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## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

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**To cite this Article** Park, Sang-Wook , Lee, Joon-Wook , Choi, Byoung-Sik and Lee, Jae-Wook(2005) 'Reaction Kinetics of Carbon Dioxide with Diethanolamine in Polar Organic Solvents', Separation Science and Technology, 40: 9, 1885 — 1898

**To link to this Article:** DOI: 10.1081/SS-200064536

**URL:** <http://dx.doi.org/10.1081/SS-200064536>

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## Reaction Kinetics of Carbon Dioxide with Diethanolamine in Polar Organic Solvents

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**Abstract:** The chemical absorption rate of carbon dioxide with diethanolamine was measured in such nonaqueous solvents as methanol, ethanol, n-propanol, n-butanol, ethylene glycol, propylene glycol, and propylene carbonate, and in water at 298 K and 101.3 kPa using a semibatch stirred tank with a plane gas-liquid interface. The overall reaction rate constant obtained under the condition of fast reaction regime from the measured rate of absorption was used to get the elementary reaction rate constants in complicated reactions represented by reaction mechanism of carbamate formation and the order of overall reaction of CO<sub>2</sub> with amine. Correlation between the elementary reaction rate constant and the solubility parameter of the solvent was presented.

**Keywords:** Absorption, carbon dioxide, diethanolamine, organic solvent

### INTRODUCTION

The removal of acid gases such as CO<sub>2</sub>, H<sub>2</sub>S, and COS by absorption using aqueous alkanolamine solutions has been widely used in the chemical industries. Particularly, the removal of CO<sub>2</sub> from the gas produced by burning fossil fuel has been of great interest owing to the global warming caused by the increase in the concentration of CO<sub>2</sub> in the atmosphere. Industrially important chemical absorbents are monoethanolamine, diethanolamine

Received 16 November 2004, Accepted 21 March 2005

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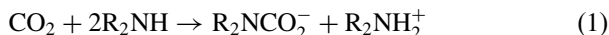
(DEA), N-methyldiethanolamine, and di-2-propanolamine (1). The kinetics of the reaction between CO<sub>2</sub> and alkanolamine were analyzed using simple mass balances resulted from the zwitterion mechanism proposed by Danckwerts (2). Some discrepancies remained according to the reaction mechanism (3), kind of amines, gas/liquid contactor, and analysis method about the rate data, i.e., the order of the overall reactions and the rate constants.

There are several industrially important reactions between CO<sub>2</sub> and amine in polar and nonpolar organic solvents (4). The addition of an amine to the solvent increases the solvent's capacity for CO<sub>2</sub> (5–7). It would be expected that the mechanism of the reaction of CO<sub>2</sub> with alkanolamine in aqueous solutions could be applied to that in nonaqueous solvents, and the condition of the fast or instantaneous reaction regime might also be satisfied in nonaqueous solvents (5–17).

In the present work, therefore, the absorption of carbon dioxide into aqueous and nonaqueous solutions of DEA was carried out using a stirred tank with a plane gas-liquid interface. The absorption rate data under a fast-reaction regime were analyzed in terms of the kinetics of carbamate formation from CO<sub>2</sub> and DEA. An attempt was made to correlate the reaction rate constants, which were derived for the different nonaqueous solvents with the physicochemical properties of each solvent.

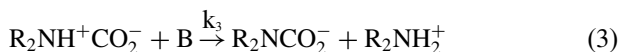
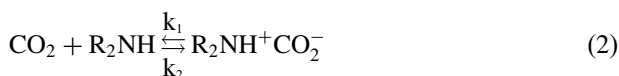
## THEORY

The overall reaction between CO<sub>2</sub> and secondary amines is



where R<sub>2</sub> represents the functional groups on the secondary amines. There has been much confusion about the overall reaction order of CO<sub>2</sub> with DEA (18). All agree that the reaction is first-order with respect to CO<sub>2</sub>. However, the reported reaction order with respect to the secondary amine DEA ranges from one to two (18). These discrepancies have led to quite different reaction schemes.

Versteeg et al. (4) cite the following two-step reaction for the formation of carbamate from CO<sub>2</sub> and alkanolamines:



where B is a base, usually a second amine molecule. The first step of the reaction is bimolecular, and the product of the first reaction step is a zwitterion. The mechanism is usually referred to as the zwitterions mechanism. In cases where an overall second-order reaction is observed, one would

assume the first step to be rate determining. Versteeg cites Caplow (19) as one who proposed this mechanism and also notes that it was later reintroduced by Danckwerts (2).

In the case of nonaqueous solvents, only the amine is considered as the base in the proton removal step (11). If the steady-state approximation is applied to the zwitterion, one gets a rate of homogeneous reaction as

$$r_A = \frac{C_A C_B}{1/k_1 + k_2/k_1 k_3 C_B} \quad (4)$$

In a recent review of the literature on the aqueous CO<sub>2</sub>-DEA reaction kinetics, Versteeg and Oyevaar (20) concluded that all results could be satisfactorily explained by the zwitterions mechanism.

If the absorption process is conducted under conditions where the liquid phase reaction may be considered first-order with respect to CO<sub>2</sub>, then the rate of reaction for CO<sub>2</sub> will be given as follows:

$$r_A = k_{ov} C_A \quad (5)$$

where the overall reaction rate constant ( $k_{ov}$ ) has the following expression.

$$k_{ov} = \frac{C_{Bo}}{1/k_1 + k_2/k_1 k_3 C_{Bo}} \quad (6)$$

Eq. (6) is rearranged to get the elementary reaction rate constants as follows:

$$\frac{C_{Bo}}{k_{ov}} = \frac{1}{k_1} + \frac{k_2}{k_1 k_3 C_{Bo}} \quad (7)$$

Thus, a plot of the left-hand side of Eq. (7) vs.  $1/C_{Bo}$  should give a straight line and permit determination of  $k_1$  and  $k_2/k_1 k_3$  from the intercept on the ordinate and the slope of the line, respectively.

The film theory material balance equation and the boundary conditions in the absorption of CO<sub>2</sub> into solution of DEA can be written as

$$D_A \frac{d^2 C_A}{dz^2} = k_{ov} C_A \quad (8)$$

$$z = 0, \quad C_A = C_{Ai} \quad (9)$$

$$z = z_L, \quad C_A = 0 \quad (10)$$

The enhancement factor of CO<sub>2</sub>, which is defined as the ratio of absorption rate of CO<sub>2</sub> with chemical reaction of DEA to that without chemical reaction, is given under the condition of fast reaction regime (21) by

$$\beta = \frac{m}{\tanh m} \quad (11)$$

where  $m^2 = k_{ov} D_A / k_L^2$ .

To conform to the fast reaction regime, the requirement that (21)

$$1 \ll Ha \ll Ei \quad (12)$$

must be fulfilled.

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

$$Ei = 1 + (D_B/D_A)\sqrt{C_{Bo}/C_{Ai}} \quad (13)$$

## EXPERIMENTAL

All chemicals in this study were reagent grade, and used without further purification. Purity of both CO<sub>2</sub> and N<sub>2</sub> was more than 99.9%. The solvents used in absorption of CO<sub>2</sub> were methanol, ethanol, n-propanol, n-butanol, ethylene glycol, propylene glycol, propylene carbonate, and water. DEA solutions were prepared from distilled solvent. The distilled solvents were degassed with boiling. DEA is Aldrich reagent grade with purity of 99.7%. The concentration of DEA solution was determined by titration of a liquid sample with HCl using methyl orange as the indicator. The DEA concentrations in this study range from 1 to 3 kmol/m<sup>3</sup>. The absorption rates of carbon dioxide into DEA solutions were measured using a semibatch stirred tank with a plane gas-liquid interface at 298 K and 101.3 kPa. The absorption vessel was constructed of glass of 0.102 m inside diameter and of 0.151 m in height. Four equally spaced vertical baffles, each one-tenth of the vessel diameter in width, were attached to the internal wall of the vessel. The gas and liquid phase were agitated with an agitator driven by a 1/4 Hp variable speed motor. A straight impeller with 0.034 m in length and 0.02 m in width was used as the liquid phase agitator, and located at the middle position of the liquid phase. The experimental value of the enhancement factor was obtained from the ratio of the specific rates of absorption of CO<sub>2</sub> with DEA and those without DEA. The absorption rate was independent of the stirring speed in the range of 40–70 rpm; all experimental runs were performed at a stirrer speed of about 50 rpm. The gas-liquid interface appeared to be carefully smoothed and therefore was well defined. The apparatus and the experimental procedure are the same as those described by Park et al. (22).

## Physicochemical Properties

Both the diffusivity and solubility of solute gas in the liquid medium affect the derived reaction rate parameters, as shown in Eq. (11). The nitrous oxide analogy was used to approximate these properties in the reactive solvents in the most papers (11, 13). Solubility of CO<sub>2</sub> in solvents does not seem to depend on the amine concentration (9). In this study the solubility of CO<sub>2</sub>

in DEA solution was assumed to be equal to that in pure solvents, and measured by the pressure measuring method, which was used by measuring the pressure difference of  $\text{CO}_2$  between, before, and after equilibrium between gas and liquid phase similar to the procedure reported elsewhere (23). The experimental procedure was duplicated as that as reported in the published research (22) in detail. The viscosity of solvent was measured using Brookfield viscometer (Brookfield Eng. Lab. Inc, USA). Diffusivity ( $D_B$ ) of DEA in aqueous DEA solution was obtained from assumption that the ratio of  $D_B$  to  $D_A$  was equal to the ratio in water (24). The diffusivity of  $\text{CO}_2$  and DEA in water at  $25^\circ\text{C}$  were taken as  $1.95 \times 10^{-9} \text{ m}^2/\text{s}$  (25) and  $6.67 \times 10^{-10} \text{ m}^2/\text{s}$  (25), respectively. The diffusivity ( $D_A$ ) of  $\text{CO}_2$  in solvent of DEA was estimated by the method of Wilke (26) corrected with the viscosity measured at the given concentration of DEA. The liquid-side mass transfer coefficient ( $k_L$ ) of  $\text{CO}_2$  in solvent was obtained using the measured rate of absorption of  $\text{CO}_2$ . The values of dielectric constant (27), solubility parameter (28), and viscosity of solvent,  $C_{Ai}$ ,  $D_A$ ,  $D_B$ , and  $k_L$  of  $\text{CO}_2$  in solvent are listed in Table 1.

## RESULTS AND DISCUSSION

The overall reaction rate constant ( $k_{ov}$ ) at the given concentration of DEA was obtained using the experimental value of enhancement factor and Eq. (11), and the experimental results are listed in Table 2.

To obtain the reaction order with respect to amine concentration,  $k_{ov}$  was plotted in the form of logarithm against DEA concentration in Fig. 1. As shown in Fig. 1, the plots satisfied the straight lines. The reaction orders were obtained from the slope of the linear relationship in Fig. 1 and were listed in Table 3. Also, the reaction orders in other references were listed in Table 3. As shown in Table 3, the values of the reaction orders were more than 1 and the values in references ranged from 1 to 2. The reaction between  $\text{CO}_2$  and MEA in aqueous solutions has already been found to be of first order with respect to both species, while for the  $\text{CO}_2$ -DEA system in aqueous solutions, the order of reaction with respect to DEA has not been determined to be of first or second (11). Danckwerts (2) proposed a reaction mechanism comprising a zwitterions followed by the removal of proton by a base (DEA) to explain such contraction of the reaction order. Sada et al. (11) explained that the reaction order would possibly range from first to second, because the deprotonation by DEA may be depressed by a basicity and the steric hindrance effect of DEA.

The reaction orders were plotted against the dielectric constant of solvent in semilogarithmic scale in Fig. 2. As shown in Fig. 2, they depended on the dielectric constant approaching 1.4 with decreasing the polarity of solvent. This result may be brought about by the deprotonation, which may occur more easily by the polarity of the solvent.

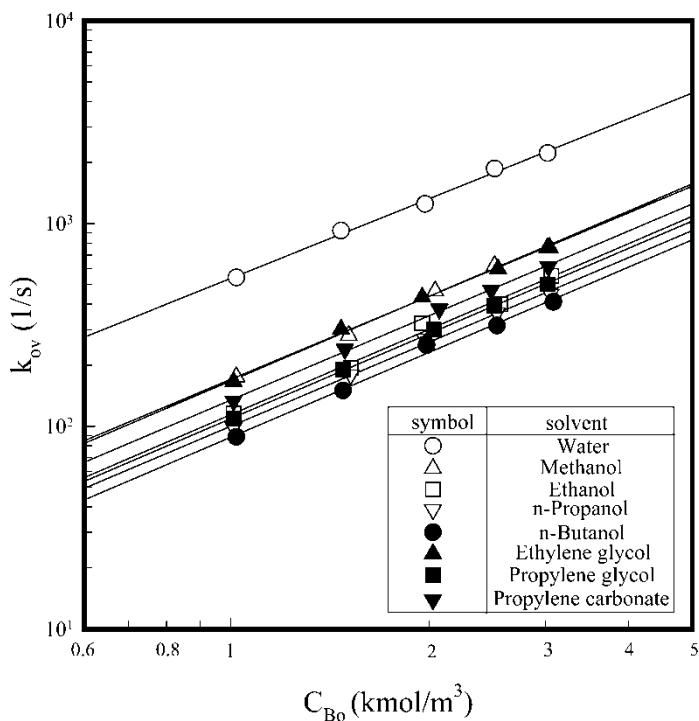
**Table 1.** Physicochemical properties of solvent and CO<sub>2</sub>/DEA at 298 K

Solvent	$\varepsilon$	$\delta$ (J/m <sup>3</sup> ) <sup>1/2</sup>	$\mu$ (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)
Water	78.5	48.1	0.894	0.035	1.95	0.667	6.505
Methanol	32.6	29.7	0.547	0.159	8.37	1.721	8.314
Ethanol	24.3	26.1	1.099	0.125	3.88	0.912	5.867
n-Propanol	20.1	23.4	1.942	0.096	2.73	0.482	4.413
n-Butanol	17.1	23.3	2.01	0.093	0.876	0.398	3.806
Ethylene glycol	37.7	29.9	17.33	0.027	0.121	0.055	1.477
Propylene glycol	32.0	25.8	42.93	0.248	0.054	0.025	0.934
Propylene carbonate	65.0	27.2	2.493	0.127	1.077	0.489	3.895

**Table 2.** Experimental data of the reaction of CO<sub>2</sub> with DEA at 289 K

Solvent	C <sub>Bo</sub> (kmol/m <sup>3</sup> )	$\beta$	k <sub>ov</sub> (1/s)	H <sub>A</sub>	E <sub>i</sub>
Water	1.02	15.69	541.48	16	173
	1.47	20.35	921.41	20	249
	1.97	23.54	1249.26	24	334
	2.51	28.62	1868.52	29	425
	3.02	30.87	2223.64	31	511
Methanol	1.02	14.26	175.34	14	30
	1.51	17.85	280.84	18	44
	2.04	22.81	464.08	23	59
	2.51	26.09	620.61	26	73
	3.02	28.75	758.98	29	87
Ethanol	1.01	11.39	116.08	11	40
	1.52	15.31	193.47	15	60
	1.95	19.59	321.68	20	77
	2.56	21.79	399.36	22	100
	3.06	25.57	552.52	26	120
n-Propanol	1.01	11.72	98.74	12	45
	1.52	15.75	179.53	16	67
	1.97	19.24	269.13	19	87
	2.53	22.33	363.00	22	111
	3.05	24.82	448.40	25	134
n-Butanol	1.02	7.13	88.65	7	75
	1.48	9.07	150.07	9	108
	1.98	11.88	251.51	12	145
	2.53	13.03	313.24	13	184
	3.08	14.50	410.74	14	224
Ethylene glycol	1.01	9.59	166.22	10	26
	1.47	12.90	301.10	13	38
	1.95	15.47	433.02	15	50
	2.54	18.17	598.08	18	64
	3.04	20.50	761.90	20	77
Propylene glycol	1.01	8.21	109.16	8	29
	1.48	10.82	189.91	11	42
	2.03	13.59	299.37	14	57
	2.51	15.55	392.64	16	70
	3.02	17.56	501.29	18	84
Propylene carbonate	1.01	9.69	133.40	10	55
	1.49	12.83	239.59	13	80
	2.07	16.07	378.27	16	111
	2.48	18.23	469.69	18	133
	3.03	20.76	613.23	21	162





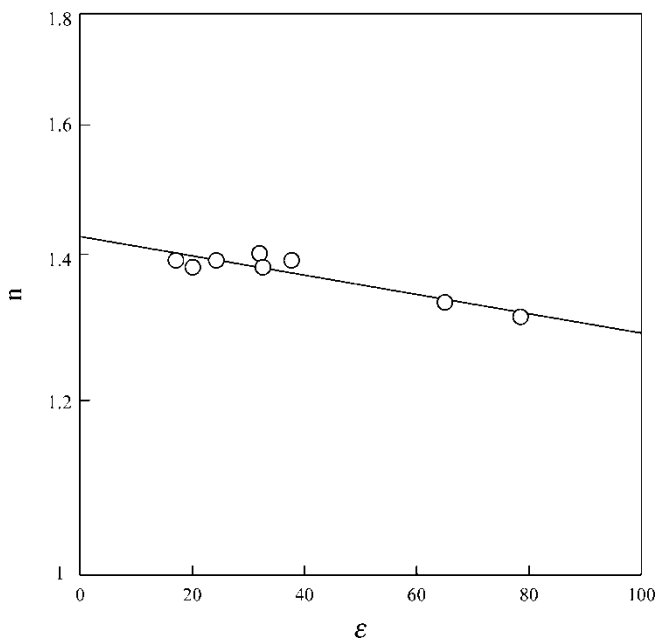
**Figure 1.** Dependence of DEA concentration on the pseudo-first-order reaction rate constant in the reaction of  $\text{CO}_2$  with DEA.

To obtain the elementary reaction rate constants using  $k_{\text{ov}}$  and  $C_{\text{Bo}}$ , the experimental results were plotted in Fig. 3 in the form of Eq. (7).

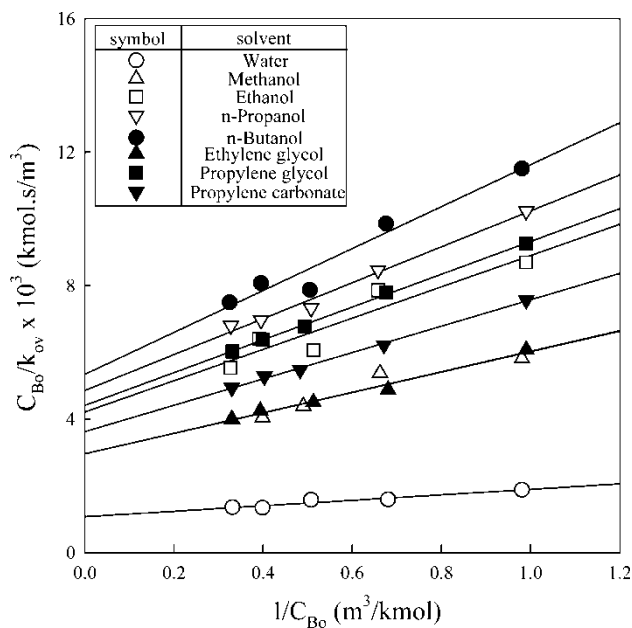
As expected, the linear relationship in Fig. 3 was in agreement with the carbamate formation mechanism. The rate constants,  $k_1$  and  $k_2/k_3$ , were

**Table 3.** The reaction orders and rate constants of  $\text{CO}_2$  in the reaction of  $\text{CO}_2$  with DEA at 298 K

Solvent	n	$k_1$	$k_2/k_3$
Water	1.31 (1 (8), 1.42 (11), 1.65 (13), 2 (30))	929 (1100 (11))	0.76 (0.83 (11))
Methanol	1.39 (1.52 (11))	338 (340 (11))	1.04 (1 (11))
Ethanol	1.4 (1.74 (11), 2 (9))	237 (290 (11))	1.11 (1.4 (11))
n-Propanol	1.38	206 (240 (11))	1.11 (1.3 (11))
n-Butanol	1.39	187 (220 (11))	1.18 (1.5 (11))
Ethylene glycol	1.36 (1.59 (16), 2 (9))	338	1.03
Propylene glycol	1.39	227	1.11
Propylene carbonate	1.38	276	1.09



**Figure 2.** Dependence of reaction order on dielectric constant of solvent in the reaction of  $\text{CO}_2$  with DEA.



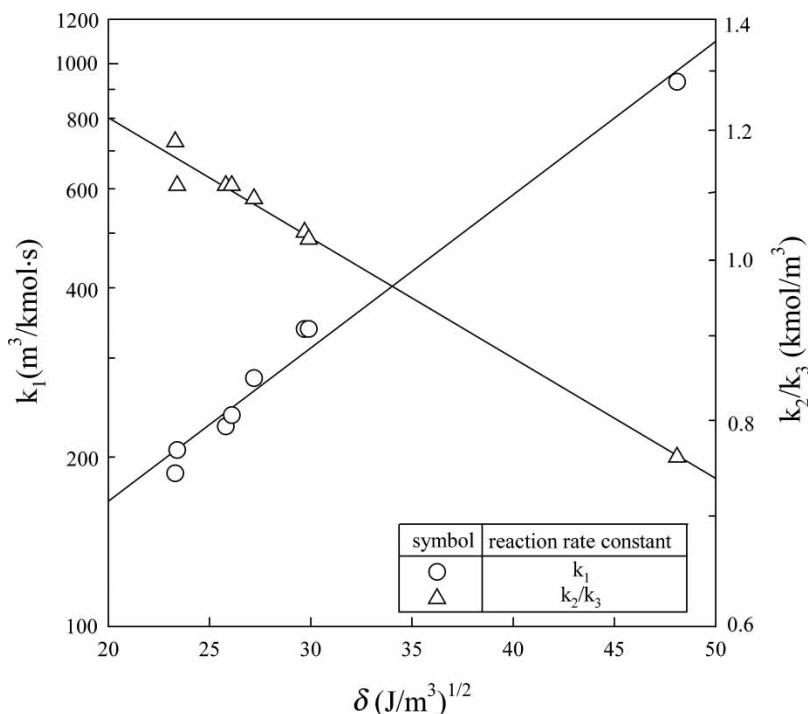
**Figure 3.**  $C_{\text{Bo}}/k_{\text{ov}}$  vs.  $C_{\text{Bo}}$  for various solvents in the reaction of  $\text{CO}_2$  with DEA.

listed in Table 3. These constants in a solvent generally reflect the solvent effect. Various empirical measures of the solvent effect had been proposed and correlated with the reaction rate constant (29). Of these, some measures had a linear relation to the solubility parameter of the solvent. Then, using the data of  $k_1$ ,  $k_2/k_3$ , and solubility parameter, the logarithms of  $k_1$  and  $k_2/k_3$  were plotted against the solubility parameter of the solvent in Fig. 4.

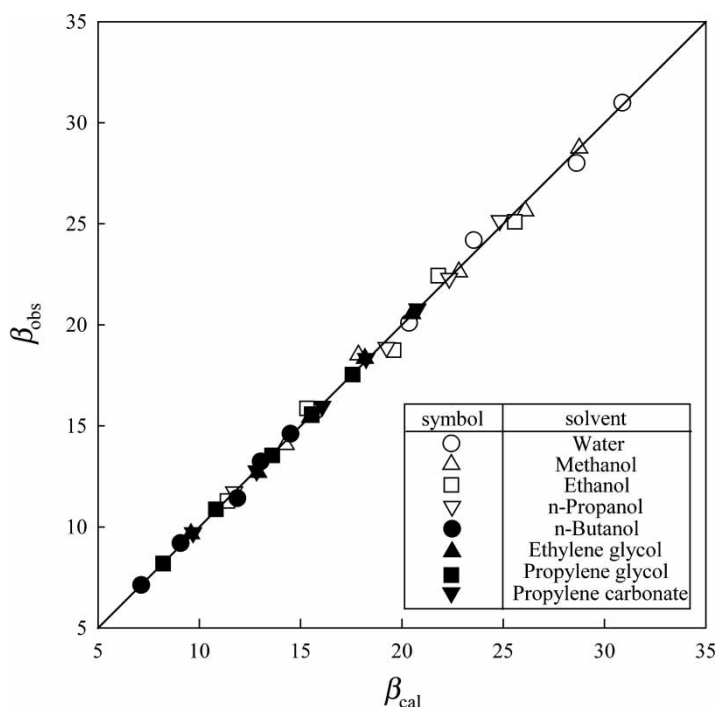
As shown in Fig. 4, the plots satisfied the linear relationship between the reaction rate constant and solubility parameter of the solvent. Thus, the magnitude of the rate constants may be a function of the degree to which the solvent is able to stabilize the zwitterions intermediate. The reaction of  $\text{CO}_2$  with DEA in polar solvents was confirmed to be expressed by the previously stated reaction scheme such as the mechanism of carbamate formation.

The values of  $H_a$  and  $E_i$  calculated by Eq. (13) are listed in Table 2. As shown in Table 2, Eq. (11) was satisfied, and then the reaction with DEA concentration of  $1\text{--}3\text{ kmol/m}^3$  can be a fast reaction regime.

The calculated and measured values of the enhancement factor were shown as solid line and symbols, respectively, in Fig. 5.



**Figure 4.** Relationship between reaction rate constant and solubility parameter of solvent in the reaction of  $\text{CO}_2$  with DEA.



**Figure 5.** Comparison of estimated enhancement factor with observed one of CO<sub>2</sub> absorption into solvent of DEA.

The observed enhancement factors agreed within an error of 4.6% with the theoretical values calculated by Eq. (11) with elementary reaction rate constants derived from the absorption rate data under the fast reaction regime.

## CONCLUSIONS

The chemical absorption rates of carbon dioxide in such solvents as methanol, ethanol, n-propanol, n-butanol, ethylene glycol, propylene glycol, propylene carbonate, and water were measured using a semibatch stirred tank with a plane gas-liquid interface at 298 K and 101.3 kPa. The rate data were used to get the overall reaction rate constant, which gave the elementary reaction rate constants according to the carbamate formation mechanism under the condition of the fast reaction regime. The reaction orders with respect to DEA concentration depended on the solvent species and approached 1.4 with decreasing the polarity of the solvent. It was found that the dependence of the logarithms of the elementary reaction rate constants on the solubility parameter of the solvent was close to linear.

## NOMENCLATURE

$C_i$	concentration of species, $i$ (kmol/m <sup>3</sup> )
$D_i$	diffusivity of species, $i$ (m <sup>2</sup> /s)
$E_i$	$1 + (D_B/D_A)\sqrt{C_{B0}/C_{Ai}}$
$H_A$	$\sqrt{k_{ov}D_A/k_L}$
$k_{ov}$	overall reaction rate constant (1/s)
$k_1$	forward reaction rate constant in reaction (2) (m <sup>3</sup> /kmol s)
$k_2$	backward reaction rate constant in reaction (2) (1/s)
$k_3$	forward reaction rate constant in reaction (3) (m <sup>3</sup> /kmol s)
$k_L$	liquid–side mass-transfer coefficient of CO <sub>2</sub> in absorbent (m/s)
$n$	reaction order with respect to DEA concentration
$z$	distance (m)
$z_L$	film thickness (m)

## Greek Letters

$\beta$	enhancement factor of CO <sub>2</sub>
$\delta$	solvent parameter (J/m <sup>3</sup> ) <sup>1/2</sup>
$\varepsilon$	dielectric constant of solvent
$\mu$	viscosity of liquid (cP)

## Subscripts

A	CO <sub>2</sub>
B	DEA
i	gas–liquid interface
o	feed

## ACKNOWLEDGMENTS

This work was supported from the Basic Research Program of the Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC), Brain Korea 21 Project in 2004, and Brain Busan 21 Program.

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