# CHEMICAL EQUILIBRIA OF ABSORPTION OF CO₂ INTO NONAQUEOUS SOLUTION OF AMINE
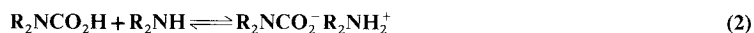
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Tokyo 152

The moles of $CO_2$ absorbed into an amine–nonaqueous solvent mixture were measured by using the stirred-cell method. The test solutions were the mixtures of amine such as butylamine, *tert*-butylamine, dibutylamine, diethylamine and dipropylamine, and solvents such as octane, triethylamine and methanol.

The equilibria of the reactions between $CO_2$ and amine in nonaqueous solvent were studied by examining the pressure dependency of the absorption of $CO_2$ at lower temperatures, and could be described by the following reactions:

$$CO_2(l) + R_2NH \rightleftharpoons R_2NCO_2H \qquad (1)$$

$$R_2NCO_2H + R_2NH \rightleftharpoons R_2NCO_2^- R_2NH_2^+ \qquad (2)$$

$$R_2NCO_2H + R_2NH \rightleftharpoons R_2NCO_2^- + R_2NH_2^+ \qquad (3)$$

where R is the alkyl group.

The equilibrium constants, $K_1$, $K_2$ and $K_3$, were estimated simultaneously by the method of least squares with respect to the pressure dependency of the absorption of $CO_2$.

The equilibria of the reactions in a nonpolar solvent were mainly described by Eqs. (1) and (2). Those in a polar solvent were described by Eqs. (1) and (3). The proposed reactions, Eqs. (1) to (3), were supported by enthalpies estimated from the Arrhenius plot of the equilibrium constant.

## Introduction

Chemical absorption of carbon dioxide into amine is applicable to a process for removing carbon dioxide from effluent gases. Some studies of the mechanism of the reactions between $CO_2$ and amine have appeared. However, most studies have focused only on the reactions of amine in aqueous solution.[1,3]

In practice, amine–nonaqueous solvent mixtures, for example, ethanolamine–methanol mixture, have been used to remove $CO_2$ effectively in some industrial processes.[2] The absorption of $CO_2$ into amine–nonaqueous solvent mixture are of practical interest because of the high solubility of $CO_2$ or the high absorption capacity.

Danckwerts suggested a mechanism derived from the concept that the proton is removed from the zwitter-ion by amine after formation of the zwitter-ion.[4] By use of this concept, Sada *et al.* made clear the kinetics of the reactions between $CO_2$ and amine in aqueous or nonaqueous solvents.[7]

The purposes of this study are to examine the relation between the chemical reactions and the absorption capacity of $CO_2$ for amine–nonaqueous sol-
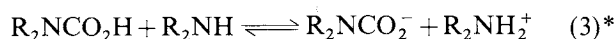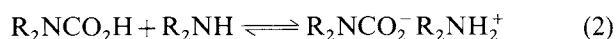
vent mixture and to determine the equilibrium constants for the absorption reactions. These constants were determined simultaneously by the method of least squares combined with the modified Newton method.
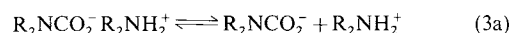
## 1. Theoretical Background

### 1.1 Absorption of CO₂ into amine solution

The absorption of $CO_2$ into amine solution is composed of physical absorption into nonaqueous solvent and chemical absorption of $CO_2$ reacting with amine. The moles of physical absorption can be estimated from Henry's law and are proportional to the partial pressure of $CO_2$.[8]

The chemical absorption of $CO_2$ into amine in nonaqueous solvent is assumed here as three step reactions:[4]

$$R_2NH + CO_2(l) \rightleftharpoons R_2NCO_2H \qquad (1)$$

$$R_2NCO_2H + R_2NH \rightleftharpoons R_2NCO_2^- R_2NH_2^+ \qquad (2)$$

$$R_2NCO_2H + R_2NH \rightleftharpoons R_2NCO_2^- + R_2NH_2^+ \qquad (3)*$$

* Dissociation of amine carbamate,

$$R_2NCO_2^- R_2NH_2^+ \rightleftharpoons R_2NCO_2^- + R_2NH_2^+ \qquad (3a)$$

can be expressed by Eqs. (2) and (3). The equilibrium constant for Eq. (3a), $K_4$, can be estimated from $K_4 = K_3/K_2$.

where $R_2NCO_2H$ and $R_2NCO_2^- R_2NH_2^+$ (ion-pair) denote carbamic acid and amine carbamate, respectively. $R_2NCO_2^-$ and $R_2NH_2^+$ denote carbamic ion and ammonium ion, respectively. $CO_2(l)$ denotes $CO_2$ dissolved physically into the liquid phase. $R_2$ means two alkyl groups for a secondary amine, or one alkyl group and hydrogen (that is, RH for a primary amine). Carbamic acid $R_2NCO_2H$ changes partially to a zwitter-ion, $R_2NH^+CO_2^-$, but there is no way to distinguish them.

### 1.2 Evaluation of the absorption capacity of $CO_2$ into amine solution

1) **Physical absorption**  The moles of physical absorption of $CO_2$ into amine solution were assumed equal to the moles of $CO_2$ dissolved physically into the solvent. Physical absorption into the amine was neglected here, because the moles of $CO_2$ dissolved physically into the amine were less than one tenth of those dissolved physically into the nonaqueous solvent.[9]

The concentration of $CO_2$ dissolved physically into the amine solution, $Cg'$, can be described by

$$Cg' = (P/H') \simeq (1 - CM/\rho)(P/H) \qquad (5)$$

where $H'$ and $H$ mean Henry's constants for the solution and for the solvent, respectively. $(CM/\rho)$ means the volume fraction of amine in the solution.

2) **Chemical absorption**  The molar absorption ratio, $Ac$, is defined as the ratio of the moles of $CO_2$ reacting with amine to the initial moles of amine in the solution. That is,

$$Ac = [\text{moles of } CO_2 \text{ absorbed chemically}]/$$
$$[\text{initial moles of amine}] \qquad (6)$$

According to Eqs. (1) to (3), $CO_2$ absorbed chemically into amine solution changes to mono-amino or di-amino complex. $Ac$ can be estimated from the sum of the ratios of the moles of carbamic acid ($X$), amine carbamate ($Y$) and carbamic ion ($Z$), to the initial moles of amine:

$$Ac = X + Y + Z \qquad (7)$$

As seen from Eqs. (1) to (3), the concentrations of $CO_2(l)$, $R_2NH$, $R_2NCO_2H$, $R_2NCO_2^- R_2NH_2^+$, $R_2NCO_2^-$ and $R_2NH_2^+$ are given by

$$[CO_2(l)] = Cg' \qquad (8)$$

$$[R_2NH] = C(1 - X - 2Y - 2Z) \qquad (9)$$

$$[R_2NCO_2H] = CX \qquad (10)$$

$$[R_2NCO_2^- R_2NH_2^+] = CY \qquad (11)$$

$$[R_2NCO_2^-] = CZ \qquad (12)$$

$$[R_2NH_2^+] = CZ \qquad (13)$$

where $C$ is the initial concentration of amine. The

effect of pressure is included in $Cg'$.

The equilibrium constants $K_1$, $K_2$ and $K_3$ for Eqs. (1) to (3) are defined by

$$K_1 = \frac{[R_2NCO_2H]}{[R_2NH][CO_2]} = \frac{X}{(1 - X - 2Y - 2Z)Cg'} \qquad (14)$$

$$K_2 = \frac{[R_2NCO_2^- R_2NH_2^+]}{[R_2NH][R_2NCO_2H]} = \frac{Y}{C(1 - X - 2Y - 2Z)X} \qquad (15)$$

$$K_3 = \frac{[R_2NCO_2^-][R_2NH_2^+]}{[R_2NH][R_2NCO_2H]} = \frac{Z^2}{(1 - X - 2Y - 2Z)X} \qquad (16)$$

From Eqs. (14) to (16), $X$, $Y$ and $Z$ are given by

$$X = \{ -(2\sqrt{K_1 K_3 Cg'} + 1 + K_1 Cg')$$
$$+ \sqrt{(2\sqrt{K_1 K_3 Cg'} + 1 + K_1 Cg')^2 + 8K_1 K_2 Cg' C} \}/4K_2 C \qquad (17)$$

$$Y = \frac{K_2 C X^2}{K_1 Cg'} \qquad (18)$$

$$Z = X \sqrt{\frac{K_3}{K_1 Cg'}} \qquad (19)$$

If $X$, $Y$ and $Z$ are introduced into Eq. (7), $Ac$ can be described as a function of $K_1$, $K_2$ and $K_3$.

$$Ac(K_1, K_2, K_3) = X + Y + Z \qquad (20)$$

### 1.3 Determination of $K_1$, $K_2$ and $K_3$

The sum of the squares of the difference between the calculated $Ac$ values and the $Ac$ values observed experimentally is expressed by $E$:

$$E = \sum_{i=1}^{n} [Ac(K_1, K_2, K_3) \mid p_i/Ac \mid p_i - 1]^2 \qquad (21)$$

$P_i$ denotes the pressure of $CO_2$ for $i$-th experimental datum. $n$ means the total number of data.

The proper values of $K_1$, $K_2$ and $K_3$ were estimated by the method of least squares, so that $E$ became minimum. The details of the numerical method are described in **Appendix**.

### 1.4 Approximation of absorption reactions by two parameters

There are two extreme cases in which the chemical reaction can be expressed by two equations.

**Type I**  The absorption reactions can be described by Eqs. (1) and (2) if the amount of carbamic ion is negligible. Then, $K_3 = 0$ and $Z = 0$ hold.

**Type II**  The absorption reactions can be described by Eqs. (1) and (3) if the amount of amine carbamate is negligible. Then, $K_2 = 0$ and $Y = 0$ hold.
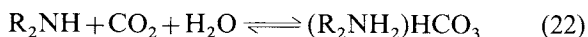
## 2. Experimental Procedures

### 2.1 Test solution

The test solution was a mixture of amine and nonaqueous solvent. The following amines and solvents were used:

| | |
|---|---|
| Primary amine | : butylamine (BA) |
| | *tert*-butylamine (TBA) |
| Secondary amine | : diethylamine (DEA) |
| | dipropylamine (DPA) |
| | dibutylamine (DBA) |
| Nonpolar solvent | : octane |
| | triethylamine (TEA) |
| Polar solvent | : methanol |

If a trace amount of water is included in amine or solvent as impurity, the following reaction with $CO_2$ takes place in the solution,

$$R_2NH + CO_2 + H_2O \rightleftharpoons (R_2NH_2)HCO_3 \qquad (22)$$

and white precipitates of amine carbonate appear. Traces of water were removed by a silica-gel column before the experiments.

### 2.2 Experimental procedures

The experimental set-up is shown in **Fig. 1**.[8] The system was mainly made of Pyrex glass. The absorption capacity was measured by the constant-pressure method. The pressure of the system was kept constant by adjusting the vertical position of the Hg-reservoir (G) which was moved upward by a variable-speed motor (H) controlled by the signals from the pressure monitor (E). The pressure level was set with the vertical position of the monitor (E). The precision of pressure control was $\pm 0.2$ mmHg.

The moles of $CO_2$ absorbed into the solution were measured with the stirred cell A ($30\phi \times 65$ mmH).

Gaseous impurity dissolving in the test solution was removed before the measurements by means of several repeated treatments utilizing the solubility difference caused by the temperature change between two discrete temperature.[8]

The moles of $CO_2$ absorbed chemically into the test solution were calculated by subtracting the moles of $CO_2$ absorbed physically given by Henry's law from the total moles of $CO_2$ absorption measured experimentally. These values were employed in the form of the molar absorption ratio $Ac$ defined by Eq. (6). The moles of absorbed $CO_2$ were estimated by the ideal gas law from the volume change of gas in the burette
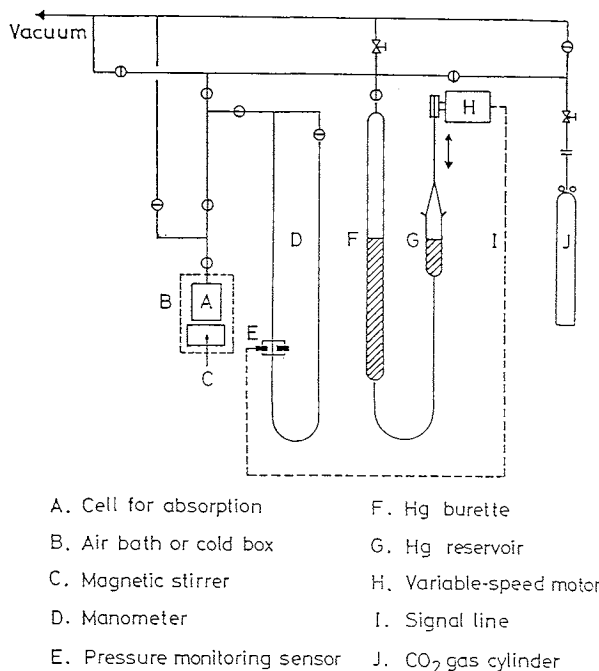


| | |
|---|---|
| A. Cell for absorption | F. Hg burette |
| B. Air bath or cold box | G. Hg reservoir |
| C. Magnetic stirrer | H. Variable-speed motor |
| D. Manometer | I. Signal line |
| E. Pressure monitoring sensor | J. $CO_2$ gas cylinder |

**Fig. 1.** Schematic diagram of the experimental apparatus
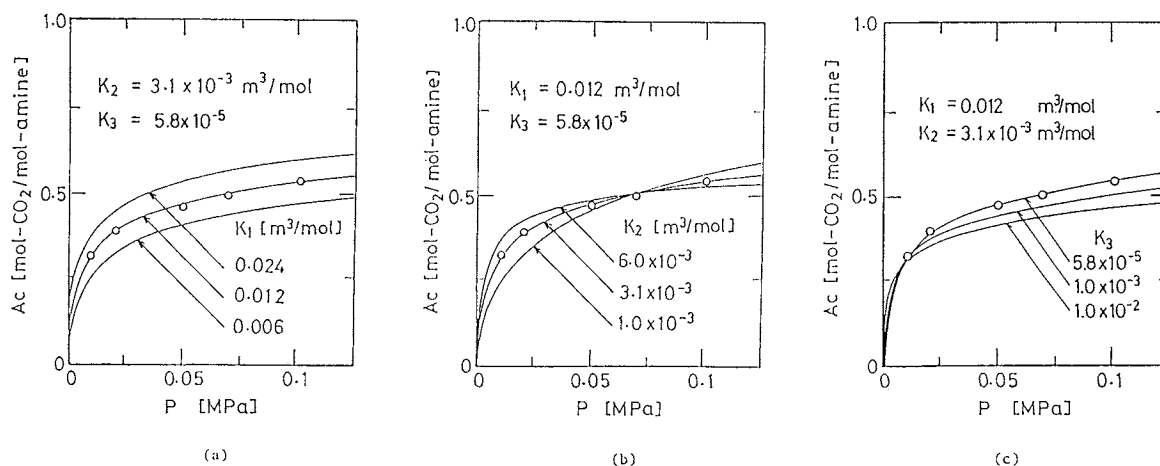


(a)  (b)  (c)

**Fig. 2.** Relation between $Ac$ and pressure of $CO_2$ in BA–octane solution. Calculated curves of $Ac$ vs. $P$ are shown by solid lines with parameters of $K_1$, $K_2$ and $K_3$.
2a) Effect of $K_1$ on $Ac$ vs. $P$ relation
2b) Effect of $K_2$ on $Ac$ vs. $P$ relation
2c) Effect of $K_3$ on $Ac$ vs. $P$ relation

(F). The pressure of $CO_2$ was obtained from the difference between the measured pressure and the sum of the vapor pressures of amine and solvent at the experimental temperature.

## 3. Results and Discussion

### 3.1 Chemical absorption of $CO_2$ in equilibrium

The moles of $CO_2$ absorbed chemically into amine–nonaqueous solvent mixture were closely related to the equilibrium constants of chemical reaction between $CO_2$ and amine.

Figures 2(a), (b) and (c) show the relations between $Ac$ and the pressure of $CO_2$ for butylamine (BA)–octane solution. It should be noted that the results obtained from the same experiment are plotted in three figures. The curves calculated from Eq. (20) show the effect of the variation of one parameter $K_i$ ($i=1,2$ or 3), when the others are fixed at the proper values of $K_1$, $K_2$ or $K_3$. One of the curves in each figure agreed sufficiently with the pressure dependency of $Ac$ observed experimentally. The proper values of $K_1$, $K_2$ and $K_3$ were $1.2 \times 10^{-2}\,\mathrm{m^3/mol}$, $3.10 \times 10^{-3}\,\mathrm{m^3/mol}$ and $5.80 \times 10^{-5}$, respectively.

It is clear that $K_1$ was a factor controlling the chemical absorption of $CO_2$ in a wide range of pressure, while $K_2$ was a factor controlling the chemical absorption in the lower pressure region. On the other hand, $K_3$ was a factor controlling the chemical absorption at higher pressures. $Ac$ increased with $K_1$ and decreased with $K_3$. On the other hand, $Ac$ increased with $K_2$ at lower pressures, but decreased with $K_2$ at higher pressures. The effects of $K_1$, $K_2$ and $K_3$ on absorption behavior were quite different.

Figure 3 shows the sensitivity analysis of $K_i$ ($i=1$ to 3) with the accuracy of experimental data. The figure shows the relations between the relative change of $K_i$, that is $\Delta K_i/K_i$, and the pressure for DBA–methanol solution. The proper values of $K_1$, $K_2$ and $K_3$ for the solution were $3.43 \times 10^{-2}\,\mathrm{m^3/mol}$, $4.03 \times 10^{-5}\,\mathrm{m^3/mol}$ and 2.36, as shown in Fig 8(b) or Table 3. $\Delta K_i$'s are the numerical changes of $K_i$'s from the proper values when one of the $Ac$ values in Fig. 8(b) increased by $+2\%$ and the others were the same as the observed ones. The sign indicated by $A$, $B$, $C$ or $D$ in Fig. 3 corresponds to the pressure at which the $Ac$ value changed by 2%. $\Delta K_2/K_2$ was largest in the lower pressure region, while $\Delta K_3/K_3$ was largest in the higher pressure region. According to the results, it is

very important to measure accurately the experimental data of $Ac$ in the lower pressure region.

### 3.2 Absorption of $CO_2$ in several systems

$K_1$, $K_2$ and $K_3$ for several systems are shown in Tables 1 to 3. The following tendencies are observed from the results:

(1)  Table 1 shows that the chemical absorption of $CO_2$ into primary amine (BA, TBA) in nonpolar solvent yields amine carbamate ($Y$) as well as carbamic acid ($X$).

(2)  Table 2 shows that the chemical absorption of $CO_2$ into secondary amine (DEA, DPA, DBA) in nonpolar solvent (octane, TEA) yields only carbamic acid ($X$) and does not yield amine carbamate ($Y$) and carbamic ion ($Z$).

(3)  $Ac$ for secondary amine is usually larger than that for primary amine.

(4)  $Ac$ for secondary amine increases inversely with the number of carbon atoms in a secondary amine molecule, $(C_nH_{2n+1})_2NH$.

(5)  Table 3 shows that amine carbamate in polar solvent (methanol) dissociates to carbamic ion and ammonium ion.

(6)  $Ac$ in nonpolar solvent is larger than that in polar solvent. The absorption reactions are influenced by the polarity of the solvent.

Figures 4(a) and (b) show the variation of $Ac$ with the concentration of amine diluted with octane. Solid
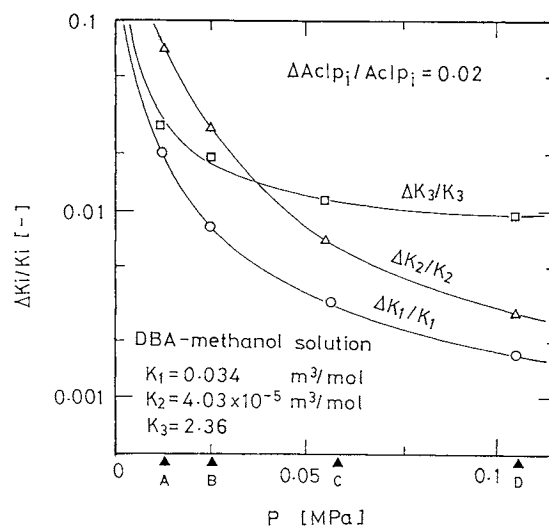
Fig. 3.  Relation between the relative sensitivity in equilibrium constant $\Delta K_i/K_i$ ($i=1$ to 3) with the change of 2% in $Ac$, and pressure of $CO_2$ in DBA–methanol mixture

Table 1.  Values of $K_1$, $K_2$ and $K_3$ for primary and secondary amine
$T=-20°C$, $P=0.101$ MPa and $C=1.00$ mol/$l$

| Amine | Solvent | $Ac$ | $X$ | $Y$ | $Z$ | $K_1$ | $K_2$ | $K_3$ |
|---|---|---|---|---|---|---|---|---|
| Butylamine (BA) | Octane | 0.531 | 0.223 | 0.308 | $1.82 \times 10^{-4}$ | $1.20 \times 10^{-2}$ | $3.10 \times 10^{-3}$ | $5.80 \times 10^{-5}$ |
| tert-Butylamine (TBA) | Octane | 0.359 | 0.085 | 0.310 | $1.29 \times 10^{-4}$ | $4.11 \times 10^{-2}$ | $3.52 \times 10^{-3}$ | $2.89 \times 10^{-5}$ |
| Dibutylamine (DBA) | Octane | 0.880 | 0.879 | $2.12 \times 10^{-4}$ | $1.21 \times 10^{-4}$ | $3.52 \times 10^{-2}$ | $1.87 \times 10^{-6}$ | $1.29 \times 10^{-6}$ |

**Table 2.** Values of $K_1$, $K_2$ and $K_3$ for alkyl group in secondary amine
$T = -20°C$, $P = 0.101$ MPa and $C = 1.00$ mol/$l$

| Amine | Solvent | $Ac$ | $X$ | $Y$ | $Z$ | $K_1$ | $K_2$ | $K_3$ |
|---|---|---|---|---|---|---|---|---|
| Diethylamine (DEA) | Octane | 0.948 | 0.947 | $1.83 \times 10^{-7}$ | $3.00 \times 10^{-6}$ | $1.40 \times 10^{-1}$ | $5.21 \times 10^{-8}$ | $2.57 \times 10^{-8}$ |
| Dipropylamine (DPA) | Octane | 0.895 | 0.894 | $2.01 \times 10^{-4}$ | $6.14 \times 10^{-5}$ | $7.12 \times 10^{-2}$ | $1.23 \times 10^{-6}$ | $5.85 \times 10^{-7}$ |
| Dibutylamine (DBA) | Octane | 0.880 | 0.879 | $2.21 \times 10^{-4}$ | $1.21 \times 10^{-4}$ | $3.52 \times 10^{-2}$ | $1.87 \times 10^{-6}$ | $1.29 \times 10^{-6}$ |

**Table 3.** Values of $K_1$, $K_2$ and $K_3$ for secondary amine mixed with solvent
$T = -20°C$, $P = 0.101$ MPa and $C = 1.00$ mol/$l$

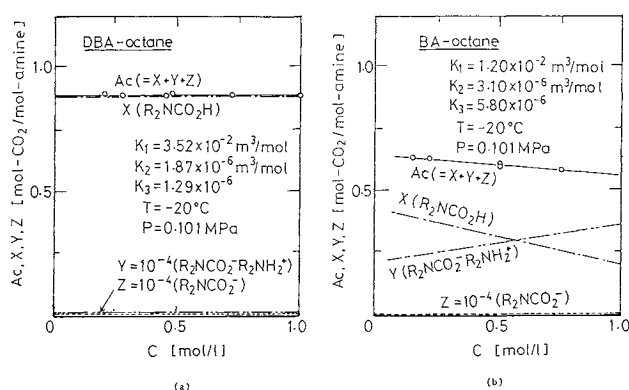| Amine | Solvent | $Ac$ | $X$ | $Y$ | $Z$ | $K_1$ | $K_2$ | $K_3$ |
|---|---|---|---|---|---|---|---|---|
| Dibutylamine (DBA) | Octane | 0.880 | 0.879 | $2.12 \times 10^{-4}$ | $1.21 \times 10^{-4}$ | $3.52 \times 10^{-2}$ | $1.87 \times 10^{-6}$ | $1.29 \times 10^{-6}$ |
| Dibutylamine (DBA) | Triethyl-amine | 0.910 | 0.909 | $1.68 \times 10^{-4}$ | $2.49 \times 10^{-5}$ | $3.40 \times 10^{-2}$ | $9.80 \times 10^{-7}$ | $9.66 \times 10^{-7}$ |
| Dibutylamine (DBA) | Methanol | 0.745 | 0.560 | $5.31 \times 10^{-4}$ | 0.185 | $3.43 \times 10^{-2}$ | $4.03 \times 10^{-5}$ | 2.36 |



**Fig. 4.** The variations of $Ac$, $X$, $Y$ and $Z$ with amine concentration. Theoretical lines were calculated from Eqs. (17) to (20) with $K_1$, $K_2$ and $K_3$ listed in Table 1
4a) DBA (dibutylamine)–octane solution
4b) BA (butylamine)–octane solution



**Fig. 5.** Relation between equilibrium constant $K_1$ and $1/T$ for DBA–nonaqueous solvent mixture

lines show $Ac$ estimated from the equilibrium constants listed in Table 1. The concentration dependency of $X$, $Y$ and $Z$ is also shown in these figures. In the secondary amine (DBA) solution, the absorbed $CO_2$ existed in the form of carbamic acid ($X$) and not in the form of amine carbamate ($Y$) or carbamic ion ($Z$). In the primary amine (BA) solution, $X$ and $Y$ were comparable with each other and $Z$ was negligibly small.

### 3.3 Determination of the heat of reaction

**Figure 5** shows the relation between ln $K_1$ and $1/T$. This relation is represented by a straight line for the results obtained from DBA in several kinds of solvent. The enthalpy of the reaction, $\Delta H_{exp}$, estimated from the slope in Fig. 5, was $-9.59$ kJ/mol. This enthalpy corresponds to the heat of the reaction expressed by Eq. (1). It is interesting to note that $\Delta H_{exp}$ in DBA–methanol mixture is the same as $\Delta H_{exp}$ in DBA–nonpolar solvent mixture. The slope of the straight line was obtained by the least squares method based on Demming's treatment.[5]
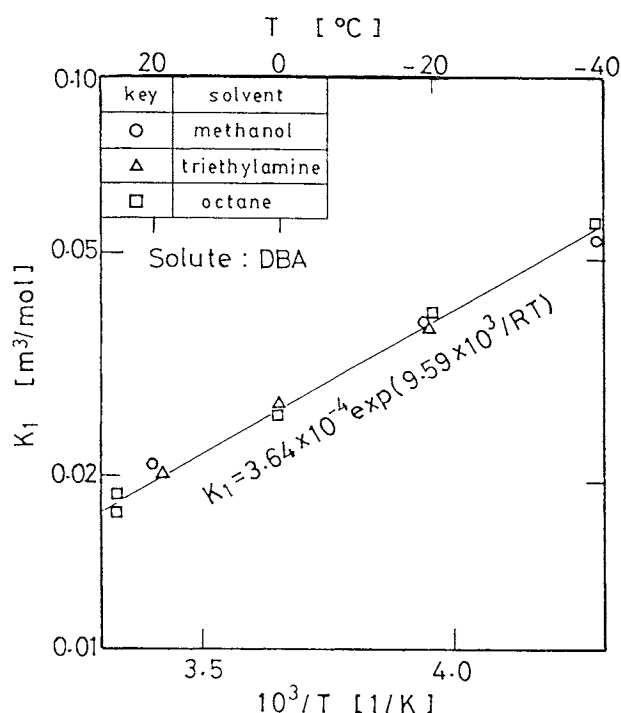
The temperature dependency of $K_1$ for DBA–octane mixture was determined as follows by a method reported in ref. 8.

$$K_1 = 3.64 \times 10^{-4} \exp(9.59 \times 10^3 / RT) \quad (23)$$

This relation agrees with the results in Fig. 5.

The heat of reaction can be evaluated from the additive law of chemical bond energy.[6] $\Delta H_{cal}$ for Eq. (1) is $-8.95$ kJ/mol. The relative difference between $\Delta H_{exp}$ and $\Delta H_{cal}$ was 6.7%.

**Figure 6** shows the relation between ln $K_3$ and $1/T$ for DBA–methanol solution. The enthalpy of the reaction estimated from the slope, $\Delta H_{exp}$, was $-68.8$ kJ/mol. This enthalpy corresponds to the heat
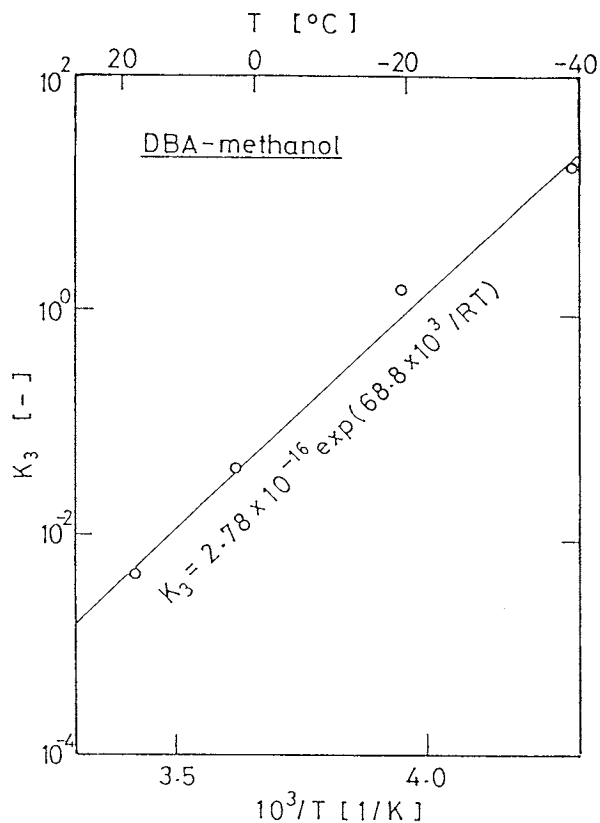
**Fig. 6.** Relation between equilibrium constant $K_3$ and $1/T$ for DBA–methanol mixture



**Fig. 7.** Relation between equilibrium constant $K_2$ and $1/T$ for amine–octane mixture

of reaction expressed by Eq. (3). $K_3$ was represented by

$$K_3 = 2.78 \times 10^{-16} \exp(68.8 \times 10^3 / RT) \qquad (24)$$

The additive law of chemical bond energy was applied to Eq. (3), and the heat of reaction, $\Delta H_{cal}$, was estimated as $-71.8 \, \text{kJ/mol}$.[6] $\Delta H_{exp}$ agrees with $\Delta H_{cal}$ within the relative difference of 4.1%.

**Figure 7** shows the relation between $\ln K_2$ and $1/T$ for butylamine (BA)–octane mixture and for *tert*-butylamine (TBA)–octane mixture. The heat of reaction of Eq. (2), $\Delta H_{exp}$, was calculated as $-52.2 \, \text{kJ/mol}$.

If the additive law of chemical bond energy is applied to Eq. (2), in which the O–N bond in amine carbamate is in the form of a covalent bond, the heat of reaction is estimated as $380 \, \text{kJ/mol}$.[6]

On the other hand, if amine carbamate is assumed to dissociate, the heat of reaction is estimated as $-71.8 \, \text{kJ/mol}$.[6]

These results suggest that the O–N bond in amine carbamate $(\Delta H_{exp} = -52.2 \, \text{kJ/mol})$ is close to the ionic dissociation $(\Delta H_{cal} = -71.8 \, \text{kJ/mol})$ rather than the covalent bond $(\Delta H_{cal} = 380 \, \text{kJ/mol})$.

### 3.4 Two parameter models for the absorption equilibrium

**Figures 8**(a) and (b) show the relations between $Ac$ and the pressure for butylamine (BA)–octane mixture
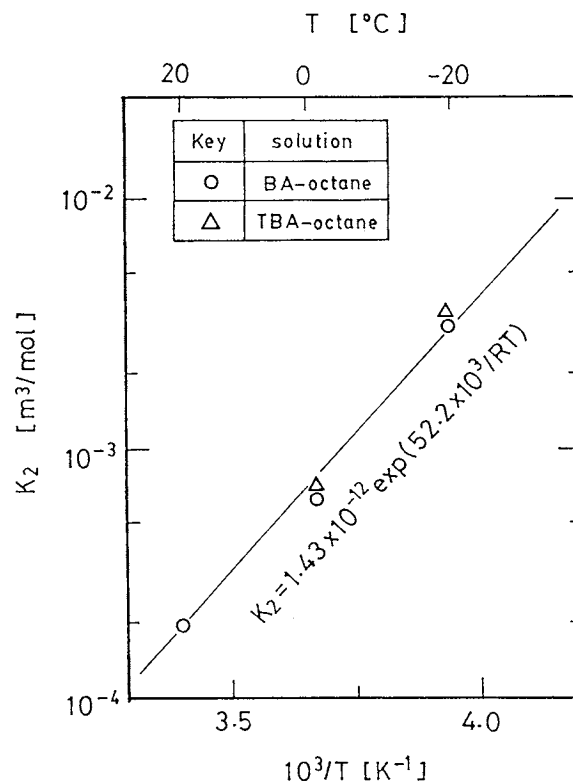


| | $K_1$ | $K_2$ | $K_3$ | $E_{min}$ |
|---|---|---|---|---|
| 3-P | 0.012 | 3.1E-3 | 5.8E-5 | 9.8E-7 |
| Type I | 0.012 | 3.1E-3 | — | 1.8E-6 |
| Type II | 0.012 | — | 1.05 | 2.3E-4 |

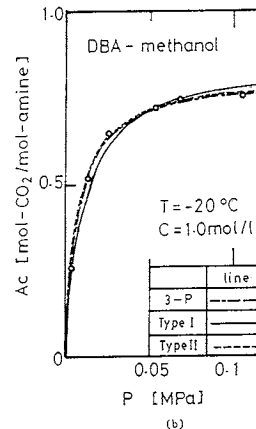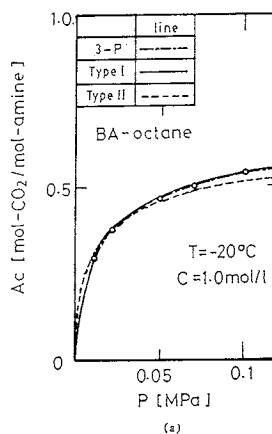| | $K_1$ | $K_2$ | $K_3$ | $E_{min}$ |
|---|---|---|---|---|
| 3-P | 0.034 | 4.0E-5 | 2.36 | 5.0E-6 |
| Type I | 0.015 | 2.9E-3 | — | 6.7E-4 |
| Type II | 0.034 | — | 2.37 | 9.0E-6 |



**Fig. 8.** Comparison of fitting curves determined by method of least squares based on three parameters, Type I or Type II model. Experimental data are obtained from:
8a) mixture of BA–nonpolar solvent (octane)
8b) mixture of DBA–polar solvent (methanol)

and dibutylamine (DBA)–methanol mixture. Three analytical results are shown.

The analytical results calculated with $K_1$, $K_2$ and $K_3$ are noted by the (3-p) model, and those calculated with $K_1$ and $K_2$ or with $K_1$ and $K_3$, are noted by the Type I or II model.

Each table in these figures shows that the minimum

value of $E$ obtained from the (3-p) model is smaller than that obtained from the Type I or II model.

Figure 8(a) shows that the minimum value of $E$ obtained from the Type I model is of the same order of magnitude as that obtained from the (3-p) model. Figure 8(b) shows that the minimum value of $E$ obtained from the Type II model is of the same order of magnitude as that obtained from the (3-p) model.

These facts suggest that the equilibria in nonpolar solvent and in polar solvent can be described by the Type I model and Type II model, respectively.

## Conclusions

(1) The moles of $CO_2$ absorbed chemically into amine–nonaqueous solvent mixture can be described by three equilibrium constants, $K_1$, $K_2$ and $K_3$.

(2) The equilibria of the absorption reactions of $CO_2$ with amine in nonaqueous (nonpolar or polar) solvent were described by two approximate models, depending on the polarity of solvent: the reactions of $CO_2$ with amine in nonpolar solvent produced amine carbamate, while those in polar solvent produced carbamic ion and ammonium ion.

(3) The absorption reactions were supported by the heat of reaction estimated from the temperature dependency of $K_1$, $K_2$ and $K_3$.

## Appendix

The following reactions hold at the minimum value of $E$.

$$\partial E/\partial K_1 = 0 \qquad (A1)$$

$$\partial E/\partial K_2 = 0 \qquad (A2)$$

$$\partial E/\partial K_3 = 0 \qquad (A3)$$

Four steps of the modified Newton method were applied to obtain the solutions of Eq. (A1) to (A3), because sometimes meaningless solutions were obtained which satisfied the pseudo-minimum condition for two variables in $K_1$, $K_2$ and $K_3$.

Step 1 Assume that $K_3 = 0$, and solve Eqs. (A1) and (A2). The solutions were expressed by $K_1'$ and $K_2'$.

Step 2 Assume the $K_2 = 0$, and solve Eqs. (A1) and (A3). The solutions were expressed by $K_1''$ and $K_3''$.

Step 3 $K_1$, $K_2$ and $K_3$ at the minimum value of $E$ were found in three ranges obtained in Step 1 and Step 2, such as $K_1' \lessgtr K_1 \lessgtr K_1''$, $0 < K_2 < K_2'$ and $0 < K_3 < K_3''$.

Step 4 Meaningful solutions were found by conditions other than Eq. (A1) to (A3):

(1) $\quad |\partial E/\partial K_1| + |\partial E/\partial K_2| + |\partial E/\partial K_3| < \varepsilon_1 \qquad (A4)$

and

(2) $\quad |\Delta K_i| < \varepsilon_2 \qquad (A5)$

where $\Delta K_i = K_i^{(N)} - K_i^{(N-1)}$, $\varepsilon_1 = 1.0 \times 10^{-5}$ and $\varepsilon_2 = 1.0 \times 10^{-6}$. $K_i^{(N)}$ expresses the value of $K_i$ at the $N$-th iteration.

If the solutions did no satisfy Eqs. (A4) and (A5) simultaneously, the procedures went back to Step 3 again. If Eqs. (A4) and (A5) were satisfied, the solutions were regarded as the solutions of the equilibrium constants.

## Nomenclature

| | | |
|---|---|---|
| $Ac$ | = molar absorption ratio defined by Eq. (6) | [mol/mol] |
| $C$ | = initial concentration of amine | [mol/m$^3$] |
| $Cg'$ | = molar concentration of $CO_2$ dissolved physically | [mol/m$^3$] |
| $E$ | = function defined by Eq. (21) | [—] |
| $H, H'$ | = Henry's constant for solvent and solution | [m$^3$/mol·Pa] |
| $\Delta H$ | = enthalpy of reaction | [J/mol] |
| $K_1$ | = equilibrium constant for Eq. (1) | [m$^3$/mol] |
| $K_2$ | = equilibrium constant for Eq. (2) | [m$^3$/mol] |
| $K_3$ | = equilibrium constant for Eq. (3) | [—] |
| $P$ | = partial pressure of $CO_2$ in equilibrium | [Pa] |
| $R$ | = gas law constant ($= 8.314$) | [J/mol·K] |
| $T$ | = temperature | [K] |
| $X, Y, Z$ | = ratio of moles of (carbamic acid, amine carbamate and carbamic ion) to initial moles of amine | [—] |
| $\rho$ | = density of amine | [g/m$^3$] |
| $\varepsilon_1, \varepsilon_2$ | = parameters in Eqs. (A4) and (A5) | [—] |

⟨Subscrits⟩

| | |
|---|---|
| cal | = calculated |
| exp | = experimental |
| $g$ | = gas phase |
| $i$ | = initial or $i$-th condition |
| $l$ | = liquid phase |

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