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Absorption of Carbon Dioxide into Aqueous Monoethanolamine Solutions

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The rates of absorption of pure carbon dioxide into aqueous monoethanolamine solutions with a surface active agent were measured at 15°, 25°, 35°, and 45°C in a liquid jet column and a wetted wall column. Experimental results were analyzed with the chemical absorption theory based on the penetration model. Physical solubility of carbon dioxide in aqueous monoethanolamine solutions was determined from the absorption rates measured in a near pseudo first-order reaction regime and was shown to be considerably larger than the physical solubility in water. The measured absorption rates were in good agreement with the theoretical predictions for gas absorption with an irreversible second-order reaction, when the variation of the physical solubility of carbon dioxide due to the change in the composition of the solution during the absorption process was taken into account.

SCOPE

The absorption of carbon dioxide from gas mixtures by aqueous monoethanolamine solutions is an important industrial process. Despite a considerable number of studies, severe disagreements exist between the previous experimental data on the absorption rate of carbon dioxide into aqueous monoethanolamine solutions and the theoretical predictions. These disagreements are attributed partly to interfacial turbulence due to Marangoni instability as suggested by Brian et al. (1967). They showed that the use of the physical mass transfer coefficient measured under conditions where the interfacial turbulence was present resulted in a considerable improvement in the agreement between the experimental data on the absorption rate of carbon dioxide into aqueous monoethanolamine solutions in a short wetted wall column and the chemical absorption theory based on the penetration model. However, it appears that this agreement is not satisfactory. Recently, Sada et al. (1976, 1977*b*) have measured the absorption rate of carbon dioxide into aqueous monoethanolamine solutions in laminar liquid jet and wetted wall column absorbers under conditions where the interfacial turbulence was suppressed by adding trace amounts of surface active agent to the solutions and concluded that the measured absorption rates were in good agreement with the theoretical predictions based on the penetration model. However, the value of the rate constant of the reaction between carbon dioxide and monoethanolamine, employed for the analysis of the experimental results, was obtained from the absorption rate data taken under pseudo first-order reaction conditions and is considerably higher than that obtained by the conventional kinetic method.

The purposes of the study described here are to obtain reliable data on the absorption rate of carbon dioxide into aqueous uncarbonated and partly carbonated monoethanolamine solutions under the conditions of no interfacial turbulence and to clarify the kinetics of chemical absorption for the present system.

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CONCLUSIONS AND SIGNIFICANCE

Experiments have been carried out on the absorption of pure carbon dioxide into uncarbonated and partly carbonated monoethanolamine solutions with a small amount of a surface active agent using a liquid jet column and a wetted wall column. In some additional experiments, carbon dioxide has also been absorbed into uncarbonated monoethanolamine solutions without surface active agent in a liquid jet column at 25°C. The measured rates of absorption into the solution without surface active agent were higher than those into the solution with surface active agent, presumably owing to interfacial turbulence driven by surface tension gradients during the chemical absorption process, as first found by Brian et al. (1967). Therefore, the absorption rates obtained for the solutions with surface active agent were used to clarify the chemical absorption mechanism of the present system. The experimental results were analyzed with the chemical absorption theory based on the penetration model.

The physical solubility of carbon dioxide in aqueous monoethanolamine solutions was determined from the absorption rates measured near the pseudo first-order reaction regime by fitting the experimental data to the theoretical equations. This was found to be considerably larger than the physical solubility of carbon dioxide in water. The absorption rates obtained with uncarbonated monoethanolamine solutions were in good agreement with the theoretical predictions for gas absorption accompanied by an irreversible second-order reaction with a stoichiometric coefficient of 2, if the variation of the physical solubility of carbon dioxide due to the change in the composition of the solution during the absorption process was taken into account. On the other hand, absorption of carbon dioxide into partly carbonated monoethanolamine solutions was treated as chemical absorption accompanied by a reversible reaction having a large value of equilibrium constant, and the observed absorption rates agreed with those predicted from the theory.

CHEMICAL ABSORPTION MECHANISM

When carbon dioxide is absorbed into aqueous MEA (monoethanolamine) solutions, the following two overall reactions should be considered (Astarita et al., 1964; Danckwerts and McNeil, 1967):

$$CO_2 + 2RNH_2 \rightleftharpoons RNH_3^+ + RNHCOO^- \tag{1}$$

$$CO_2 + RNHCOO^- + 2H_2O \rightleftharpoons RNH_3^+ + 2HCO_3^- \tag{2}$$

where R refers to $HOCH_2CH_2$. At very short exposure times of the liquid to the gas encountered in industrial absorbers, the effect of reaction (2) can be neglected, and only reaction (1) affects the absorption rate of carbon dioxide (Sada et al., 1976). Reaction (1) takes place in two steps:

$$CO_2 + RNH_2 \rightleftharpoons H^+ + RNHCOO^- \tag{3}$$

$$H^+ + RNH_2 \rightleftharpoons RNH_3^+ \tag{4}$$

The equilibrium constants of reactions (3) and (4) are of the order of 10^{-5} and 10^{10} 1/g-mole, respectively (Danckwerts and McNeil, 1967). The second-step reaction (4) is ionic and virtually instantaneous, whereas the first-step reaction (3) is second order, that is, first order with respect to both carbon dioxide and MEA, and is rate controlling. Thus, the overall reaction (1) can be treated as an irreversible second-order reaction with a stoichiometric coefficient of 2, the equilibrium constant being of the order of 10^5 1/g-mole.

When the absorption of solute gas A is accompanied by an irreversible reaction, the average rate of absorption N_A is represented by

$$N_A = \beta(2\sqrt{D_A/\pi t})A_i \tag{5}$$

For absorption with a second-order reaction of the form A + 2B → products, the penetration model solution for the reaction factor can be closely approximated by the following equation (Hikita and Asai, 1963; 1964):

$$\beta = \left(\gamma\eta + \frac{\pi}{8\gamma\eta}\right)\mathrm{erf}\left(\frac{2\gamma\eta}{\sqrt{\pi}}\right) + \frac{1}{2}\exp\left(-\frac{4\gamma^2\eta^2}{\pi}\right) \tag{6}$$

where γ is a dimensionless parameter defined as

$$\gamma = (\sqrt{\pi}/2)\sqrt{kB_0 t} \tag{7}$$

and η is also a dimensionless parameter given by

$$\eta = \sqrt{B_i/B_0} \tag{8a}$$

$$= \sqrt{(\beta_\infty - \beta)/(\beta_\infty - 1)} \tag{8b}$$

Here β_∞ represents the reaction factor for absorption with an instantaneous reaction and can be obtained from (Danckwerts, 1950):

$$\beta_\infty = 1/\mathrm{erf}(\sigma) \tag{9}$$

$$\mathrm{erfc}(\sqrt{D_A/D_B}\,\sigma)\exp[(D_A/D_B - 1)\sigma^2] = \sqrt{D_B/D_A}(B_0/2A_i)\mathrm{erf}(\sigma) \tag{10}$$

If carbon dioxide is absorbed into highly carbonated MEA solutions, the liquid bulk concentration A_0 of free carbon dioxide is not negligible compared to its interfacial concentration A_i, and reaction (1) can no longer be regarded as irreversible. In this case, the absorption rate is given by

$$N_A = \beta(2\sqrt{D_A/\pi t})(A_i - A_0) \tag{11}$$

and the reaction factor can be approximated by Equations (6) to (8*b*) (Danckwerts and McNeil, 1967), if the value given by the following equation is used as β_∞ in Equation (8*b*):

$$\beta_\infty = 1 + \sqrt{\frac{D_B}{D_A}}\left(\frac{B_0}{2A_i}\right)\frac{1}{1 + \sqrt{A_0/A_i}} \tag{12}$$

This equation was derived by Hikita et al. (1971) for absorption with an instantaneous reversible reaction of

Table 1. Compositions of Aqueous MEA Solutions Used

Solution	Temp., °C	Total MEA conc., g-mole/l	Total CO_2 conc., g-mole/l	Carbonation ratio, α	Free MEA conc., B_0, g-mole/l	RNH_3^+ conc., g-ion/l	$RNHCOO^-$ conc., g-ion/l	CO_3^{2-} conc. $\times 10^3$, g-ion/l	HCO_3^- conc., g-ion/l	OH^- conc. $\times 10^5$, g-ion/l	Equil. press. of CO_2, p_A, mmHg
a	25	0.125	0	0	0.125	0	0	0	0	0	0
b	25	0.25	0	0	0.25	0	0	0	0	0	0
c	25	0.50	0	0	0.50	0	0	0	0	0	0
d	25	1.0	0	0	1.0	0	0	0	0	0	0
e	25	2.0	0	0	2.0	0	0	0	0	0	0
f	15	1.0	0	0	1.0	0	0	0	0	0	0
g	35	1.0	0	0	1.0	0	0	0	0	0	0
h	45	1.0	0	0	1.0	0	0	0	0	0	0
i	15	2.0	0	0	2.0	0	0	0	0	0	0
j	35	2.0	0	0	2.0	0	0	0	0	0	0
k	45	2.0	0	0	2.0	0	0	0	0	0	0
l	25	2.0	0.52	0.26	0.969	0.522	0.509	1.62	0.0105	5.94	0
m	25	2.0	0.82	0.41	0.399	0.822	0.779	1.57	0.0391	1.55	0
n	25	2.0	1.04	0.52	0.0972	1.041	0.861	1.37	0.177	0.299	8.8
o	25	2.0	1.44	0.72	0.0123	1.441	0.547	0.630	0.893	0.0272	330

the form $A + 2B \rightleftharpoons E + F$ with a very large equilibrium constant.

EXPERIMENTAL

Apparatus and Procedure

Absorption experiments were carried out using a liquid jet column and a wetted wall column.

The liquid jet column was similar to that used by Hikita et al. (1968, 1973, 1976, 1977*a*) in previous work. The laminar liquid jet was formed by a bell shaped glass nozzle with an exit diameter of 1.16 mm. The exposure time of the liquid to the gas was varied from 0.0010 to 0.023 s by changing the liquid flow rate and the jet length. Absorption rate was determined volumetrically by means of a soap-film meter.

The wetted wall column used in this study was of a modified form and was the same as that used by Hikita et al. (1967, 1976) in previous work. The exposure time was varied from 0.052 to 1.07 s by changing the liquid flow rate and the film height. Absorption rate was again measured by means of a soap-film meter.

All the experiments were conducted at atmospheric pressure and at 15°, 25°, 35°, and 45°C. The gas phase was always pure carbon dioxide saturated with water vapor at the temperature of the experiment. The absorbents used were aqueous solutions of uncarbonated and partly carbonated MEA. The partly carbonated MEA solutions were obtained by bubbling carbon dioxide into uncarbonated MEA solutions and prepared at least 24 hr before starting the experimental runs in order to ensure that the solutions were in equilibrium. To prevent rippling on the falling liquid film and to suppress the interfacial turbulence due to Marangoni effect, 0.01 to 0.05 vol % of a surface active agent, Scourol 100 (Kao-Atlas Co.), was added to the absorbent. In the experiments with the liquid jet column, the absorbents without surface active agent were also used to check the presence of the interfacial turbulence.

The total MEA concentration in the solution was determined by titrating the liquid sample with standard hydrochloric acid by use of methylorange as an indicator. The total carbon dioxide concentration was determined by adding sulfuric acid solution to the sample and measuring the volume of evolved carbon dioxide gas by means of a gas burette. The concentrations of free MEA and various ionic species, such as RNH_3^+, $RNHCOO^-$, CO_3^{2-}, HCO_3^-, and OH^- ions, were calculated from the measured concentrations of total MEA and total carbon dioxide using the calculated results by Astarita et al. (1963). The equilibrium partial pressure of carbon dioxide over partly carbonated MEA solutions was estimated from the data of Mason and Dodge (1936). The compositions of the solutions are given in Table 1.

Results

Experimental results for the absorption of carbon dioxide into aqueous solutions of uncarbonated MEA with and without surface active agent obtained at 25°C in the liquid jet column are shown in Figure 1, where the average absorption rate N_A of carbon dioxide is plotted against the exposure time t on logarithmic coordinates. It can be seen that the absorption rate into the solution without surface active agent, in general, is higher than that into the solution with surface active agent, and that the difference between the both absorption rates becomes larger as the MEA concentration and the exposure time increase. This higher absorption rate observed in the case of the solution without surface active agent may be attributed to interfacial turbulence, presumably produced by surface tension gradients during the chemical absorption process, as found by Brian et al. (1967) and Sada et al. (1977*b*) for the present system and by Hikita et al. (1968, 1971, 1977*a*) for the other

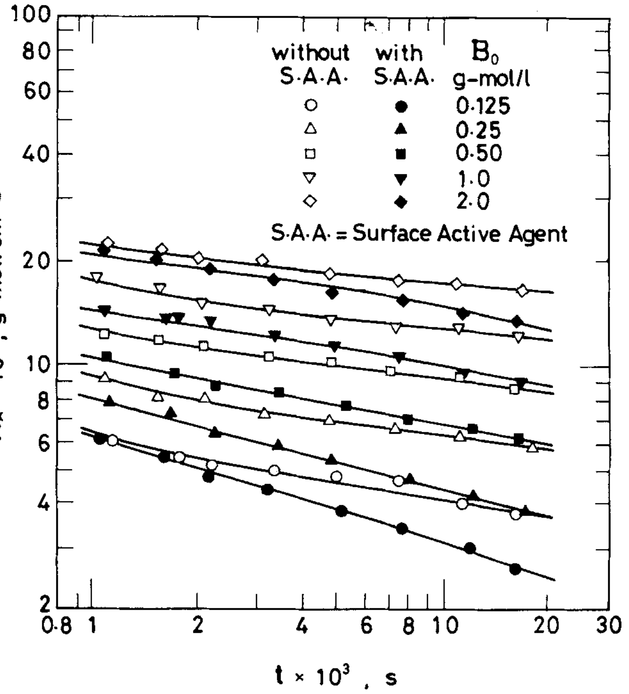

Fig. 1. Absorption rate of carbon dioxide into aqueous uncarbonated MEA solutions with and without surface active agent in a liquid jet column at 25°C.

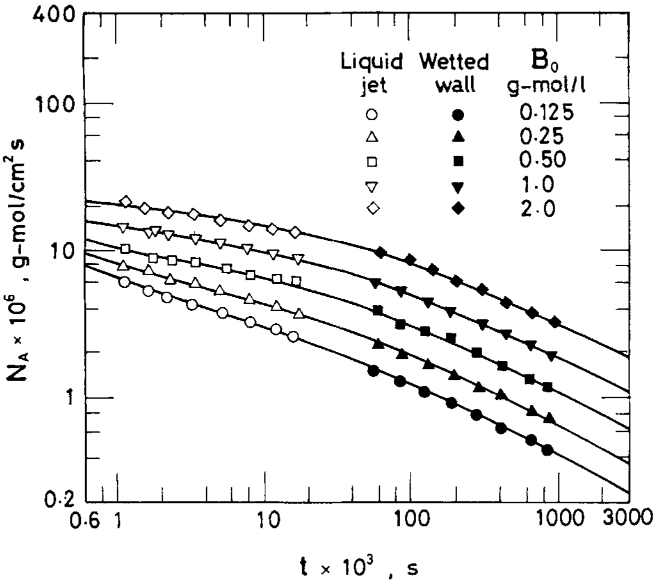

Fig. 2. Absorption rate of carbon dioxide into aqueous uncarbonated MEA solutions at 25°C.

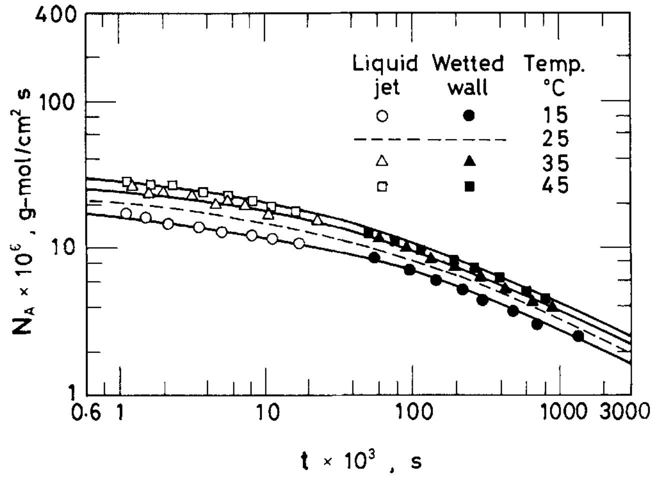

Fig. 3. Absorption rate of carbon dioxide into 2.0 g-mole/l aqueous uncarbonated MEA solution at 15°, 35°, and 45°C.

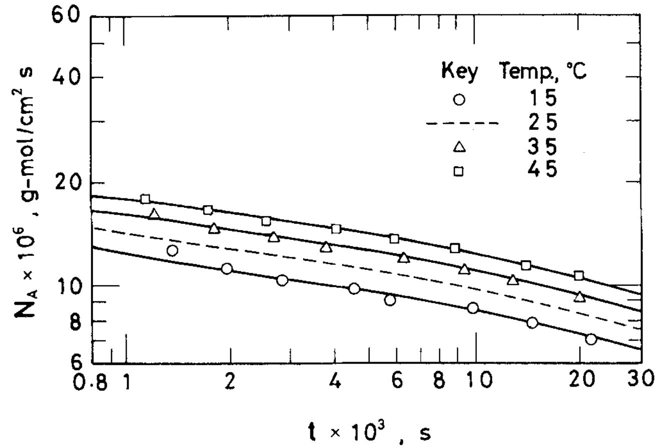

Fig. 4. Absorption rate of carbon dioxide into 1.0 g-mole/l aqueous uncarbonated MEA solution in a liquid jet column at 15°, 35°, and 45°C.

gas-liquid systems. Therefore, in comparing the experimental results with the chemical absorption theory, the data obtained for the solutions with surface active agent were employed. These data are shown in Figures 2 to 5. Figures 2, 3, and 4, and 5 represent the effects of the MEA concentration, temperature, and the carbonation ratio on the absorption rate, respectively.

DISCUSSION OF RESULTS

Prediction of Physical Properties

In order to compare the experimental results with the theoretical equations described above, it is necessary to know the values of the physical properties such as A_i, D_A, D_B, k, etc. of the present system. These physical properties except A_i were assumed to be constant and were evaluated under the condition of an irreversible pseudo first-order reaction, that is, approximately for the composition of the feed solution.

The liquid phase diffusivity D_A of carbon dioxide in aqueous MEA solutions was predicted from the value of 1.97×10^{-5} cm^2/s, measured at 25°C for carbon dioxide in water (Peaceman, 1951), by correcting for the temperature and viscosity of the solution according to the well-known Stokes-Einstein relation. The ratio of the liquid phase diffusivity of MEA to that of carbon dioxide, that is, D_B/D_A, was assumed to be equal to that in water and to be independent of temperature. The estimated value of D_B/D_A was 0.558 which was evaluated at 25°C using the D_B value of 1.10×10^{-5} cm^2/s measured at 25°C for MEA in water (Thomas and Furzer, 1962).

The forward second-order reaction rate constant k of reaction (1) was calculated from the empirical equation

$$\log k = 10.99 - 2\,152/T \qquad (13)$$

which correlates well the data obtained by Hikita et al. (1977*b*) using a conventional kinetic method. Several investigators (Clarke, 1964; Sharma, 1964, 1965; Leder, 1971; Sada et al., 1976) have also reported the values of k for the present system. These k values were obtained from absorption rate measurements in pseudo first-order

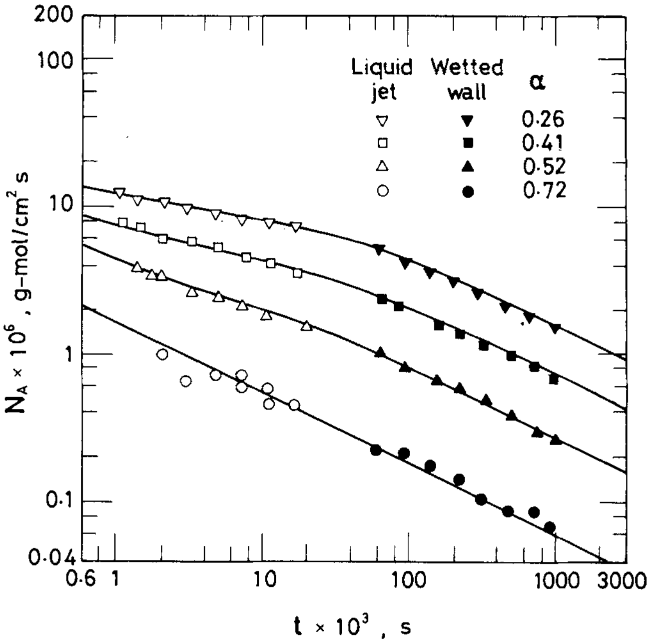

Fig. 5. Absorption rate of carbon dioxide into aqueous partly carbonated MEA solutions at 25°C.

reaction regime and are 19 to 42% higher than those given by Equation (13). This discrepancy may be attributed partly to the underestimate of the physical solubility of carbon dioxide in aqueous MEA solutions which was used in the analysis of the absorption rate data, as described below, and partly to the interfacial turbulence driven by surface tension gradients, as described above. Equation (13) is based on the data, which are completely free from such uncertain factors, and is believed to give the most reliable k values.

There is presently neither an adequate theory nor a useful empirical correlation for predicting the solubility of the gas in nonelectrolyte solutions. Thus, in the previous work, most of the investigators (Astarita, 1964; Clarke, 1964; Sharma, 1964; Brian et al., 1967; Danckwerts and McNeil, 1967) have assumed that the physical solubility of carbon dioxide in aqueous MEA solutions is the same as that in water. Recently, Sada et al. (1976) have estimated the solubility of carbon dioxide in aqueous MEA solutions from the measured solubilities of nitrous oxide and ethylene in the same solutions (Sada and Kito, 1972) by correcting for the differences in the contributions of solute gases to the salting out parameters in the same manner as in the case of electrolyte solutions. Their estimated solubility of carbon dioxide in aqueous MEA solutions shows a salting out effect.

In the present work, the physical solubility A_i of carbon dioxide in aqueous MEA solutions was determined from the absorption rates N_A measured at very short exposure times in a liquid jet column using Equations (5) to (10) and the physical properties predicted by the methods described above. The absorption rate data obtained under the conditions where the depletion of MEA at the gas-liquid interface is less than 30%, that is, $B_i/B_0 > 0.70$, were used in calculating the A_i values. Figure 6 shows a semilogarithmic plot of the carbon dioxide solubility in aqueous MEA solutions determined in this manner against the interfacial MEA concentration B_i. As can be seen in this figure, the carbon dioxide solubility in aqueous MEA solutions is much larger than that in water at high MEA concentrations. Such a salting in effect is not so unusual. Sada and Kito (1972) and Sada et al. (1977*a*, 1978) have reported that the physical solubilities of ethylene and acetylene in aqueous solutions of various amines increase with increasing amine concentration. Hikita et al. (1971) have observed the salting in effect for the physical solubility of carbon dioxide in aqueous ammonia solutions. The salting in effect for the present system is of the same magnitude as that for the carbon dioxide-aqueous ammonia solution system. The evaluated values of A_i were well correlated by

$$\log\left(\frac{A_i}{A_{iw}}\right) = \frac{0.3\,B_i}{1 + \kappa B_i} \tag{14}$$

The value of A_{iw} was taken from the book of Linke and Seidell (1958). The values of κ at 15°, 25°, 35°, and 45°C were found to be 1.75, 0.963, 0.821, and 0.781, respectively. The solid lines in Figure 6 represent Equation (14).

In this work, the value of the carbon dioxide solubility A_i in aqueous MEA solutions under the pseudo first-order reaction regime A_{i1} was estimated from Equation (14). Under the instantaneous reaction regime, an aqueous $RNH_3OOCHNR$ ($RNH_3^+ + RNHCOO^-$) solution exists in the region between the gas-liquid interface and the reaction plane. Therefore, the value of the carbon dioxide solubility in this solution, A_{i2}, should be taken as the A_i value and can be estimated from

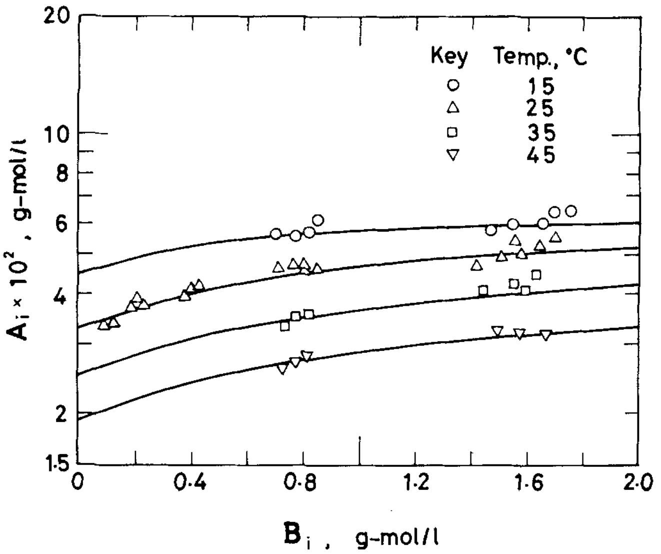

Fig. 6. Physical solubility of carbon dioxide in aqueous uncarbonated MEA solutions.

$$\log(A_i/A_{iw}) = -k_s I \tag{15}$$

with

$$k_s = i_g + i_+ + i_- \tag{16}$$

The salting out parameter k_s for the reaction product $RNH_3OOCHNR$ is not known and was assumed to be zero. A similar assumption was adopted in the previous work (Hikita et al., 1971) for the analysis of the carbon dioxide-ammonia system and was found to introduce an insignificant error.

In the case of the partly carbonated MEA solutions, there exists RNH_3^+, $RNHCOO^-$, HCO_3^-, CO_3^{2-}, and OH^- ions together with RNH_2 in the solution, the concentrations being given in Table 1, and hence the salting out effects due to these ionic species should be taken into account in predicting the A_i values. The carbon dioxide solubility in partly carbonated MEA solutions under the pseudo first-order reaction regime A_{i1} was estimated from

$$\log\left(\frac{A_i}{A_{iw}}\right) = \frac{0.3\,B_i}{1 + \kappa B_i} - \Sigma k_s I \tag{17}$$

The contribution i_+ of RNH_3^+ ions was assumed to be equal to i_+ of NH_4^+ ions. The values of i for carbon dioxide and NH_4^+, OH^-, CO_3^{2-}, and HCO_3^- ions were taken from the data of van Krevelene and Hoftijzer (1948) and of Hikita et al. (1974). The carbon dioxide solubility in partly carbonated MEA solutions under the instantaneous reaction regime A_{i2} was calculated from Equation (17) without the first term on the right-hand side.

The estimated value of the carbon dioxide solubility under the instantaneous reaction regime is considerably different from that under the pseudo first-order reaction regime. Therefore, in the present study, the variation of the A_i value due to the change in the interfacial composition of the solution with the exposure time of the liquid to the gas was taken into account.

The bulk concentration of unreacted carbon dioxide in partly carbonated MEA solutions, A_0, was predicted from Equation (17) using the value of A_{iw} corresponding to the equilibrium partial pressure of carbon dioxide p_A and the value of the free MEA concentration B_0.

The predicted values of the physical properties for the uncarbonated and partly carbonated MEA solutions are listed in Table 2.

Table 2. Physical Properties for Carbon Dioxide-Aqueous MEA Solution System

Solution	B_0, g-mole/l	$A_0 \times 10^2$, g-mole/l	$A_{i1} \times 10^2$, g-mole/l	$A_{i2} \times 10^2$, g-mole/l	$D_A \times 10^5$ cm²/s	k 1/(g-mole) (s)
a	0.125	0	3.55	3.28	1.94	5 930
b	0.25	0	3.77	3.28	1.91	5 930
c	0.50	0	4.15	3.28	1.82	5 930
d	1.0	0	4.67	3.28	1.63	5 930
e	2.0	0	5.27	3.28	1.35	5 930
f	1.0	0	5.75	4.47	1.22	3 330
g	1.0	0	3.65	2.50	2.22	10 200
h	1.0	0	2.85	1.94	2.85	19 600
i	2.0	0	6.08	4.47	1.01	3 330
j	2.0	0	4.21	2.50	1.98	10 200
k	2.0	0	3.32	1.94	2.60	16 900
l	0.969	0	4.63	3.27	1.25	5 930
m	0.399	0	3.96	3.24	1.21	5 930
n	0.0972	0.0394	3.31	3.11	1.18	5 930
o	0.0123	1.48	2.52	2.50	1.14	5 930

$D_B/D_A = 0.588$

Calculation of Theoretical Absorption Rates

The relation between the theoretical absorption rate N_A and the exposure time t can be easily obtained by the following procedure:

1. Assign a value of B_i within the range of 0 to B_0 for a given MEA solution.
2. Estimate the value of A_i from Equation (17).
3. Calculate the value of β_∞ from Equations (9) and (10) for the case of $A_0/A_i = 0$ or from Equation (12) for the case of $A_0/A_i \neq 0$.
4. Substitute the value of B_i into Equation (8*a*) to obtain the value of η.
5. Calculate the value of β from Equation (8*b*).
6. Determine the value of $\gamma\eta$ from Equation (6).
7. Divide the value of $\gamma\eta$ by the value of η to get the value of γ.
8. Evaluate the value of t from Equation (7).
9. Substitute the values of t, A_i, β, and A_0 into Equation (11) to obtain the value of N_A.
10. Repeat steps 1 to 9 for various values of B_i.

Comparison of Experimental Results with Theory

Figure 7 shows the comparison of the measured absorption rates of carbon dioxide into uncarbonated 2.0 g-mole/l MEA solution containing surface active agent at 25°C with the theoretical absorption rates calculated from Equations (5) to (10). In this figure, the dashed and dash-dot lines represent the theoretical lines for the case of constant A_i equal to the values in the pseudo first-order reaction regime and the instantaneous reaction regime A_{i1} and A_{i2}, respectively. On the other hand, the solid line shows the theoretical line for the case where the variation of A_i during the absorption process is taken into account. It can be seen that the measured absorption rates are in good agreement with the solid line. The theoretical lines for the case of varying A_i are shown in Figures 2 to 4 as solid lines and compared with the measured absorption rates of carbon dioxide into uncarbonated MEA solutions. The agreement of the measured absorption rates with the theoretical lines is fairly good. In Figure 5, a similar comparison between the theoretical and measured absorption rates of carbon dioxide into partly carbonated MEA solutions at 25°C is shown. The measured absorption rates agree well with the theoretical lines calculated from Equations (11), (6) to (8), and (12), taking into account the variation of A_i during the absorption process.

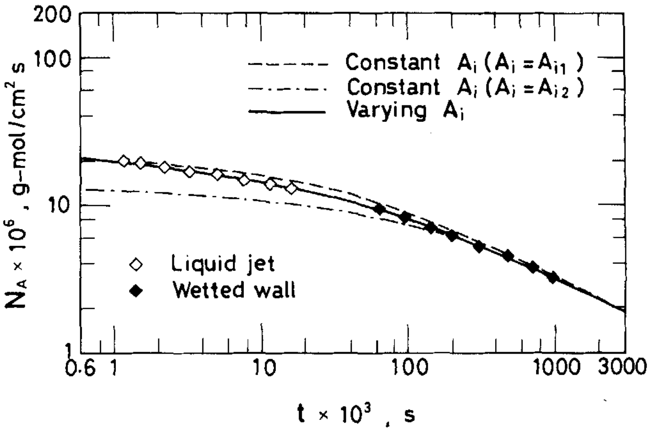

Fig. 7. Comparison between measured and calculated absorption rates of carbon dioxide into 2.0 g-mole/l aqueous uncarbonated MEA solution at 25°C.

In Figure 8, the experimental data of Sada et al. (1976) on the absorption rate of carbon dioxide into uncarbonated MEA solutions containing surface active agent in a liquid jet column and a wetted wall column at 25°C are compared with the theoretical predictions. The

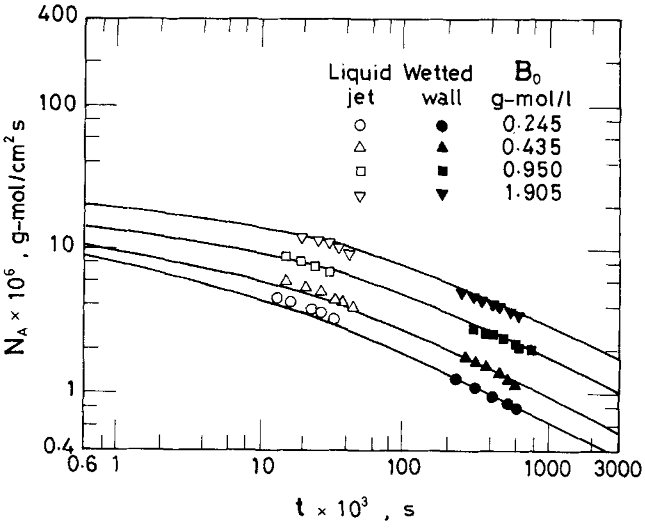

Fig. 8. Comparison of data of Sada et al. with theoretical predictions.

solid lines are the theoretical lines calculated from Equations (5) to (10) using the values of the physical properties estimated in the same manner as used in the present work and taking into account the variation of the A_i value during the absorption process. The measured absorption rates are in good agreement with the theoretical lines.

From the results described above, it may be concluded that under the conditions of no interfacial turbulence, the absorption of carbon dioxide into aqueous uncarbonated MEA solutions can be treated as absorption accompanied by an irreversible second-order reaction represented by the forward part of reaction (1) if the variation of the physical solubility of carbon dioxide due to the change in the interfacial composition of the solution during the absorption process is taken into account. It may also be concluded that the absorption of carbon dioxide into aqueous partly carbonated MEA solutions can be regarded as absorption accompanied by a reversible reaction represented by reaction (1) having a large value of equilibrium constant.

NOTATION

A_i = interfacial concentration or physical solubility of carbon dioxide in solution, g-mole/l
A_{iw} = physical solubility of carbon dioxide in water, g-mole/l
A_0 = concentration of unreacted carbon dioxide in bulk of solution, g-mole/l
B_i = interfacial concentration of MEA in solution, g-mole/l
B_0 = concentration of MEA in bulk of solution, g-mole/l
D_A = liquid phase diffusivity of carbon dioxide in solution, cm^2/s
D_B = liquid phase diffusivity of MEA in solution, cm^2/s
I = ionic strength of aqueous electrolyte solution, g-ion/l
i_g, i_+, i_- = contributions of solute gas, positive ions, negative ions to salting out parameter, 1/g-ion
k = second-order reaction rate constant of reaction (1), 1/(g-mole) (s)
k_s = salting out parameter, 1/g-ion
N_A = average absorption rate of carbon dioxide, g-mole/(cm^2) (s)
p_A = equilibrium partial pressure of carbon dioxide over partly carbonated MEA solutions, mmHg
T = absolute temperature of solution, °K
t = exposure time of liquid to gas, s

Greek Letters

α = carbonation ratio
β = reaction factor
β_∞ = reaction factor for the case when reaction (1) is instantaneous
γ = parameter defined by Equation (7)
η = parameter defined by Equation (8)
κ = constant in Equation (14)
σ = parameter to be determined from Equation (10)

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The Effect of Gas and Solids Maldistribution on the Performance of Moving-bed Reactors: The Reduction of Iron Oxide Pellets with Hydrogen

A mathematical formulation is presented describing the reduction of iron oxide pellets with hydrogen in a counterflow moving-bed arrangement under conditions such that both the gaseous and the solids streams may be maldistributed. This maldistribution is imposed on the system by prescribing a radial variation in the void fraction and the particle size, together with a radial variation in the axial velocity of the solid stream.

In the formulation, allowance has been made for realistic chemical kinetics and nonisothermal behavior. Computer results are presented for both the maldistributed system and for base line cases where uniform gas and solids flow have been postulated.

It was found that maldistribution may play a very marked role in affecting the performance of the system, in particular, when the gas and the solid streams are mismatched, for example, preferential flow of gas near the walls and preferential flow of solids in the central core.

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SCOPE

The countercurrent contacting of gaseous and solids streams in a packed-bed arrangement is of considerable practical interest in many materials processing operations (Yagi et al. 1968; Spitzer et al. 1968; Ishida and Wen 1971; Hara et al. 1976*a*, *b*). In the early work, it has been assumed that the axial velocity in the gaseous and solids streams was spatially uniform.

In recent work, Radestock and Jeschar (1970, 1971*a*, *b*), Stanek and Szekely (1972, 1973, 1974), and Szekely and Poveromo (1975) have shown that the postulate of spatially uniform velocity fields in packed beds may introduce serious errors. The effect of spatially nonuniform gas flows on the performance of moving packed-bed reactors has been studied very recently by Yagi and Szekely (1977*a*, *b*) and also by Kuwabara and Muchi (1976) who have shown that the overall conversion may indeed be affected quite markedly by the gas flow maldistribution. While these authors assumed a flat velocity profile for the solid stream, there are strong indications in the literature, notably due to the work of Chatlynne and Resnick (1973), Novosad and Surapati (1968), and Takahashi and Yanai (1973), that, in general, solids flow also tends to be maldistributed. In particular, for moving beds, the central portion of the solids would tend to move faster than the region close to the wall.

The purpose of this paper is to present a general formulation describing a reaction between a stream of particulate solids and a gas stream, contacted in a countercurrent moving-bed arrangement, under conditions that both the gaseous and the solid streams may be maldistributed. The particular system to be studied is the reaction between iron oxide pellets and hydrogen. The computed results will be compared with two sets of standard cases, corresponding to flat velocity profiles in both the gaseous and the solid streams and gas maldistribution with a flat solid velocity profile, respectively. As a result, a quantitative assessment will be presented of the part played by gas and solids flow maldistribution in affecting conversion in moving-bed reactors.

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