Carbon Dioxide Absorption into Promoted Carbonate Solutions

CO_2 absorption rates into diethanolamine (DEA)-promoted carbonate solutions were measured over a wide range of carbonate conversions and temperatures. Analysis of the data showed that the CO_2-DEA reaction rate was controlled by the rate of formation of zwitterion intermediate for carbonate conversions below 30%, and was controlled by the rate of abstraction of proton from the zwitterion intermediate for carbonate conversions greater than 30%. Hydroxyl ion, free amine, and carbonate ion were identified to act as bases to abstract the proton from the zwitterion. The modeling of the CO_2 absorption rates and the effects of carbonate conversion and amine concentration on the CO_2-DEA reaction kinetics were investigated.

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Introduction

The removal of CO_2 from gas mixtures by regenerative absorption with a chemically active liquid solution is important in the chemical and petroleum industries. Among the processes for the removal of CO_2, the amine-promoted hot carbonate process provides an economic and efficient way for removing large quantities of CO_2 from synthesis gases. In this process, the amine generally provides high absorption rates, while the carbonate-bicarbonate buffer offers advantages of large capacity for CO_2 and ease of regeneration.

When CO_2 is absorbed into a carbonate-bicarbonate buffer, the carbonate ion is converted stoichiometrically to the bicarbonate ion, but the local rate of reaction of CO_2 is proportional to the concentration of hydroxyl ion, rather than to the concentration of carbonate ion:

$$CO_2 + OH^- \rightarrow HCO_3^- \qquad (1)$$

$$\text{Rate (gmol/L} \cdot \text{s)} = k_{OH}[CO_2][OH^-]$$

where k_{OH} is the second-order rate constant, and its value at infinite dilution was given by Pinsent et al. (1956):

$$\log_{10} k_{OH} = 13.635 - \frac{2{,}895}{T} \ (T \text{ in } K) \qquad (2)$$

The actual value of the rate constant k_{OH} in a solution containing the hydroxyl ion is complicated by the effect of ionic strength so that a modified Pinsent equation was offered (Astarita et al., 1983):

$$\log_{10} k_{OH} = 13.635 - \frac{2{,}895}{T} + 0.08I \qquad (3)$$

where I is the ionic strength of the solution.

Amines and aminoalcohols represent another class of bases which have been commonly used in gas treating processes. In aqueous amine solutions (e.g., secondary amines R_1R_2NH), CO_2 absorption is accompanied by the following overall chemical reactions:

$$CO_2 + 2R_1R_2NH \rightarrow R_1R_2NCO_2^- + R_1R_2NH_2^+ \qquad (4a)$$

$$CO_2 + R_1R_2NH + H_2O \rightarrow HCO_3^- + R_1R_2NH_2^+ \qquad (4b)$$

The relative extent of these two reactions depends on the structure of amine, particularly the steric hindrance of the N site. There has been considerable disagreement in the literature over the kinetics of CO_2 reactions with amines in aqueous solutions (Laddha and Danckwerts, 1981; Blauwhoff et al., 1983; Savage and Kim, 1985), especially in the case of diethanolamine (DEA). The reaction order of CO_2 with DEA with respect to free DEA concentration has been reported as 1, 2, and some intermediate values; the magnitudes of the rate constants also vary because of inconsistencies in the reaction order.

Caplow (1968) suggested that CO_2 reacts with primary and

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secondary amines via the formation of a "zwitterion" intermediate:

$$CO_2 + R_1R_2NH \underset{k_z}{\overset{k_{CO_2-Am}}{\rightleftharpoons}} R_1R_2N^+HCOO^- \text{ (zwitterion } [Z]) \quad (5)$$

followed by removal of the proton by water:

$$R_1R_2N^+HCOO^- + H_2O \xrightarrow{k'_{z-H_2O}} R_1R_2NCOO^- + H_3O^+ \quad (6)$$

Danckwerts (1979) proposed a model based on the zwitterion mechanism and included water, hydroxyl ion, and amines as the bases that can react with the zwitterion to remove the proton. Later, Laddha and Danckwerts (1981) used the model to attempt to explain the controversies over the reaction kinetics between CO_2 and amines, but they considered only the amine as the base in the proton abstraction step. Then, they postulated that the rate-controlling step in the zwitterion mechanism could be the formation of the zwitterion, Eq. 5, or the proton abstraction from the zwitterion, Eq. 6 (but with amine as the base rather than water), depending on the concentration and the steric hindrance of the amine. This explained how the reaction order with respect to amine could range from one to two depending on which reaction was considered to be the rate-controlling step. Blauwhoff et al. (1983) analyzed CO_2 absorption rate data for several types of aqueous amines by using Danckwerts' (1979) model, and suggested that the CO_2-DEA reaction rate could be controlled by the abstraction of proton from the zwitterion intermediate. Blauwhoff et al. incorporated all bases (water, hydroxyl ion, and free amine) into the zwitterion reaction scheme, and derived values for the rate constants.

The combination of amine and carbonate solution offers advantages for gas treating in terms of both efficiency and capacity. The addition of amines and other additives to carbonate-bicarbonate buffers to enhance CO_2 absorption has been known for a long time (Killeffer, 1937). In 1960, Ellis studied CO_2 absorption rates in mixtures of potassium carbonate and monoethanolamine (MEA) and observed a significant rate-promotion effect. Although the absorption rates were expressed in terms of overall gas-phase mass transfer coefficients, the author indicated that the absorption rates were controlled by liquid film conditions. Jeffreys and Bull (1964) explained the rate-promotion effect of amines and other additives by means of surface phenomena. McNeil and Danckwerts (1964) questioned the role of surface phenomena. Recent studies have considered two different chemical mechanisms to elucidate the conspicuous effect of the rate-promoting additives. A so-called shuttle mechanism has been proposed to describe the action of amine-type promoters at low temperatures (Shrier and Danckwerts, 1969). In this mechanism, the rate promoter acts as a carrier to provide an additional pathway for the transport of CO_2 from the gas-liquid interface to the bulk liquid. Another mechanism, called homogeneous catalysis, has been suggested for arsenious acid. The rate promoter in this mechanism acts as a homogeneous catalyst by first forming an intermediate with CO_2; the intermediate is then hydrolyzed to produce the final product, bicarbonate ion. From an analysis of the chemistry and mass transfer for both mechanisms, Astarita et al. (1981) concluded that the two mechanisms are different only quantitatively, not qualitatively. A recent publication (Savage et al., 1984) indicated that the rate-promotion effect of amine in carbonate solutions can be described very well from the viewpoint of homogeneous catalysis.

For the ease of analyzing the chemical reaction rate that accompanies the mass transfer, experiments can be conducted under certain conditions such that the dissolved gas (e.g., CO_2) undergoes a pseudofirst-order reaction, and the concentrations of the other reactants in the neighborhood of the gas-liquid interface are very little different from those in the bulk of the liquid. In this case, the gas absorption rate can be expressed as (Danckwerts and Sharma, 1966):

$$N_{CO_2} = AC_i\sqrt{k_L^{o2} + D_{CO_2}k_B[B]} \quad (7)$$

This relationship holds true for any type of chemical system in which the reaction of CO_2 is first order or pseudofirst-order.

Taking into account the reverse reaction, the rate of CO_2 absorption into carbonate-bicarbonate buffer is given by:

$$N_{CO_2} = A(C_i - C_b)\sqrt{k_L^{o2} + D_{CO_2}k_{OH}[OH^-]} \quad (8)$$

With a rate-promoter, *Prom*, in the carbonate-bicarbonate buffer, Danckwerts and Sharma extended the above expression to the following:

$$N_{CO_2} = A(C_i - C_b)\sqrt{k_L^{o2} + D_{CO_2}k_{OH}[OH^-] + D_{CO_2}k_B[Prom]} \quad (9)$$

In the present study, we performed a series of CO_2-absorption experiments to measure the absorption rates into unpromoted and DEA-promoted carbonate solutions over a wide range of conversions of carbonate to bicarbonate and temperatures using a single sphere absorber. For DEA-promoted solution, the rate data under the pseudofirst-order fast-reaction regime were analyzed by the use of two models with different assumptions about the rate-controlling step. In one model it was assumed that the formation of the zwitterion intermediate was the rate-controlling step in the CO_2-DEA reaction kinetics. In another it was assumed that proton abstraction from the zwitterion intermediate was rate-controlling. The validity of the models, magnitudes of reaction rate constants, orders of reactions, and effects of carbonate conversion and amine concentration on CO_2 absorption rate were investigated.

Experimental Method

Apparatus

The single-sphere absorber used in this work is shown schematically in Figure 1. This absorber was the same as that used previously for the measurement of CO_2 absorption rates into hot carbonate solutions (Savage et al., 1980) and aqueous amine systems (Savage and Kim, 1985). For each of our experiments the total charge of potassium carbonate solution was 2.6 kg, and the solution circulation rate to the single sphere was 163 cm³/min. The total pressure in the sphere chamber was kept at 153 kPa for all the experiments. Both the solution and the gas feed were preheated to the operating temperature (50 to 103°C)

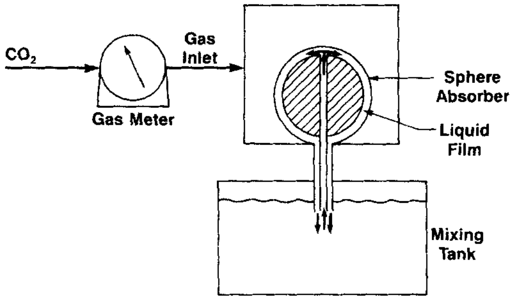

Figure 1. Sphere absorber for rate measurement.

before entering the chamber. The actual partial pressure of CO$_2$ was calculated by subtracting the partial pressure of water from the measured total pressure:

$$P_{CO_2} = P_{tot} - P_{H_2O} \tag{10}$$

where the saturation partial pressure of water P_{H_2O} was obtained as a function of weight percentage of potassium carbonate, carbonate conversion, and temperature from the experimental work of Tosh et al. (1959). The partial pressures of CO$_2$ used in our experiments with temperatures of 50–103°C ranged from 50 to 140 kPa. The absorption rates were determined from the wet-test gas meter readings, which were in good agreement with the rates determined from the carbonate conversions in the solutions obtained by HCl titration.

Chemicals

Potassium carbonate and potassium hydroxide were purchased from Mallinckrodt, Inc. Diethanolamine (DEA) was purchased from Aldrich Chemical Co. The chemicals with purities higher than 99% were used in the experiments without further purification.

Equations for Calculation of Concentrations in Solution

Definition of carbonate conversion

In this work we defined carbonate conversion by taking into account the equilibrium reactions among CO$_2$ and hydroxyl, carbonate, and bicarbonate ions in the carbonate-bicarbonate solution:

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3 \tag{11}$$

$$2KOH + CO_2 \rightleftharpoons K_2CO_3 + H_2O \tag{12}$$

$$KOH + CO_2 \rightleftharpoons KHCO_3 \tag{13}$$

The relationship among these species can be expressed as follows:

$$2KOH \xleftarrow[+H_2O]{-CO_2} K_2CO_3 \xrightarrow[+H_2O]{+CO_2} 2KHCO_3 \tag{14}$$

KHCO$_3$ is viewed as it is generated from K$_2$CO$_3$ by absorbing CO$_2$. On the other hand, KOH is generated from K$_2$CO$_3$ by losing (or desorbing) CO$_2$. The carbonate conversion is thus defined as moles CO$_2$ absorbed per mole K$_2$CO$_3$. This is the same as the conventional definition, but it covers a wider range of carbonate conversions with the following modifications:

$$\text{Mol CO}_2\text{ absorbed} = \tfrac{1}{2}[KHCO_3] - \tfrac{1}{2}[KOH] \tag{15}$$

$$\text{Mol K}_2\text{CO}_3 = [K_2CO_3] + \tfrac{1}{2}[KHCO_3] + \tfrac{1}{2}[KOH] \tag{16}$$

Carbonate conversion

$$= \frac{[KHCO_3] - [KOH]}{2[K_2CO_3] + [KHCO_3] + [KOH]} \tag{17}$$

Calculation of hydroxyl ion and free amine concentrations

The two equilibrium reactions in the carbonate-bicarbonate buffer are:

$$H_2O \overset{K_w}{\rightleftharpoons} H^+ + OH^- \tag{18}$$

$$HCO_3^- \overset{K_2}{\rightleftharpoons} H^+ + CO_3^= \tag{19}$$

The hydroxyl ion concentration can therefore be expressed as:

$$[OH^-] = \frac{K_w}{K_2}\frac{[CO_3^=]}{[HCO_3^-]} \tag{20}$$

By the conventional definition of carbonate conversion, the hydroxyl ion concentration was derived as a simple function of the carbonate conversion x_o:

$$[OH^-] = \frac{K_w}{K_2}\frac{1 - x_o}{2x_o} \tag{21}$$

The expression gave $[OH^-] = \infty$ at zero carbonate conversion and failed to give the hydroxyl ion concentrations in lean loading solutions.

In the present study, the hydroxyl ion and free amine concentrations were obtained by solving simultaneous equations based on chemical equilibria and material and charge balances. Besides the two equilibrium reactions, Eqs. 18 and 19, taken into account earlier, the following chemical reactions and material and charge balances were also considered:

Protonation of amine

$$R_1R_2NH_2^+ \overset{K_a}{\rightleftharpoons} R_1R_2NH + H^+ \tag{22}$$

Carbamate hydrolysis

$$R_1R_2NCO_2^- + H_2O \overset{K_5}{\rightleftharpoons} R_1R_2NH + HCO_3^- \tag{23}$$

Definition of carbonate conversion

$$x_o = \frac{[HCO_3^-] - [OH^-]}{[K^+]} \tag{24}$$

Electroneutrality

$$[K^+] + [H^+] + [R_1R_2NH_2^+] = [OH^-] + 2[CO_3^=] + [HCO_3^-] + [R_1R_2NCO_2^-] \quad (25)$$

Material balance

$$[R_1R_2NH]_o = [R_1R_2NH_2^+] + [R_1R_2NH] + [R_1R_2NCO_2^-] \quad (26)$$

Values of equilibrium constants in the above reactions were obtained from previous literature data (Kent and Eisenberg, 1976), as listed in Table 1. With known potassium ion and total amine concentrations, the values of unknown concentrations for hydrogen, hydroxyl, carbonate, bicarbonate, protonated amine, and carbamate ions, and free amine were calculated as a function of carbonate conversion x_o by solving the above equations numerically. A sample plot of the calculated concentration profiles is shown in Figure 2.

Results and Discussion

Estimation of physical mass transfer coefficient

The magnitude of the physical mass transfer coefficient k_L^o is controlled by the fluid mechanics of the liquid flowing over the spherical gas-liquid contactor. Davidson and Cullen (1957), Astarita (1967), and Astarita et al. (1983) proposed equations—Eqs. 27 and 28, respectively—for the theoretical calculation of k_L^o for a single-sphere absorber:

$$k_L^o = \frac{(12 \times 1.68)^{1/2}(2\pi g/3\nu)^{1/6} D^{1/2} L^{1/3} R^{7/6}}{4\pi R^2} \quad (27)$$

$$k_L^o = 0.583\ \sqrt{D}\left(\frac{gL^2\rho}{\mu d_s^5}\right)^{1/6} \quad (28)$$

Under our typical experimental conditions (sphere dia. = 5 cm, liquid flow rate = 163 cm^3/min, and 25% K_2CO_3 solution), the values of k_L^o for CO_2 at 90°C predicted by Eqs. 27 and 28 were 0.580 and 0.466 cm/min, respectively (using $D_{CO_2} = 2.34 \times 10^{-5}$ cm^2/s obtained from Savage et al., 1980).

Savage et al. (1980) conducted experiments to measure the physical mass transfer coefficient k_L^o by absorbing CO_2 into sucrose-water solution, which had approximately the same viscosity as the carbonate solution. The value of k_L^o obtained from their experiments was twice as large as the theoretical value predicted by Eq. 28. It was explained that for a sphere absorber of rather large diameter (5 cm), some rippling of the gas-liquid interface does occur. Therefore, we used Eq. 28 to calculate k_L^o and multiplied it by a factor of 2 to be the k_L^o for the present study. That is, k_L^o was 0.93 cm/min for our typical experimental conditions at 90°C.

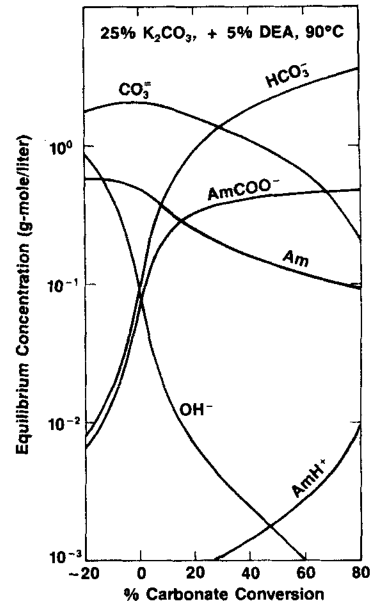

Figure 2. Equilibrium concentrations as a function of carbonate conversion.

Profiles of reactants and products in 25% K_2CO_3/5% DEA solution

Assumptions for the film model of pseudofirst-order fast-reaction regime

The concentration profiles of reactants and unreacted CO_2 gas according to the film model of the pseudofirst-order fast-reaction regime are shown schematically in Figure 3. In the reaction zone from the gas-liquid interface to the distance δ, the CO_2 gas undergoes pseudofirst-order reaction, and the concentrations of other reactants are fairly constant. Outside the reaction zone, i.e., in the bulk solution and the region in the mass transfer boundary layer (gas-liquid film) between the reaction zone δ and the bulk solution, chemical equilibria prevail. In the mass transfer boundary layer, a steady state is assumed.

Estimation of interfacial concentrations

With the assumption of steady state in the mass transfer boundary layer, the absorption rate of CO_2 having reaction with reactive species in the reaction zone should be equal to the rates of diffusion of the physically and chemically absorbed CO_2 species (unreacted CO_2, and carbonate, bicarbonate, and carbamate ions) from the reaction zone to the bulk solution. This can

Table 1. Values of Equilibrium Constants

Equilib. Constant, K_i*	Units	A	$B \times 10^{-4}$	$C \times 10^{-8}$	$D \times 10^{-10}$	$E \times 10^{-12}$
K_a	L/gmol	2.5510	0.5652	0	0	0
K_2	gmol/L	−294.74	36.439	−1.8416	4.1579	−3.5429
K_5	gmol/L	4.8255	−0.18848	0	0	0
K_w	gmol^2/L^2	39.555	−9.879	0.56883	−1.4645	1.3615

*$K_i = \exp(A + B/T + C/T^2 + D/T^3 + E/T^4)$ for T in K.

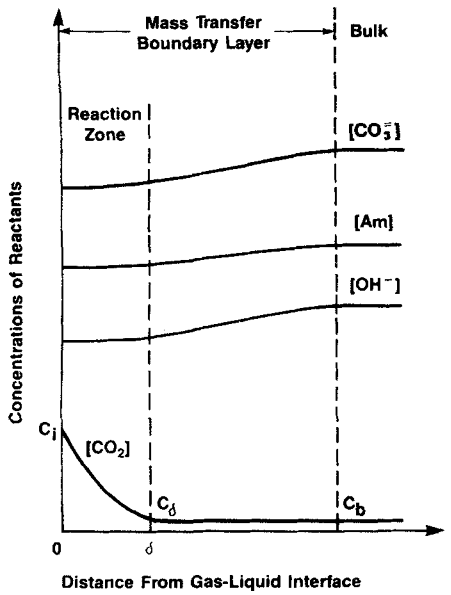

Figure 3. Concentration of reactants and unreacted CO$_2$ gas.

Profiles according to film model of pseudofirst-order fast-reaction regime

be expressed in the following equation:

$$N_{CO_2} = k_L A (C_i - C_\delta) = k_L^\circ A (\psi_\delta - \psi_b) \tag{29}$$

where ψ is the total concentration of the physically and chemically absorbed CO$_2$ species (ψ = [CO$_2$] + [carbonate ion] + [bicarbonate ion] + [carbamate ion]). This equation can be used to relate the interfacial concentrations of the reactive species in the reaction zone to their concentrations in the bulk solution. Using this equation, together with the case that chemical equilibria prevail in the bulk solution and the region between the reaction zone δ and the bulk solution, we were able to calculate the interfacial concentrations of the reactive species in the reaction zone (e.g., C_δ, [carbonate ion]$_\delta$, $[Am]_\delta$, and $[OH^-]_\delta$) from the physical transfer coefficient k_L° and the measured CO$_2$ absorption rate N_{CO_2}. (C_δ could be approximated well by C_b, and C_b was less than 10% of C_i in our experiments.) The interfacial concentrations and the corresponding interfacial carbonate conversion were used for expressing our experimental data and in our modeling work.

Carbon dioxide absorption into unpromoted carbonate solution

CO$_2$ absorption into hot carbonate solutions without promoters has been studied in depth (Astarita et al., 1983; Savage et al., 1980). A few unpromoted carbonate runs were performed in this work to cross-check the earlier results and verify that the equipment was operating properly. In Figure 4, CO$_2$ absorption rates into unpromoted carbonate solutions of 50, 70, and 90°C, expressed in terms of the overall liquid-film mass transfer coefficient k_L, are plotted as a function of interfacial carbonate conversion. The experimental data of k_L were calculated from the measured CO$_2$ absorption rates by means of the following equation:

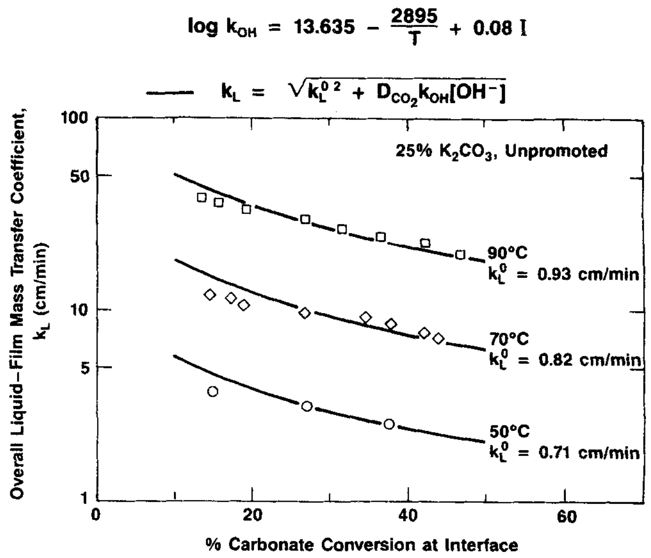

Figure 4. Rate constant for reaction with hydroxyl ion obtained from unpromoted carbonate solution.

$$N_{CO_2} = A(C_i - C_b)k_L$$
$$= A \frac{(P_{CO_2,i} - P_{CO_2,b})}{H} k_L \tag{30}$$

where $P_{CO_2,i}$ is the partial pressure of CO$_2$ at the gas-liquid interface (obtained from Eq. 10), and $P_{CO_2,b}$ is the equilibrium vapor pressure of CO$_2$ corresponding to the bulk liquid composition. Values of Henry's law constant and $P_{CO_2,b}$ used in the above equation were taken from the available vapor-liquid equilibrium (VLE) data (Tosh et al., 1959; Savage et al., 1980). The data under the pseudofirst-order fast-reaction regime were analyzed by the use of Eq. 8, in terms of k_L expressed in the following equation:

$$k_L = \sqrt{k_L^{\circ 2} + D_{CO_2} k_{OH} [OH^-]} \tag{31}$$

The physical mass transfer coefficient k_L° term was very small compared with the CO$_2$—OH$^-$ reaction term, and therefore the k_L° term could be neglected. The rate constant k_{OH} was used as the adjustable parameter to analyze the experimental data with the model. As shown in Figure 4, the pseudofirst-order reaction model fitted the experimental data very well. The k_{OH} obtained was in excellent agreement with the modified Pinsent equation, Eq. 3, reported by Astarita et al. (1983).

Carbon dioxide absorption into DEA-promoted carbonate solutions

Experimental k_L data on CO$_2$ absorption into diethanolamine (DEA)-promoted carbonate solutions were obtained from a series of single-sphere absorber runs by the use of Eq. 30, in which $P_{CO_2,b}$ values were determined from the VLE data for DEA-promoted carbonate solutions (Savage et al., 1984). Under our experimental conditions, values of $P_{CO_2,b}$ were relatively small (accounting for only 1 to 10%) compared with $P_{CO_2,i}$ and therefore presented only a minor effect on the unreacted CO$_2$

concentration driving force. The value of Henry's law constant was assumed to be the same as in the unpromoted carbonate solution.

At first, k_L data under the pseudofirst-order fast-reaction regime were analyzed assuming that the formation of the zwitterion intermediate, Eq. 5, is rate-controlling. In this case the absorption rate is enhanced by the CO_2-amine reaction rate that is proportional to the product of unreacted CO_2 and the free amine concentration in the solution. The expression for k_L is:

$$k_L = \sqrt{D_{CO_2} k_{OH}[OH^-] + D_{CO_2} k_{CO_2-Am}[Am]} \qquad (32)$$

Values of the rate constant k_{OH} at various temperatures were those obtained from the modeling work described above with unpromoted carbonate solutions, Eq. 3. We obtained the rate constant related to CO_2-amine reaction, k_{CO_2-Am}, by the least-square fitting of Eq. 32 to our experimental data with 2 and 5% DEA concentrations at temperatures ranging from 50 to 103°C. In the fitting, we imposed the rate constant k_{CO_2-Am} to have the Arrhenius dependency with temperature:

$$k_{CO_2-Am} = \exp\left[a + (b/T)\right] \qquad (33)$$

Thus, a and b were the adjustable parameters in the least-square fitting. As shown in Figures 5 and 6, our modeling efforts revealed that this model fitted the absorption rate data for carbonate conversions lower than 30%, but not for carbonate conversions higher than 30%. The results indicated that zwitterion formation was the rate-controlling step only in the region of the low carbonate conversions.

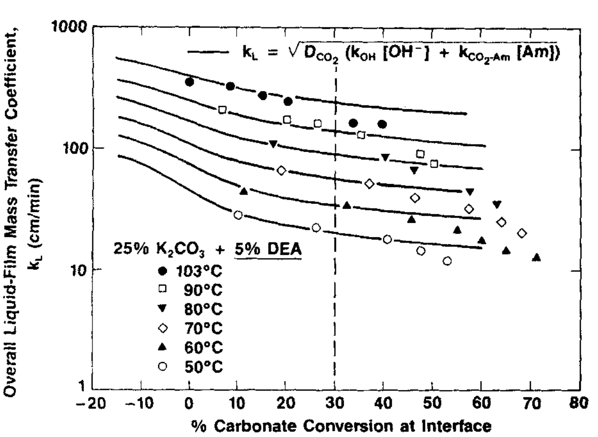

Figure 5. Model results with zwitterion formation assumption, 5% DEA.

Model assuming zwitterion formation as rate-controlling step fits rate data for low carbonate conversions, but not for conversions greater than 30% for 5% DEA-promoted carbonate solution

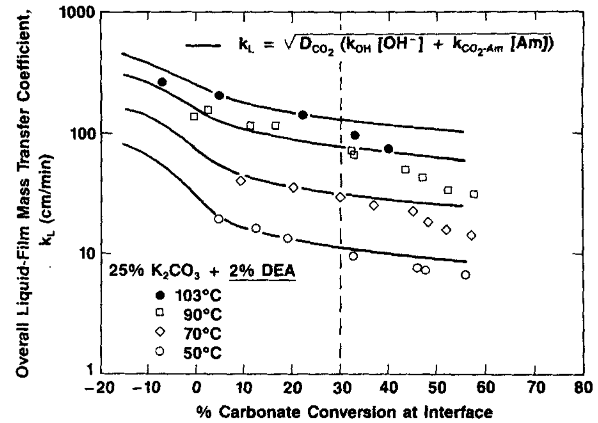

Figure 6. Model results with zwitterion formation assumption, 2% DEA.

Assumption: same as Figure 5, 2% DEA-promoted carbonate solution

We next examined the case in which it was assumed that the abstraction of proton from the zwitterion intermediate by bases (e.g., water in Eq. 6), is rate-controlling. The CO_2-amine reaction rate in this case would be proportional to the product of the concentrations of the zwitterion and the bases:

$$\text{Rate} = \Sigma k'_{Z-B}[\text{zwitterion}][B] \qquad (34)$$

while the concentration of zwitterion is proportional to the product of the concentrations of free amine and unreacted CO_2. This can be reconciled with Danckwerts' (1979) model in the following:

$$\frac{\text{Rate}}{[CO_2][Am]} = \frac{k_{CO_2-Am}}{1 + \dfrac{k_Z}{\Sigma k'_{Z-B}[B]}} \qquad (35)$$

When the second term in the denominator is much greater than 1, owing to the abstraction of proton from the zwitterion intermediate, Eq. 6, as the rate-controlling step, we get:

$$\text{Rate} = \Sigma k'_{Z-B}\left(\frac{k_{CO_2-Am}}{k_Z}\right)[CO_2][Am][B] \qquad (36)$$

Therefore, the CO_2 mass transfer coefficient into DEA-promoted carbonate solution under the pseudofirst-order fast-reaction regime can be expressed by the following model:

$$k_L = \sqrt{D_{CO_2} k_{OH}[OH^-] + D_{CO_2}\Sigma k_{Z-B}[Am][B]} \qquad (37)$$

Considering that hydroxyl ion, free amine, carbonate ion, and water may act as the bases and react with the zwitterion intermediate in the amine-promoted carbonate solution,

$$R_1R_2N^+HCOO^- + OH^- \xrightarrow{k'_{Z-OH}} HCO_3^- + R_1R_2NH \qquad (38)$$

$$R_1R_2N^+HCOO^- + R_1R_2NH \xrightarrow{k'_{Z-Am}} R_1R_2NCOO^- + R_1R_2NH_2^+ \qquad (39)$$

$$R_1R_2N^+HCOO^- + CO_3^{=} \xrightarrow{k'_{Z-CO_3}} HCO_3^- + R_1R_2NCOO^- \qquad (40)$$

$$R_1R_2N^+HCOO^- + H_2O \xrightarrow{k'_{Z-H_2O}} HCO_3^- + R_1R_2NH_2^+ \quad (41)$$

The mass transfer coefficient under the pseudofirst-order fast-reaction regime can be expressed as follows:

$$k_L = \sqrt{D_{CO_2}(k_{OH}[OH^-] + k_{Z-OH}[Am][OH^-] + k_{Z-Am}[Am][Am] + k_{Z-CO_3}[Am][CO_3^=] + k_{Z-H_2O}[Am][H_2O])} \quad (42)$$

The first term in the square root takes into account the absorption rate enhancement due to the CO_2-hydroxyl ion reaction; the second through the fifth terms represent contributions from the zwitterion proton abstraction reactions with hydroxyl ion, free amine, carbonate ion, and water, respectively.

We obtained the rate constants k_{Z-B} related to the zwitterion-hydroxyl ion reaction k_{Z-OH}, the zwitterion-amine reaction k_{Z-Am}, the zwitterion-carbonate ion reaction k_{Z-CO_3}, and the zwitterion-water reaction k_{Z-H_2O}, by the least-square fitting of the proposed model, Eq. 42, to our experimental data with 2 and 5% DEA concentrations at the temperatures ranging from 50 to 103°C for carbonate conversions greater than 30%. In the fitting, again, we imposed each rate constant to have the Arrhenius dependency with temperature:

$$k_{Z-B} = \exp\,[c + (d/T)] \quad (43)$$

Thus, c and d for each rate constant were the adjustable parameters in the least-square fitting. As shown in Figures 7 and 8, the model was able to fit the experimental data very well for carbonate conversions greater than 30%. Our modeling work indicated that the effect of the zwitterion-H_2O reaction on the CO_2 absorption rate is not significant in the presence of the other stronger bases and therefore can be neglected in the absorption rate expression, Eq. 42.

The overall modeling results showed that the CO_2 absorption rates into DEA-promoted carbonate solutions for carbonate conversions below 30% can be represented very well by the pseudofirst-order fast-reaction regime model assuming the zwitterion formation as the rate-controlling step in the CO_2-DEA reaction, whereas those for carbonate conversions greater than 30% can be represented very well by the proposed model assuming the proton abstraction from the zwitterion as the rate-controlling step. The CO_2-DEA reaction rate was controlled by the formation of the zwitterion intermediate at carbonate conversions below 30%, and it was controlled by the abstraction of proton from the zwitterion at carbonate conversions greater than 30%.

Values of rate constants related to the zwitterion formation and the proton abstraction reactions obtained from the present work on DEA-promoted carbonate solutions are plotted in Figure 9. The Arrhenius expressions of the rate constants and the derived values of their activation energies are listed in Table 2. Similar to Blauwhoff et al.'s (1983) results on aqueous amine systems, an increase in the relative magnitudes of the individual rate constants was found with increasing basicity of the bases (in the increasing order of carbonate ion, DEA, and hydroxyl ion) in the proton abstraction reactions of the zwitterion intermediate. The magnitudes of the derived individual activation energies were also comparable with those "apparent" activation energies (ranging from 23 to 55 kJ/gmol) reported in previous studies (Nunge and Gill, 1963; Danckwerts and Sharma, 1966; Hikita et al., 1977; Blanc and Demarais, 1981; Leder, 1971; Barth et al., 1986). The zwitterion-hydroxyl ion reaction had the lowest activation energy because of the highest basicity of hydroxyl ion. On the other hand, the zwitterion-free amine reaction had the highest activation energy possibly due to the steric hindrance effect, as discussed by Barth et al. (1986).

However, the magnitudes of rate constants obtained from the present work for the reactions related to the CO_2-DEA system in promoted carbonate solutions were much higher than those derived from aqueous amine solutions. As compared with Blau-

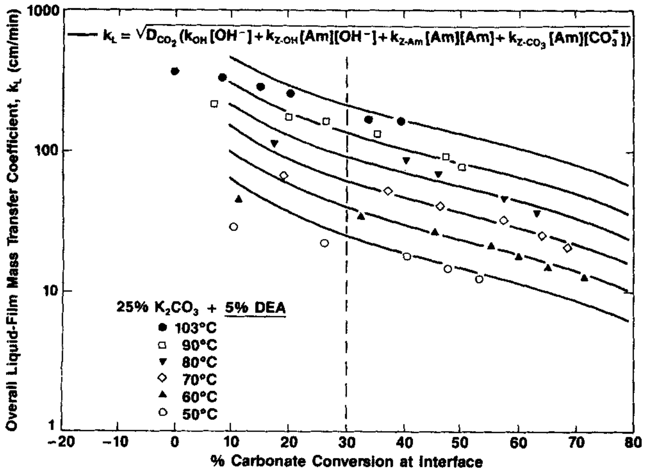

Figure 7. Model results with zwitterion-base reaction assumption, 5% DEA.

Model assuming zwitterion reaction with bases as rate-controlling step fits rate data for carbonate conversions greater than 30% for 5% DEA-promoted carbonate solution

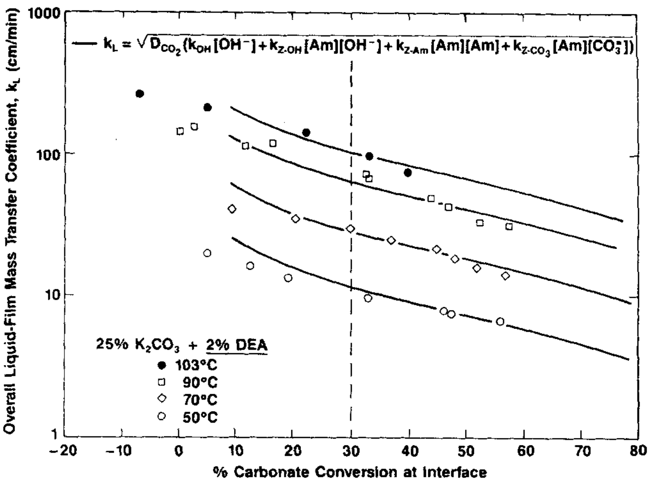

Figure 8. Model results with zwitterion-base reaction assumption, 2% DEA.

Assumption: same as Figure 7, 2% DEA-promoted carbonate solution

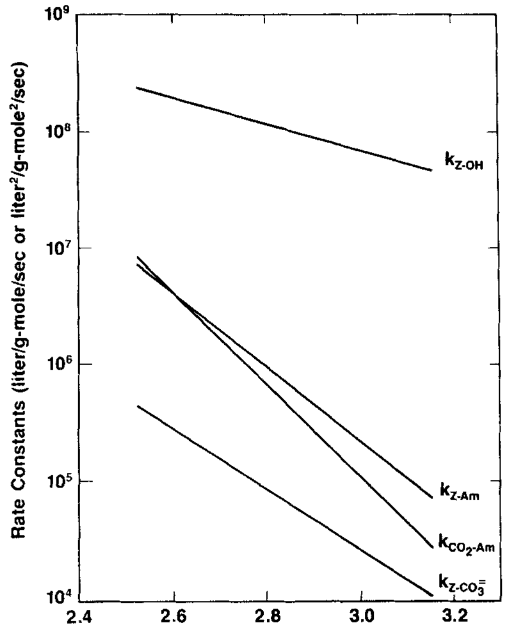

Figure 9. Arrhenius plots for derived rate constants related to zwitterion formation and proton abstraction reactions.

whoff et al.'s results at 25°C, the rate constant related to zwitterion-free amine reaction differed by an order of magnitude, while the rate constant corresponding to zwitterion-hydroxyl ion reaction differed by more than two orders of magnitude. This suggested that the CO_2-DEA reaction kinetics in concentrated carbonate solutions is quite different from that in aqueous solutions. Danckwerts (1979) also indicated that DEA enhanced the CO_2 absorption rate in carbonate solution more than could be accounted for by an additive effect, and suggested that the carbonate ion might catalyze the CO_2-DEA reaction. Savage et al. (1984) found that the kinetic constant for the reaction of CO_2 with a hindered diamine promoter in hot carbonate solution was extremely (incredibly) large. It is well known that the rate constant k_{OH} for CO_2-hydroxyl ion reaction can be increased significantly in high ionic strength environment, Eq. 3. It is then a question if the abstraction of proton from the zwitterion intermediate could also be accelerated in amine-promoted carbonate solutions, which provide very high ionic strength. Further work is needed to investigate this phenomenon.

Table 2. Rate Constants and Activation Energies Related to Zwitterion Formation and Proton Abstraction Reactions from Present Work

Rate Constants	Unit	Rate Expression	Activation Energy kJ/gmol
$k_{CO_2\text{-}Am}$	L/gmol · s	exp [38.51 − (8,964/T)]	74.5
$k_{Z\text{-}OH}$	L²/gmol² · s	exp [25.63 − (2,513/T)]	20.9
$k_{Z\text{-}Am}$	L²/gmol² · s	exp [33.98 − (7,220/T)]	60.0
$k_{Z\text{-}CO_3}$	L²/gmol² · s	exp [27.96 − (5,922/T)]	49.2

CO_2-DEA reaction kinetics

In Figure 10, percentage contributions from individual reactions to the overall CO_2 absorption rate are plotted as a function of carbonate conversion at 90°C for promoted carbonate solutions containing 2 and 5% diethanolamine (DEA) concentrations, respectively. The hydroxyl ion is involved in both the reaction directly with CO_2 and the proton abstraction reaction with the zwitterion intermediate. As shown in this figure, the direct reaction between CO_2 and hydroxyl ion is very significant in very lean solutions ($x_o < 0\%$), but it accounts for less than 15% of the overall absorption rate when the carbonate conversion is higher than 15%. Also shown in this figure, the proton abstraction reaction between the zwitterion and hydroxyl ion is more significant at lower carbonate conversions (closer to 30% carbonate conversion) because the chemical equilibria favor higher hydroxyl ion concentrations at lower carbonate conversions.

Laddha and Danckwerts (1981) postulated that CO_2-amine reactions in aqueous solutions may be first or second order with respect to free amine concentration because the steric hindrance of amine or the variation in amine concentration may change the rate-controlling step in the zwitterion reaction scheme. Our experimental and modeling work indicated that the proton abstraction from the zwitterion intermediate was rate-controlling in the CO_2-DEA reaction for the promoted carbonate solutions when the carbonate conversions were greater than 30%. But the apparent reaction order was not necessarily 2 with respect to free amine concentration due to the important roles of hydroxyl and carbonate ions in the zwitterion proton abstraction

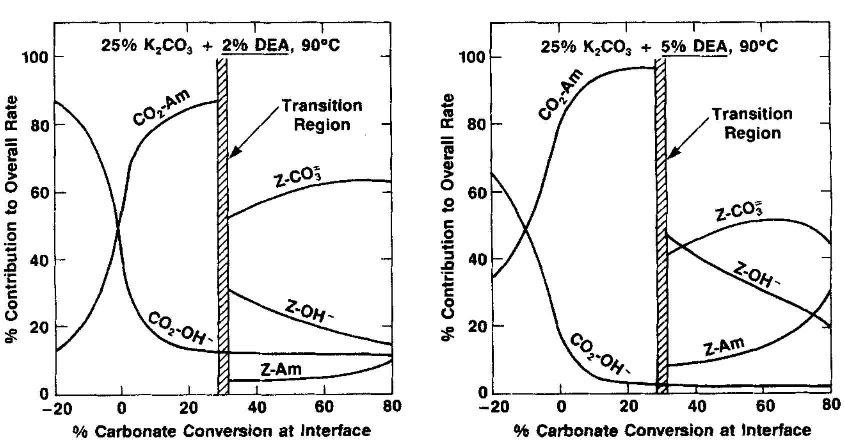

Figure 10. Absorption rate and reaction kinetics influenced by carbonate conversion and amine concentration.

reactions. Several previous publications also reported significant dependence of CO_2-amine reaction rates on hydroxyl ion concentration (Jorgensen, 1956; Caplow, 1968; Blauwhoff et al., 1983) or carbonate conversion (Coldrey and Harris, 1976), which actually reflected the hydroxyl and carbonate ion concentrations in the solution.

The observed reaction order with respect to amine can be 1, 2, or some intermediate value depending on the relative concentrations of the hydroxyl ion, free amine, and carbonate ion in the solution. Carbonate conversion and total amine concentration can affect the apparent reaction order because the relative concentrations of hydroxyl ion, free amine, and carbonate ion change with these variables as shown in Figure 10. At low carbonate conversions and the low amine concentration, the zwitterion-hydroxyl ion and zwitterion-carbonate ion reactions are the major contributions to the overall absorption rate, as shown in Figure 10, and the overall reaction is thus nearly first order with respect to free amine concentration. On the other hand, at high carbonate conversions and high amine concentration, the zwitterion-free amine reaction becomes significant, and the apparent reaction order with respect to free amine concentration could be closer to 2.

A recent article by Sada et al. (1985) described the reaction kinetics of CO_2 with ethanolamines in nonaqueous solvents. The results provide information that is relevant to the present discussion regarding the CO_2-DEA reaction kinetics because hydroxyl and carbonate ions and water are not existent in nonaqueous solvents. When proton abstraction reaction became the rate-controlling step in the absence of hydroxyl and carbonate ions and water, the overall reaction rate would be slower and the observed reaction order would be 2 with respect to the free amine concentration because amine was the only base existing in the solution to react with the zwitterion intermediate. Excluding the effect of alcohol-type solvent on the zwitterion stability (which may cause changes in the rate-controlling step), the orders of reaction with respect to ethanolamines in various nonaqueous solvents were closer to 2. This result is in line with our results.

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Notation

A = surface area of gas-liquid contacting, cm^2
Am = amine; concentration expressed as $[Am]$, gmol/L
B = base; concentration expressed as $[B]$, gmol/L
C = concentration of unreacted CO_2; gmol/L
d_s = diameter of single sphere, cm
D = diffusivity of gas, cm^2/s
D_{CO_2} = diffusivity of CO_2, cm^2/s
DEA = diethanolamine
g = acceleration of gravity, cm/s^2
H = Henry's law constant, kPa · L/gmol
I = ionic strength of solution, gmol/L
k_B = rate constant of CO_2 reaction with base B, L/gmol · s
k_L = overall liquid-film mass transfer coefficient, cm/min
k_L° = physical mass transfer coefficient, cm/min
k_{OH} = rate constant of CO_2-hydroxyl ion reaction, L/gmol · s
k_{CO_2-Am} = rate constant of CO_2-amine reaction for zwitterion formation
k_Z = rate constant for the conversion of zwitterion to CO_2 and amine, s^{-1}
k_{Z-Am} = $(k_{CO_2-Am}/k_Z)k'_{Z-Am}$, $L^2/gmol^2 \cdot s$
k'_{Z-Am} = rate constant of zwitterion-amine reaction, L/gmol · s
k_{Z-B} = $(k_{CO_2-Am}/k_Z)k'_{Z-B}$, $L^2/gmol^2 \cdot s$
k'_{Z-B} = rate constant of zwitterion reaction with base B, L/gmol · s
k_{Z-CO_3} = $(k_{CO_2-Am}/k_Z)k'_{Z-CO_3}$, $L^2/gmol^2 \cdot s$
k'_{Z-CO_3} = rate constant of zwitterion-carbonate ion reaction, L/gmol · s
k_{Z-H_2O} = $(k_{CO_2-Am}/k_Z)k'_{Z-H_2O}$, $L^2/gmol^2 \cdot s$
k'_{Z-H_2O} = rate constant of zwitterion-H_2O reaction, L/gmol · s
k_{Z-OH} = $(k_{CO_2-Am}/k_Z)k'_{Z-OH}$, $L^2/gmol^2 \cdot s$
k'_{Z-OH} = rate constant of zwitterion-hydroxyl ion reaction, L/gmol · s
K_2 = dissociation constant of HCO_3^-, gmol/L
K_5 = hydrolysis constant of carbamate, gmol/L
K_a = deprotonation constant of amine, gmol/L
K_w = ionic product of water, $gmol^2/L^2$
L = liquid flow rate to single sphere, cm^3/s
N_{CO_2} = absorption rate of CO_2, gmol/s
P_{CO_2} = partial pressure of CO_2, kPa
P_{H_2O} = partial pressure of water, kPa
Prom = rate promoter
P_{tot} = total pressure, kPa
R = radius of single sphere, cm
T = absolute temperature, K
x_o = carbonate conversion

Greek letters

μ = viscosity, g/cm · s
ψ = total concentration of physically and chemically absorbed CO_2 species, gmol/L
ρ = density of flowing liquid, g/cm^3
ν = kinematic viscosity, cm^2/s
δ = reaction zone thickness, cm

Subscripts

b = bulk liquid
i = gas-liquid interface
o = total concentration for Eq. 26
δ = at reaction zone thickness δ

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