Absorption of carbon dioxide into non-aqueous solutions of *N*-methyldiethanolamine

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Abstract–The chemical absorption rate of carbon dioxide was measured in non-aqueous solvents, which dissolved *N*-methyldiethanoamine (MDEA), such as methanol, ethanol, n-propanol, n-butanol, ethylene glycol, propylene glycol, and propylene carbonate, and water at 298 K and 101.3 kPa using a semi-batch stirred tank with a plane gas-liquid interface. The overall reaction rate constant obtained from the measured rate of absorption of carbon dioxide under the condition of fast pseudo-first-order reaction regime was used to get the apparent reaction rate constant, which yields the second-order reaction rate constant and the reaction order of the overall reaction. There was approximately linear dependence of the logarithm of the rate constant for the overall second-order reaction on the solubility parameter of the solvent. In non-aqueous solutions of (MDEA), dissolved carbon dioxide is expected to react with solvated (MDEA) to produce an ion pair.

Key words: Absorption, Carbon Dioxide, *N*-Methyldiethanoamine

INTRODUCTION

The removal of acid gases such as CO_2, H_2S, and COS by absorption using aqueous alkanolamine solutions has been widely used in the chemical industries. Particularly, the removal of CO_2 from the gas produced by burning fossil fuel has been of great interest owing to the global warming caused by the increase of the concentration of CO_2 in the atmosphere. Industrially important chemical absorbents are monoethanolamine, diethanolamine, triethanolamine (TEA), MDEA [Astarita et al., 1983]. Due to the instantaneous reaction rate for the reaction of H_2S with tertiary alkanolamine (TEA, MDEA) and a very slow reaction rate for the reaction of CO_2 with the aqueous alkanolamine solutions they are frequently used as a selective solvent for selectively absorbing H_2S while permitting CO_2 unabsorbed [Astarita et al., 1983].

Although many studies have been done towards the mechanisms and kinetics of the reaction between CO_2 and various alkanolamines, the reaction media are limited to aqueous solutions [Danckwerts, 1970]. In practice, non-aqueous systems comprising methanol solution of alkanolamine have been commercially employed for absorption of CO_2, H_2S, 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 CO_2 and alkanolamine was analyzed by using simple mass balances resulting from the zwitterion mechanism of the reaction of CO_2 with alkanolamine such as primary and secondary amine proposed by Danckwerts [1979]. It would be expected that the mechanism of the reaction of CO_2 with alkanolamine in aqueous solutions could be applied to that in non-aqueous solvents, and the condition of the fast or instantaneous reaction re-

gime might also be satisfied in non-aqueous solvents. Tertiary alkanolamines such as TEA and MDEA 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 MDEA was carried out by 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 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 CO_2 in Aqueous Alkanolamine Solutions

The first reaction to be considered is the hydration of CO_2:

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \tag{1}$$

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

The second reaction is the bicarbonate formation with hydroxyl ion:

$$CO_2 + OH^- \leftrightarrow HCO_3^- \tag{2}$$

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 CO_2 with OH^- can be described [Pinsent et al., 1956]:

$$R_{CO2\text{-}OH}^- = k_{OH}^- [CO_2][OH^-] \tag{3}$$

For the reaction of CO_2 in aqueous solution with tertiary alkanola-

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

Solvent	$\delta(J/m^3)^{1/2}$	μ (cP)	C_{Ai} (kmol/m³)	$D_A \times 10^9$ (m²/s)	$D_B \times 10^{10}$ (m²/s)	k_L (m/s)	k_2 (m³/kmol·s)	n
Water	48.1	0.894	0.035	1.95	8.38	6.505	4.79	1.02
Methanol	29.7	0.547	0.159	8.37	15.62	8.314	2.22	1.05
Ethanol	26.1	1.099	0.125	3.88	8.28	5.867	1.91	0.98
n-Propanol	23.4	1.942	0.096	2.73	4.37	4.413	1.72	1.07
n-Butanol	23.3	2.01	0.093	0.876	3.61	3.806	1.75	1.04
Ethylene glycol	29.9	17.33	0.027	0.121	0.55	1.477	2.21	1.13
Propylene glycol	25.8	42.93	0.248	0.054	0.22	0.934	1.91	0.99
Propylene carbonate	27.2	2.493	0.127	1.077	4.44	3.895	2.36	0.92

mine (R_3N), Donaldson and Nguyen [1980] proposed the following reaction mechanism:

$$CO_2+R_3N+H_2O \leftrightarrow R_3NH^+ + HCO_3^- \qquad (4)$$
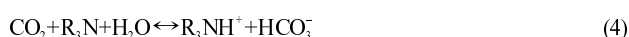
The forward reaction for the reaction of CO_2 with R_3N in Eq. (4) can be described:

$$R_{CO2\text{-}MDEA}=k_2\,[CO_2][MDEA] \qquad (5)$$

Mono- or diethanolame can react with CO_2 to form a zwitterionic intermediate [Danckwerts, 1979], but tertiary alkanolamine cannot react directly with CO_2, because its reaction mechanism is essentially a based-catalyzed hydration of CO_2 as shown in Eq. (4).

For the absorption of CO_2 into $MDEA+H_2O$, the CO_2 overall reaction rate can be expressed as follows:

$$R_{ov}=R_{CO2\text{-}MDEA}+R_{CO2\text{-}OH}^- \qquad (6)$$

In most literature [Blauwhoff et al., 1984; Versteeg and van Swaaij, 1988a] on CO_2 kinetics with tertiary alkanolamines, it is assumed that reaction of CO_2 with MDEA is a pseudo-first-order reaction combining Eq. (3), (5) and (6), and one has

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

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

$$k_{ov}=k_2\,[MDEA]+k_{OH}^-\,[OH^-] \qquad (8)$$

On the other hand, the apparent reaction rate constant (k_{app}) is defined as k_2 [MDEA], and is obtained as follows:

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

The enhancement factor (β) of CO_2, which is defined as the ratio of absorption rate of CO_2 with chemical reaction of MDEA to that without one for a pseudo-first-order reaction of Eq. (7), is given [Daraiswany and Sharma, 1984] by

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

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

**2. Reactions of CO₂ in Non-Aqueous Alkanolamine Solutions**

Because tertiary alkanolamines such as TEA and MDEA 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 CO_2 and MDEA in non-aqueous solution. Sada et al. [1989] have proposed that in non-aqueous solutions of

tertiary alkanolamine the dissolved carbon dioxide will react with solvated tertiary alkanolamine to form an ion pair as follows:

$$R_3NH(HSol)+CO_2 \rightarrow R_3NH^+CO_2Sol^- \qquad (11)$$

where Hsol designates solvent.

It is assumed that reaction of CO_2 with MDEA is a pseudo-first-order reaction in non-aqueous solutions as follows:

$$R_{CO2\text{-}MDEA(Hsol)}=k_2\,[CO_2][MDEA(Hsol)]=k_{ov}\,[CO_2] \qquad (12)$$
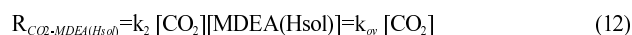
and the overall reaction rate constant (k_{ov}) has the following expression

$$k_{ov}=k_2\,[MDEA(Hsol)] \qquad (13)$$

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

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

EXPERIMENTAL

1. Chemicals and Absorption Rate of CO₂

All chemicals in this study were of reagent grade, and used with-
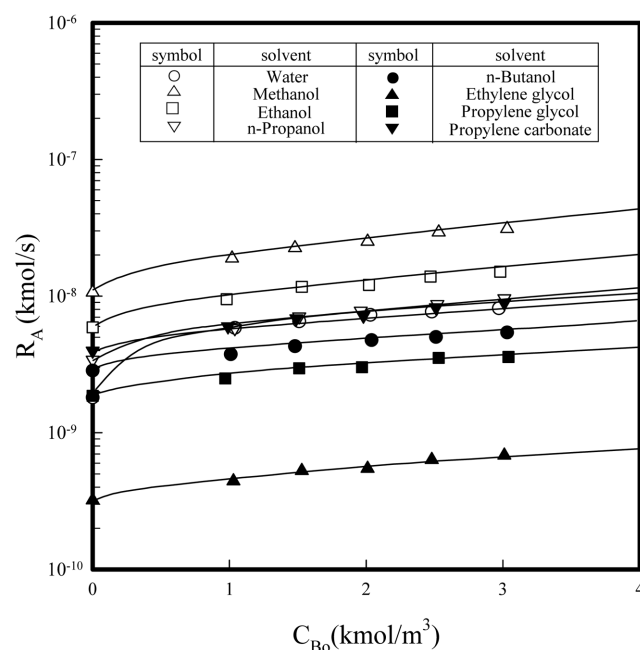

Fig. 1. Effect of MDEA concentration on R_A.

out further purification. The purity of both CO_2 and N_2 was more than 99.9%. The solvents used in the absorption of CO_2 were methanol, ethanol, n-propanol, n-butanol, ethylene glycol, propylene glycol, propylene carbonate, and water. MDEA solutions were prepared from distilled solvent. The distilled solvents were degassed with boiling. MDEA was Aldrich reagent grade with purity of 99.7%. The concentration of MDEA solution was determined by titration of a liquid sample with HCl by using methyl orange as an indicator. The MDEA concentrations in this study range from 1 to 3 $kmol/m^3$.

The absorption rates of carbon dioxide into MDEA solutions were measured by using a semi-batch stirred tank with a plane gas-liquid interface at 298 K and 101.3 kPa. The experimental enhancement factor of CO_2 by reaction of CO_2 with MDEA was obtained from the ratio of the specific rates of absorption of CO_2 with MDEA and those without MDEA. 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 experimental procedure to get the absorption rate was duplicated as reported in published research [Park et al., 2004] in detail.

2. Physicochemical Properties

Table 2. Experimental data of the reaction of CO_2 with MDEA at 289 K

Solvent	C_{Bo} (kmol/m³)	$R_A \times 10^9$ (kmol/s)	k_{ov} (1/s)	k_{app} (1/s)	H_A	E_i
Water	1.04	5.85	22.49	4.97	3.22	198
	1.51	6.53	28.12	7.00	3.60	287
	2.03	7.30	35.21	10.72	4.03	386
	2.48	7.69	39.09	12.02	4.24	471
	2.97	8.13	43.70	14.08	4.49	564
Methanol	1.02	18.90	2.25	2.25	1.65	29
	1.48	22.50	3.46	3.46	2.05	41
	2.01	25.10	4.42	4.42	2.31	56
	2.53	29.30	6.16	6.16	2.73	70
	3.03	31.10	6.97	6.97	2.91	83
Ethanol	0.98	9.50	1.83	1.83	1.44	37
	1.53	11.70	3.19	3.19	1.89	58
	2.02	12.10	3.45	3.45	1.97	76
	2.47	13.90	4.73	4.73	2.31	92
	2.98	15.10	5.66	5.66	2.53	111
n-Propanol	1.04	5.81	1.72	1.72	1.55	44
	1.51	7.08	2.84	2.84	1.99	64
	1.96	7.81	3.55	3.55	2.23	82
	2.52	8.71	4.51	4.51	2.51	106
	3.01	9.61	5.55	5.55	2.79	126
n-Butanol	1.01	3.75	1.67	1.67	1.01	71
	1.48	4.30	2.80	2.80	1.30	103
	2.04	4.76	3.81	3.81	1.52	142
	2.51	5.01	4.38	4.38	1.63	174
	3.03	5.42	5.37	5.37	1.80	210
Ethylene glycol	1.03	0.44	2.22	2.22	1.11	258
	1.53	0.53	3.95	3.95	1.48	383
	2.01	0.55	4.39	4.39	1.56	503
	2.48	0.63	6.42	6.42	1.89	620
	3.01	0.68	7.68	7.68	2.06	753
Propylene glycol	0.97	2.50	1.77	1.77	1.05	26
	1.51	2.96	3.21	3.21	1.41	40
	1.97	3.02	3.40	3.40	1.45	52
	2.53	3.53	5.18	5.18	1.79	66
	3.04	3.59	5.41	5.41	1.83	79
Propylene carbonate	0.99	5.99	2.36	2.36	1.29	51
	1.49	6.86	3.54	3.54	1.58	76
	1.98	7.18	3.99	3.99	1.68	101
	2.51	8.26	5.64	5.64	2.00	128
	3.01	8.92	6.72	6.72	2.18	153

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

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

The hydroxyl ion concentration for very small amount of the CO_2 loading in alkanolamine solution was estimated from the relations given by Astatita et al. [1983]:

$$[OH^-] = (K_w C_{Bo}/K_p)^{1/2} \tag{16}$$

K_w is the dissociation constant for water and its value is 1×10^{-14} $kmol^2/m^6$ at 298 K, and pK_p, where K_p is the protonation constant of MDEA, was obtained from Littel et al. [1990], and its value was 8.63.

A 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 CO_2 in MDEA 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 CO_2 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 published research [Park et al., 2002] in detail.

The diffusivity (D_A) of CO_2 and diffusivity (D_B) of MDEA in solvent were estimated by the method of Wilke [Danckwerts, 1970]. The diffusivity of MDEA in MDEA solution was obtained from the assumption that the ratio of D_B to D_A was equal to the ratio in solvent [Nijsing et al., 1959]. The diffusivity of CO_2 in water at 25 °C was taken as 1.95×10^{-9} m^2/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 CO_2 in solvent was obtained by using the measured rate of absorption of CO_2.

The values of solubility parameter [Brandrup and Immergut, 1975], viscosity of solvent, C_{Ai}, D_A, D_B, and k_L of CO_2 in solvent are listed in Table 1.

RESULTS AND DISCUSSION

To get the reaction rate constant in the reaction of CO_2 with MDEA, the absorption rates of CO_2 were measured according to the change of MDEA concentration in each solvent, and shown in Fig. 1.

As shown in Fig. 1, R_A increases as the MDEA concentration increases. The enhancement factor was estimated by using R_A. The k_{ov} at the given MDEA concentration was obtained from the measured 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 by using Eq. (9) and (14) for aqueous and non-aqueous solution, respectively. The experimental results are listed in Table 2.

As shown in Table 2, the k_{app} increases as MDEA concentration increases, and a comparison of the values of k_{ov} and k_{app} shows that the contribution of the CO_2-OH^- reaction cannot be neglected in aqueous solution.

To obtain the reaction rate constant and reaction order, the k_{app} was plotted in logarithmic form against MDEA concentration in
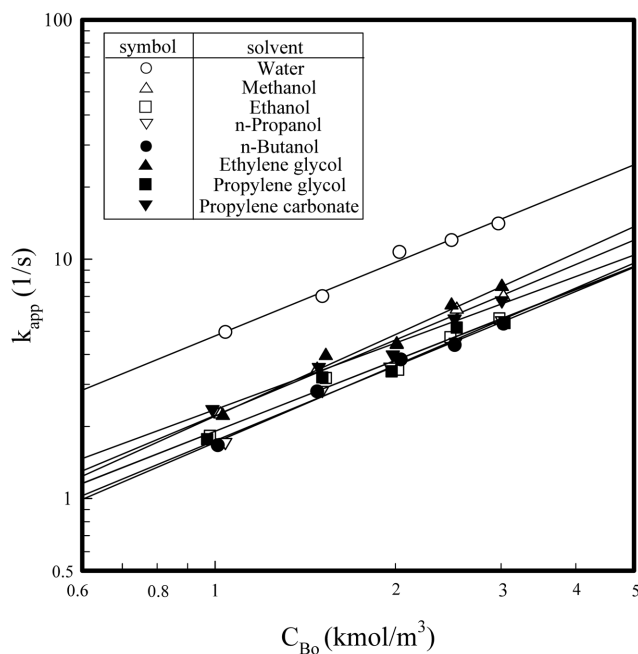

Fig. 2. Effect of MDEA concentration on k_{app}.

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 alkanolamine can be presented in terms of Eq. (11). The slope and intercept of the plots in Fig. 1 and Eq. (13) 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 MDEA can be described as the first order with respect to MDEA, and 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 conditions were used [Daraiswany and Sharma, 1984]:

$$1 \ll Ha \ll Ei \tag{17}$$

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

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

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 MDEA concentration higher than 1.0-3.0 $kmol/m^3$ 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 a linear relationship, except one point at $\delta = 27.2 (J/m^3)^{1/2}$ with experimental error, between the
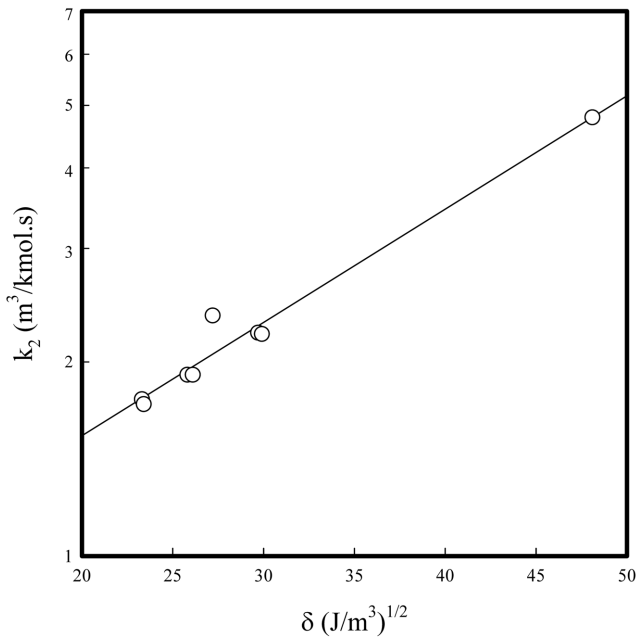
Fig. 3. Relationship between reaction rate constant and solubility parameter of solvent in the reaction of CO_2 with MDEA.

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 increase of stability and solvation of $R_3NH^+CO_2Sol^-$ due to the increase of solvent polarity makes the formation reaction of $R_3NH^+CO_2Sol^-$ and the reaction between $R_3NH(HSol)$ and CO_2 in Eq. (11) by solvation [Morrison and Boyd, 1983] easier, respectively, and then, k_2 increases as increasing the solubility parameter as shown in Fig. 3.

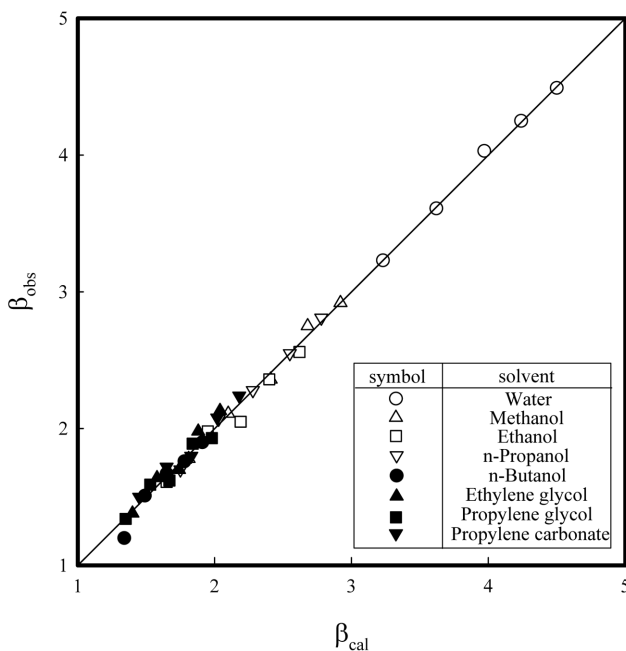The comparison of observed and calculated enhancement fac-

Fig. 4. Comparison of estimated enhancement factor with observed values of absorption of CO_2 into solvent of MDEA.

tors in the total concentration range of 1-3 molar MDEA is shown in Fig. 4. The observed enhancement factors agreed within an error of 4.6% 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 MDEA in solvents such as methanol, ethanol, n-propanol, n-butanol, ethylene glycol, propylene glycol, propylene carbonate, and water were investigated via chemical absorption technique by using a stirred tank with a plane gas-liquid interface at 298 K and 101.3 kPa. Based on the condition of the pseudo-first-order fast reaction in the CO_2 absorption, the overall pseudo-first-order 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 MDEA, dissolved carbon dioxide is expected to react with solvated MDEA to produce an ion pair.

NOMENCLATURE

C_i : concentration of species, i [kmol/m^3]
D_i : diffusivity of species, I [m^2/s]
k_{app} : apparent reaction rate constant in reaction (9) and (14) [1/s]
k_{ov} : overall reaction rate constant in reaction (6) and (11) [1/s]
k_2 : second-order reaction rate constant in reaction (5) and (12) [1/s]
k_L : liquid-side mass transfer coefficient of CO_2 in absorbent [m/s]

Greek Letters
β : enhancement factor of CO_2
δ : solvent parameter [J/m^3]$^{1/2}$

Subscripts
A : CO_2
B : MDEA
i : gas-liquid interface
o : feed

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