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# Absorption of carbon dioxide into glycidyl methacrylate solution with quaternary onium salts

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**Abstract**−Carbon dioxide was absorbed into organic solutions of glycidyl methacrylate (GMA) in a semi-batch stirred tank with a plane gas-liquid interface at 101.3 kPa to measure absorption rates of carbon dioxide, from which the reaction kinetics between carbon dioxide and GMA with quaternary onium salts as catalysts was obtained. The reaction rate constants were estimated by the mass transfer mechanism accompanied by the pseudo-first-order reaction method. An empirical correlation formula between the reaction rate constants and the solubility parameters of solvents such as toluene, N-methyl-2-pirrolidinone, and dimethyl sulfoxide was presented.

Key words: Absorption, Carbon Dioxide, Gglycidyl Methacrylate, Quaternary Onium Salt

## INTRODUCTION

The chemical fixation of carbon dioxide has received much attention in view of environmental problems. An attractive strategy to deal with this situation is converting $CO_2$ into valuable substances [1]. The reaction of carbon dioxide with oxiranes leading to 5-membered cyclic carbonates is well known [1]. These cyclic carbonates can be used as polar aprotic solvents, electrolytes for batteries and sources for reactive polymers [2]. The synthesis of cyclic carbonates by the reaction of $CO_2$ with oxirane has been performed using Lewis acids, transition metal complexes, and organometallic compounds as catalysts at high pressure such as 10-50 atm [3,4]. Some articles [5-9] reported the synthesis of 5-membered cyclic carbonates under mild conditions at atmospheric pressure in the presence of metal halides or quaternary onium salts.

The papers [3-9] about oxirane-$CO_2$ reactions have mainly focused on the reaction mechanism, the overall reaction kinetics, and the effect of the catalyst on the conversion. But, because the diffusion may have an effect on the reaction kinetics [10] in the mass transfer accompanied by chemical reactions, we believe that it is worthwhile to investigate the effect that diffusion has on the reaction kinetics of the gas-liquid heterogeneous reaction such as the oxirane-$CO_2$ reaction.

There is little information about the effect of diffusion on the reaction kinetics in the gas absorption. Park et al. [11-17] used tetrabutylammonium bromide [11], Aliquat 336 [12], tetraoctylammonium chloride [13], immobilized tetraoctylammonium chloride [14], immobilized tetrabutylammonium chloride [15], immobilized tetrahexylammonium bromide [16], immobilized tetraethylammonium chloride [17] as a catalyst to obtain the reaction kinetics of the reaction between $CO_2$ and glycidyl methacrylate (GMA) using the measured rate of $CO_2$ absorption. They presented the pseudo-first-order reaction method based on the reaction mechanism [4] with two steps to obtain the elementary reaction rate constants.

To investigate the effect of diffusion on the gas-liquid heterogeneous reaction and the catalytic activity of quaternary onium salts in GMA-$CO_2$ reaction in series, tetrabutylammonium iodide, tetraethylammonium chloride, tetrabutylammonium chloride, tetrabutylphosphonium bromide, and tetrahexylammonium chloride were selected as catalysts. Toluene, N-methyl-2-pirrolidinone (NMP), and dimethyl sulfoxide (DMSO) were used as organic solvents for $CO_2$ absorption.

## THEORY

It is necessary for the reaction kinetics between oxirane and carbon dioxide using a catalyst such as a quaternary onium salt to set up the reaction mechanism of their reactions. Although the reaction mechanism shown in Eq. (i) have been proposed for the oxirane-$CO_2$ reaction by many researchers [4-9], no reliable evidence has yet been reported. It was found that the rate-determining step is the attack of the anion part of the catalyst to oxirane. The importance of the anion part of the catalyst can be explained by this mechanism. That is, the overall reaction between $CO_2$ and GMA to form five-membered cyclic carbonate, 2-oxo-1,3-dioxolan-4-yl) methacrylate (DOMA), is presented as follows:

$$CO_2+GMA\rightarrow DOMA \tag{i}$$

The overall reaction in Eq. (i) with the rate-determining step of the attack of the anion part of the catalyst to GMA [7] is assumed to consist of two steps [4] as follows:

1) A reversible reaction between B and QX to form an intermediate complex ($C_1$), 2) An irreversible reaction between A and $C_1$ to form QX and DOMA(C)

$$B+QX\underset{k_2}{\overset{k_1}{\rightleftarrows}}C_1 \tag{ii}$$

$$A+C_1\xrightarrow{k_3}C+QX \tag{iii}$$

The reaction rate of $CO_2$ under the condition of steady-state approximation to formation of $C_1$ is presented as follows:

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$$r_A=\frac{C_BQ_o}{\frac{1}{k_1}+\frac{k_2}{k_1k_3C_A}+\frac{C_B}{k_3C_A}} \tag{1}$$

As shown in Eq. (1), the reaction rate of $CO_2$ is proportional to the total concentration of the catalyst.

If the value of $k_1$ is very large and then $1/k_1$ approaches to 0, Eq. (1) is arranged to

$$r_{Af}=\frac{C_AC_BQ_o}{\frac{k_2}{k_1k_3}+\frac{C_B}{k_3}} \tag{2}$$

It is assumed that species B and QX are nonvolatile and gas phase resistance to absorption is negligible by using pure species A, and thus, the concentration of species A at the gas-liquid interface corresponds to equilibrium with the partial pressure of species A in the bulk gas phase.

Under the assumptions mentioned above, the mass balances of species A and B with the film theory [18] accompanied by a chemical reaction and the boundary conditions are given as follows:

$$D_A\frac{d^2C_A}{dz^2}=r_{Af} \tag{3}$$

$$D_B\frac{d^2C_B}{dz^2}=r_{Af} \tag{4}$$

$$z=0;\ C_A=C_{Ai};\ \frac{dC_B}{dz}=0 \tag{5}$$

$$z=0;\ C_A=C_{AL};\ C_B=C_{B0} \tag{6}$$

If the diffusion rate of A is greater than or equal to the reaction rate, and the amount of the dissolved A that reacts in the diffusion film adjacent to the phase boundary compared to that which reaches the bulk liquid phase in the unreacted state is negligible, the concentration of A in the bulk liquid phase is a finite quantity ($C_{AL}$) [10], obtained from the following equation:

$$k_La_V(C_{Ai}-C_{AL})=\frac{C_{AL}C_{Bo}Q_o}{\frac{k_2}{k_1k_3}+\frac{C_{Bo}}{k_3}} \tag{7}$$

The enhancement factor of $CO_2$ defined as ratio of the flux of $CO_2$ with chemical reaction to that without chemical reaction is shown as follows:

$$\beta=-\left.\frac{da}{dx}\right|_{x=0} \tag{8}$$

where, $a=C_A/C_{Ai}$, $x=z/z_L$.

The absorption rate of $CO_2$ can be estimated as follows:

$$R_A=\beta k_LC_{Ai}S \tag{9}$$

If the physico-chemical properties such $C_{Ai}$, $D_A$, $D_B$, $k_2/k_1$, and $k_3$ are given at fixed $C_{Bo}$ and $Q_o$, the $\beta$ can be obtained from the numerical solution of the simultaneous differential equations of Eqs. (3) and (4) using FEMLAB@ program.

It is convenient to use the pseudo-first-order reaction method [10] to obtain $k_2/k_1$ and $k_3$ as follows:

$C_B$ becomes to be constant as $C_{Bo}$ and $r_{Af}$ of Eq. (2) is shown as

$$r_{A1}=k_oC_A \tag{10}$$

where, $k_o$ is the pseudo-first-order reaction constant and

$$k_o=\frac{C_{Bo}Q_o}{\frac{k_2}{k_1k_3}+\frac{C_{Bo}}{k_3}} \tag{11}$$

The mass balance of species A with the film theory accompanied by a pseudo-first-order reaction is given as follows:

$$D_A\frac{d^2C_A}{dz^2}=r_{A1} \tag{12}$$

If the $C_{AL}$ is zero, $\beta$ is presented from the exact solution of Eq. (12) as follows:

$$\beta=\frac{Ha}{\tanh Ha} \tag{13}$$

where Ha is called as Hatta number of $\sqrt{k_oD_A}/k_L$

Eq. (11) is rearranged as follows:

$$\frac{Q_oC_{Bo}}{k_o}=\frac{k_2}{k_1k_3}+\frac{C_{Bo}}{k_3} \tag{14}$$

The values of $k_2/k_1$ and $k_3$ are obtained from the intercept and slope of the plots of $Q_oC_{Bo}/k_o$ against $C_{Bo}$ using Eq. (14) and the measured $\beta$.

## EXPERIMENTAL

### 1. Chemicals

All chemicals in this study were reagent grade, and used without further purification. Purity of both $CO_2$ and $N_2$ was more than 99.9%. GMA, tetrabutylammonium iodide (TBAI), tetraethylammonium chloride (TEAC), tetrabutylammonium chloride (TBAC), tetrabutylphosphnium bromide (TBPB), and tetrahexylammonium chloride (THAC) were used as reagent grade supplied by Aldrich chemical company, U.S.A. without purification.

### 2. Absorption Rate of $CO_2$

The gas-liquid contactor used was a stirred tank made of glass of 0.075 m inside diameter and of 0.13 m in height with a plane unbroken gas-liquid interface, and was operated continuously with respect to the gas and batchwise with respect to the liquid phase. Four equally spaced vertical baffles, each one-tenth of the vessel diameter in width, were attached to the internal wall of the vessel. The contact area between gas and liquid was obtained as a ratio of the volume (0.3 $dm^3$) of the added liquid to the measured height (0.07 m) of the liquid in the vessel, and its value was $4.286\times10^{-3}$ $m^2$. The liquid phase was agitated with an agitator driven by a 1/4 Hp variable speed motor without agitation in gas phase because of pure $CO_2$ gas. A straight impeller with 0.034 m in length, 0.017 m in width and 0.005 m in thickness was used as the liquid phase agitator, and located at the middle position of the liquid phase of 0.3 $dm^3$. Carbon dioxide was saturated with solvent vapor and fed into the absorber. The absorber and saturator were kept constant at a given temperature in a water bath and the gas flow meters were kept at the same temperature in an air bath. The gas flow rate was maintained at 50 $cm^3$/min. The flow rate of outlet gas was measured us-

**Table 1. Physicochemical properties of the $CO_2$/GMA system**

| Temp. (°C) | Solvent | μ (cp) | $C_{Ai}$ (kmol/m$^3$) | $D_A\times10^9$ (m$^2$/s) | $D_B\times10^9$ (m$^2$/s) | $k_L\times10^5$ (m/s) |
|---|---|---|---|---|---|---|
| 80 | Toluene | 0.322 | 0.0783 | 9.379 | 3.665 | 1.268 |
| | NMP | 0.848 | 0.0711 | 3.694 | 1.444 | 1.204 |
| | DMSO | 0.857 | 0.0612 | 3.245 | 1.268 | 2.595 |
| 85 | Toluene | 0.307 | 0.0727 | 9.977 | 3.898 | 1.472 |
| | NMP | 0.797 | 0.0679 | 3.986 | 1.558 | 2.285 |
| | DMSO | 0.808 | 0.0576 | 3.490 | 1.364 | 2.864 |
| 90 | Toluene | 0.294 | 0.0698 | 10.563 | 4.128 | 1.946 |
| | NMP | 0.750 | 0.0629 | 4.295 | 1.678 | 1.998 |
| | DMSO | 0.764 | 0.0544 | 3.743 | 1.463 | 3.110 |

ing a mass flow meter (Brook Instrument, U.S.A). The absorption rate was obtained from the difference between inlet and outlet flow rates of $CO_2$ in the concentrations of GMA ranged from 0.5 to 3.0 kmol/m$^3$ and catalyst of 0.05 kmol/m$^3$ at reaction temperature in range of 80-90 °C. The experimental procedure to get the absorption rate was duplicated that as reported in published research [17] in detail.

The solubility of $CO_2$ in such organic solvents as toluene, NMP, and DMSO at 101.3 kPa was obtained by measuring the pressure difference of $CO_2$ between before and after equilibrium between gas and liquid phase similar to the procedure reported elsewhere [19]. The mass transfer coefficient ($k_L$) of $CO_2$ was obtained by using the measured rate of absorption of $CO_2$ and solubility of $CO_2$ at the impeller speed of 50 rpm. The diffusivity of $CO_2$ and GMA in solvent was estimated from the Wilke-Chang equation [18]. The viscosity of solvent was measured with Cannon-Fenske viscometer. The values of the viscosity of solvent, solubility, mass transfer coefficient, diffusivity of $CO_2$ and GMA in the solvent are given in Table 1.

### 3. Analysis of the Five-membered Cyclic Carbonate and Physico-chemical Properties of $CO_2$ and GMA

DOMA, produced from the reaction between $CO_2$ and GMA, was confirmed by the instrumental analysis such as FT-IR (cyclic carbonate C=O peak at wavelength of 1,800 cm$^{-1}$) and $^{13}$C-NMR (cyclic carbonate C=O at 160 ppm).

## RESULTS AND DISCUSSION

To obtain $k_o$, the absorption rates ($R_{Aexp}$) of $CO_2$ in such solvents as toluene, NMP, and DMSO were measured from the difference between the input- and output flow rate of $CO_2$ for GMA concentration ranging from 0.5 to 3.0 kmol/m$^3$. The input rate of $CO_2$, as mentioned in the text, was fixed at 50 cm$^3$/min. The absorption rate of $CO_2$ was $7.07\times10^{-9}$ kmol/s at typical condition of DMSO, 85 °C and output rate of 40.50 cm$^3$/min, The chemical absorption rate of $CO_2$ was $8.67\times10^{-9}$ kmol/s at $Q_o$=0.05 kmol/m$^3$, THAC and output rate of 38.35 cm$^3$/min. These absorption rates were plotted against $C_{Bo}$ of 0 and 0.5 kmol/m$^3$, respectively, in Fig. 1.

Fig. 1 shows the plots of $R_{Aexp}$ against the concentration of GMA using a typical THAC of 0.05 kmol/m$^3$ at 85 °C. The solid line in Fig. 1 is the absorption rate calculated from Eq. (9) with the known values of $k_3$ and $k_2/k_1$, which are obtained along the procedure mentioned below. As shown in Fig. 1, $R_{Aexp}$ increase gradually with increasing GMA concentration and increase in toluene, NMP, DMSO order. These results are exhibited equally for the other temperatures and catalysts.

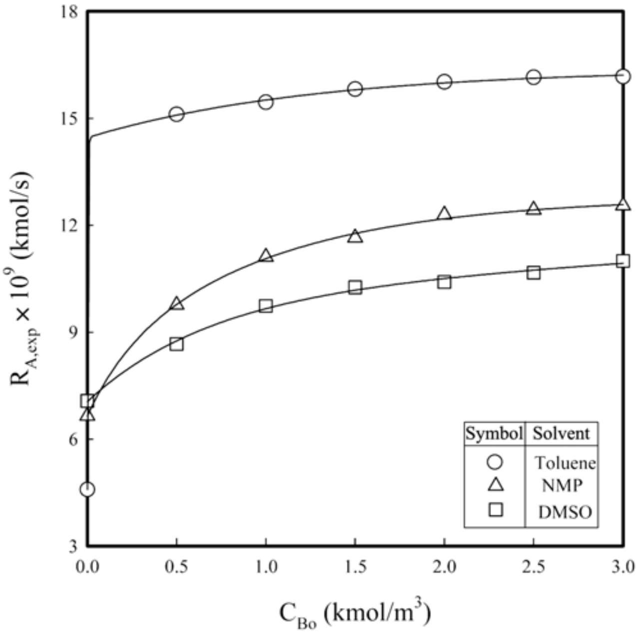

**Fig. 1. Absorption rates of carbon dioxide into various solvents in the reaction of $CO_2$ and GMA with THAC at 85 °C.**

The values of $k_o$ were obtained from $R_{Aexp}$ and Eq. (13) by using the physico-chemical properties in Table 1, and plotted in Fig. 2. The solid line in Fig. 2 is the calculated value from Eq. (11) with the known values of $k_3$ and $k_2/k_1$, which are obtained along the procedure mentioned below. As shown in Fig. 2, $k_o$ increase gradually with increasing GMA concentration. Fig. 3 shows plots of $Q_oC_{Bo}/k_o$ against $C_{Bo}$ and the plots satisfied straight lines. These results of linear relationship are exhibited equally for the other temperatures and catalysts. The $k_3$ and $k_2/k_1$ were obtained from the slope and intercept of the straight line. These values were used to estimate $R_A$ and $k_o$ to be shown as solid lines in Fig. 1 and 2. All the values of $k_3$ and $k_2/k_1$ including those in references are listed in Table 2.

Using the values of $k_3$ and $k_2/k_1$ at the given $C_{Bo}$, and $Q_o$, Eq. (3) and (4) were solved by a finite element method of FEMLAB$^@$ to give the profiles of $C_B$ at $Q_o$=0.05 kmol/m$^3$ and 85 °C. The typical profiles of $C_B$ for various $C_{Bo}$ at $Q_o$=0.05 kmol/m$^3$ and 85 °C are shown in Fig. 4. As shown, the values of $C_B/C_{Bo}$ at the gas-liquid

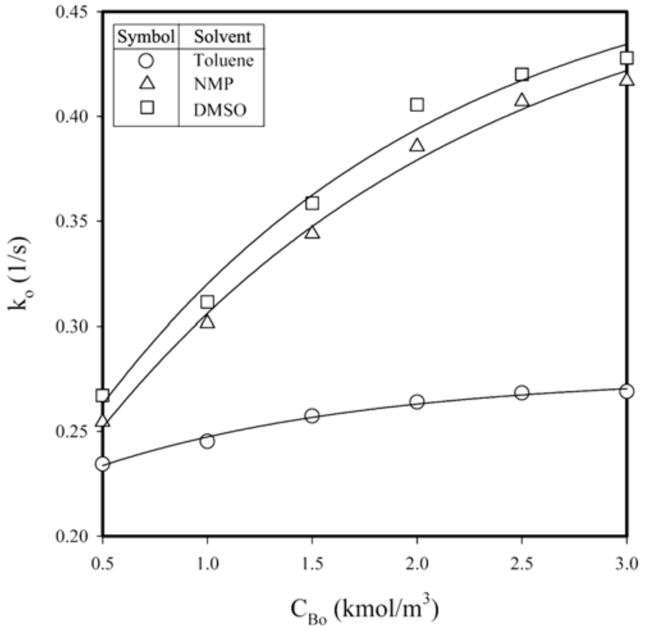

**Fig. 2. Pseudo-first-order reaction rate constant for various solvents in reaction of $CO_2$ and GMA with THAC t 85 °C.**

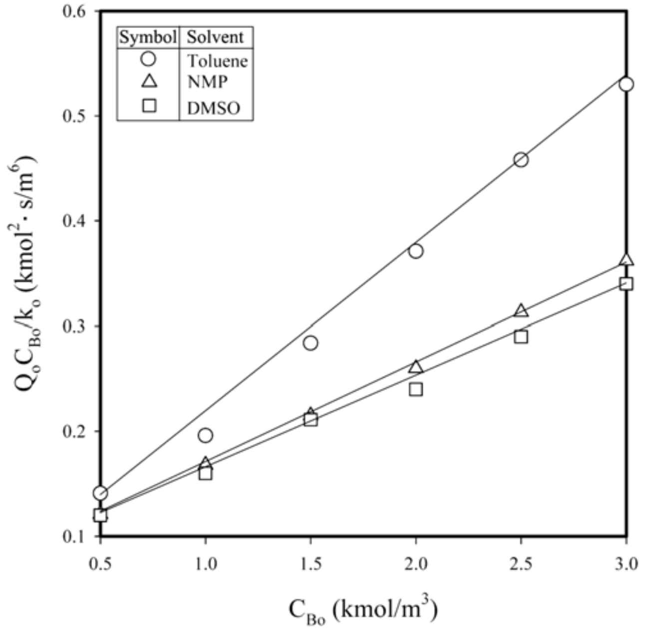

**Fig. 3. $Q_oC_{Bo}/k_o$ vs. $C_{Bo}$ for various solvents in the reaction of $CO_2$ with GMA using THAC at 85 °C.**

**Table 2. Reaction rate constants and activation energies for various catalysts in the reaction of $CO_2$ and GMA**

| Catalyst | Temp. (°C) | $k_3$ (m$^3$/kmol·s) | $k_2/k_1$ (kmol/m$^3$) | ΔE (kJ/mol) |
|---|---|---|---|---|
| Aliquat 336 [12] | 80 | 4.092 | 0.366 | 55.03 |
| | 85 | 5.696 | 0.429 | |
| | 90 | 6.859 | 0.650 | |
| TBAI | 80 | 5.544 | 0.451 | 49.21 |
| | 85 | 6.782 | 0.594 | |
| | 90 | 8.806 | 0.732 | |
| TBAB [11] | 80 | 6.218 | 0.619 | 58.05 |
| | 85 | 8.023 | 0.866 | |
| | 90 | 10.732 | 1.141 | |
| TEAC | 80 | 6.518 | 0.671 | 53.36 |
| | 85 | 8.118 | 0.874 | |
| | 90 | 10.766 | 1.201 | |
| TBPB | 80 | 6.819 | 0.565 | 58.18 |
| | 85 | 8.904 | 0.886 | |
| | 90 | 11.781 | 1.211 | |
| TBAC | 80 | 7.123 | 0.840 | 54.06 |
| | 85 | 9.180 | 1.093 | |
| | 90 | 11.840 | 1.435 | |
| THAC | 80 | 9.427 | 0.887 | 55.73 |
| | 85 | 12.053 | 1.192 | |
| | 90 | 15.919 | 1.670 | |
| TOAC [13] | 80 | 10.564 | 1.033 | 52.67 |
| | 85 | 13.652 | 1.430 | |
| | 90 | 17.329 | 1.782 | |

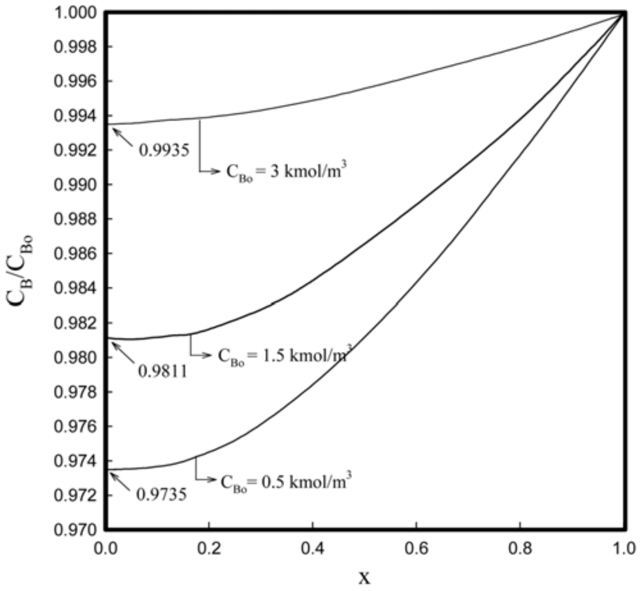

**Fig. 4. Dimensionless concentration profile of GMA using THAC.**

interface were larger than 0.97 and the change of $C_B$ in the film was small. This means that the reaction between $CO_2$ and GMA could be assumed to be pseudo-first-order with respect to $CO_2$ concentration.

The rate constants in organic reaction in a solvent generally reflect the solvent effect. Various empirical measures of the solvent effect have been proposed and correlated with the reaction rate constant [20]. Of these, some measures have a linear relation with the solubility parameter of the solvent. Then, using the data of $k_3$, $k_2/k_1$ and solvent parameter [21] of toluene, NMP, and DMSO of 18.2, 23.1, and 24.6(J/m$^3$)$^{0.5}$, respectively, the logarithms of $k_3$ and $k_2/k_1$ were plotted against the solubility parameter of the solvent under the typical conditions of THAC catalyst and 85 °C in Fig. 5.

As shown in Fig. 5, the plots satisfied the linear relationship between the reaction rate constant and solubility parameter of the sol-

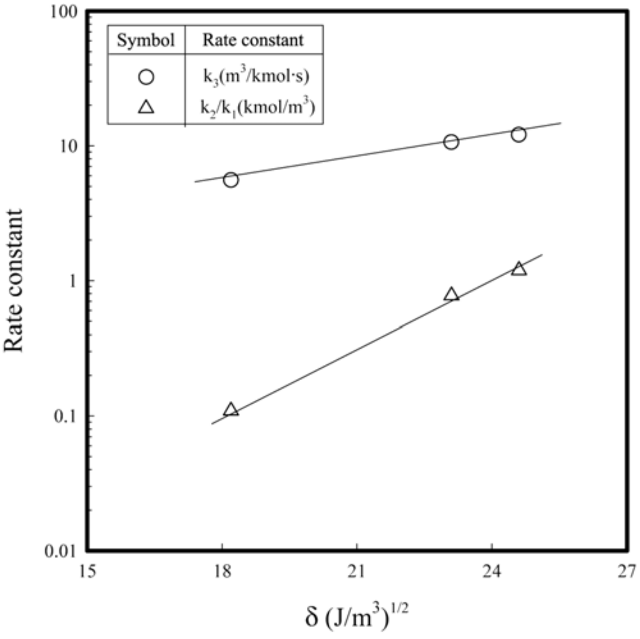

**Fig. 5. Relationship between reaction rate constant and solubility parameter of solvent in the reaction of $CO_2$ with GMA using THAC at 85 °C.**

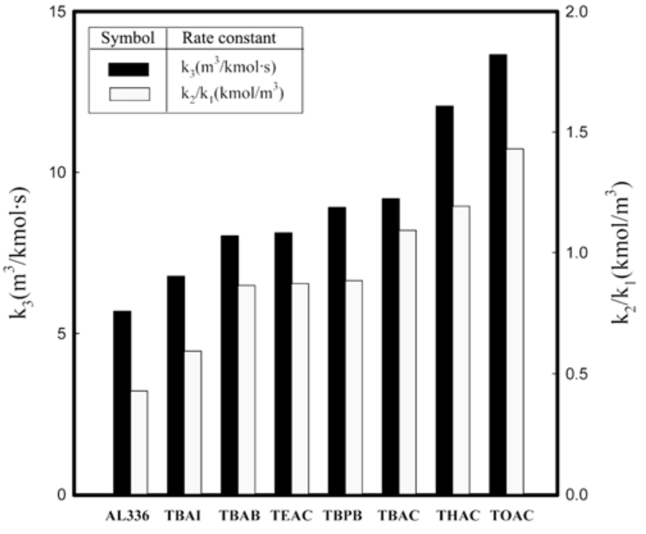

**Fig. 6. Reaction rate constants for various catalysts in the reaction of $CO_2$ with GMA in DMSO at 85 °C.**

vent. These results of linear relationship are exhibited equally for the other temperatures and catalysts.

To compare the catalytic activity one another, $k_3$ and $k_2/k_1$ were plotted against the kinds of catalysts under typical DMSO and 85 °C in Fig. 6.

As shown in Fig. 6, the values of $k_3$ and $k_2/k_1$ increase in Aliquat 336, TBAI, TBAB, TEAC, TBPB, TBAC, THAC and TOAC order.

The chemical species that are usually involved in the rate-determining step are the catalyst, anion and solvent. The structure of cation and species of anion in quaternary onium salts, and solvent affect the catalyst reactivity. A quantitative parameter for characterizing accessibility was suggested [22] based on the strong dependence of electrostatic interaction on the distance of closest approach between cation and anion (which is determined by steric factors). This parameter, termed q, is simply the sum of the reciprocals of the length of the linear alkyl chains attached to the central nitrogen of the quaternary ammonium cation. Accessibility of cation to anion is easier as the value of q becomes larger. For example, q value of Aliquat 336 is 11/8 and that of TBAC is 1; therefore, the better accessibility of TBAC makes the attack of anion to GMA stronger than Aliquat 336, and then, the reaction rate constants in TBAC are larger than those in Aliquat 336. Therefore, the reaction rate constants increase in Aliquat 336, TEAC, TBAC, THAC, TOAC order, as shown in Fig. 6. Because anion is hard base in $Cl^-$, $Br^-$, $I^-$ order and DMSO, soft solvent, the solvation of anion in DMSO is large in $I^-$, $Br^-$, $Cl^-$ order. Then, the reaction rate constants are large in TBAI, TBAB, TBAC order as shown in Fig. 6. Because the element of phosphorus in TBPB has smaller electric density and weaker bond strength between cation and anion than nitrogen in TBAB, the reaction rate constants in TBPB are larger than those in TBAB as shown in Fig. 6.

To observe the effect of reaction temperature on the reaction rate constants, $k_3$ and $k_2/k_1$, absorption rates of $CO_2$ were measured according to the change of reaction temperature of the range of 80-90 °C for all solvents and catalysts to get the reaction rate constants, $k_3$ and $k_2/k_1$. Fig. 7 shows plots of the reaction rate constants against 1/T in a semi-logarithm scale under a typical THAC and DMSO. As shown in Fig. 7, the plots satisfied straight lines. These results of linear relationship are exhibited equally for the other catalysts and solvents. The activation energy ($\Delta E$) in the reaction of Eq. (iii) for $k_3$ was obtained from the slope of the line, and its value was 55.73 kJ/mol.

The values of $\Delta E$ for all the catalysts are listed in Table 2. As shown, they were in the range of 49-59 kJ/mol.

To confirm the use of Eq. (13), the value of $C_{AL}$ was calculated

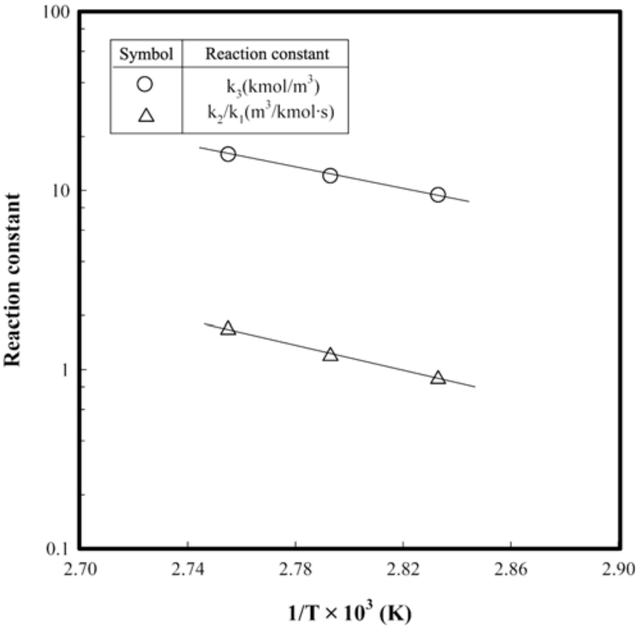

**Fig. 7. Dependence of reaction temperature on reaction rate constant in the reaction of $CO_2$ with GMA using THAC in DMSO.**

from Eq. (7), Tables 1 and 2. For example, under the condition of $C_{Ai}$=0.0544, $k_3$=80806, $k_2/k_1$=0.732, $k_L$=$3.11\times10^{-5}$ at $Q_o$=0.05, $C_{Bo}$=0.5, T=90 °C, QX=TBAI and solvent=DMSO, the value of $C_{AL}$ is $1.35\times10^{-4}$ kmol/m$^3$, which is only 0.25% of $C_{Ai}$. This means that $C_{AL}$ could be taken as zero.

## CONCLUSIONS

The overall reaction between $CO_2$ and GMA using quaternary onium salt as a catalyst was assumed to consist of two elementary reactions such as a reversible reaction of GMA and catalyst to form an intermediate and an irreversible reaction of this intermediate and carbon dioxide to form five-membered cyclic carbonate. Absorption data for $CO_2$ in the solution at 101.3 kPa were interpreted to obtain pseudo-first-order reaction rate constant, which was used to obtain the elementary reaction rate constants. The effect of the solubility parameter of solvent such as toluene, N-methyl-2-pirrolidinone, and dimethyl sulfoxide on the rate constant was presented. The catalytic reactivity was explained with the accessibility of cation to anion and solvation of anion.

## NOMENCLATURE

$a_v$ : the specific interfacial area [m$^2$/m$^3$]
$C_{Ai}$ : solubility of $CO_2$ in absorbent [kmol/m$^3$]
$C_i$ : concentration of component, i [kmol/m$^3$]
$D_i$ : diffusivity of component, i [m$^2$/s]
Ha : Hatta number
$k_o$ : pseudo-first-order reaction constant [1/s]
$k_L$ : mass transfer coefficient of $CO_2$ in absorbent [m/s]
$k_1$ : forward reaction rate constant in reaction (ii) [m$^3$/kmol s]
$k_2$ : backward reaction rate constant in reaction (ii) [1/s]
$k_3$ : reaction rate constant in reaction (iii) [m$^3$/kmol s]
$r_A$ : reaction rate of $CO_2$ [kmol/m$^3$s]
$r_{A1}$ : reaction rate of $CO_2$ for the pseudo-first-order reaction [kmol/m$^3$s]
$R_A$ : absorption rate of $CO_2$ [kmol/s]
$R_{Aexp}$ : measured absorption rate of $CO_2$ [kmol/s]
$Q_o$ : total concentration of catalyst [kmol/m$^3$]
QX : catalyst
S : contact area of gas-liquid interface [m$^2$]
z : distance [m]
$z_L$ : film thickness [m]

### Greek Letters

$\beta$ : enhancement factor of $CO_2$
$\delta$ : solvent parameter (J/m$^3$)$^{1/2}$
$\mu$ : viscosity of solvent [cP]

### Subscripts

A : $CO_2$
B : GMA
$C_1$ : intermediate complex
i : gas-liquid interface
o : feed

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