

Chemical absorption of carbon dioxide with triethanolamine in non-aqueous solutions

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Abstract—Carbon dioxide was absorbed into non-aqueous solvents such as methanol, ethanol, n-propanol, n-butanol, ethylene glycol, propylene glycol, and propylene carbonate, and into water in a stirred semi-batch tank with a planar gas-liquid interface at 298 K and 101.3 kPa. Triethanolamine (TEA) was used as a reactant with carbon dioxide. The reaction rate constants of the reaction between carbon dioxide and TEA were estimated by the mass transfer mechanism, which was accompanied by a fast pseudo-first-order reaction. An empirical correlation between the reaction rate constants and the solubility parameter of the solvent is presented. In non-aqueous solutions of TEA, dissolved carbon dioxide is expected to react with solvated TEA to produce an ion pair.

Key words: Carbon Dioxide, Absorption, Triethanolamine, Non-aqueous Solutions

INTRODUCTION

Monoethanolamine, diethanolamine, triethanolamine (TEA), and *N*-methyldiethanolamine (MDEA) are used as industrially important chemical absorbents for removing acid gases such as CO₂, H₂S, and COS. Due to the instantaneous reaction rate for the reaction of H₂S with tertiary amine such as TEA and MDEA, and a much slower reaction rate for the reaction of CO₂ with these amines, the aqueous tertiary amine solutions are frequently used as a selective solvent for selectively absorbing H₂S while permitting CO₂ unabsorbed [Astarita et al., 1983].

Although many studies have been done towards the mechanisms and kinetics of the reaction between CO₂ and various amines, the reaction media are limited to aqueous solutions [Danckwerts, 1970]. In practice, non-aqueous systems comprising a methanol solution of alkanolamine have been commercially employed for absorption of CO₂, H₂S, and COS, etc., because of their high solubility and capacity, their low corrosiveness, and their low energy consumption during generation of used liquor [Astarita et al., 1983]. Non-aqueous systems, which are essentially used in a closed loop, should be considered more for acid gas removal.

The kinetics of reaction between CO₂ and amine was analyzed by using simple mass balances resulting from the zwitterion mechanism of the reaction of CO₂ with alkanolamine such as primary and secondary amine proposed by Danckwerts [1979]. It would be expected that the mechanism of the reaction of CO₂ with alkanolamine in aqueous solutions could be applied to that in non-aqueous solvents. Tertiary alkanol amines do not form carbamates since there is no hydrogen atom to be displaced by carbon dioxide [Sada et al., 1989]. It has been reported that TEA and MDEA act as homogeneous base catalysts for carbon dioxide hydrolysis and that negligible monoalkylcarbonate formation takes place [Ko and Li, 2000]. In view of the possibility of base catalysis in carbon dioxide hydrolysis, it is of interest to investigate the reaction kinetics in non-

aqueous solvents.

In the present work, therefore, the absorption of carbon dioxide into aqueous and non-aqueous solutions of TEA was carried out by using a stirred tank with a planar gas-liquid interface. The absorption rate data under a fast-reaction regime were analyzed in terms of the chemical absorption theory of second-order reactions. An attempt was made to correlate the reaction rate constants, which were derived for the different non-aqueous solvents with the physicochemical properties of each solvent.

THEORY

1. Reactions of CO₂ in Aqueous Solutions

The first reaction to be considered is the hydration of CO₂:



This reaction is very slow [Pinsent et al., 1956] and may usually be neglected.

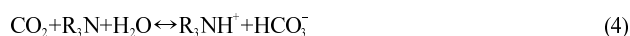
The second reaction is the bicarbonate formation with hydroxyl ion:



This reaction is fast and can enhance mass transfer even when the concentration of hydroxyl ion is low. The forward reaction for the reaction of CO₂ with OH⁻ can be described [Pinsent et al., 1956]:

$$R_{\text{CO}_2\text{-OH}^-} = k_{\text{OH}^-} [\text{CO}_2] [\text{OH}^-] \quad (3)$$

For the reaction of CO₂ in aqueous solution with tertiary alkanolamines (R₃N), Donaldson and Nguyen [1980] proposed the following reaction mechanism:



The forward reaction for the reaction of CO₂ with R₃N in Eq. (4) can be described:

$$R_{\text{CO}_2\text{-TEA}} = k_2 [\text{CO}_2] [\text{TEA}] \quad (5)$$

Mono- or diethanolamine can react with CO₂ to form a zwitterionic

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intermediate [Danckwerts, 1979], but tertiary amine cannot react directly with CO₂, because its reaction mechanism is essentially a based-catalyzed hydration of CO₂ as shown in Eq. (4).

For the absorption of CO₂ into TEA+H₂O, the CO₂ overall reaction rate (R_{ov}) can be expressed as follows:

$$R_{ov} = R_{CO_2-TEA} + R_{CO_2-OH} \quad (6)$$

In most literature [Blauwhoff et al., 1984; Versteeg and van Swaaij, 1988a] on CO₂ kinetics with tertiary amines, it is assumed that reaction of CO₂ with TEA is a pseudo-first-order reaction combining Eq. (3), (5) and (6), and one has

$$R_{ov} = k_{ov}[CO_2] \quad (7)$$

The overall reaction rate constant (k_{ov}) in Eq. (7) has the following expression:

$$k_{ov} = k_2[TEA] + k_{OH}^- [OH^-] \quad (8)$$

On the other hand, the apparent reaction rate constant (k_{app}) is defined as k₂[TEA], and is obtained as follows:

$$k_{app} = k_{ov} - k_{OH}^- [OH^-] \quad (9)$$

The enhancement factor (β) of CO₂, which is defined as the ratio of absorption rate of CO₂ with chemical reaction of TEA to that without one for a pseudo-first-order reaction of Eq. (7), is given [Daraiswany and Sharma, 1984] by

$$\beta = \frac{m}{\tanh m} \quad (10)$$

where $m^2 = k_{ov} D_A / k_2^2$ and m is defined as Hatta number (Ha).

2. Reactions of CO₂ in Non-aqueous Solutions

Because tertiary amines do not form carbamates and act as homogeneous base catalysts for carbon dioxide hydrolysis, the reaction (4) cannot be used to explain the reaction mechanism between CO₂ and TEA in non-aqueous solution. Sada et al. [1989] have proposed that in non-aqueous solutions of tertiary amine the dissolved carbon dioxide will react with solvated tertiary amine to form an ion pair as follows:



where Hsol designates solvent.

It is assumed that the reaction of CO₂ with TEA is a pseudo-first-order reaction in non-aqueous solutions as follows:

$$R_{CO_2-TEA(Hsol)} = k_{ov}[CO_2] \quad (12)$$

and the overall reaction rate constant (k_{ov}) has the following expression

$$k_{ov} = k_2[TEA(Hsol)] \quad (13)$$

The apparent reaction rate constant (k_{app}) is defined as follows:

$$k_{app} = k_{ov} \quad (14)$$

EXPERIMENTAL

1. Chemicals

All chemicals were of reagent grade, and used without further purification. Purity of both CO₂ and N₂ was more than 99.9%. Meth-

anol, ethanol, n-propanol, n-butanol, ethylene glycol, propylene glycol, propylene carbonate, and TEA are Aldrich reagent grade. TEA solutions were prepared from distilled solvent, which was degassed with boiling. The concentration of TEA solution was determined by titration of a liquid sample with HCl by using methyl orange as the indicator.

2. Absorption Rate of Carbon Dioxide

Absorption experiments were carried out in an agitated vessel at 25 °C and atmospheric pressure. The absorption vessel was constructed of glass of 0.102 m inside diameter and 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 phases were agitated with an agitator driven by a 1/4 hp speed variable 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 gas-liquid interface appeared to be carefully smoothed, and therefore, was well defined. 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 solute gas, 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 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 inlet and outlet flow rates of CO₂ in the concentrations of TEA ranged from 1 to 4.5 kmol/m³. The experimental enhancement factor of CO₂ by reaction of CO₂ with TEA was obtained from the ratio of the specific rates of absorption of CO₂ with TEA and those without TEA. The experimental procedure to get the absorption rate was duplicated as reported in published research [Park et al., 2004] in detail.

3. Physicochemical Properties

The reaction rate constant (k_{OH}⁻) for the reaction of the bicarbonate formation was estimated by the following equation [Pinsent et al., 1956]

$$\log(k_{OH}^-) = 13.635 - 2895/T \quad (15)$$

The hydroxyl ion concentration for very small amount of the CO₂ loading in amine solution was estimated from the relations given by Astarita et al. [1983]:

$$[OH^-] = (K_w B_o / K_p)^{1/2} \quad (16)$$

K_w is the dissociation constant for water and its value is 1 × 10⁻¹⁴ kmol²/m⁶ at 25 °C, and pK_p, where K_p is the protonation constant of TEA, was obtained from Littel et al. [1990], and its value was 7.88.

The nitrous oxide analogy to get the solubility was used to approximate these properties in the reactive solvents in the most papers [Ko and Li, 2000; Sada et al., 1989]. But, in this study, the solubility of CO₂ in TEA 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 CO₂ between before and after equilibrium in gas and liquid phase similar to the procedure reported elsewhere [Kennard and Meisen, 1984]. The experimental procedure was duplicated as reported in the pub-

Table 1. Physicochemical properties of solvent and CO₂/TEA at 298 K

Solvent	δ (J/m ³) ^{1/2}	μ (cP)	C_{Ai} (kmol/m ³)	$D_A \times 10^9$ (m ² /s)	$D_B \times 10^{10}$ (m ² /s)	k_L (m/s)	k_2 (m ³ /kmol·s)	n
Water	48.1	0.894	0.035	1.95	7.11	6.505	3.06	0.98
Methanol	29.7	0.547	0.159	8.37	14.01	8.314	1.13	0.95
Ethanol	26.1	1.099	0.125	3.88	7.43	5.867	0.89	0.92
n-Propanol	23.4	1.942	0.096	2.73	3.92	4.413	0.71	1.07
n-Butanol	23.3	2.01	0.093	0.876	3.24	3.806	0.66	1.07
Ethylene glycol	29.9	17.33	0.027	0.121	0.45	1.477	1.18	0.92
Propylene glycol	25.8	42.93	0.248	0.054	0.20	0.934	0.93	0.91
Propylene carbonate	27.2	2.493	0.127	1.077	3.98	3.895	0.90	1.01

lished research [Park et al., 2002] in detail.

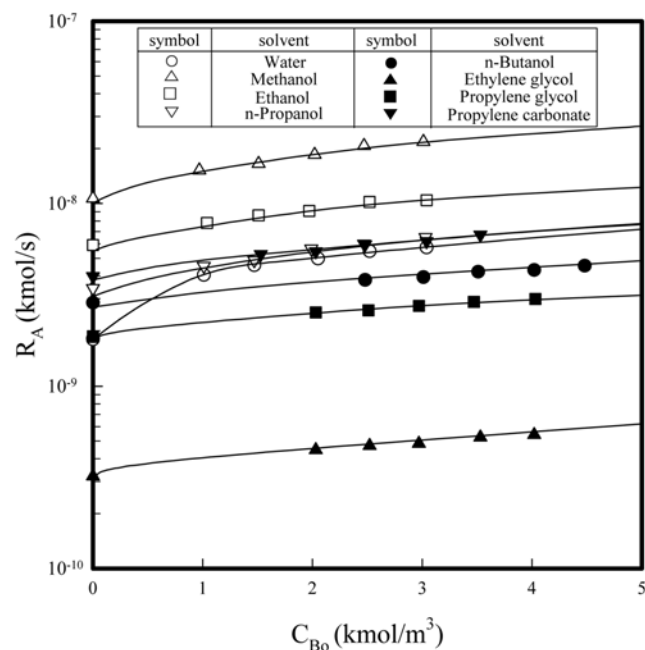
The diffusivity (D_A) of CO₂ and diffusivity (D_B) of TEA in solvent was estimated by the method of Wilke [Danckwerts, 1970]. The diffusivity of TEA in TEA solution was obtained from the assumption that the ratio of D_B to D_A was equal to the ratio in solvent [Nijssing et al., 1959]. The diffusivity of CO₂ in water at 25 °C was taken as 1.95×10^{-9} m²/s [Danckwerts and Sharma, 1966]. The viscosity of solvent was measured with a Brookfield viscometer (Brookfield Eng. Lab. Inc., USA).

The liquid-side mass transfer coefficient (k_L) of CO₂ in solvent was obtained by using the measured rate of absorption of CO₂.

The values of solubility parameter [Brandrup and Immergut, 1975], viscosity of solvent, C_{Ai} , D_A , D_B , and k_L of CO₂ in solvent are listed in Table 1.

RESULTS AND DISCUSSION

To obtain the reaction rate constant in the reaction of CO₂ with TEA, the absorption rates of CO₂ were measured according to the change of TEA concentration in each solvent, and shown in Fig. 1.

**Fig. 1. Absorption rate of CO₂ as a function of TEA concentration.**

As shown in Fig. 1, R_A increases as the TEA concentration increases. The enhancement factor was estimated by using R_A . The k_{ov} at the given TEA concentration was obtained by using the experimental enhancement factor and Eq. (10). The values of k_{OH} and OH⁻ concentration were estimated from Eq. (15) and (16). The k_{app} was obtained from Eqs. (9) and (14) for aqueous and non-aqueous solution, respectively. The results are listed in Table 2.

As shown in Table 2, the k_{app} increases as TEA concentration increases, and a comparison of the values of k_{ov} and k_{app} shows that the contribution of the CO₂-OH⁻ reaction cannot be neglected in aqueous solution.

To obtain the reaction rate constant (k_2) and reaction order (n), the k_{app} was plotted in form of logarithm against TEA concentration in Fig. 2.

As shown in Fig. 2, an approximately straight line can be drawn. Thus, the reaction mechanism in non-aqueous solution by the solvated amine can be used in terms of Eq. (11). The slope and intercept of the plots in Fig. 1 yield the reaction order and k_2 , and these values are listed in Table 1. As shown in Table 1, the values of the slopes are almost constant as 1.0. Thus, the reaction order for TEA can be described as the first order with respect to TEA concentration, the same as the results of references [Versteeg and van Swaaij, 1988b].

To ensure the pseudo-first-order fast reaction as shown in Eq. (7), the following condition was used [Daraiswany and Shama, 1984]:

$$1 \ll Ha \ll Ei \quad (17)$$

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

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

The calculated values of Ha and Ei are listed in Table 2. As shown in Table 2, Eq. (17) is satisfied, and then the reaction with TEA concentration of 1-4.5 kmol/m³ can be a pseudo-first-order fast reaction regime.

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 [Herbrandson and Neufeld, 1966]. Of these, some measures have a linear relation to the solubility parameter of the solvent. Then using the data of k_2 and solubility parameter of solvent (listed in Table 1), the logarithms of k_2 were plotted against the solubility parameter of the solvent in Fig. 3.

As shown in Fig. 3, the plots satisfied the linear relationship be-

Table 2. Experimental data of the reaction of CO₂ with TEA at 289 K

Solvent	C _{Bo} (kmol/m ³)	R _A × 10 ⁹ (kmol/s)	k _{ov} (1/s)	k _{app} (1/s)	H _d	E _i
Water	1.01	4.05	10.31	3.03	2.18	177
	1.47	4.58	13.50	4.72	2.49	258
	2.05	4.98	16.13	5.75	2.73	359
	2.52	5.47	19.60	8.09	3.01	441
	3.04	5.73	21.56	8.92	3.15	532
Methanol	0.97	15.20	1.16	1.16	1.18	26
	1.51	16.50	1.52	1.52	1.36	40
	2.02	18.50	2.12	2.12	1.60	53
	2.47	20.70	2.83	2.83	1.85	65
	3.01	21.80	3.21	3.21	1.97	78
Ethanol	1.04	7.80	0.81	0.81	1.01	37
	1.51	8.60	1.33	1.33	1.23	54
	1.97	9.10	1.61	1.61	1.35	70
	2.52	10.20	2.24	2.24	1.59	89
	3.04	10.40	2.36	2.36	1.63	107
n-Propanol	1.01	4.53	0.66	0.66	1.02	41
	1.47	4.87	0.99	0.99	1.18	59
	1.99	5.64	1.58	1.58	1.49	79
	2.48	5.95	1.84	1.84	1.60	99
	3.03	6.52	2.33	2.33	1.81	120
n-Butanol	2.48	3.79	1.75	1.75	1.03	163
	3.01	4.01	2.20	2.20	1.11	198
	3.51	4.22	2.63	2.63	1.26	231
	4.02	4.31	2.82	2.82	1.31	264
	4.48	4.55	3.34	3.34	1.42	294
Ethylene glycol	2.03	0.45	2.30	2.30	1.13	460
	2.52	0.47	2.78	2.78	1.24	570
	2.97	0.49	3.07	3.07	1.30	672
	3.53	0.52	3.89	3.89	1.47	798
	4.02	0.54	4.26	4.26	1.54	909
Propylene glycol	2.03	2.52	1.83	1.83	1.06	51
	2.51	2.59	2.04	2.04	1.12	63
	2.97	2.74	2.50	2.50	1.24	74
	3.47	2.88	2.95	2.95	1.35	86
	4.03	2.99	3.31	3.31	1.43	100
Propylene carbonate	1.53	5.26	1.45	1.45	1.01	74
	2.03	5.45	1.68	1.68	1.09	98
	2.47	6.00	2.37	2.37	1.30	119
	3.04	6.19	2.62	2.62	1.36	147
	3.53	6.73	3.35	3.35	1.54	170

tween the reaction rate constant and solubility parameter of the solvent. The solvent polarity is increased by the increase of solubility parameter of the solvent. It may be assumed that the increase of stability and solvation of R₃NH(HSol) due to the increase of solvent polarity makes the formation reaction of R₃NH⁺CO₂So⁻ and the reaction between R₃NH(HSol) and CO₂ in Eq. (11) by solvation [Morrison and Boyd, 1983] easier, respectively, and then, k₂ increases as increasing the solubility parameter as shown in Fig. 3.

The comparison of observed and calculated enhancement factors in the total concentration range of 1-4.5 molar TEA is shown in Fig. 4. The observed enhancement factors agreed within an error

of 2.1% with the theoretical values calculated with estimates of rate constants derived from the absorption rate data under the fast reaction regime.

CONCLUSIONS

The reaction kinetics of carbon dioxide with TEA in solvent such as methanol, ethanol, n-propanol, n-butanol, ethylene glycol, propylene glycol, propylene carbonate, and water were investigated via chemical absorption technique using a stirred tank with a plane gas-liquid interface at 298 K and 101.3 kPa. Based on the condi-

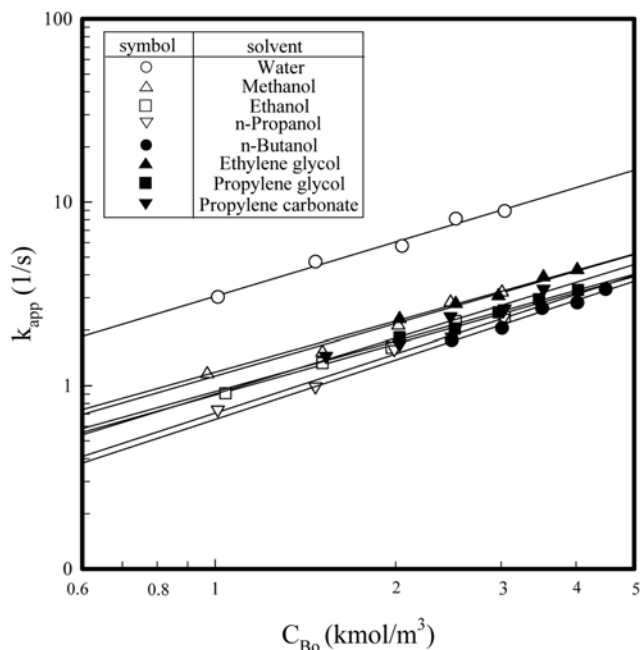


Fig. 2. Apparent reaction rate constant as a function of TEA concentration.

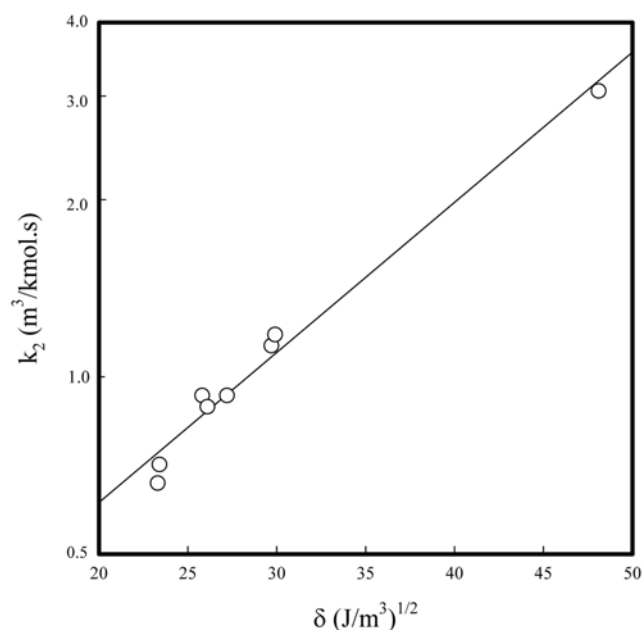


Fig. 3. Relationship between reaction rate constant and solubility parameter of solvent in the reaction of CO₂ with TEA.

tion of the pseudo-first-order fast reaction in non-aqueous solutions, the overall reaction rate constants were determined from the kinetic data measurements. The logarithm of the rate constant for the overall second-order reaction depended linearly on the solubility parameter of the solvent. In non-aqueous solutions of TEA, dissolved carbon dioxide is expected to react with solvated TEA to produce an ion pair.

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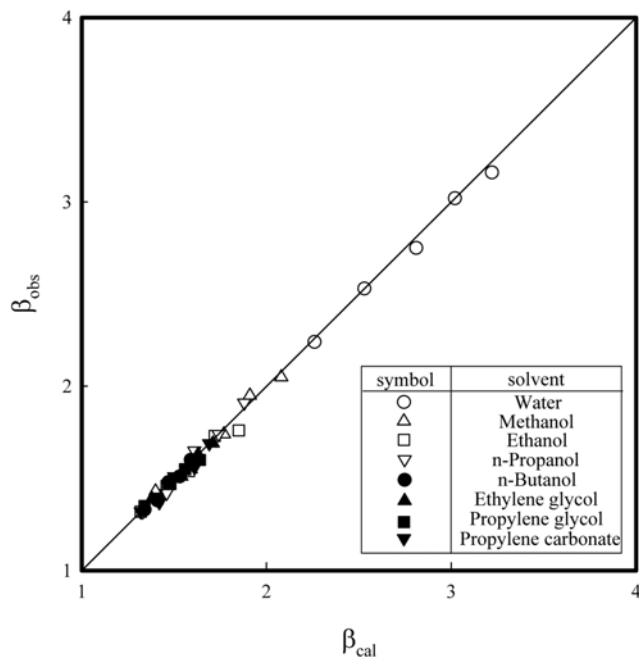


Fig. 4. Comparison of estimated enhancement factor with observed one of CO₂ absorption into solvent of TEA.

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NOMENCLATURE

- C_i : concentration of species i [kmol/m³]
 D_i : diffusivity of species i [m²/s]
 k_{app} : apparent reaction rate constant in reaction (10) and (15) [1/s]
 k_{ov} : overall reaction rate constant in reaction (9) and (13) [1/s]
 k_2 : second-order reaction rate constant in reaction (5) and (12) [1/s]
 k_L : liquid-side mass transfer coefficient of CO₂ in absorbent [m/s]

Greek Letters

- β : enhancement factor of CO₂
 δ : solubility parameter of solvent [J/m³]^{1/2}

Subscripts

- A : CO₂
 B : TEA
 i : gas-liquid interface
 o : feed

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