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Chemical kinetics of the reaction between carbon dioxide and phenyl glycidyl ether using Aliquat 336 as a catalyst

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Abstract

The kinetics of the reaction of carbon dioxide with phenyl glycidyl ether using Aliquat 336 as a catalyst in such nonaqueous solvents as toluene, *N*-methyl-2-pirrolidinone and dimethyl sulfoxide were studied using a stirred tank absorber with a plane gas–liquid interface at 358 and 0.1013 MPa. A mathematical model accompanied by a chemical absorption mechanism of carbon dioxide was presented to obtain the values of the rate parameters for which the predicted rate of absorption of CO_2 matched the experimental value. The relationship between the rate parameter and the solubility parameter of the solvent was presented.

Keywords: Chemical absorption; Carbon dioxide; PGE; Aiquat 336

1. Introduction

Recently, the chemistry of carbon dioxide has received much attention [1] and its reaction with oxiranes leading to five-membered cyclic carbonate (oxirane–CO_2 reaction) is well-known among many examples [2–3]. These carbonates can be used as aprotic polar solvent and sources for polymer synthesis [4]. In the oxirane–CO_2 reaction, high pressure (5–50 atm) of CO_2 has been thought to be necessary [2]. The oxirane–CO_2 reactions under atmospheric pressure have been reported [4] only recently. Many organic and inorganic compounds including amines, phosphines, quaternary ammonium salts and alkali metal salts are known to catalyze the oxirane–CO_2 reaction [3]. Most purpose of these papers have been to show the reaction mechanism, the pseudo-first-order reaction rate constant with respect to the concentration of oxirane, and the catalyst dependence of its conversion.

In the mass transfer accompanied by a chemical reaction, the diffusion may have an effect on the reaction kinetics. It is considered worthwhile to investigate the effect of diffusion on the reaction kinetics of the gas–liquid heterogeneous reaction such as the oxirane–CO_2 reaction.

In this study, the absorption rates of carbon dioxide into the solution of phenyl glycidyl ether (PGE) and Aliquat 336(QX) in such nonaqueous solvents as toluene, *N*-methyl-2-pirrolidinone and dimethyl sulfoxide was measured to determine the apparent second-order rate constant (k) of the overall reaction of CO_2 with PGE by matching the predicted rate of absorption with the experimental value, and these values of k were used to find the rate parameters of the elementary reactions, which were obtained from modeling of the overall reaction.

2. Theory

It is necessary for the reaction kinetics between oxirane (ex. PGE) and carbon dioxide using a catalyst such as a quaternary onium salts to set up the reaction mechanism of its reactions. Although the reaction mechanism shown in Eq. (1) has been proposed for the oxirane–CO_2 reaction by many researchers [3,5–8], 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 PGE to form five-membered cyclic carbonate is presented as follows:

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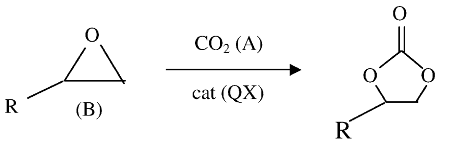
Nomenclature

C_A	concentration of CO_2 component (kmol/m^3)
C_{Ai}	solubility of CO_2 in absorbent (kmol/m^3)
C_B	concentration of PGE (kmol/m^3)
C_{Bo}	feed concentration of PGE (kmol/m^3)
D_A	diffusivity of CO_2 (m^2/s)
D_B	diffusivity of PGE (m^2/s)
C_{C_1}	concentration of C_1 component (kmol/m^3)
C_{QX}	concentration of QX component (kmol/m^3)
H_A	Hatta number defined as $\sqrt{D_A k_2 C_B}/k_L$
k	apparent reaction rate constant (m^3/kmol s)
k_1	forward reaction rate constant in reaction (2) (m^3/kmol s)
k_1'	backward reaction rate constant in reaction (2) (s^{-1})
k_2	reaction rate constant in reaction (3) (m^3/kmol s)
k_L	mass transfer coefficient of CO_2 in absorbent (m/s)
$\bar{N}_A$	mean molar flux of CO_2 with chemical reaction during contact time (kmol/m^2 s)
$\bar{N}_A^o$	mean molar flux of CO_2 without chemical reaction during contact time (kmol/m^2 s)
r_A	reaction rate of CO_2 (kmol/m^3 s)
R_A	absorption rate of CO_2 (kmol/s)
R_{Aexp}	measured absorption rate of CO_2 (kmol/s)
R_{Ao}	absorption rate of CO_2 without chemical reaction (kmol/s)
Q_o	total concentration of catalyst (kmol/m^3)
t	contact time of gas between gas and liquid, or reaction time (s)
z	distance (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	PGE
i	gas-liquid interface
o	feed



(1)

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

(i) A reversible reaction between PGE(B) and Aliquat 336(QX) to form an intermediate complex (C_1).

(ii) An irreversible reaction between C_1 and carbon dioxide(A) to form QX and five-membered cyclic carbonate.

$$B + QX \underset{K_2'}{\overset{K_1}{\rightleftarrows}} C_1 \tag{2}$$

$$A + C_1 \xrightarrow{K_2} C + QX \tag{3}$$

An expression for the rate of reaction for CO_2 can be derived based on the assumption, that steady-state approximation is applied to the formation of C_1, as follows:

$$r_A = -\frac{dC_A}{dt} = \frac{C_A C_B Q_o}{k_1'/k_1 k_2 + C_A/k_1 + C_B/k_2} \tag{4}$$

The mass balance of the catalyst is shown as follows:

$$Q_o = C_{C_1} + C_{QX} \tag{5}$$

The experimental absorption data obtained in this study are interpreted to give an apparent second-order rate constant (k), which is given in terms of the fundamental rate constants by comparison with Eq. (4), as follows:

$$k = \frac{Q_o}{k_1'/k_1 k_2 + C_A/k_1 + C_B/k_2} \tag{6}$$

The chemical reaction of Eq. (1) is assumed to be an apparent second-order with Eqs. (4) and (6) as follows:

$$r_A = k C_A C_B \tag{7}$$

Species B is a nonvolatile solute, which has been dissolved into 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 corresponds to equilibrium with the partial pressure of species A in the bulk gas phase.

Under the assumptions mentioned above, the conservation equations of species A and B are given as Eqs. (8) and (9).

$$D_A \frac{\partial^2 C_A}{\partial z^2} = \frac{\partial C_A}{\partial t} + k C_A C_B \tag{8}$$

$$D_B \frac{\partial^2 C_B}{\partial z^2} = \frac{\partial C_B}{\partial t} + k C_A C_B \tag{9}$$

Boundary and initial conditions to be imposed are

$$z = 0,\ t > 0; \quad C_A = C_{Ai} \tag{10}$$

$$z > 0,\ t = 0; \quad C_A = 0 \tag{11}$$

$$z = \infty,\ t > 0; \quad C_A = 0 \tag{12}$$

Eqs. (8)–(12) are put into the dimensionless form as follows:

$$\frac{\partial^2 a}{\partial x^2} = \frac{\partial a}{\partial \theta} + ab \tag{13}$$

$$\frac{\partial^2 b}{\partial x^2} = r\frac{\partial b}{\partial \theta} + rq\,ab \tag{14}$$

$$x = 0,\ \theta > 0; \quad a = 1,\ \frac{\partial b}{\partial \theta} = 0 \tag{15}$$

$$x > 0,\ \theta = 0; \quad a = 0,\ b = 1 \tag{16}$$

$$x = \infty,\ \theta > 0; \quad a = 0,\ b = 1 \tag{17}$$

where $a = C_A/C_{Ai}$, $b = C_B/C_{Bo}$, $x = z\sqrt{kC_{Bo}/D_A}$, $\theta = kC_{Bo}t$, $r = D_A/D_B$, $q = C_{Ai}/C_{Bo.}$ The mean molar flux of CO_2 during contact time (t_0) is written as

$$\bar{N}_A = -\frac{D_A}{t}\int_0^{t_0} \frac{\partial C_A}{\partial Z}\bigg|_{z=0} \mathrm{d}t \tag{18}$$

where t_0 is the contact time of $4D_A/\pi k_L^2$ [9].

The mean molar flux of CO_2 without chemical reaction based on the penetration model during contact time has been derived as follows [9]:

$$\bar{N}_A^o = 2C_{Ai}\sqrt{\frac{D_A}{\pi t_0}} \tag{19}$$

The enhancement factor (β) here defined as the ratio of mean molar flux with chemical reaction to that without chemical reaction ($\bar{N}_A/\bar{N}_A^o$) is described as follows:

$$\beta = -\frac{\pi}{4H_A}\int_0^{\theta} \frac{\partial a}{\partial x}\bigg|_{x=0} \mathrm{d}\theta \tag{20}$$

where $H_A = \sqrt{D_A k C_{Bo}}\,/k_L$, and the value of $\partial a/\partial x|_{x=0}$ is estimated from a numerical solution of the dimensionless partial differential Eqs. (13) and (14) with conditions of Eqs. (15)–(17).

The predicted value of the absorption rate of CO_2 can be obtained as follows:

$$R_A = \beta R_{Ao} = \beta k_L a C_{Ai} \tag{21}$$

where a is contact area at interface of gas–liquid per liquid volume.

3. Experimental

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%. PGE (phenyl glycidyl ether) was used as reagent grade supplied by Aldrich chemical company, USA without purification.

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 measured as $4.286 \times 10^{-3}\ m^2$. 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. The solute gas, carbon dioxide was saturated with solvent vapor and fed into the absorber. The absorber and saturator were kept constant at 358 K 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 using a mass flow meter (Brook Instrument, USA). The absorption rate was calculated from the difference between inlet and outlet flow rates of CO_2 in the concentrations of PGE ranged from 0.5 to 3 kmol/m^3 and Aliquat 336 of 0.05 and 0.1 kmol/m^3 in such nonaqueous solvents as toluene, *N*-methyl-2-pirrolidinone and dimethyl sulfoxide.

4. Analysis of the five-membered cyclic carbonate and physico-chemical properties of CO_2 and PGE

Phenoxy methyl ethylene carbonate (PMEC), which was produced from the reaction between CO_2 and PGE was confirmed by the instrumental analysis such as FT-IR(cyclic carbonate C=O peak at wavelength of 1800 cm^{-1}, C–O peak at 1200cm^{-1} and aromatic C=C peak at 1500 cm^{-1}), ^1H NMR (1H and OCH_2CHCH_2 at 4.6 ppm, 2H, OCH_2CHCH_2 and 2H, OCH_2CHCH_2 at 4.1–4.4 ppm), and ^{13}C NMR (cyclic carbonate C=O at 160 ppm).

The solubility of CO_2 in such nonaqueous solvents as toluene, *N*-methyl-2-pirrolidinone and dimethyl sulfoxide at 358 K and 0.1013 MPa 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 [10]. The experimental procedure was duplicated that as reported in published research [11] in detail. The mass transfer coefficient (k_L) of CO_2 was calculated using the measured rate of absorption of CO_2 and solubility of CO_2 at the impeller speed of 50 rev/min. The diffusivity of CO_2 and PGE in solvent was estimated from Wilke–Chang equation [12]. The viscosity of solvent was measured with Cannon–Fenske viscometer. The viscosity of solvent, solubility, mass transfer coefficient, diffusivity of CO_2 and diffusivity of PGE in the solvent are given in Table 1.

Table 1
Physicochemical properties of the CO_2/PGE system

Solvent	$\mu \times 10^4$	$D_A \times 10^9$	$D_B \times 10^9$	C_{Ai}	$k_L \times 10^5$	k_2	k_1/k_2	δ
Toluene	3.29	9.309	3.544	0.0727	1.842	0.0563	0.0072	18.2
NMP	8.09	3.927	1.495	0.0691	2.345	0.293	0.2632	23.1
DMSO	8.5	3.318	1.263	0.0597	2.764	0.5074	1.4187	24.6

5. Results and discussion

To get the apparent second-order rate constant (k), the rate (R_{Aexp}) of absorption of CO_2 in such nonaqueous solvents as toluene, *N*-methyl-2-pirrolidinone (NMP) and dimethyl sulfoxide (DMSO) was measured for PGE concentration ranging from 0 to 3 kmol/m^3 at QX of 0.1 kmol/m^3. Fig. 1 shows the plots of R_{Aexp} against the concentration of PGE. As shown in Fig. 1, R_{Aexp} increase gradually with increasing PGE concentration.

To determine the apparent second-order rate constant (k) in Eq. (7) from the measured rate of absorption, the partial differential Eqs. (13) and (14) are solved iteratively to find the value of k for which the predicted rate of absorption matches the experimental value with the parameters such as k_L, C_{Ai}, D_A and D_B. For example, the value of R_{Aexp} at C_{Bo} of 2.0 kmol/m^3 and Q_o of 0.1 kmol/m^3 was 7.352×10^{-9} kmol/s for DMSO, and this value matched the predicted value of R_A obtained from Eq. (21) at k of 0.0138 m^3/kmol s.

To analyze the reaction kinetics with the experimental data of the absorption rate of CO_2, Eq. (4) is rearranged as follows:

$$r_A = \frac{C_B Q_o}{k_1'/k_1 k_2 C_A + 1/k_1 + C_B/k_2 C_A} \tag{22}$$

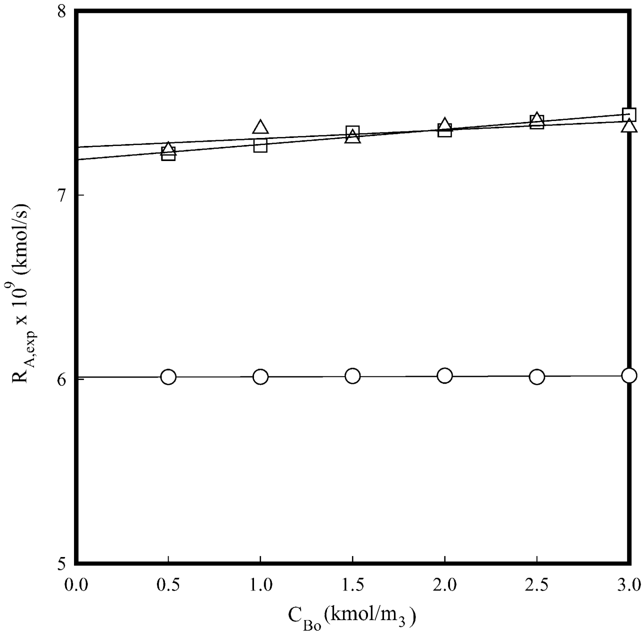


Fig. 1. Absorption rates of carbon dioxide into the solution of PGE (○: Toluene, Δ: NMP, □ : DMSO).

When the kinetics results with the apparent second-order rate constant are fitted to the reaction mechanism of Eqs. (2) and (3), we find the term, $1/k_1$, where k_1 is the kinetic rate coefficient for the formation of C_1 component is equal to zero within the precision of the data. This indicates that the formation of C_1 component is not the rate-limiting step. Thus, Eq. (22) is given by

$$r_A = kC_A C_B \tag{7}$$

$$k = \frac{k_1 k_2 Q_o}{k_1' + k_1 C_B} \tag{23}$$

As shown in Eq. (23), the apparent rate constant (k) appearing is expressed a function of concentrations of PGE and catalyst, and is composed of reaction rate parameters such as k_1, k_1' and k_2. Eq. (23) is rearranged as follows:

$$\frac{Q_o}{k} = \frac{k_1'}{k_1 k_2} + \frac{C_B}{k_2} \tag{24}$$

Thus Eq. (24) suggests that the rate parameters (k_2 and k_1'/k_1) can be evaluated, respectively, from the slope and intercept of the plot of Q_o/k versus C_{Bo}. Figs. 2–4 show such plots in solvent of toluene, NMP and DMSO, respectively, and there appear linear relationships. The derived rate constants of k_2 and k_1'/k_1 are shown in Table 1.

To ascertain the effect of chemical reaction on the specific rate of mass transfer in a heterogeneous system such as gas

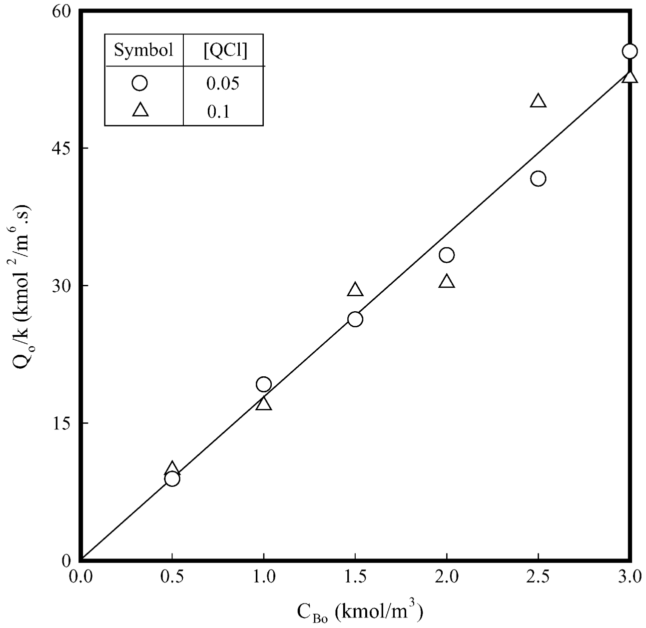


Fig. 2. Q_o/k vs. C_{Bo} in toluene solution.

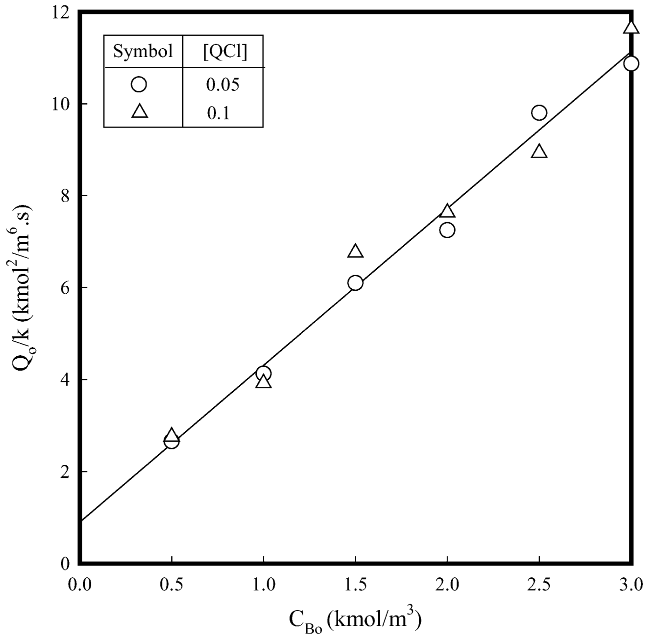


Fig. 3. Q_o/k vs. C_{Bo} in NMP solution.

absorption into liquid, depending on the relative rates of diffusion and reaction for convenience the system may be classified into four regimes such as very slow reactions, slow reactions, fast reactions and instantaneous reactions [13].

The values of $k_L a C_{Ai}$, $k C_{Ai} C_{Bo}$ and Ha (=$\sqrt{D_A k C_{Bo}}/k_L$) were calculated using the physicochemical properties such as D_A, D_B, k, C_{Ai} in the range of the PGE concentration of 0.5 ~ 3 kmol/m^3. The calculated values of H_A were smaller than one and those of $k C_{Ai} C_{Bo}$ were larger than those of $k_L a C_{Ai}$. This means that the amount of the dissolved CO$_2$ that reacts in the diffusion film adjacent to the interface of gas–liquid contact compared to that which reaches the liquid phase in the unreacted state is negligible and the reaction rate is larger than the transferred rate of CO$_2$. Therefore, the system of chemical reaction of CO$_2$ with PGE is the slow reaction regime [13].

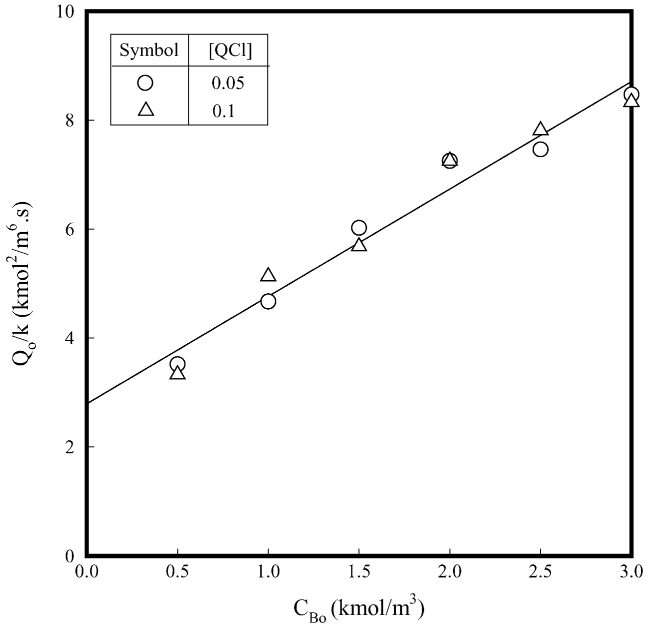


Fig. 4. Q_o/k vs. C_{Bo} in DMSO solution.

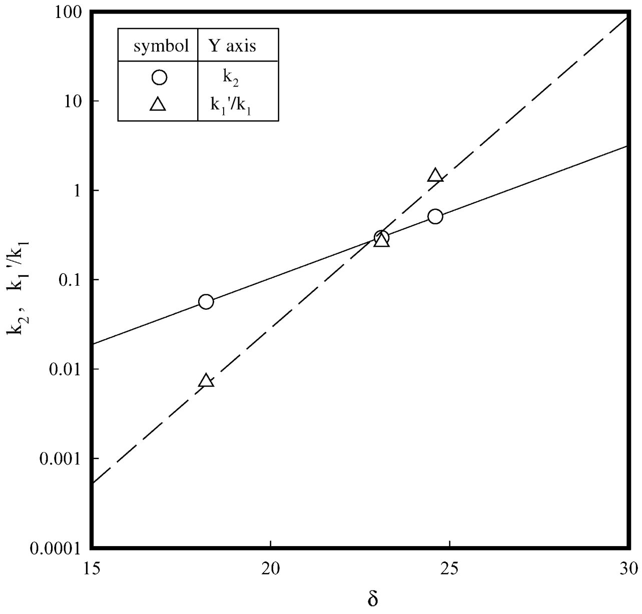


Fig. 5. Relationship between reaction rate parameter and solubility parameter of the solvent in the carbon dioxide-PGE system.

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 [14]. Of these, some measures have a linear relation to the solubility parameter of the solvent. Then using the data of k_2, k_1'/k_1 and solvent parameter of toluene, NMP and DMSO [15] in Table 1, the logarithms of k_2 and k_1'/k_1 were plotted against the solubility parameter of the solvent. Fig. 5 shows this relationship. As shown in Fig. 5, the plots satisfied the linear relationship between the reaction rate parameter and solubility parameter of the solvent.

6. Conclusions

The overall reaction between CO$_2$ and PGE using Aliquat 336 as a catalyst in such solvents as toluene, *N*-methyl-2-pirrolidinone and dimethyl sulfoxide was assumed to consist of two elementary reactions such as a reversible reaction of PGE and Aliquat 336 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 358 K and 0.1013 MPa were interpreted to obtain an apparent second-order kinetic rate coefficient of the overall reaction and the rate parameters of the elementary reactions. The effect of the solubility parameter of the solvent on the rate parameter was presented.

Acknowledgements

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