Chemical Kinetics of Carbon Dioxide Reactions With Diethanolamine and Diisopropanolamine in Aqueous Solutions

Differential rates of carbon dioxide absorption into aqueous monoethanolamine (MEA), diethanolamine (DEA), and diisopropanolamine (DIPA) were measured over a wide range of carbonation ratios. Analysis of the chemical-reaction-rate-controlled data showed that the chemical reaction rates for all three aminoalcohols are first order with respect to the free-amine concentration.

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SCOPE

Despite widespread use in gas treating of aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), and diisopropanolamine (DIPA) for regenerative CO_2 removal from gases, the underlying chemical reaction kinetics are not fully understood. It is generally agreed that the reaction of MEA with dissolved CO_2 proceeds by second-order kinetics, i.e., first order with respect to the free amine concentration. For the DEA reaction, however, serious discrepancies exist among results of recent studies. The reaction order with respect to the free DEA concentration was proposed to be unity, two, or intermediate between one and two. Danckwerts postulated that the change in kinetics from second order for MEA to third-order for DEA may originate from the increased steric requirements of DEA as compared with MEA. This postulate would thus predict that an amine with further increased steric crowding would give third-order kinetics. Accordingly, we undertook to examine the reaction of DIPA, an amine which is sterically more crowded than DEA. For this purpose, CO_2 absorption rates into 1–3 molar aqueous solutions of MEA, DEA, DIPA were measured at 323 K using a single-sphere absorber. The chemical-reaction-controlled absorption rate data, obtained over a wide range of carbonation ratios, were then analyzed to determine the chemical kinetics.

CONCLUSION AND SIGNIFICANCE

The rates of CO_2 absorption at 323 K into 2 and 3M DEA and 1M DIPA solutions were found to be chemical-reaction-rate-controlled. A thermodynamic model was derived to estimate the free amine concentrations at various carbonation ratios. The absorption rate results were rigorously analyzed using Danckwerts' theoretical model. The resultant chemical reaction rates showed dependencies on the free amine concentration to the power of 1.13 in the DEA system and 0.93 in the DIPA system. This result shows that the order of chemical reaction with respect to the free amine concentration is close to unity for both DEA and DIPA. Thus, the present study suggests that MEA, DEA, and DIPA all follow the same kinetics. No evidence for shifting to higher-order kinetics owing to increasing steric crowding of the amine structure was observed.

BACKGROUND

The removal of CO_2 from gases by regenerative absorption into aqueous amine solutions is an important industrial process. The gas-liquid mass transfer aspect was treated quantitatively by Danckwerts (1970), who established a theory correlating the absorption rate from the gas phase with chemical reaction rate in solution. Among industrially important amines, diethanolamine (DEA) is perhaps the most widely studied system.

The chemical kinetics of the DEA-CO_2 reaction have been scrutinized by various techniques. These include analysis of competitive CO_2-OH^- and CO_2-DEA reactions (Jensen et al., 1954; Jorgensen, 1956); deduction from mass transfer data using theoretical models (Sharma, 1965; Danckwerts and Sharma, 1966; Sada et al., 1976; Alvarez-Fuster et al., 1980; Hikita et al., 1980; Laddha and Danckwerts, 1981); direct measurements using a rapid-mix method (Coldrey and Harris, 1976; Hikita et al., 1977); and analysis of CO_2 transport across a membrane containing a DEA solution (Donaldson and Nguyen, 1980). The results of these investigations are, however, not consistent. Serious discrepancies exist both in terms of the magnitude of the rate and the order of reaction with respect to amine concentration. As pointed out by Danckwerts (1979) the inconsistencies in the DEA system are puzzling in light of the generally good agreement among results for the monoethanolamine (MEA) system which were obtained in parallel experiments with DEA.

Several previous studies led to the conclusion that the order of chemical reaction with respect to amine concentration changes from unity for MEA to two for DEA. A possible explanation of this result has been given (Danckwerts, 1979; Laddha and Danckwerts, 1981) in terms of changing rate determining step in the following scheme:

$$R_2NH + CO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2\overset{+}{N}HCO_2^- \qquad (1)$$

$$R_2\overset{+}{N}HCO_2^- + R_2NH \xrightarrow{k_2} R_2NCO_2^- + R_2\overset{+}{N}H_2 \qquad (2)$$

It was argued that the rate-determining step for the MEA-CO_2 reaction is the forward reaction 1, while that for the DEA-CO_2 reaction corresponds to the proton-transfer step, reaction 2. The rationale behind this argument was that the increased steric requirements of DEA as compared with MEA retard the reaction step 2 to the extent that it becomes the controlling step (Danckwerts, 1979). This view would predict that amines with further increased steric requirements such as diisopropanolamine (DIPA) would give third order kinetics.

To study this point further we conducted absorption rate measurements using a single-sphere absorber to derive chemical kinetic information on CO_2-DEA and CO_2-DIPA reactions.

EXPERIMENTAL

Apparatus and Procedure

The description and the procedure of using a single-sphere absorber (d = 5 cm) were given previously (Savage et al., 1980). All runs in the present study were conducted at 323 K using pure CO_2 at 152 kN/m^2 total pressure. After correcting for the water vapor pressure, the net CO_2 partial pressure is 140 kN/m^2. The solution (3 liter total charge) was circulated to the sphere at 220 cm^3/min and periodic liquid samples were taken for CO_2 analysis. The absorption rates were determined based on wet test meter readings which were in good agreement with the solution CO_2 data. The vapor space in the sphere chamber was filled with CO_2 from a CO_2 source under pressure. The rate of absorption was calculated from the rate at which CO_2 was drawn into the chamber to maintain constant pressure.

Materials

Amines were purchased from the Aldrich Chem. Co. and the MC/B Manufacturing Chem. and used without purification after analyzing by gas chromatography and titration.

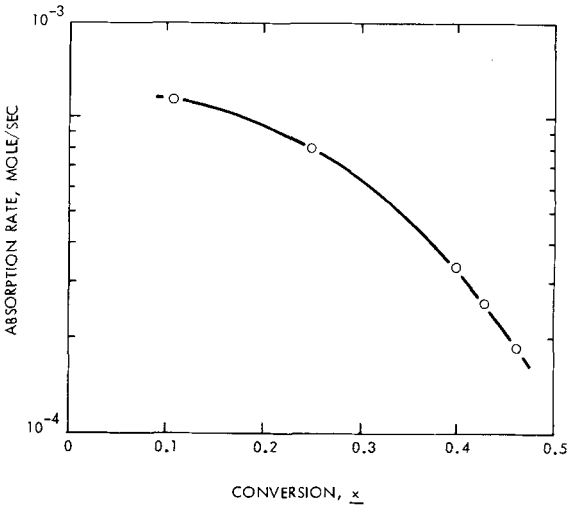


Figure 1. Rates of CO_2 absorption into 2M MEA solution at 323 K, P_{CO_2} = 140 kN/m^2, and interfacial area of 81 cm^2.

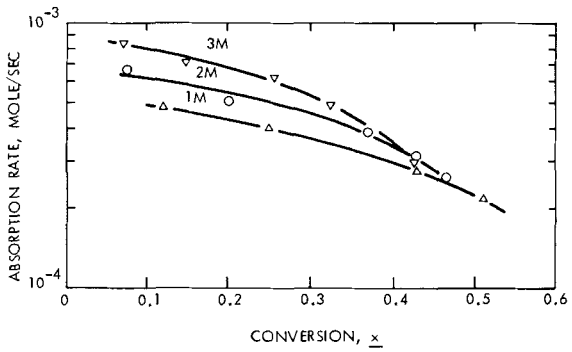


Figure 2. Rates of CO_2 absorption into aqueous DEA solutions at 323 K, P_{CO_2} = 140 kN/m^2, and interfacial area of 81 cm^2.

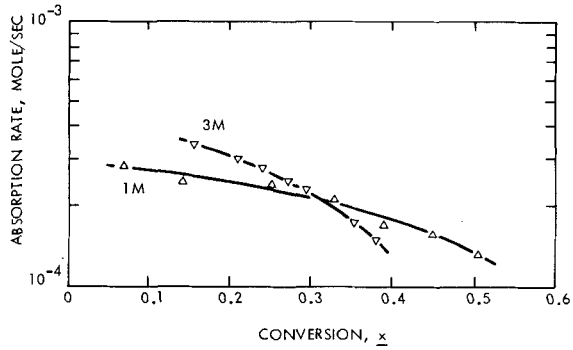


Figure 3. Rates of CO_2 absorption into aqueous DIPA solution at 323 K, P_{CO_2} = 140 kN/m^2, and interfacial area of 81 cm^2.

RESULTS

The rates of CO_2 absorption into MEA (2M), DEA (1, 2 and 3M), and DIPA (1 and 3M) solutions were measured at 323 K and P_{CO_2} = 140 kN/m^2. The results are shown in Figures 1, 2 and 3 by plotting the observed rates (moles CO_2/s) against the conversion (carbonation ratio), x, which is defined as moles of CO_2/mol amine. The first aspect of interest is the correlation between the absorption rate and the free amine concentration, for this is expected to provide a basis to evaluate whether the absorption is diffusion-controlled or chemical-reaction-controlled according to the criteria suggested by Danckwerts and Sharma (1966).

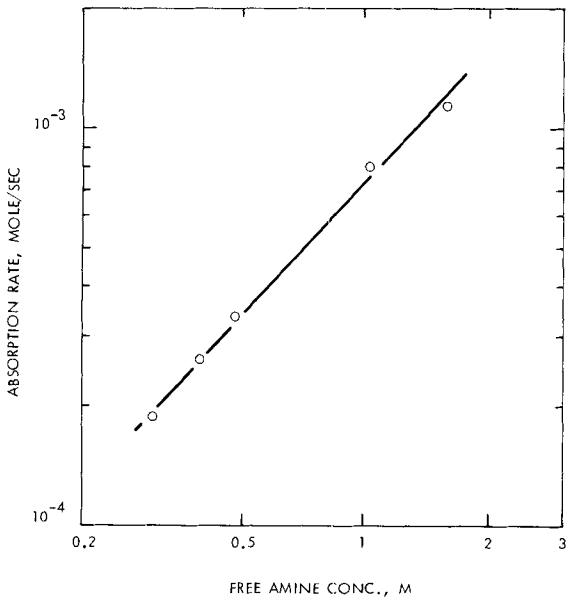


Figure 4. Correlation between absorption rates into 2M MEA solutions and free amine concentration.

To calculate the free amine concentration as a function of conversion (x), it is necessary to incorporate the equilibrium constants of reactions 4 and 5 into consideration:

$$2Am + CO_2 \rightleftharpoons AmH^+ + AmCO_2^- \quad (3)$$

$$AmCO_2^- + H_2O \overset{Q}{\rightleftharpoons} Am + HCO_3^- \quad (4)$$

$$Am + HCO_3^- \rightleftharpoons AmH^+ + CO_3^{--} \quad (5)$$

Reaction 4 is the carbamate hydrolysis reaction; the equilibrium constant Q at 323 K was estimated from the data of Kent and Eisenberg (1975) to be 0.060 M^{-1} (MEA), 0.38 M^{-1} (DEA), and 0.40 M^{-1} (DIPA). The proton exchange reaction 5 becomes significant only when the basicity of the amine is high. At 323 K the pk_A values are 8.81 for MEA and 8.30 for DEA according to Perrin (1965), and a value of 8.27 for DIPA was estimated from the reported pk_A value of 8.97 at 293 K (Alner and Kahn, 1964). These numbers are significantly lower than the pk_A value of 10.18 for HCO_3^- at 323 K. Accordingly, the contribution of reaction 5 will be neglected in subsequent considerations. Thus, the free amine concentration can be calculated using the quadratic Eq. 6.

$$[Am] = 1/2[Am]_0(1 - q - 2x + \sqrt{(q+1)^2 - 4x(1-x)}) \quad (6)$$

Other species concentrations are given by the following equations;

$$[AmCO_2^-] = 1/2[Am]_0(q + 1 - \sqrt{(q+1)^2 - 4x(1-x)}) \quad (7)$$

$$[AmH^+] = [Am]_0 - [Am] - [AmCO_2^-] = x[Am]_0 \quad (8)$$

where:

$[Am]_o$ = initial amine concentration, M
$x = ([HCO_3^-] + [AmCO_2^-])/[Am]_o$
$q = Q/[Am]_o$

The results of such calculations were used to plot absorption rates against free amine concentration.

For the MEA run, Figure 4, the absorption rate is closely related to the first power of free amine concentration. According to the criterion of Danckwerts, this suggests that diffusion of MEA to the surface is controlling the absorption rate and the following correlation may be applied:

$$E = \frac{R}{k_L C^*} \simeq E_i \quad (9)$$

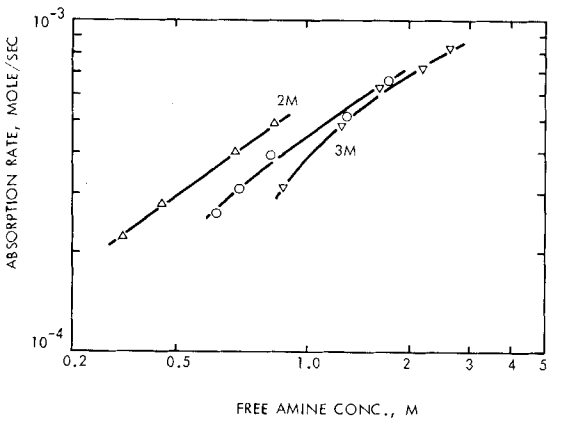


Figure 5. Correlation between absorption rates into DEA solutions and free amine concentration.

$$E_i = 1 + \frac{[Am]}{ZC^*}\sqrt{\frac{D_{Am}}{D}} \quad (10)$$

where:

E = enhancement factor by which the rate of absorption is increased by reaction
E_i = enhancement factor corresponding to instantaneous reaction
R = absorption rate per unit area, mol/cm²·s
k_L = physical mass transfer coefficient in the absence of reaction, cm/s
C^* = physically dissolved CO_2 concentration in equilibrium with gas phase, mol/cm³
Z = stoichiometric number = 2 in the present amine-CO_2 reactions
D_{Am} = diffusivity of amine, cm²/s
D = diffusivity of CO_2 in solution, cm²/s

As a condition of $C^* \ll [AM]$ is generally met in the present study, R becomes equal to $1/2\, k_L[Am]\sqrt{D_{Am}D}$ and, hence, the term $k_L\sqrt{D_{Am}/D}$ can be estimated from the slope of an R vs $[Am]$ plot. For the MEA case, a value of 0.022 cm/s was obtained for $k_L\sqrt{D_{Am}/D}$. This value is higher than an estimated theoretical k_L value of ~0.01 cm/s, which suggests the existence of interfacial turbulence.

In the cases of the DEA and DIPA runs, Figure 5 and 6, the slope of the log R vs. log $[Am]$ plot varies in the range of 0.5 to 1.0. This may initially be taken to imply that the system is in a borderline region between chemical reaction rate control and diffusion control. Assuming that the value of 0.022 cm/s can also be applied to represent $k_L\sqrt{D_{Am}D}$ value for the DEA and DIPA systems, we can determine whether the pseudo-first-order condition (Eqs. 11 and 12) is satisfied:

$$E = \frac{R}{C^*k_L} \leqslant 1/2E_i \simeq 1/2\,\frac{[Am]}{ZC^*}\sqrt{\frac{D_{Am}}{D}} \quad (11)$$

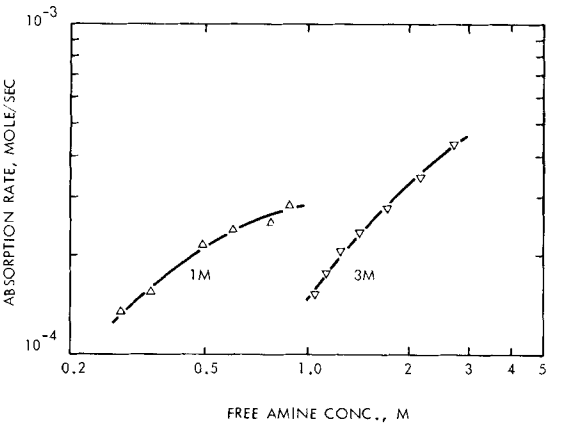


Figure 6. Correlation between absorption rates into DIPA solutions and free amine concentration.

TABLE 1. TABULATION OF CHEMICAL RATE TERM, $k_A[Am]^n$ FROM ABSORPTION RATE DATA

Conversion x	Absorption Rate 10^6 mol/cm²·s	Free Amine Concentration 10^3 mol/cm³	$C^* - C_{eq}$ 10^5 mol/cm³	$k_A[Am]^n$ 10^{-3} s^{-1}
2M DEA				
0.075	8.15	1.73	2.50	6.00
0.20	6.30	1.29	2.47	3.69
0.37	4.83	0.77	2.26	2.58
0.43	3.90	0.62	2.03	2.07
0.465	3.22	0.53	1.80	1.80
3M DEA				
0.070	10.1	2.61	2.40	11.1
0.15	8.90	2.17	2.38	8.69
0.26	7.65	1.61	2.33	6.77
0.33	5.93	1.27	2.22	4.45
0.43	3.83	0.84	1.78	2.90
1M DIPA				
0.070	3.48	0.88	2.50	1.26
0.14	3.06	0.77	2.49	0.98
0.25	2.98	0.60	2.46	0.95
0.33	2.62	0.49	2.39	0.78
0.39	2.16	0.41	2.30	0.57
0.45	1.90	0.35	2.15	0.51

or

$$R \leq 1/4(k_L\sqrt{D_{Am}/D})[Am] \quad (12)$$

It was found that the data for the 1M DEA run do not meet this condition while the remaining data more or less satisfy the condition of Eq. 12. This allows us to set the following correlation:

$$R = \frac{1}{\alpha}(C^* - C_{eq})\sqrt{k_L^2 + dk_{OH}[OH^-] + Dk_A[Am]^n} \quad (13)$$

where n is the order of the chemical reaction with respect to the free amine concentration and α is a small factor corresponding to the deviation from the ideal pseudofirst-order behavior of $E = \sqrt{M}$ ($= \sqrt{Dk_a[Am]^n}/k_2$) when $E <<< E_i$. Namely, in the present cases ($E_i/E \simeq 2$–3) E at a given value of $\sqrt{M}$ is slightly smaller than that in the ideal case and thus α was estimated at 1.3 from Figures 5–6 of Danckwerts (1970). The term C_{eq}, is the equilibrium CO_2 concentration set by Eq. 14:

$$2Am + CO_2 \overset{K}{\rightleftharpoons} AmH^+ + AmCO_2^- \quad (14)$$

The equilibrium constant can be obtained by a relationship of log $K = pk_A$ (amine) $- pK_a(CO_2) - \log Q$, where pk_A (DEA) = 8.30, pK_a (DIPA) = 8.27, pk_A (CO_2) = 6.31, and the Q values are as given previously. As the concentrations of free amine, protonated amine, and carbamate can be computed as functions of $[Am]_o$ and x (Eqs. 6–8), C_{eq} can be readily calculated. The relative magnitudes of k_L^2 and $Dk_{OH}[OH^-]$ can also be evaluated and the combined contribution was estimated to be less than 1% of the observed rate. Accordingly, Eq. 13 can be reduced to Eq. 15:

$$R = 1/\alpha(C^* - C_{eq})\sqrt{Dk_A[Am]^n} \quad (15)$$

Thus, if we know C^* and D, we can compute the $k_A[Am]^n$ term.

The common practice in evaluating C^* and D is to use data obtained for nitrous oxide (N_2O) according to the following correlations:

$$(C^*/C^*_{H_2O})_{N_2O} = (C^*/C^*_{H_2O})_{CO_2} \quad (16)$$

$$(D/D_{H_2O})_{N_2O} = (D/D_{H_2O})_{CO_2} \quad (17)$$

The nitrous oxide data of Sada et al. (1977, 1968) were used assuming the ratios determined at 298 K are unchanged at 323 K. The concentration of physically dissolved CO_2 in pure water at 323 K and $P_{CO_2} = 140$ kN/m² is determined to be 2.67×10^{-5} mol/cm³, and the diffusivity of CO_2 in pure water at 323 K was set at 3.8×10^{-5} cm²/s, which is the average of two values: 4.1×10^{-5} by the procedure of Davidson-Cullen (1957), and 3.6×10^{-5} by the Wilke-Chang correlation (1955). The final results of C^* and D values are shown below:

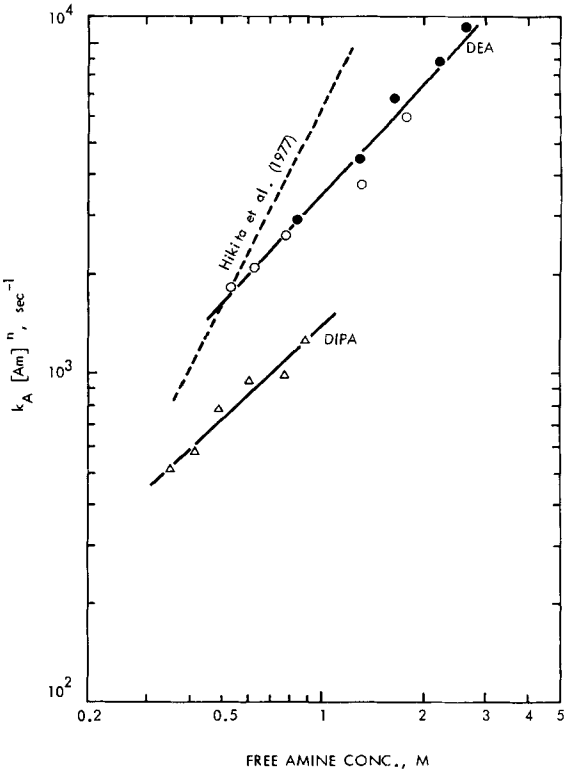


Figure 7. Correlation between $k_A[Am]^n$ and free amine concentration.

● Data from 3M DEA run

○ Data from 2M DEA run

△ Data from 1M DIPA run

	10^5 C^*, mol/cm³	10^5 D, cm²/s
DEA 1M	2.6	3.3
2M	2.5	3.0
3M	2.4	2.7
DIPA 1M	2.5	2.6

It should be noted that in the DIPA case, both C^* and D decrease precipitously with increasing concentration beyond the 1M level (Sada et al., 1978). Accordingly, the data for the 3M DIPA solution cannot be analyzed further in this study and a question remains unresolved as to whether the observed behavior of 3M DIPA in Figure 6 is due to diffusion limitation or to the occurrence of third-order kinetics similar to that observed by Nunge and Gill (1963) for the pure DEA system.

The final results of the calculations are shown in Table 1, and the plots of log $k_A[Am]^n$ vs. log $[Am]$ are illustrated in Figure 7. The straight lines are the results of linear regression analysis and the n value thus determined is 1.13 for DEA (correlation coefficient = 0.987) and 0.93 for DIPA (correlation coefficient = 0.972). These results are thus consistent with a view that the chemical rates of CO_2-DEA and CO_2-DIPA reaction are first order with respect to the free amine concentration.

As to the magnitude of the rate, comparisons with literature data are shown in Figure 8. Because the proposed order of CO_2-DEA reaction varies among different researchers, a quantity, $k_A[Am]^n$ at $[Am]$ = 1M, was chosen for the purpose of comparison. Here, the earlier data of Jensen et al. (1954) and Jorgensen (1956) were not included because their values are unreasonably high. Their rate, determined by product analysis of competitive CO_2 reaction with DEA/NaOH mixtures is almost identical to the rate of CO_2-OH^-

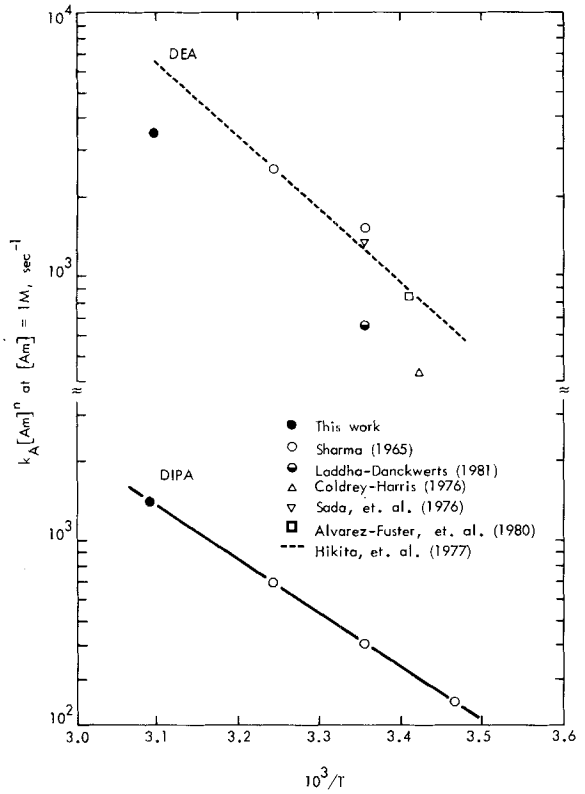


Figure 8. Comparison of rates with literature data.

reaction. It seems very likely that a rapid product equilibration was taking place at their experimental conditions.

Our rate for the DEA system is generally consistent with other literature data. Hikita's correlation, shown by a dotted line in both Figure 7 and 8, converges with our data at $[Am] = 0.5$ M. Our data for the DIPA system are in an excellent agreement with Sharma's results (1965).

DISCUSSION

The results of this study show that the chemical rate of CO_2-DEA reaction is best represented by second-order kinetics, i.e., first-order with respect to the free amine concentration. This does not agree with the third order kinetics reported by Hikita et al. (1977; 1980) and by Alvarez-Fuster et al. (1980). Very recently, Laddha and Danckwerts (1981) observed that the rates of CO_2 absorption into aqueous DEA solutions in a stirred cell can be accounted for by chemical kinetics of mixed order; an apparent 1.5th-order with respect to the DEA concentration was obtained in the amine concentration range of 0.48–2.88M. To explain this result they advanced a theory that predicts shifting kinetic order with respect to the amine concentration from 2 at low amine concentrations (below 0.3M) to 1 at high amine concentration (above 4M). The available literature data summarized in Table 2, however, show considerable deviations from this theory and also reveal seemingly irreconcilable discrepancies among results of different studies.

The problem of inconsistencies among kinetic results for the CO_2-DEA reaction was pointed out by Danckwerts (1979; Laddha and Danckwerts, 1981). A possible cause of this puzzling situation may be connected with the fact that most of the studies except this study and that of Donaldson and Nguyen (1980) were conducted using uncarbonated DEA solutions. Coldrey and Harris (1976) observed in their rapid-mix experiments that the reaction at the exit end of the reaction tube can be adequately described by second-order kinetics (first-order with respect to the free amine concentration), but at the entrance of the tube where uncarbonated DEA solutions were freshly mixed with CO_2 solutions, the reaction becomes very complex. As the contribution by the hydroxyl ion (OH^-) was ruled out, the above observation suggests that the kinetics of CO_2-DEA reaction may vary with carbonation. Accordingly, it seems desirable to repeat some of the previous studies using precarbonated solutions.

In view of the above uncertainties concerning the experimental data, discussions on the reaction mechanism might seem premature at this time. However, if one accepts the standpoint that MEA, DEA, and DIPA all follow second-order kinetics, the following comments on the mechanism proposed by Danckwerts may be in order.

Assuming that the CO_2-amine reaction occurs via a path represented by reactions 18 and 19:

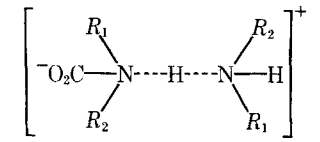
$$R_2NH + CO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2\overset{+}{N}HCO_2^- \tag{18}$$

$$R_2\overset{+}{N}HCO_2^- + R_2NH \xrightarrow{k_2} R_2NCO_2^- + R_2\overset{+}{N}H_2 \tag{19}$$

the overall rate expression is given by Eq. 20:

$$-\frac{d[CO_2]}{dt} = \frac{k_1k_2[Am]^2[CO_2]}{k_{-1} + k_2[Am]} \tag{20}$$

The essence of Danckwerts' proposal (1979; Laddha and Danckwerts, 1981) is that a condition of $k_{-1} \ll k_2[Am]$ is satisfied in the MEA system but not in the DEA system. This was rationalized by a theory that the increased steric requirements of the DEA molecule as compared with MEA retard the proton transfer (k_2) step. Indeed, if we presume that the transition state of this proton transfer step can be depicted by the structure shown below,



MEA: $R_1 = H$ $R_2 = CH_2CH_2OH$
DEA: $R_1 = R_2 = CH_2CH_2OH$
DIPA: $R_1 = R_2 = CH_2CHOH$
CH_3

TABLE 2. RECENT LITERATURE INTERPRETATIONS ON THE KINETICS OF CO_2-DEA REACTION

	Experimental Method*	Reaction Order with Respect to Free Amine Conc.	Applicable Free Amine Conc. Range, M
Coldrey-Harris (1976)	A	Apparently 1	0.1–1.0
Hikita et al. (1977)	A	2	0.174–0.719
Alverez-Fuster et al. (1980)	B	2	0.25–0.82
Hikita et al. (1980)	B	2	0.25–2.0
Donaldson-Nguyen (1980)	C	Apparently 1	<0.08
Laddha-Danckwerts (1981)	D	2	<0.3
	B	1–2	0.48–2.88
	D	1	>4
This Study	B	1	0.5–2.5

* A = direct measurements by rapid-mix method; B = analysis of CO_2 absorption rates; C = analysis of transport rates across membrane; D = predicted by theory.

the structure for DEA shows a much higher steric crowding than that for MEA. The steric crowding in this structure is perhaps much more severe than that in a carbamate structure which can be qualitatively represented by the carbamate hydrolysis constant, Q. It may thus be reasonable to assume that the structure for DIPA would be even more crowded than that for DEA, and accordingly, Danckwerts' theory would predict a shift toward third-order kinetics. However, the results of this study showed that DIPA follows second-order kinetics instead.

The chemical literature suggests that proton transfer as in reaction 19 is likely to occur through solvent molecules in the solvation shell (Lowenstein and Meiboom, 1956; Grunwald and Ralph, 1971; Bell, 1973). The solvent-assisted proton transfer reaction is known to be subject to little steric effect (Grunwald and Ku, 1968). In this line, Caplow (1968), who studied CO_2 reaction with various amines in aqueous solutions, proposed a reaction sequence involving a discrete step of proton transfer from the zwitterion intermediate to a water molecule. Caplow's scheme may be represented by Eqs. 21, 22, and 23:

$$R_2NH + CO_2 \rightleftharpoons R_2\overset{+}{N}HCO_2^- \tag{21}$$

$$R_2\overset{+}{N}HCO_2^- + H_2O \rightleftharpoons R_2NCO_2^- + H_3O^+ \tag{22}$$

$$H_3O^+ + R_2NH \rightarrow R_2\overset{+}{N}H_2 + H_2O \tag{23}$$

According to this scheme, the kinetics of CO_2-amine reactions become second-order if either reaction 21 or 22 is rate-limiting, and third-order if reaction 23 is limiting. Caplow proposed that for amines in the pk_A range of about 6–11, reaction 22 becomes the rate-limiting step, and accordingly, the rate was formulated to be first order with respect to the free amine concentration. This view, however, is not in agreement with the interpretation that reaction 21 is the rate-determining step in the CO_2-MEA reaction. As far as the kinetic behavior is concerned, our results are consistent with Caplow's theory and also with the traditional view that formation of the zwitterion intermediate is rate-limiting. Finally, it should be noted again that resolution of the inconsistencies among results shown in Table 2 is prerequisite to definitive discussions on the reaction mechanism.

ACKNOWLEDGMENT

The authors would like to thank G. Astarita for stimulating discussions and Mr. J. N. Begasse for excellent laboratory assistance.

NOTATION

$|Am|$ = free amine concentration, M
$|AmCO_2^-|$ = carbamate ion concentration, M
$|AmH^+|$ = protonated amine concentration, M
$|Am|_o$ = $|Am| + |AmCO_2^-| + |AmH^+|$
C^* = physically dissolved CO_2 concentration in equilibrium with gas phase, mol/cm^3
C_{eq} = instantaneous chemical equilibrium CO_2 concentration set by Eq. 14, mol/cm^3
E = enhancement factor by which the rate of absorption is increased by reaction
E_i = enhancement factor corresponding to instantaneous reaction
k_A = overall reaction rate constant for amine-CO_2 reaction
k_1, k_{-1}, k_2 = reaction rate constants defined in Eqs. 1 and 2
k_L = physical mass transfer coefficient, cm/s
K = equilibrium constant defined in Eq. 14
n = reaction order with respect to free amine concentration
p =
Q = equilibrium constant defined in Eq. 4
q = $Q/|Am|_o$
R = CO_2 absorption rate per unit area, mol/cm^2·s
x = conversion or carbonation ratio defined in Eq. 8
Z = stoichiometric number in amine-CO_2 reaction

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Manuscript received May 17, 1983; revision received Nov. 14, 1983, and accepted Nov. 15.