

## Reaction rate of carbon dioxide in glycidyl methacrylate solution using tricapyrylmethylammonium chloride as a catalyst

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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 were studied by using tricapyrylmethylammonium chloride catalyst. The reaction rate constants of the reaction were estimated by using the mass transfer mechanism accompanied by the pseudo-first-order reaction. 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, Tricapyrylmethyl-ammonium Chloride

### INTRODUCTION

Recently, the chemistry of carbon dioxide has received much attention [Inoue, 1982]; its reaction with oxiranes, leading to five-membered cyclic carbonate, is well-known among many examples [Peppel, 1958; Kihara et al., 1993]. In the oxirane-CO<sub>2</sub> reaction, a high pressure (5-50 atm) of CO<sub>2</sub> was believed to be necessary [Peppel, 1958], but recently oxirane-CO<sub>2</sub> reactions that occur at atmospheric pressure have been reported [Rokicki, 1985]. Many organic and inorganic compounds, including amines, phosphines, quaternary ammonium salts, and alkali metal salts, are known to catalyze the reaction of CO<sub>2</sub> with oxirane [Kihara et al., 1993]. Most of above papers have focused on the reaction mechanism, the pseudo-first-order reaction rate constant with respect to the concentration of oxirane, and the effect of the catalyst on the conversion.

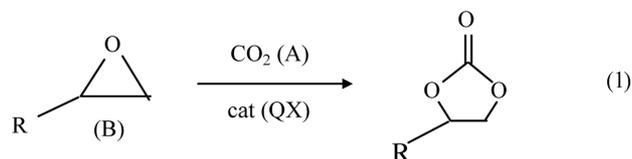
In mass transfer processes that accompany chemical reactions, diffusion may have an effect on the reaction kinetics [Park et al., 2003a]. We believe that it is worthwhile to investigate the effect that diffusion has on the reaction kinetics of the gas-liquid heterogeneous reaction such as the oxirane-CO<sub>2</sub> reaction.

In our previous work [Park et al., 2003], we studied the kinetics of CO<sub>2</sub> reaction with glycidyl methacrylate (GMA) using 18-crown-6 catalyst to get the reaction rate constants. In this study, the same reaction was performed using tricapyrylmethylammonium chloride as a catalyst. We measured the absorption rates of carbon dioxide into solutions of glycidyl methacrylate (GMA) in organic solvents such as toluene, *N*-methyl-2-pyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) to determine the pseudo-first-order reaction constant, which we used to obtain the elementary reaction rate constants.

### THEORY

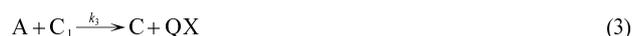
To determine the reaction kinetics between an oxirane and carbon dioxide using a catalyst, such as a quaternary onium salt, it is

necessary to understand the reaction mechanism. Although the reaction mechanism shown in Eq. (1) has been proposed by many researchers for oxirane-CO<sub>2</sub> reaction [Aida and Inoue, 1983; Rokicki et al., 1985; Kihara and Endo, 1992; Kihara et al., 1993; Nishikubo et al., 1993], no reliable evidence has yet been reported. It has been found that the rate-determining step is the attack of the anion part of the catalyst to the oxirane. The importance of the anion part of the catalyst can be explained by this mechanism. That is, the overall reaction between CO<sub>2</sub> and GMA to form five-membered cyclic carbonate is presented as follows:



The overall reaction (1) in this study is assumed to consist of two steps:

(i) A reversible reaction between GMA (B) and Aliquat 336 (QX) to form an intermediate complex (C<sub>1</sub>), (ii) An irreversible reaction between C<sub>1</sub> and carbon dioxide (A) to form QX and five-membered cyclic carbonate (C).



The reaction rate of CO<sub>2</sub> under the condition of steady-state approximation to formation of C<sub>1</sub> is presented as follows:

$$r'_A = \frac{C_B Q_o}{\frac{1}{k_1} + \frac{k_2}{k_1 k_3 C_A} + \frac{C_B}{k_3 C_A}} \quad (4)$$

If the value of k<sub>1</sub> is very large, such that 1/k<sub>1</sub> approaches to 0, Eq. (4) becomes

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$$r_A = \frac{C_A C_B Q_o}{\frac{k_2}{k_1 k_3} + \frac{C_B}{k_3}} \quad (5)$$

Species B is a nonvolatile solute, which is dissolved in the liquid phase prior to its introduction into the gas absorber. It is assumed that 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, using film theory accompanied by a chemical reaction, and the boundary conditions are given as follows:

$$D_A \frac{d^2 C_A}{dz^2} = r_A \quad (6)$$

$$D_B \frac{d^2 C_B}{dz^2} = r_A \quad (7)$$

$$z = 0; C_A = C_{Ai}; \frac{dC_B}{dz} = 0 \quad (8)$$

$$z = z_L; C_A = 0; C_B = C_{Bo} \quad (9)$$

The enhancement factor of CO<sub>2</sub>, defined as ratio of the flux of CO<sub>2</sub> with chemical reaction to that without chemical reaction, is shown as follows:

$$\beta = - \left. \frac{da}{dx} \right|_{x=0} \quad (10)$$

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

The value of  $\beta$  can be obtained from the numerical solution of the simultaneous differential Eqs. (6) and (7) by using finite element method and Eq. (10), by applying the known values of  $D_A$ ,  $D_B$ ,  $k_1$ ,  $k_2$ , and  $k_3$ , and the given values of  $C_{Bo}$  and  $Q_o$ .

The absorption rate of CO<sub>2</sub> can be estimated as follows:

$$R_A = \beta k_L C_{Ai} S \quad (11)$$

where  $\beta$  is obtained from Eq. (10),  $D_A$ ,  $D_B$ ,  $k_L$  and  $C_{Ai}$  from Table 2.

It is impossible to solve the non-linear differential Eqs. (6) and (7) if the reaction rate constants, such as  $k_1$ ,  $k_2$ , and  $k_3$ , are not known. The pseudo-first-order reaction method [Doraiswamy and Sharma, 1984] can be used to obtain the reaction rate constants in the following situation.

If the concentration of B is constant as  $C_{Bo}$ , the reaction between CO<sub>2</sub> and GMA is assumed to be pseudo-first-order reaction with respect to the concentration of CO<sub>2</sub>, and  $r_A$  of Eq. (5) is given by

$$r_A = k_o C_A \quad (12)$$

$$\text{where, } k_o = \frac{C_{Bo} Q_o}{\frac{k_2}{k_1 k_3} + \frac{C_{Bo}}{k_3}} \quad (13)$$

Eq. (13) rearranges to

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

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

$$D_A \frac{d^2 C_A}{dz^2} = k_o C_A \quad (15)$$

From the exact solution of Eq. (15),  $\beta$  is presented as follows:

$$\beta = \frac{\text{Ha}}{\tanh \text{Ha}} \quad (16)$$

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

The  $k_o$  is obtained from the experimental value of Eq. (16) at given values of  $C_{Bo}$  and  $Q_o$ . The values of  $k_3$  and  $k_2/k_1$  can be evaluated from the slopes and intercepts of plots of  $Q_o C_{Bo}/k_o$  against  $C_{Bo}$  in Eq. (14).

Depending on the relative rates of diffusion and reaction in the heterogeneous system, for convenience the system may be classified into four regimes: very slow reactions, slow reactions, fast reaction, and instantaneous reactions.

To ensure the pseudo-first-order fast reaction as shown in Eq. (12), the following condition is used [Doraiswamy and Sharma, 1984]:

$$1 \ll \text{Ha} \ll \text{Ei} \quad (17)$$

Ei is an enhancement factor for an instantaneous reaction and defined as follows:

$$\text{Ei} = 1 + (D_B/D_A) \sqrt{C_{Bo}/C_{Ai}} \quad (18)$$

## EXPERIMENTAL

### 1. Experimental Procedure

All chemicals were of reagent grade and used without further purification. Purity of both CO<sub>2</sub> and N<sub>2</sub> was more than 99.9%. GMA was supplied by Aldrich chemical company, U.S.A.

The gas-liquid contactor used was a stirred tank made of glass (7.5 cm inside diameter, 13 cm height) having a planar unbroken gas-liquid interface; it was operated continuously with respect to the gas and batch-wise with respect to the liquid phase. Four equally spaced vertical baffles, each one-tenth of the vessel diameter in height, were attached to the internal wall of the vessel. The contact area between gas and liquid was measured as  $4.286 \times 10^{-3} \text{ m}^2$ . The liquid phase was agitated with an agitator driven by a 1/4 hp variable-speed motor without agitation in gas phase, because it was pure CO<sub>2</sub> gas. A straight impeller (3.4 cm length, 1.7 cm width, and 0.5 cm thickness) was used as the liquid phase agitator; it was located at the middle position of the liquid phase of 0.3 dm<sup>3</sup>. The solute gas, carbon dioxide, was saturated with solvent vapor, and fed into the absorber. The absorber and saturator were maintained at a constant given temperature in a water bath and the gas flow meters were maintained at the same temperature in an air bath. The gas flow rate was maintained at 50 cm<sup>3</sup>/min. The flow rate of outlet gas was measured with a mass flow meter (Brook Instrument, U.S.A). The absorption rate was calculated from the difference between the inlet and outlet flow rates of CO<sub>2</sub> at the concentrations of GMA ranging from 0.5 to 3 kmol/m<sup>3</sup>, catalyst of 0.01 kmol/m<sup>3</sup> and at reaction temperature in range of 80-90 °C. The organic solvents used in this study were toluene, NMP, and DMSO. The experimental procedure to obtain the absorption rate duplicated the reported research [Park et al., 2004]. The measured values of the absorption rates ( $R_{A,exp}$ ) and  $\beta$  of CO<sub>2</sub> in solvents such as toluene, NMP, and DMSO at GMA concentrations ranging from 0.5 to 3 kmol/m<sup>3</sup> and the reaction temperature

**Table 1. Experimental date for the reaction of CO<sub>2</sub> with GMA**

Temp. (°C)	C <sub>Bo</sub>	R <sub>A</sub> , exp × 10 <sup>9</sup>	β	k <sub>o</sub>	H <sub>i</sub>	E <sub>i</sub>
80	0.5	7.048	1.035	0.0222	1.327	6.11
	1.0	7.139	4.109	0.0307	1.385	11.21
	1.5	7.170	1.053	0.0336	1.402	16.32
	2.0	7.185	1.056	0.0350	1.411	21.43
	2.5	7.189	1.056	0.0354	1.413	26.54
	3.0	7.199	1.058	0.0363	1.418	31.64
85	0.5	7.381	1.044	0.0312	1.365	6.43
	1.0	7.456	1.055	0.0389	1.407	11.85
	1.5	7.513	1.063	0.0447	1.436	17.28
	2.0	7.528	1.065	0.0462	1.443	22.71
	2.5	7.534	1.066	0.0468	1.446	28.13
	3.0	7.574	1.071	0.0509	1.466	33.56
90	0.5	7.521	1.037	0.0291	1.335	6.75
	1.0	7.641	1.054	0.0421	1.404	12.49
	1.5	7.697	1.061	0.0483	1.432	18.24
	2.0	7.732	1.066	0.0521	1.449	23.98
	2.5	7.749	1.069	0.0540	1.457	29.73
	3.0	7.771	1.072	0.0564	1.467	35.48

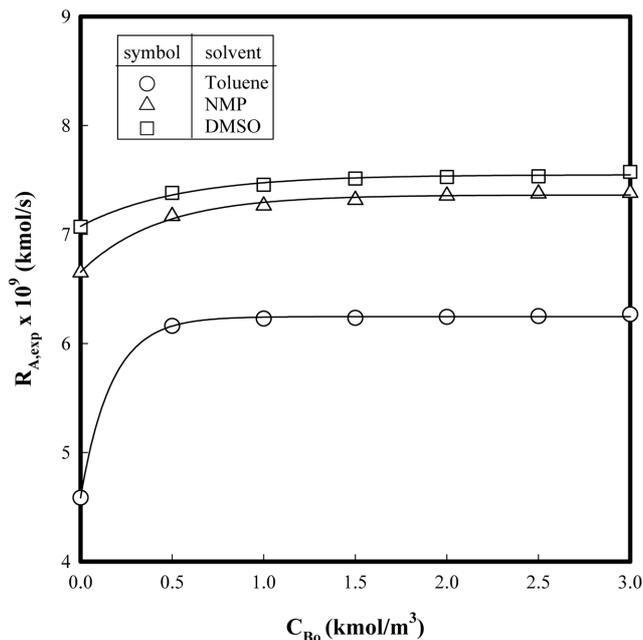
in range of 80-90 °C are given in Table 1.

## 2. Physical Properties

The solubilities of CO<sub>2</sub> in organic solvents such as toluene, NMP, and DMSO at 101.3 kPa at 101.3 kPa were obtained by measuring the pressure difference of CO<sub>2</sub> before and after equilibrium between the gas and liquid phases, similar to the procedure reported elsewhere [Kennard and Meisen, 1984]. The mass transfer coefficient (k<sub>t</sub>) of CO<sub>2</sub> was calculated by using the measured rate of absorption of CO<sub>2</sub> and solubility of CO<sub>2</sub> at an impeller speed of 50 rpm. The diffusivity of CO<sub>2</sub> and GMA in solvent was estimated from the Wilke-Chang equation [Danckwerts, 1970]. The viscosity of the solvent was measured with a Cannon-Fenske viscometer. The viscosity of solvent, solubility, mass transfer coefficient, diffusivities of CO<sub>2</sub>, and GMA in the solvent are given in Table 2.

## 3. Analysis of the Five-membered Cyclic Carbonate and Physico-chemical Properties of CO<sub>2</sub> and GMA

The presence of (2-oxo-1,3-dioxolan-4-yl)methacrylate (DOMA), which was produced from the reaction between CO<sub>2</sub> and GMA, was confirmed by instrumental analysis, such as FT-IR (cyclic car-



**Fig. 1. Absorption rates of carbon dioxide into various solvents in the reaction of CO<sub>2</sub> with GMA using Aliquat 336 at 85 °C.**

bonate C=O peak at wavelength of 1,800 cm<sup>-1</sup>) and <sup>13</sup>C-NMR (cyclic carbonate C=O at 160 ppm) spectra.

## RESULTS AND DISCUSSION

The values of R<sub>A,exp</sub> are plotted typically according to the change of the concentration of GMA at Aliquat 336 of 0.01 kmol/m<sup>3</sup> at 85 °C in Fig. 1. As shown in Fig. 1, R<sub>A,exp</sub> increased gradually with increasing GMA concentration and increased in the order toluene, NMP, DMSO. The solid line in Fig. 1 is the absorption rate calculated from Eq. (11) using the known values of k<sub>3</sub> and k<sub>2</sub>/k<sub>1</sub>, which are obtained by following the procedure mentioned below.

The values of k<sub>o</sub> were obtained from R<sub>A,exp</sub> and Eq. (16) using the physicochemical properties in Table 2; they are plotted in Fig. 2. The solid line in Fig. 2 is the value calculated from Eq. (13) using the known values of k<sub>3</sub> and k<sub>2</sub>/k<sub>1</sub>, which are obtained by following the procedure mentioned below. As shown in Fig. 2, k<sub>o</sub> increases gradually with increasing GMA concentration. Fig. 3 shows plots of Q<sub>c</sub>C<sub>Bo</sub>/k<sub>o</sub> against C<sub>Bo</sub>; these plots satisfy straight lines. The values

**Table 2. Physicochemical properties of CO<sub>2</sub>/GMA system**

Temp. (°C)	Solvent	μ (cp)	C <sub>Ai</sub> (kmol/m <sup>3</sup> )	D <sub>A</sub> × 10 <sup>9</sup> (m <sup>2</sup> /s)	D <sub>B</sub> × 10 <sup>9</sup> (m <sup>2</sup> /s)	k <sub>L</sub> × 10 <sup>5</sup> (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

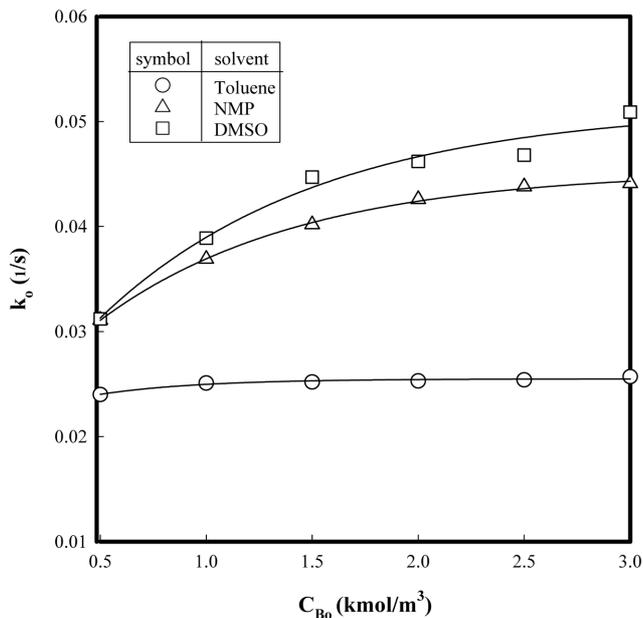


Fig. 2. Pseudo-first-order reaction rate constant for various solvents in reaction of  $\text{CO}_2$  and GMA with Aliquat 336 of 0.01 kmol at  $85^\circ\text{C}$ .

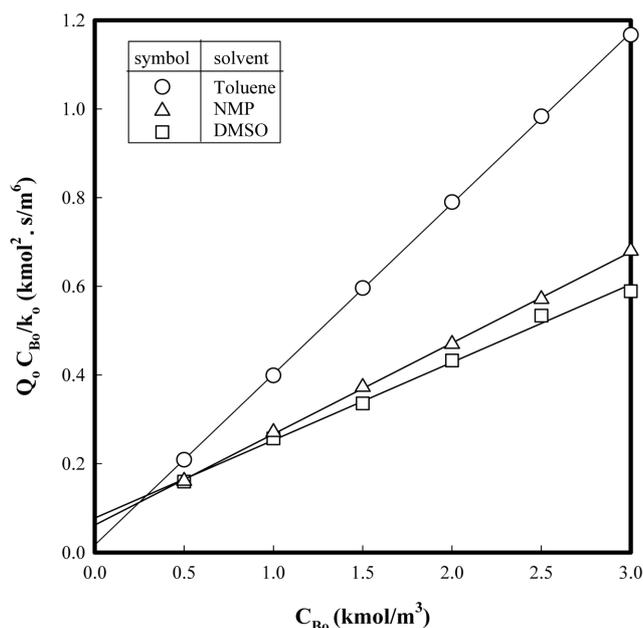


Fig. 3.  $Q_0 C_{B0}/k_0$  vs.  $C_{B0}$  for various solvents in the reaction of  $\text{CO}_2$  with GMA using Aliquat 336 at  $85^\circ\text{C}$ .

of  $k_3$  and  $k_2/k_1$  were obtained from the slopes and intercepts of the straight lines. These values were used to estimate  $R_d$  and  $k_0$ , which were then presented as solid lines in Fig. 1 and 2.

To ensure the reaction in Eq. (12) to be a pseudo-first-order reaction, the values of  $Ha$  and  $Ei$  are calculated from Eq. (18) using the obtained  $k_0$  and the known data in Table 2, and are given in Table 1. As shown in Table 1, Eq. (17) was satisfied, and then the reaction with GMA concentration of  $0.5\text{--}3\text{ kmol/m}^3$  can be a pseudo-first-order reaction regime.

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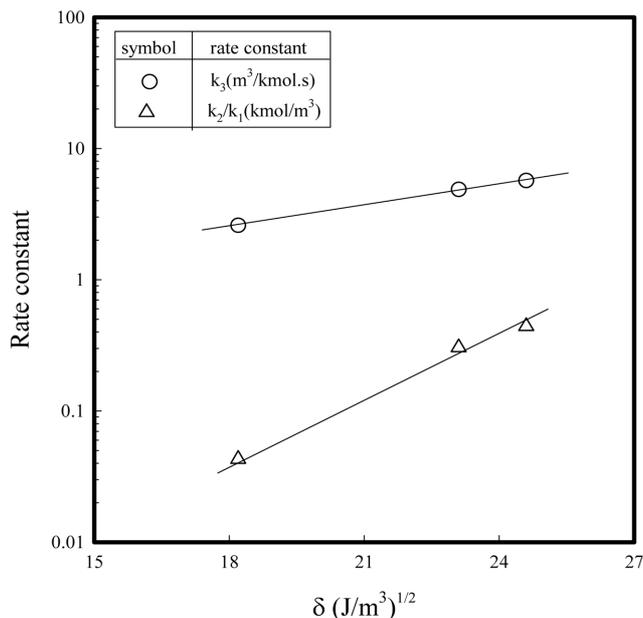


Fig. 4. Relationship between reaction rate constant and solubility parameter of solvent in the reaction of  $\text{CO}_2$  with GMA using Aliquat 336 at  $85^\circ\text{C}$ .

The rate constants of organic reactions in solvents generally reflect the solvent effect. Various empirical measures of the solvent effect have been proposed to correlate with the reaction rate constant [Herbrandson and Neufeld, 1966]. Of these, some measures have a linear relationship to the solubility parameter of the solvent. Using data of  $k_3$ ,  $k_2/k_1$  and solubility parameter [Brandrup and Immergut, 1975] of toluene, NMP and DMSO of 18.2, 23.1, and 24.6  $(\text{J}/\text{m}^3)^{0.5}$ , respectively, the logarithms of  $k_3$  and  $k_2/k_1$  were plotted against the solubility parameter of the solvent. Fig. 4 demonstrates this relationship; the plots satisfy the linear relationships between the reaction rate constant and solubility parameter of the solvent. The solvent polarity is increased when the solubility parameter of the solvent is increased. It may be assumed that the increased instability and solvation of  $C_1$  arising from the increased solvent polarity enhance the dissociation reaction of  $C_1$  and the reaction between  $C_1$  and  $\text{CO}_2$ , such as  $\text{SN}_1$  by solvation [Morrison and Boyd, 1983], respectively; thus, the values of  $k_2/k_1$  and  $k_3$  increase upon increasing the solubility parameter, as shown in Fig. 4.

To observe the effect that the reaction temperature has on the reaction rate constants,  $k_3$  and  $k_2/k_1$ , the absorption rates of  $\text{CO}_2$  were measured according to the changes of reaction temperature over the range  $80\text{--}90^\circ\text{C}$  in a particular solvent, e.g., DMSO, and to obtain the reaction rate constants,  $k_3$  and  $k_2/k_1$ . Fig. 5 shows plots of the reaction rate constants against  $1/T$  on a semi-logarithm scale; these plots satisfy straight lines. The activation energy of reaction (3) was obtained from the slope of the line for  $k_3$ ; its value is 13.15 kcal/mol.

## CONCLUSION

The overall reaction between  $\text{CO}_2$  and GMA using tricaprylylmethylammonium chloride as a catalyst was assumed to consist of two elementary reactions: a reversible reaction of GMA and the catalyst to form an intermediate, and an irreversible reaction of this

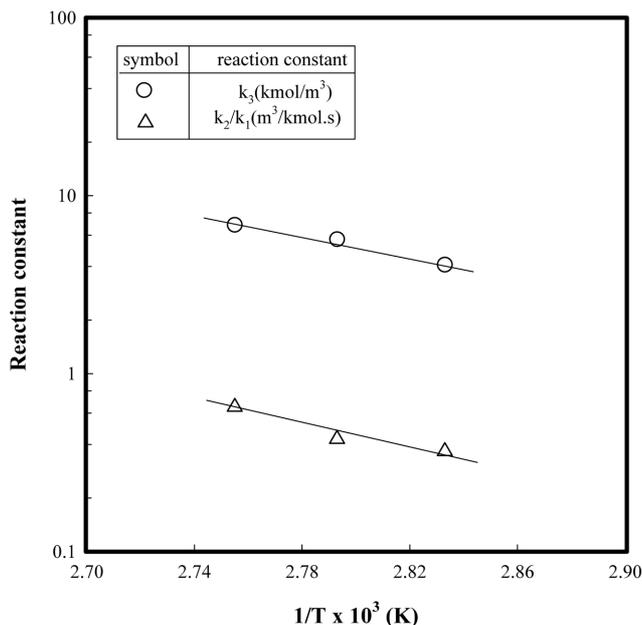


Fig. 5. Dependence of reaction temperature on reaction rate constant in the reaction of  $\text{CO}_2$  with GMA using Aliquat 336 and DMSO.

intermediate with carbon dioxide to form five-membered cyclic carbonate. Absorption data for  $\text{CO}_2$  in the solution at 101.3 kPa were interpreted to obtain a pseudo-first-order reaction rate constant, which was used to obtain the elementary reaction rate constants. The effects that the solubility parameters of solvent such as toluene, *N*-methyl-2-pyrrolidinone, and dimethyl sulfoxide have on the rate constant were determined.

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#### NOMENCLATURE

- $C_{,di}$  : solubility of  $\text{CO}_2$  in absorbent [ $\text{kmol/m}^3$ ]  
 $C_i$  : concentration of component, *i* [ $\text{kmol/m}^3$ ]  
 $D_i$  : diffusivity of component, *i* [ $\text{m}^2/\text{s}$ ]  
 $k_o$  : pseudo-first-order reaction constant [ $1/\text{s}$ ]  
 $k_3$  : reaction rate constant in reaction (3) [ $\text{m}^3/\text{kmol s}$ ]  
 $k_L$  : mass transfer coefficient of  $\text{CO}_2$  in absorbent [ $\text{m/s}$ ]  
 $k_1$  : forward reaction rate constant in reaction (2) [ $\text{m}^3/\text{kmol s}$ ]  
 $k_2$  : backward reaction rate constant in reaction (2) [ $1/\text{s}$ ]  
 $r'_A$  : reaction rate of  $\text{CO}_2$  in Eq. (4) [ $\text{kmol/m}^3 \text{s}$ ]  
 $r_A$  : reaction rate of  $\text{CO}_2$  in Eq. (5) [ $\text{kmol/m}^3 \text{s}$ ]  
 $R_A$  : absorption rate of  $\text{CO}_2$  [ $\text{kmol/s}$ ]  
 $R_{A,exp}$  : measured absorption rate of  $\text{CO}_2$  [ $\text{kmol/s}$ ]  
 $Q_o$  : total concentration of catalyst [ $\text{kmol/m}^3$ ]  
 $S$  : contact area of gas-liquid interface [ $\text{m}^2$ ]  
 $z$  : distance [ $\text{m}$ ]  
 $z_L$  : film thickness [ $\text{m}$ ]

#### Greek Letters

- $\beta$  : enhancement factor of  $\text{CO}_2$   
 $\delta$  : solvent parameter [ $(\text{J/m}^3)^{1/2}$ ]  
 $\mu$  : viscosity of solvent [ $\text{cP}$ ]

#### Subscripts

- A :  $\text{CO}_2$   
 B : GMA  
 $C_1$  : intermediate complex  
 QX : Aliquat 336  
 i : gas-liquid interface  
 o : initial

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