

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-pyrrolidinone, and dimethyl sulfoxide was presented.

Key words: Absorption, Carbon Dioxide, Glycidyl 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 CO₂ 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 CO₂ 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-CO₂ 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-CO₂ 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 CO₂ and glycidyl methacrylate (GMA) using the measured rate of CO₂ 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-CO₂ reaction in series, tetrabutylammonium iodide, tetraethylammonium chloride, tetrabutylammonium chloride, tetrabutylphosphonium bromide, and tetrahexylammonium chloride were selected as catalysts. Toluene, N-methyl-2-pyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) were used as organic solvents for CO₂ 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-CO₂ 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 CO₂ and GMA to form five-membered cyclic carbonate, 2-oxo-1,3-dioxolan-4-yl) methacrylate (DOMA), is presented as follows:



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 (C₁), 2) An irreversible reaction between A and C₁ to form QX and DOMA(C)



The reaction rate of CO₂ under the condition of steady-state approximation to formation of C₁ is presented as follows:

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$$r_A = \frac{C_B Q_o}{\frac{1}{k_1} + \frac{k_2}{k_1 k_3 C_A} + \frac{C_B}{k_3 C_A}} \quad (1)$$

As shown in Eq. (1), the reaction rate of CO₂ 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

$$r_{Af} = \frac{C_A C_B Q_o}{\frac{k_2}{k_1 k_3} + \frac{C_B}{k_3}} \quad (2)$$

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:

$$D_A \frac{d^2 C_A}{dz^2} = r_{Af} \quad (3)$$

$$D_B \frac{d^2 C_B}{dz^2} = r_{Af} \quad (4)$$

$$z=0; \quad C_A = C_{Ai}; \quad \frac{dC_B}{dz} = 0 \quad (5)$$

$$z=0; \quad C_A = C_{AL}; \quad C_B = C_{Bo} \quad (6)$$

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:

$$k_L a_V (C_{Ai} - C_{AL}) = \frac{C_{AL} C_{Bo} Q_o}{\frac{k_2}{k_1 k_3} + \frac{C_{Bo}}{k_3}} \quad (7)$$

The enhancement factor of CO₂ defined as ratio of the flux of CO₂ with chemical reaction to that without chemical reaction is shown as follows:

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

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

The absorption rate of CO₂ can be estimated as follows:

$$R_A = \beta k_L C_{Ai} S \quad (9)$$

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 β 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

$$r_{Af} = k_o C_A \quad (10)$$

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

$$k_o = \frac{C_{Bo} Q_o}{\frac{k_2}{k_1 k_3} + \frac{C_{Bo}}{k_3}} \quad (11)$$

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

$$D_A \frac{d^2 C_A}{dz^2} = r_{Af} \quad (12)$$

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

$$\beta = \frac{Ha}{\tanh Ha} \quad (13)$$

where Ha is called as Hatta number of $\sqrt{k_o D_A}/k_L$.

Eq. (11) is rearranged as follows:

$$\frac{Q_o C_{Bo}}{k_o} = \frac{k_2}{k_1 k_3} + \frac{C_{Bo}}{k_3} \quad (14)$$

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

EXPERIMENTAL

1. Chemicals

All chemicals in this study were reagent grade, and used without further purification. Purity of both CO₂ and N₂ was more than 99.9%. GMA, tetrabutylammonium iodide (TBAI), tetraethylammonium chloride (TEAC), tetrabutylammonium chloride (TBAC), tetrabutylphosphonium 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 CO₂

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 dm³) of the added liquid to the measured height (0.07 m) of the liquid in the vessel, and its value was 4.286×10^{-3} m². 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 CO₂ 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 dm³. 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 cm³/min. The flow rate of outlet gas was measured us-

Table 1. Physicochemical properties of the CO₂/GMA system

Temp. (°C)	Solvent	μ (cp)	C_{Ai} (kmol/m ³)	$D_A \times 10^9$ (m ² /s)	$D_B \times 10^9$ (m ² /s)	$k_L \times 10^5$ (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 CO₂ in the concentrations of GMA ranged from 0.5 to 3.0 kmol/m³ and catalyst of 0.05 kmol/m³ 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 CO₂ in such organic solvents as toluene, NMP, and DMSO at 101.3 kPa was obtained by measuring the pressure difference of CO₂ between before and after equilibrium between gas and liquid phase similar to the procedure reported elsewhere [19]. The mass transfer coefficient (k_L) of CO₂ was obtained by using the measured rate of absorption of CO₂ and solubility of CO₂ at the impeller speed of 50 rpm. The diffusivity of CO₂ 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 CO₂ and GMA in the solvent are given in Table 1.

3. Analysis of the Five-membered Cyclic Carbonate and Physico-chemical Properties of CO₂ and GMA

DOMA, produced from the reaction between CO₂ 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 ¹³C-NMR (cyclic carbonate C=O at 160 ppm).

RESULTS AND DISCUSSION

To obtain k_o , the absorption rates (R_{Aexp}) of CO₂ in such solvents as toluene, NMP, and DMSO were measured from the difference between the input- and output flow rate of CO₂ for GMA concentration ranging from 0.5 to 3.0 kmol/m³. The input rate of CO₂, as mentioned in the text, was fixed at 50 cm³/min. The absorption rate of CO₂ was 7.07×10^{-9} kmol/s at typical condition of DMSO, 85 °C and output rate of 40.50 cm³/min. The chemical absorption rate of CO₂ was 8.67×10^{-9} kmol/s at $Q_o = 0.05$ kmol/m³, THAC and output rate of 38.35 cm³/min. These absorption rates were plotted against C_{Bo} of 0 and 0.5 kmol/m³, 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/m³ 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 in-

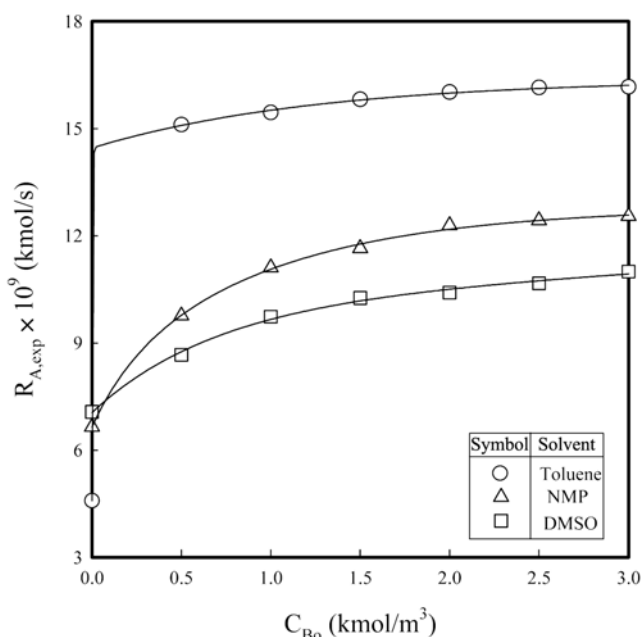


Fig. 1. Absorption rates of carbon dioxide into various solvents in the reaction of CO₂ and GMA with THAC at 85 °C.

creasing GMA concentration and increase in toluene, NMP, DMSO order. These results are exhibited equally for the other temperatures and catalysts.

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 $Q_o C_{Bo}/k_o$ 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/m³ and 85 °C. The typical profiles of C_B for various C_{Bo} at $Q_o = 0.05$ kmol/m³ and 85 °C are shown in Fig. 4. As shown, the values of C_B/C_{Bo} at the gas-liquid

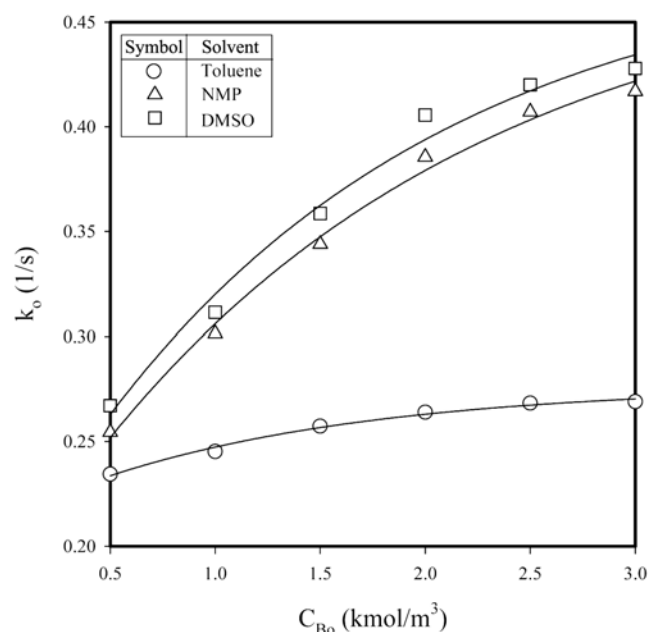


Fig. 2. Pseudo-first-order reaction rate constant for various solvents in reaction of CO₂ and GMA with THAC at 85 °C.

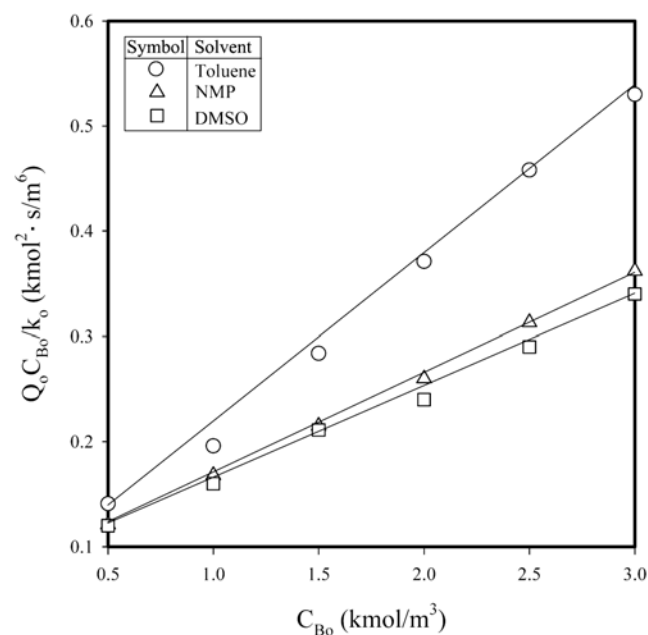


Fig. 3. $Q_o C_{B0} / k_o$ vs. C_{B0} for various solvents in the reaction of CO₂ with GMA using THAC at 85 °C.

interface were larger than 0.97 and the change of C_B in the film was small. This means that the reaction between CO₂ and GMA could be assumed to be pseudo-first-order with respect to CO₂ 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 relationship 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/m³)^{0.5}, respectively, the logarithms of k_3 and k_2/k_1

Table 2. Reaction rate constants and activation energies for various catalysts in the reaction of CO₂ 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	

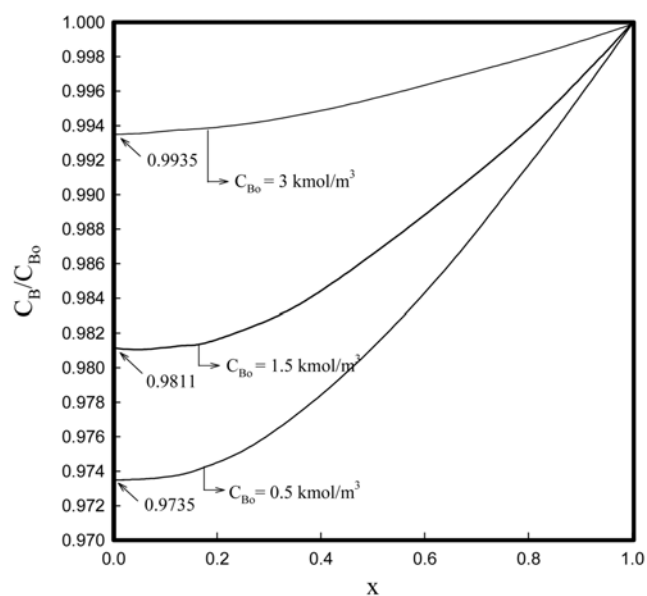


Fig. 4. Dimensionless concentration profile of GMA using THAC.

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-

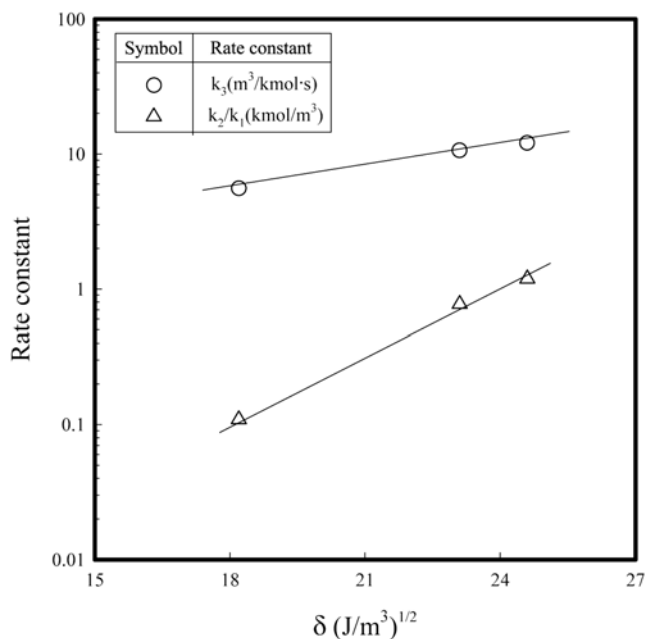


Fig. 5. Relationship between reaction rate constant and solubility parameter of solvent in the reaction of CO_2 with GMA using THAC at 85°C .

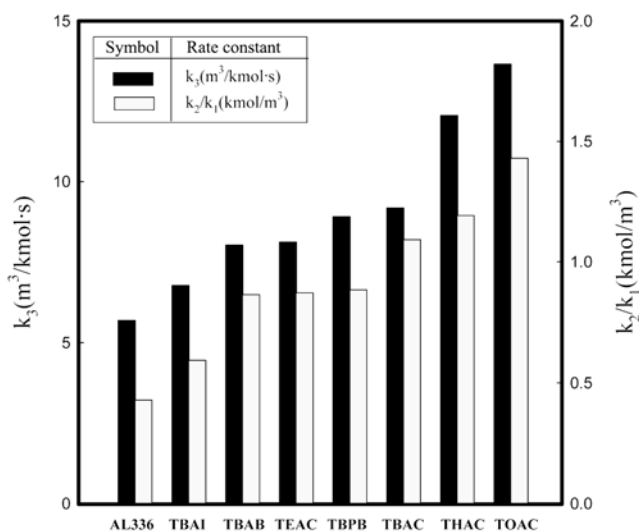


Fig. 6. Reaction rate constants for various catalysts in the reaction of CO_2 with GMA in DMSO at 85°C .

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 (ΔE) 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 ΔE 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

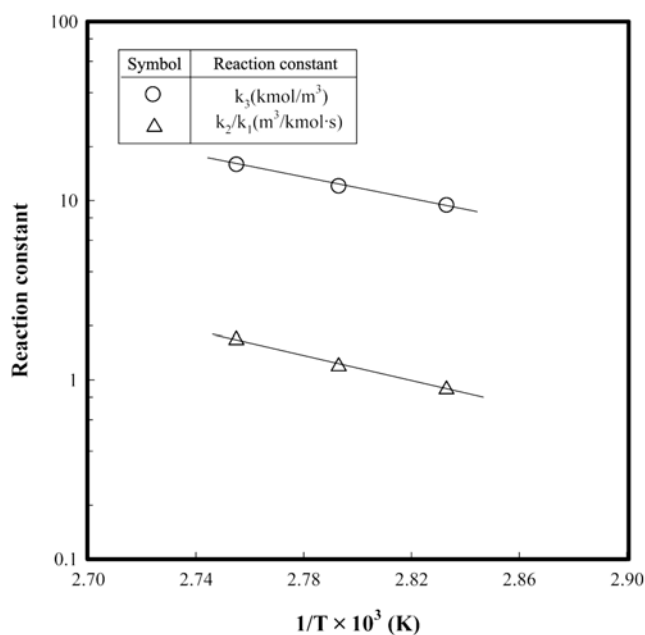


Fig. 7. Dependence of reaction temperature on reaction rate constant in the reaction of CO_2 with GMA using THAC in DMSO.

from Eq. (7), Tables 1 and 2. For example, under the condition of $C_{Ai}=0.0544$, $k_3=80806$, $k_2/k_1=0.732$, $k_L=3.11\times 10^{-5}$ at $Q_o=0.05$, $C_{Bo}=0.5$, $T=90^\circ\text{C}$, $QX=\text{TBAI}$ and solvent=DMSO, the value of C_{AL} is 1.35×10^{-4} kmol/m³, which is only 0.25% of C_{Ai} . This means that C_{AL} could be taken as zero.

CONCLUSIONS

The overall reaction between CO₂ 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 CO₂ 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-pyrrolidone, 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

β	: enhancement factor of CO ₂
δ	: solvent parameter (J/m ³) ^{1/2}
μ	: viscosity of solvent [cP]

Subscripts

A	: CO ₂
B	: GMA
C_1	: intermediate complex

i	: gas-liquid interface
o	: feed

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