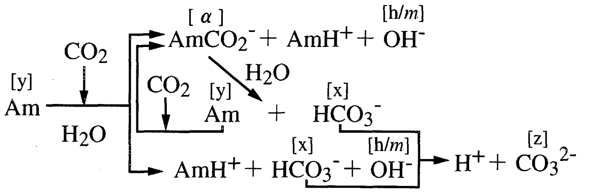
The ratio of the quantities of carbonate ion to those of other amine species can be determined directly by the integration of each peak in the spectra. Quantitative determination of the above five chemical species can be explained using the following scheme by referring to the dissolved species present in the reaction process.



preparation conditions

concentration of amine	:	30 wt%
amounts of solution	:	100 g
temperature	:	40 ± 0.5 °C
flow of gas	:	1 $dm^3 min^{-1}$
absorption time	:	30~120 min

Figure 1. Preparation of the samples containing different amounts of CO_2 in 30 wt% aqueous amine.



The concentration of [AmH^+] is sum of α , x , 2z , and h/*m* (on the basis of charge balance, amount of [H^+] being negligibly little). If we consider the total amine in the aqueous system $\{$ [$AmCO_2^-$] + [Am] + [AmH^+] $\}$ to be 100%, equation (1) is obtained where *m* is molar concentration of amine in the system.

$$\alpha + y + \alpha + x + 2z + h/m = 1 \qquad (1)$$

From NMR spectra, peak area of carbamate ion and another area of other peaks are assigned a and b, respectively. Equation (2) is obtained.

$$[\text{carbamate}] / ([\text{free amine}] + [\text{protonated amine}])$$
$$= a / b = [AmCO_2^-] / ([Am] + [AmH^+]) = \alpha / \beta \qquad (2)$$

where we employ equation (3).

$$y + \alpha + x + 2z + h/m = \beta \qquad (3)$$

Therefore, [$AmCO_2^-$]: $\alpha = \alpha / (\alpha + \beta) = a / (a + b)$ (4)

$$\beta = (1 - \alpha) / (\alpha + \beta) = b / (a + b) \qquad (5)$$

From experimental data, we can get CO_2 / total amine (θ), that is, CO_2 / total amine = ([$AmCO_2^-$] + [HCO_3^-] + [CO_3^{2-}]) / ([$AmCO_2^-$] + [Am] + [AmH^+]) = $(\alpha + x + z) / (\alpha + \beta) = \theta$.

From these parameters, we can calculate each concentration of [HCO_3^-], [Am], and [AmH^+] according to the following equations.

[HCO_3^-]: $x = \theta \times \beta - (1 - \theta) \times \alpha - z$
[Am]: $y = (1 - \theta) \times \beta - \theta \times \alpha - z - h/m$
[AmH^+]: $\theta + z + h/m$

where z and h are obtained, respectively, by applying the next three equations concerning on the dissociation constant.

$$[Am] [H^+] / [AmH^+] = Kp$$
$$[OH^-] [H^+] = Kw$$
$$[H^+] [CO_3^{2-}] / [HCO_3^-] = K_{C2}$$

Figure 2 indicates the distribution of five chemical species in the MEA system. The results in this study are plotted with points in the figure and are very similar to that calculated by Austgen *et al.*[11] according to equilibrium of the system where carbamate formation shows maximum at half of molar loading. The proposed method based on NMR measurement, as is shown above, is considered to be the facile method to calculate distribution of chemical species in CO_2-Amine-H_2O system. Application of this method to three secondary amine systems indicates clearly that the carbamate formation is retarded and bicarbonate forms at lower CO_2 molar loading than those in MEA system. The results on EAE are shown in Figure 3 as one of the representatives of secondary amines. In the case of MDEA, the results being not shown in the figure, the concentrations of both $MDEAH^+$ and HCO_3^- increase with an increase in CO_2 molar loading in a similar manner as curves of $MEAH^+$ and $EAEH^+$ while free MDEA decreases monotonously because of the lack of carbamate species. The maximum concentration of the carbamate anions examined in this study ranges in the next order;

$$\text{MEA} > \text{MAE} > \text{EAE} \approx \text{BEA} > \text{MDEA} = 0 .$$

It is suggested in secondary amine systems that the carbamate may be easily converted by the hydrolysis to both bicarbonate ion and free amine which interacts with another CO_2 gas, resulting in further increment of absorbed amount. The CO_2 absorption rate also may be concerned with the carbamate formation since tertiary amine depresses remarkably the absorption rate. The highest ability of secondary amine in CO_2 absorption may be ascribed for the process through the formation of carbamate followed by the easy decomposition to bicarbonate even at low CO_2 partial pressures because of its moderate carbamate stability.

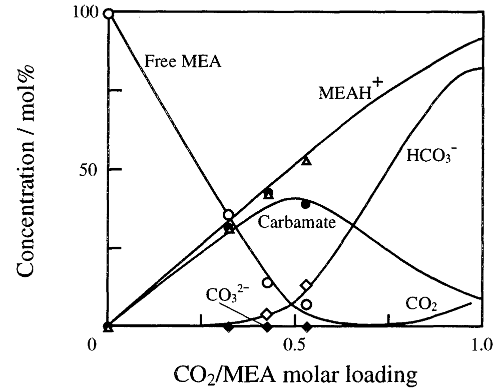


Figure 2. Plots of concentration of chemical species against CO_2/ MEA molar loading (points are obtained in this work, lines from the results of D. M. Austgen, *et al.*).

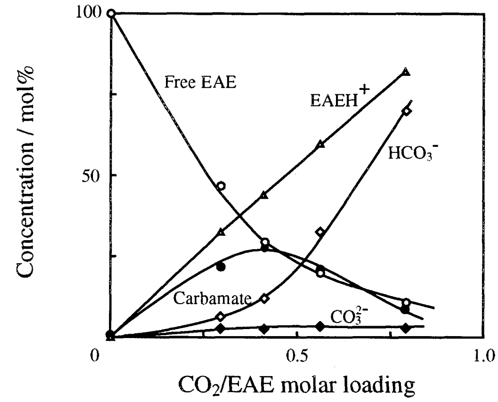


Figure 3. Plots of concentration of chemical species against CO_2/ EAE molar loading.

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