Chemical Kinetics of the Reaction of Carbon Dioxide with Ethanolamines in Nonaqueous Solvents

The kinetics of the reaction of carbon dioxide with mono- and diethanolamine in such nonaqueous solvents as methanol, ethanol, and 2-propanol and in water were studied using a stirred tank absorber with a plane gas-liquid interface at 303 K. The reaction was found to be of first order with respect to carbon dioxide for every solvent. The order of reaction with respect to ethanolamine was found to be unity only for an aqueous solution of monoethanolamine and for the other solutions, ranged from 1.4 to 2, depending on the solvent species. The reaction order was increased in the order of water, methanol, ethanol, and 2-propanol. The variation of the reaction order with the solvent species could be explained in terms of a reaction scheme via a zwitterion. Almost linear dependence of the logarithm of the reaction rate constant on the solubility parameter of the solvent was derived.

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SCOPE

Gas purification by chemical absorption is of great industrial importance. Alkanolamine solutions are frequently used for the removal of acid gases (Wall, 1975). Although many studies have been done toward the mechanisms and kinetics of the reaction between carbon dioxide and various amines (Blauwhoff et al., 1983), the reaction media are limited to aqueous solutions. In practice, nonaqueous systems comprising methanol solution of alkanolamine have been commercially employed for absorption of carbon dioxide, hydrogen sulfide, carbonyl sulfide, etc., because of their high solubility and capacity, their low corrosiveness, and their low energy consumption during regeneration of used liquor (Bratzler and Doerges, 1974). Nonaqueous systems, which are essentially used in a closed loop, should be considered more for acid gas removal.

The reaction between carbon dioxide and monoethanolamine in aqueous solutions has already been found to be of first order with respect to both species, while for the carbon dioxide-diethanolamine system in aqueous solutions, the order of reaction with respect to diethanolamine has not been determined to be of first or second order. Danckwerts (1979) and Laddha and Danckwerts (1981) proposed a new reaction mechanism comprising formation of a zwitterion followed by the removal of proton by a base (diethanolamine) to explain such contradiction of the reaction order. It would be expected that the order of reaction with respect to ethanolamine ranges from first to second order in nonaqueous solvents. The variation of the reaction order with a physicochemical property of the solvent and the resultant reaction rate constants seem to be of practical interest.

In the present work, the kinetics of the reaction of carbon dioxide with mono- and diethanolamine in such nonaqueous solvents as methanol, ethanol, and 2-propanol were investigated using a stirred tank absorber with a plane gas-liquid interface. The absorption rate data under the fast reaction regime were analyzed in terms of the reaction mechanism proposed by Danckwerts (1979). An attempt was made to correlate the derived reaction rate constants in different nonaqueous solvents with physicochemical properties of the solvent.

CONCLUSIONS AND SIGNIFICANCE

Nonaqueous systems for acid gas absorption into ethanolamines seem to be of practical interest because of their high solubility and capacity, their low energy consumption during regeneration of used liquor, etc. However, little systematic work has been done on the reaction kinetics in nonaqueous solvents. The rates of carbon dioxide absorption into alcoholic (methanol, ethanol, and 2-propanol) solutions of mono- and diethanolamine were measured using a semibatch stirred tank with a plane gas-liquid interface at 303 K and 1 atm (101.3 kPa) pressure. The rate data under the fast reaction regime were analyzed by chemical absorption theory incorporating a reaction mechanism via a zwitterion. To evaluate the reaction rate constants and the order of reaction, the combined physicochemical property ($\sqrt{D_A}/H_A$) was measured in a wetted-wall column. It was found that the order of reaction with respect to carbon dioxide

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is unity for every system. The order of reaction with respect to amine was unity only for an aqueous solution of monoethanolamine, and for the other systems had a value ranging from 1.4 to 2. The reaction order with respect to amine depended on the solvent species, and was increased in the order of water, methanol, ethanol, and 2-propanol. The variation of the reaction order with the solvent species was interpreted in terms of the reaction mechanism via a zwitterion. It was found that the dependence of the logarithms of the reaction rate constants on the solubility parameter of the solvent is close to linear.

THEORETICAL BACKGROUND

It has been reported that the stoichiometrical equation of reaction of carbon dioxide with ethanolamine in an aqueous solution can be expressed by

$$CO_2 + 2RNH_2 \rightarrow RNHCO_2^- + RNH_3^+ \qquad \text{(i)}$$

and

$$CO_2 + 2R_2NH \rightarrow R_2NCO_2^- + R_2NH_2^+ \qquad \text{(ii)}$$

where the radical R denotes $HO{\cdot}CH_2{\cdot}CH_2{\cdot}$. These reactions have been found to be of first order with respect to carbon dioxide, but it has not been established whether the order of reaction with respect to diethanolamine is of first or second order. Danckwerts (1979) suggested a reaction mechanism that explains the different reaction order in amine. As regards diethanolamine, the reaction takes place in two steps:

$$CO_2 + R_2NH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R_2NH^+CO_2^- \qquad \text{(iii)}$$

$$R_2NH^+CO_2^- + R_2NH \xrightarrow{k_3} R_2NCO_2^- + R_2NH_2^+ \qquad \text{(iv)}$$

That is, the mechanism is composed of the formation of a zwitterion followed by the removal of a proton by amine. If the steady state approximation is applied to the zwitterion, one gets a homogeneous rate of reaction as

$$r = -\frac{dC_A}{dt} = \frac{C_A C_B}{\dfrac{1}{k_1} + \dfrac{k_2}{k_1 k_3 C_B}}. \qquad (1)$$

If the first term in the denominator is much smaller than the second term (i.e., k_3 small), the reaction becomes of second order in amine (B) and the rate constant of the overall third-order kinetics is expressed as k_1k_3/k_2. On the contrary, if the first term in the denominator is much larger than the second term, there is an overall second-order kinetics with the rate constant k_1. In nonaqueous solvents, thus, the order of reaction with respect to ethanolamine (even monoethanolamine) would possibly range from first to second, because the deprotonation by amine may be depressed.

The process considered is formulated by an absorption of gaseous reactant A into a liquid medium containing the liquid phase reactant B accompanied by reactions (iii) and (iv). The film theory material balance equation can be written as

$$D_A \frac{d^2C_A}{dz^2} = \frac{C_A C_{BO}}{\dfrac{1}{k_1} + \dfrac{k_2}{k_1 k_3 C_{BO}}} \qquad (2)$$

when the concentration of liquid phase reactant is much higher than that of dissolved gas. The boundary conditions can be given by

$$\text{at } z = 0,\ C_A = C_{Ai} \qquad (3)$$

$$\text{at } z = z_L,\ C_A = 0. \qquad (4)$$

For the regime of the fast-pseudofirst-order chemical reaction, the absorption rate is expressed as

$$N_A = C_{Ai}\sqrt{\frac{D_A C_{BO}}{\dfrac{1}{k_1} + \dfrac{k_2}{k_1 k_3 C_{BO}}}}. \qquad (5)$$

Replacing C_{Ai} by the partial pressure of A at the gas-liquid interface ($p_{Ai} = H_A C_{Ai}$) in Eq. 5, and rearranging the resultant equation, yields

$$C_{BO} D_A \left(\frac{p_{Ai}}{H_A N_A}\right)^2 = \frac{1}{k_1} + \frac{k_2}{k_1 k_3}\frac{1}{C_{BO}}. \qquad (6)$$

Accordingly, the second-order rate constant (k_1) and the third-order rate constant (k_1k_3/k_2) can be obtained, respectively, by the intercept and slope of the plot: $C_{BO}D_A(p_{Ai}/H_AN_A)^2$ vs. $1/C_{BO}$.

To calculate the values of the lefthand term of Eq. 6, it is necessary to know a physicochemical property ($\sqrt{D_A}/H_A$) composed of diffusivity and solubility of carbon dioxide in liquid medium with different amine concentrations. Such a property can be derived from physical absorption runs as described in the following.

For a physical absorption into a falling liquid film, the absorption rate is written, according to penetration theory, by

$$N_A = 2\sqrt{\frac{D_A}{\pi t_c}}\frac{p_{Ai}}{H_A} \qquad (7)$$

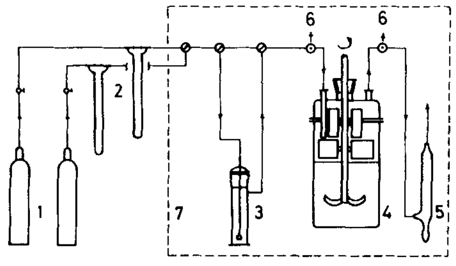
when the gas-liquid contact time t_c is short enough to assume that the penetration depth of dissolved gas is much thinner than the thickness of the falling liquid film. The combined physicochemical property ($\sqrt{D_A}/H_A$) can be determined on the basis of Eq. 7 from the measurements of absorption rate N_A at various gas-liquid contact times.

EXPERIMENTAL

The gas-liquid contactor used was a stirred tank made of glass, with a plane unbroken gas-liquid interface (I.D. 75 mm), and was operated continuously with respect to the gas phase and batchwise with respect to the liquid phase (liquid volume 330 cm^3). The gas phase stirrer was a fan turbine with six blades and was mounted in the center of the gas phase. The liquid phase stirrer was of anchor type and was placed at half of the liquid depth. Both gas and liquid phase stirrers were driven by the same shaft at 124 rpm.

The experimental setup is shown in Figure 1. The solute gas, carbon dioxide, was diluted with nitrogen, saturated with solvent vapor, and fed into the absorber. The total gas flow rate was measured with the help of a soap film meter. The concentration of carbon dioxide in the gas phase into and from the absorber was determined by gas chromatography (column packing: silica gel). The absorber and saturator were kept constant at 303 K in a water bath and the gas flow meters were kept constant at the same temperature in an air bath. The total gas flow rate was maintained at 6 N·cm^3/s. The concentration of carbon dioxide in the feed stream was varied from 1 to 10 mol%. The concentration of amine (mono- and diethanolamine) ranged from 0.2 to 1.5 ~ 2.5 mol/dm^3. The absorption rate was calculated from the difference between inlet and outlet concentrations of carbon dioxide and the gas flow rate.

A cylindrical wetted-wall column was used to measure the combined physicochemical property ($\sqrt{D_A}/H_A$) of carbon dioxide in pure solvents (alcohols). However, the combined property of carbon dioxide in alcohols



1 Cylinder, 2 Orifice flowmeter, 3 Saturater
4 Absorber, 5 Soap film meter, 6 Sampling
7 Thermostat bath

Figure 1. Schematic diagram of experimental apparatus.

with different concentrations of amine cannot presently be measured directly because of the chemical reaction. In such cases, nitrous oxide, which is similar in mass and molecular interaction parameters to carbon dioxide (Sada et al., 1976), was used as an absorbing gas. The wetted-wall section was an outer surface of glass tube (O.D.: 25 mm) and the wetted-wall height was varied between 2 and 14 cm with the liquid flow rate maintained at 2–3 cm^3/s. To prevent rippling on the surface of the falling film, 0.035 to 0.35 vol.% of surface active agent, Tween 80 (polyoxyethylene solbitan monoleate), was added to the solution. The rate of absorption of pure carbon dioxide or nitrous oxide under semibatch conditions for the gas phase was measured volumetrically with the help of a soap film meter.

In all the experimental runs, measurements were made at atmospheric pressure and a constant temperature of 303 K.

EXPERIMENTAL RESULTS AND DISCUSSION

Combined Physiocochemical Property

Both the diffusivity and solubility of solute gas in the liquid medium greatly affect the derived reaction rate parameters, as seen in Eq. 6. The measurements of $\sqrt{D_A}/H_A$ of carbon dioxide in pure alcohols and water in previous works are listed in Table 1, and there seems a considerable difference among them. In the present work, the values of $\sqrt{D_A}/H_A$ were measured in the wetted-wall column and are shown in the last row of the table.

The experimental results on $\sqrt{D_A}/H_A$ of nitrous oxide in aqueous and alcoholic solutions of amines are shown in Tables 2 and 3. Measurements of density and viscosity of the solutions are also listed. The values of $\sqrt{D_A}/H_A$ of carbon dioxide in aqueous and alcoholic solutions of mono- and diethanolamine were assumed to be equal to the corresponding values of nitrous oxide multiplied by the ratio of $(\sqrt{D_A}/H_A)_{CO_2}$ to $(\sqrt{D_A}/H_A)_{N_2O}$ in pure solvents (water and alcohols).

TABLE 1. VALUES OF $\sqrt{D_A}/H_A$ OF CARBON DIOXIDE IN WATER AND ALCOHOLS

Investigators	Temp K	$\sqrt{D_A}/H_A \times 10^{12}$, mol/Pa·cm²·s^1/2 In Water	In Methanol	In Ethanol	In 2-Propanol
Takeuchi et al. (1975)	298	1.57	9.24	5.77	3.84*
Alvarez-Fuster et al. (1980, 1981)	293	1.65		6.88	
Won et al. (1981)	298	1.51	14.3	7.69	4.96*
Imaishi et al. (1981)	303	1.28	11.4		
Present Work	303	1.40	9.01	6.69	4.35

* 1-propranol

TABLE 2. PHYSICOCHEMICAL PROPERTY ($\sqrt{D_A}/H_A$) OF NITROUS OXIDE IN AQUEOUS AND ALCOHOLIC SOLUTIONS OF MONOETHANOLAMINE AT 303 K

Solvent	Amine Conc. mol/dm³	$\sqrt{D_A}/H_A \times 10^{12}$ mol/Pa·cm²·s^1/2	Solution Viscosity × 10³ Pa·s	Solution Density g/cm³
Water	0	0.984	0.800	0.996
	0.287	0.979	0.836	0.996
	0.759	0.933	0.917	0.997
	1.19	0.909	0.983	0.998
	1.68	0.892	1.06	0.999
Methanol	0	7.74	0.514	0.782
	0.231	7.62	0.538	0.787
	0.515	7.40	0.567	0.792
	0.766	7.14	0.592	0.796
	1.07	6.97	0.620	0.801
	1.43	6.78	0.677	0.809
	1.62	6.68	0.704	0.812
Ethanol	0	7.21	0.995	0.781
	0.340	6.97	1.05	0.786
	0.644	6.63	1.11	0.791
	0.914	6.39	1.15	0.796
	1.25	6.20	1.21	0.801
	1.49	6.02	1.26	0.805
2-Propanol	0	5.39	1.76	0.776
	0.332	5.43	1.83	0.781
	0.639	5.32	1.90	0.786
	0.980	5.23	1.99	0.791
	1.53	5.03	2.13	0.799

Reaction Kinetics

Order of Reaction with Respect to Carbon Dioxide. The influence of carbon dioxide concentration on the absorption rate was investigated at a constant amine concentration. Experimental results are indicated in Figures 2 and 3 as a plot of absorption rate against partial pressure of carbon dioxide at the gas-liquid interface, which was evaluated by taking the gas-film resistance into consideration. The gas-side mass transfer coefficient (k_G) at 124 rpm of stirrer speed was determined by absorption of solute SO_2 into an aqueous solution of 0.5 M Na_2SO_3, which can be regarded as a completely gas-film controlled process, in the same manner as the earlier work (Sada et al., 1981) ($k_G = 3.46 \times 10^{-10}$ mol/s·cm²·Pa at 124 rpm). The gas-film resistance was evaluated to be less than about 30% of the total resistance. In these figures, there appears to be a linear relationship with the slope of almost unity for every solvent. So the order of reaction with respect to carbon dioxide can be determined to be unity. This is in complete agreement with the previous works on aqueous amine solutions.

Order of Reaction with Respect to Ethanolamine. When the reaction is regarded as m-order with respect to carbon dioxide and n-order with respect to ethanolamine and the process of chemical absorption lies under the fast reaction regime, then the absorption rate can be expressed as

$$N_A = \sqrt{\frac{2}{m+1} k_{m,n} C_{Ai}^{m+1} C_{BO}^{n} D_A}\,. \tag{8}$$

For this case, Eq. 8 reduces to

TABLE 3. PHYSICOCHEMICAL PROPERTY ($\sqrt{D_A}/H_A$) OF NITROUS OXIDE IN AQUEOUS AND ALCOHOLIC SOLUTIONS OF DIETHANOLAMINE AT 303 K

Solvent	Amine Conc. mol/dm^3	$\sqrt{D_A}/H_A$ × 10^{12} mol/ Pa·cm^2·s$^{1/2}$	Solution Viscosity × 10^3 Pa·s	Solution Density g/cm^3
Water	0.102	0.965	0.824	0.997
	0.181	0.951	0.489	0.998
	0.418	0.929	0.920	1.00
	0.618	0.898	1.01	1.00
	0.950	0.866	1.12	1.01
	1.46	0.835	1.36	1.01
	1.56	0.819	1.43	1.01
Methanol	0.212	7.54	0.556	0.790
	0.447	6.99	0.612	0.799
	0.661	6.68	0.660	0.806
	1.06	6.34	0.766	0.819
	1.33	6.06	0.859	0.829
	1.59	5.79	0.948	0.837
Ethanol	0.237	6.46	1.10	0.789
	0.446	6.27	1.18	0.796
	0.670	6.05	1.30	0.804
	0.970	5.71	1.48	0.814
	1.29	5.26	1.68	0.824
	1.54	4.98	1.89	0.832
2-Propanol	0.194	5.30	1.91	0.783
	0.488	5.07	2.20	0.793
	0.819	4.82	2.54	0.803
	1.20	4.48	3.01	0.815
	1.57	4.13	3.56	0.828

$$N_A = C_{Ai}\sqrt{k_{1,n}D_A C_{BO}^n}. \qquad (9)$$

The fast reaction regime is fulfilled by

$$3 < \sqrt{M} \ll \Phi_\infty,$$

and therein the enhancement factor Φ is equal to $\sqrt{M}$. According to Eq. 5, the reaction rate constant $k_{1,n}$ in Eq. 9 should depend on the amine concentration, but if the range of amine concentrations covered in chemical absorption runs is not so wide, $k_{1,n}$ can be regarded as constant. Figures 4 and 5 show the plot of $N_A/C_{Ai}\sqrt{D_A}$ vs. C_{BO} on the basis of Eq. 9.

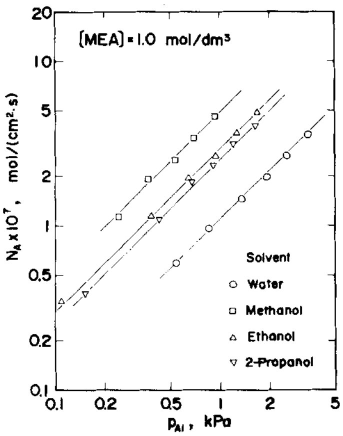


Figure 2. Rates of absorption of carbon dioxide into aqueous and alcoholic solutions of monoethanolamine.

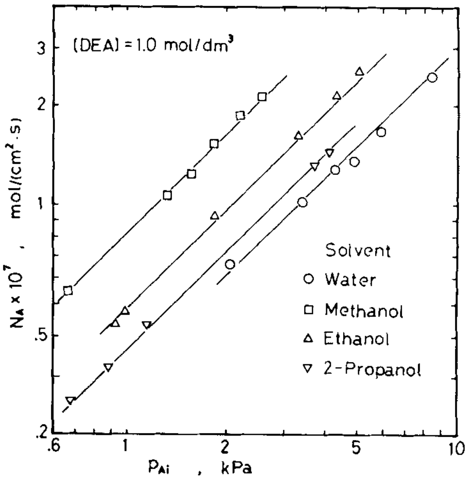


Figure 3. Rates of absorption of carbon dioxide into aqueous and alcoholic solutions of diethanolamine.

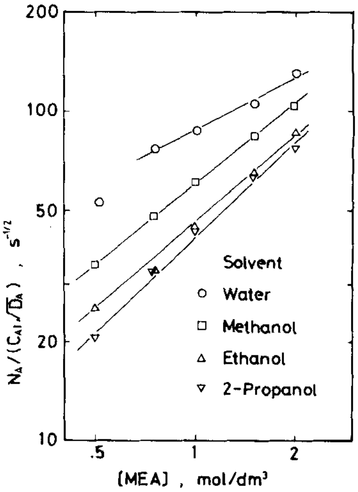


Figure 4. Effect of monoethanolamine concentration on $N_A/(C_{Ai}\sqrt{D_A})$.

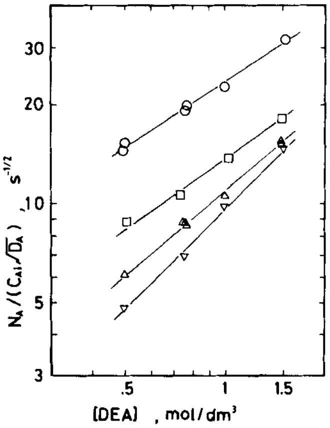


Figure 5. Effect of diethanolamine concentration on $N_A/(C_{Ai}\sqrt{D_A})$. Keys as in Figure 4.

TABLE 4. ORDER OF REACTION WITH RESPECT TO AMINE FOR REACTION BETWEEN CARBON DIOXIDE AND AMINE IN AQUEOUS AND ALCOHOLIC SOLUTIONS

	Solvent			
Amine	Water	Methanol	Ethanol	2-Propanol
Monoethanol amine	~1	1.62	1.72	1.90
Diethanol amine	1.42	1.52	1.74	~2
ϵ(25°C	78.5	32.6	24.3	18.0
δ(25°C) $(\mathrm{J \cdot mol^{-1} \cdot cm^{-3}})^{1/2}$	48.1	29.7	26.1	23.4

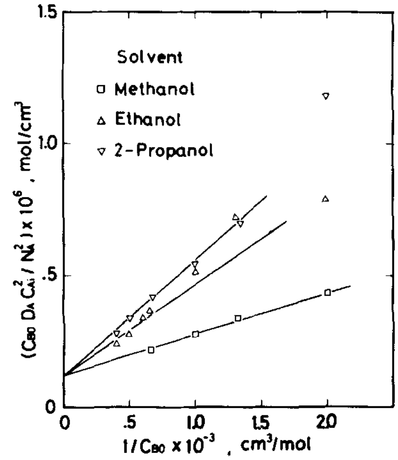


Figure 6. Plot of $C_{BO}D_AC_A^2/N_A^2$ vs. $1/C_{BO}$ for monoethanolamine.

To check the validity of the fast reaction regime for eight kinds of solutions (i.e., aqueous and alcoholic solutions of mono- and diethanolamine), the values of $\sqrt{M}$ and Φ_∞ will be evaluated as follows. One of the requirements, $\sqrt{M} > 3$, is fulfilled for amine concentrations greater than 0.5 mol/dm^3. Concerning the other requirement, $\sqrt{M} \ll \Phi_\infty$, $\Phi_\infty/\sqrt{M}$ is greater than 6 for aqueous solutions of monoethanolamine and greater than 10 for any other solutions. Here the value of diffusivity of amine in each solvent at infinite dilution was estimated by the method of Wilke (1949) and was employed without any correction of amine concentration for the calculation of Φ_∞. That is, the process of chemical absorption for amine concentrations above 0.5 mol/dm^3 can be regarded as lying under the fast reaction regime. (This seems a somewhat lenient approximation for aqueous monoethanolamine solutions.) Figures 4 and 5 show a linear relationship for $C_{BO} > 0.5$ mol/dm^3 in every solution. The slope of the line, $n/2$, enables one to determine the order of reaction with respect to amine. The derived reaction orders for eight solutions are listed in Table 4. The values of dielectric constant ϵ(25°C) and solubility parameter δ(25°C) for every solvent are also listed. It should be noted that in the strict sense, the values of apparent reaction order n are usable only in the region of amine concentrations lying under the fast reaction regime. It was found that the order of reaction with respect to both mono- and diethanolamine approaches 2 with decreasing the polarity of the solvent.

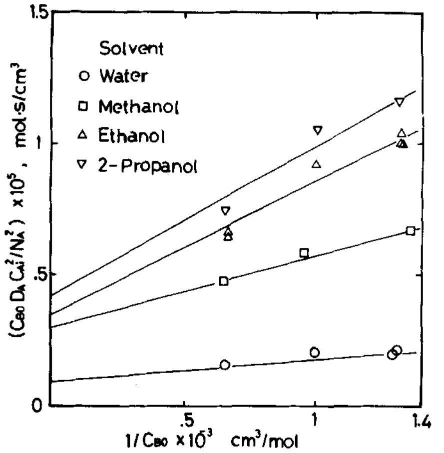


Figure 7. Plot of $C_{BO}D_AC_A^2/N_A^2$ vs. $1/C_{BO}$ for diethanolamine.

Effect of Solvent Species on Reaction Rate Parameters. According to the mechanism via zwitterion proposed by Danckwerts (1979), the reaction rate constant $k_{1,n}$ appearing in Eq. 9 should be a function of amine concentration and is composed of rate constants of second-order and third-order reactions (k_1 and k_1k_3/k_2). Equation 6 suggests that the second- and third-order reaction rate constants can be evaluated, respectively, from the intercept and slope of the plot of $C_{Ai}^2D_AC_{BO}/N_A^2$ vs. $1/C_{BO}$. Figures 6 and 7 show such plots, and there appear linear relationships. The derived rate constants and second- and third-order reactions are shown in Table 5 for monoethanolamine solutions and Table 6 for diethanolamine solutions. For the sake of comparison, in the same tables are also listed the reaction rate constants derived in earlier works.

TABLE 5. RATE PARAMETERS FOR REACTION BETWEEN CARBON DIOXIDE AND MONOETHANOLAMINE IN AQUEOUS AND ALCOHOLIC SOLUTIONS

Solvent	Investigators	Amine Conc. mol/dm^3	Reaction Temp., K	$k_1\times10^{-6}$ cm^3/mol·s	$k_1k_3/k_2\times10^{-9}$ cm^6/mol^2·s	$k_2/k_3\times10^3$ mol/cm^3
Water	Hikita et al (1977)	0.0152–0.177	303	7.72	$\gg k_1$	—
	Alvarez-Fuster et al. (1980)	0.20–2.02	293	4.3	$\gg k_1$	—
	Laddha and Danckwerts (1981)	0.49–1.71	298	5.87	$\gg k_1$	—
	Present Work	0.5–2.0	303	7.74	$\gg k_1$	—
Methanol	Present Work	0.5–2.0	303	8.33	6.49	1.28
Ethanol	Alvarez-Fuster et al. (1981)	0.2–1.0	293	$\gg k_1k_3/k_2$	2.87	
	Present Work	0.5–2.0	303	8.33	2.91	2.86
2-Propanol	Present Work	0.5–2.0	303	8.33	2.28	3.66

Table 6. Rate Parameters for Reaction Between Carbon Dioxide and Diethanolamine in Aqueous and Alcoholic Solutions

Solvent	Investigators	Amine Conc. mol/dm^3	Reaction Temp., K	$k_1 \times 10^{-6}$ cm^3/mol·s	$k_1k_3/k_2 \times 10^{-9}$ cm^6/mol^2·s	$k_2/k_3 \times 10^3$ mol/cm^3
Water	Hikita et al. (1977)	0.174–0.719	303	$\gg k_1k_3/k_2$	1.79	—
	Alvarez-Fuster et al. (1980)	0.25–0.82	293	$\gg k_1k_3/k_2$	0.84	—
	Laddha and Danckwerts (1981)	0.46–2.88	298	1.41	1.20	1.18
	Present Work	0.5–1.5	303	1.10	1.32	0.83
Methanol	Present Work	0.5–1.5	303	0.34	0.34	1.0
Ethanol	Alvarez-Fuster et al. (1981)	0.3–2.2	293	$\gg k_1k_3/k_2$	0.13	
	Present Work	0.5–1.5	303	0.29	0.20	1.4
2-Propanol	Present Work	0.5–1.5	303	0.24	0.18	1.3

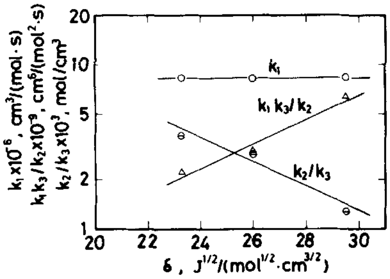


Figure 8. Relationships between reaction rate parameters and solubility parameter of the solvent for carbon dioxide-monoethanolamine.

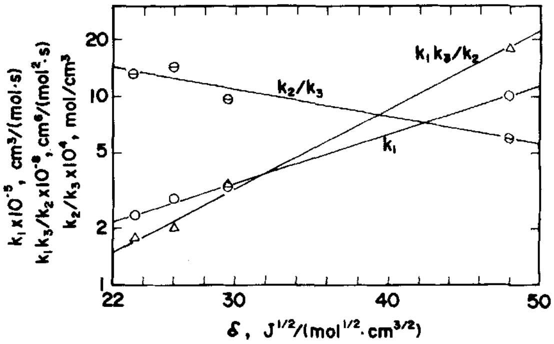


Figure 9. Relationships between reaction rate parameters and solubility parameter of the solvent for carbon dioxide-diethanolamine.

The apparent order of reaction with respect to monoethanolamine depends on the solvent species. As shown in Table 4, the reaction order varies from ~1.0 (for water) to 1.90 (for 2-propanol) in the reverse order of the solvent polarity. As monoethanolamine is a strong base that can be easily ionized in water and almost every zwitterion is deprotonated before it reverts to carbon dioxide and amine, the order of reaction with respect to monoethanolamine in water is close to unity. In nonaqueous solvents, the deprotonation is not so easy as in water. Table 5 shows that k_2/k_3 is increased in the order of methanol, ethanol, and 2-propanol. Accordingly, the apparent order of reaction with respect to amine increases first to second in the same order. For diethanolamine, the values of k_1 and k_1k_3/k_2 are considerably smaller than those of monoethanolamine because of base weakness and the fact that the approach of a carbon dioxide molecule to the nitrogen in diethanolamine and the deprotonation of the zwitterion are difficult. The apparent order of reaction with respect to diethanolamine depends on the solvent species and is increased in the order of water, methanol, ethanol, and 2-propanol.

The rate constant of organic reaction in a solvent generally reflects 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 those, some measures have a linear relation to the solubility parameter of the solvent. Then the logarithms of the second-order rate constant (k_1), the third-order reaction rate constant (k_1k_3/k_2), and k_2/k_3 were plotted against the solubility parameter of the solvent. Figures 8 and 9 show those relationships for mono- and diethanolamine, respectively. There are almost linear relationships, though the logarithm of k_1 for monoethanolamine is independent of the solubility parameter. In those figures the logarithms of both second-order reaction rate constant and the third-order reaction rate constant increase linearly with the solubility parameter of the solvent (δ), while the logarithm of k_2/k_3 decreases linearly with δ. As there is a good linear relationship between solubility parameter and dielectric constant (ϵ) of the solvent, it follows that both the logarithms of k_1 and k_1k_3/k_2 are increased with ϵ and the logarithm of k_2/k_3 is decreased linearly with ϵ. The value of k_1 for monoethanolamine is constant (8.33×10^6 cm^3/mol·s) irrespective of the solvent. The rate constant of the second-order reaction in water can be determined to be 7.74×10^6 cm^3/mol·s in Figure 5 (7.80×10^6 cm^3/mol·s) by Hikita et al. (1977) and is close to those for alcohols.

NOTATION

C = concentration in liquid phase, mol/dm^3 or mol/cm^3

D = diffusivity in liquid phase, cm^2/s

H = Henry's law constant, Pa·cm^3/mol

k^o_{LA} = physical liquid-side mass transfer coefficient of solute gas, cm/s

$\sqrt{M}$ = reaction-diffusion modulus defined by

$$\sqrt{\frac{2}{m+1} k_{m,n} C^n_{BO} C^{m-1}_{Ai} / k^o_{LA}}$$

N_A = absorption rate of solute gas, mol/s·cm^2

$k_1, k_2, k_3, k_{m,n}$ = reaction rate constants defiend in Eqs. iii, iv, and 8

p = partial pressure, Pa

r = rate of reaction between carbon dioxide and amine in aqueous and alcoholic solutions, mol/s·cm^3
t_c = gas-liquid contact time, s
z = distance into liquid phase from gas-liquid interface, cm
z_L = thickness of liquid film in film theory concept, cm

Greek Letter

δ = solubility parameter of solvent, J$^{1/2}$/mol$^{1/2}$·cm$^{3/2}$
ϵ = dielectric constant of solvent
ν = stoichiometric coefficient appearing in the reaction $A + \nu B \rightarrow$ products
Φ = enhancement factor
Φ_∞ = enhancement factor for an instantaneous reaction defined by $1 + (D_B/D_A)(C_{BO}/\nu C_{Ai})$ for film theory

Subscripts

A = solute gas component (carbon dioxide or nitrous oxide)
B = liquid phase reactant (amine)
i = gas-liquid interface
m,n = order of reaction with respect to carbon dioxide and amine, respectively
O = bulk liquid phase

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