Measurement of Diffusion Coefficients Important in Modeling the Absorption Rate of Carbon Dioxide into Aqueous *N*-Methyldiethanolamine

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Absorption rates of gaseous CO_2 into aqueous *N*-methyldiethanolamine (MDEA) solutions were measured in a quiescent, inverted-tube diffusiometer by monitoring the rate of pressure drop. The absorption rate was found to be insensitive to the diffusion coefficient of CO_2 in solution but very sensitive to the diffusion rate of bicarbonate and protonated MDEA ions. Evidence also suggested that chemical reaction equilibrium is rapid relative to diffusion. A numerical model was developed on the basis of these observations. The model was used to regress diffusion coefficients of bicarbonate and protonated amine, which must be equivalent by electroneutrality arguments, from measured absorption rates. Complete modeling of the absorption process also required data for the diffusion coefficient of MDEA in water. These were measured using a Taylor dispersion apparatus. CO_2 absorption rates and diffusion coefficients of bicarbonate and protonated MDEA were obtained at 298.2 K and 318.2 K in solutions containing 20, 35, and 50 mass % MDEA in water.

Introduction

Natural gas processors use amine treating processes to remove the acid gases H_2S and CO_2 from gas streams. Because the amines react with the acid gases, enhanced absorption and removal can be obtained. The tertiary amine *N*-methyldiethanolamine (MDEA) is commonly used in gas-treating, often in conjunction with diethanolamine because of its selectivity for H_2S over CO_2. Economical and efficient process design for selective absorption of these acid gases requires accurate fundamental property values including gas solubility, diffusion coefficients, kinetic rate data, and heats of absorption. As part of a project to supply some of the required data, mutual diffusion coefficients of MDEA in water were measured. Absorption rates of CO_2 into aqueous MDEA solutions were also measured in order to obtain indirectly diffusion coefficients of species present in the reacting mixture.

Because of the complexities involved when both reactions and diffusion are involved in the absorption process, very few measurements of diffusion coefficients in reacting mixtures have been attempted. When such measurements have been made, they are generally for a system in which a single reaction is known to occur, generally a first-order reversible reaction. More often, clever methods have been developed to measure the diffusion coefficients in a slightly modified system that eliminates the complexity of the reaction(s). For example, Tang and Sandall (1995) measured the diffusion coefficient of chlorine in water by acidifying the solution to block the formation of HOCl. Attempting to measure the diffusion coefficient for CO_2 in aqueous MDEA, Rinker *et al.* (1995) used the "N_2O analogy" (Clarke, 1964). Because N_2O has the same molecular weight and approximately the same structure as CO_2 but does not react with MDEA, measurements of the diffusion coefficient of N_2O in aqueous MDEA can be used to infer the diffusion coefficient of CO_2 in the amine solution. These methods eliminate the complexity of the reaction and make the diffusion measurement straightforward, but they rely on the assumption that the diffusion coefficient is not affected by the reaction-blocking mechanism. Laddha *et al.* (1981) provide some evidence that for low CO_2 concentrations, the N_2O analogy probably does not introduce more than about 5% error.

Much effort has been expended in obtaining an effective estimate of the diffusion coefficient of CO_2 in aqueous MDEA because it has been assumed that the absorption rate is controlled by the diffusion rate of CO_2. However, this assumes that the reaction is irreversible and that the reaction products therefore only affect the absorption rate by changing the properties of the solution. Most models for the solubility of CO_2 in aqueous MDEA are based on reversible reactions. In this case, the diffusion rate of the reaction products could have substantial effect on the absorption rate and may even be rate determining.

The solubility of CO_2 in aqueous MDEA has been modeled by Kent and Eisenberg (1976), Cornelissen (1980), Jou *et al.* (1982), and Chakma and Meisen (1987). Experimental solubilities were quite accurately modeled in all of these studies with the reversible reactions

$$\mathrm{MDEA} + CO_2 + H_2O \rightleftharpoons \mathrm{MDEAH}^+ + HCO_3^- \qquad (1)$$

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^- \qquad (2)$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (3)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad (4)$$

In this work, we use this model to regress species diffusion coefficients from experimental absorption-rate data. The model indicates that diffusion coefficients of MDEA, MDEAH^+, HCO_3^-, H^+, OH^-, and CO_3^{2-} in aqueous solutions might be required, in addition to the diffusion coefficient of CO_2, in order to accurately model the absorption of CO_2 into aqueous MDEA. A rigorous model would require the diffusion coefficients of these species in the multicomponent mixture, but we will make the simplifying

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Table 1. Measured Diffusivities of Methanol in Various Solvents at Infinite Dilution and 40 °C

solvent	$D/10^{-9}$ m^2·s^{-1}	$D_{\rm lit}/10^{-9}$ m^2·s^{-1}	$100(D - D_{\rm lit})/D_{\rm lit}$	ref
toluene	3.283	3.26	0.80	Sun and Chen (1987)
benzene	3.054	3.05	0.13	Sun and Chen (1987)
water	2.207	2.22	−0.59	Lee and Li (1991)

Table 2. Measured Diffusivities of MDEA in Water

	$D/10^{-9}$ m^2·s^{-1}			
T/K	0 mass % MDEA	20 mass % MDEA	35 mass % MDEA	50 mass % MDEA
298.2	0.736 ± 0.014	0.507 ± 0.009	0.333 ± 0.003	0.326 ± 0.003
323.2	1.33 ± 0.01	0.911 ± 0.014	0.648 ± 0.009	0.555 ± 0.006
348.2	1.98 ± 0.03	1.44 ± 0.03	1.12 ± 0.06	0.890 ± 0.009
373.2			1.76 ± 0.02	1.41 ± 0.02

assumption from the start that binary mutual diffusion coefficients of each species in water are adequate to model the system. This is clearly an approximation, albeit a necessary one, and neglects the dependence of diffusion coefficients upon changes in solvent properties. We will further assume that the concentrations of some of the ionic species will be small enough that not all of the diffusion coefficients for the above species will be required to model the absorption−reaction−diffusion process.

Chemicals

MDEA was obtained from Aldrich Chemical Co. with a stated purity of 99%. No additional purification was attempted. To avoid contamination with CO_2 in the air, the MDEA was initially transferred to smaller bottles in an Ar-filled glovebox. The smaller bottles were only opened and used once. Water was distilled, deionized, and degassed. The water was passed through a Shodex filter/degasser and then further degassed by boiling under vacuum until approximately 20% of the water had been removed. Carbon dioxide was obtained from Air Liquide and had a stated purity of 99.89%. All MDEA + water mixtures were made gravimetrically and then stored under their own vapor pressure before introduction into an ISCO high-pressure micropump.

Measurement of the MDEA−Water Mutual Diffusion Coefficient

The mutual diffusion coefficient of MDEA in water was measured as a function of composition and temperature using the Taylor dispersion method. The specifications of the instrument, its use, and accuracy have been previously reported (Rowley *et al.*, 1988). The detector for the instrument was an HP 1037A differential refractometer equipped with thermostated prisms. The resolution of the refractometer is about 5×10^{-9} refractive index units. The digital output from the refractometer was transferred to a data acquisition system and stored on disk. Analysis of the data was done by fitting the data to a normal distribution using a nonlinear least-squares regression program to directly obtain the first and second moments of the peak from which the diffusion coefficient was obtained. Rigorous corrections to the moments were applied, though they were generally insignificant due to the appropriate design of the apparatus. Details of the analysis are given by Rowley *et al.* (1988).

Operation and accuracy of the diffusiometer were checked by measuring infinite dilution diffusion coefficients of methanol in toluene, benzene, and water at 40 °C. The results of these measurements in comparison to published literature values are shown in Table 1. These results indicate an uncertainty in the instrument of about 1%, which is consistent with previous calibrations and measurements made with it.

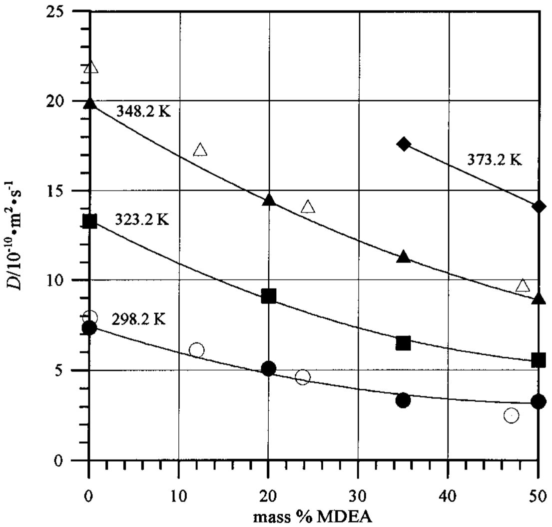

Figure 1. Mutual diffusion coefficients for MDEA in water at 298.2 K (●), 323.2 K (■), 348.2 K (▲), and 373.2 K (◆). The corresponding open symbols are values reported by Snijder *et al.* (1993).

The mutual diffusion coefficients of MDEA in water were measured at 0, 20, 35, and 50 mass % MDEA and at 25, 50, and 75 °C. The higher concentrations of MDEA (35 and 50%) lowered the vapor pressure sufficiently that measurements could also be made at 100 °C for these compositions. Generally, four replicate measurements were made at each temperature and composition and the results averaged. Table 2 contains the results of these measurements. The standard deviations from the replicates were used to obtain the 95% probability confidence intervals shown in Table 2. From these data, we estimate the relative uncertainty of the measured diffusion coefficients to be less than 2%; from experience with the apparatus, we estimate the absolute uncertainty to be less than 3.5%. Mutual diffusion coefficients of MDEA in water have also been measured by Snijder *et al.* (1993), and Figure 1 shows a comparison between those values and values measured in this work. The smoothing curves in the figure were obtained by fitting

$$D_{12}/10^{-10}\ \mathrm{m^2{\cdot}s^{-1}} = d_0 + d_1 w_{\rm MDEA} + d_2 w_{\rm MDEA}^{\ 2} \qquad (5)$$

to our experimental data. In this equation, *w* is mass fraction and values of the parameters d_i are given in Table 3.

Measurement of CO_2 Absorption

Apparatus. The absorption of CO_2 into aqueous MDEA solutions was measured in an inverted tube (liquid on top, held up by capillary action) diffusion apparatus. The intent was to fit absorption rate data to the model by adjusting

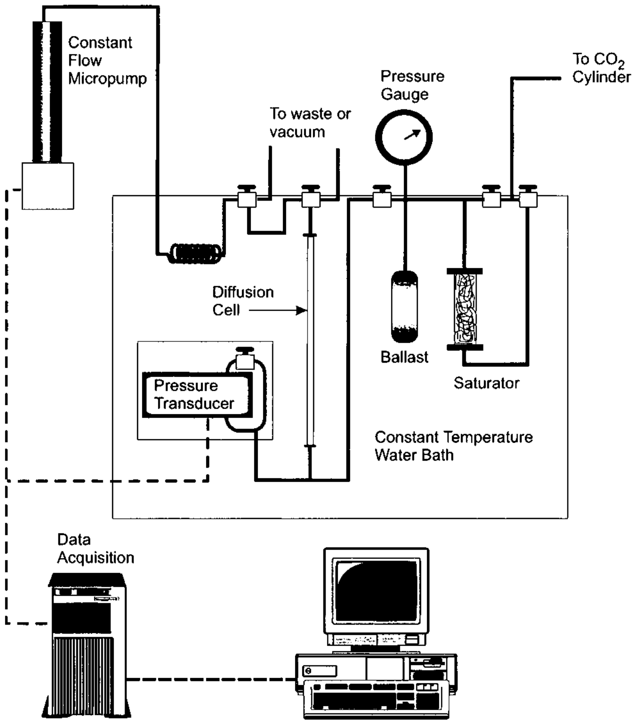

Figure 2. Schematic of inverted-tube liquid diffusion apparatus.

Table 3. Values of d_i for Use in Eq 5

T/K	d_0	d_1	d_2
298.2	7.429	−16.2	15.26
323.2	13.351	−26.5	21.47
348.2	19.807	−30.7	17.78
373.2	25.767	−23.3	0

one or more diffusion coefficients. Absorption was measured by monitoring the decrease in pressure as a function of time after contact of the CO_2 with the liquid solution. The inverted tube method was used to avoid free convection due to the increase in density of the solution with CO_2 loading (Al-Ghawas *et al.*, 1989). A schematic of the apparatus is shown in Figure 2.

The apparatus consisted of a 15 cm glass diffusion tube with a 2.0 mm inner diameter. The inner surface of the glass cell was coated with a monolayer of alkylsilane by soaking the cell in a GLASSCLAD 18 (Petrarch Systems, Inc.) solution and then curing the coating in a drying oven at 312 K for 1 h. Subsequent submersion of the tubes in MDEA solutions showed no signs of dissolution of the cured alkylsilane.

All parts of the apparatus were submerged and thermostated in a water bath controlled to within ±5.0 mK. Temperature control was done with a Tronac model 450 controller, and the temperature was monitored with an HP model 2804A quartz thermometer. The diffusion tube was connected directly to a three-way valve using Swagelock fittings with Teflon ferrules to seal against the glass. All valves and tubing were 316 stainless steel with Swagelock connectors and stainless steel ferrules.

The pressure detector was a Rosemount model 3051C differential pressure transducer with a variable pressure range from 0.125 to 6.23 kPa. The differential pressure range was set and calibrated using a manometer attached to the pressure transducer and a common pressure source. The entire transducer including electronics was enclosed in a polycarbonate case and submerged in the constant temperature bath. An electrical lead-through was provided from the submerged case to the surface of the water bath to avoid contact of the pressure transducer and its leads with the water. Thermostating of the pressure transducer was important for two reasons. First, the molar uptake rate of CO_2, hence the pressure drop, during the experiment was generally quite small, and variations in temperature were found to have a large effect on the measured pressures. Second, it was important to maintain the temperature of the dead volume in the pressure transducer at least as high as the rest of the apparatus to avoid water condensation which would change the dead volume available to the CO_2. The combined dead volume of the measurement side of the pressure transducer, the tubing, and the diffusion cell was measured to be 36.831 cm^3 by pressurizing the system with N_2 and isothermally expanding the gas into a previously evacuated cylinder of known volume. The ideal gas equation of state was used to obtain the dead volume from the pressure change measured.

The voltage output from the differential pressure transducer was collected using a Computer Boards CIO-DAS08/Jr data acquisition system and converted to pressure drop and molar uptake rates. These data were then saved to disk for later analysis. The computer also controlled an ISCO model 100 DM microsyringe pump operating in constant flow mode. The pump was used to infuse the aqueous amine solution into the diffusion cell at the beginning of the experiment.

Procedure. In prepartion for the measurement, the pump was filled with the degassed amine solution previously prepared at the desired composition. The cell, differential pressure transducer, and all stainless steel tubing were initially evacuated. These lines were then slowly flooded with CO_2 from a high-pressure cylinder. The gas entered through a sparger or saturator filled with metal turnings and about half full of water. Slow bubbling of the CO_2 up through the water saturated the CO_2 with water vapor at the run temperature. This was done to eliminate vaporization of water from the solvent during the run and the corresponding effect on the pressure. The vapor pressure of the amine is low enough that it does not evaporate during the run. Once the dead volume of the measurement portion of the cell was flooded and pressurized (generally to about 0.117 MPa) with the saturated CO_2, several consecutive runs were made without changing the CO_2. Often the first run in a series deviated somewhat from subsequent runs, and so it was never used in the analysis. We suspect that the water vapor was not yet in equilibrium with the solution during the first run because pure water was used in the sparger to saturate the CO_2 while the vapor pressure of the water above the solution would be lowered by the amine.

The gas−liquid interface was created by quickly injecting a known volume of the solvent using the microsyringe pump. The injected solution was infused through a coiled heat exchanger to thermally equilibrate the liquid to the same temperature as the CO_2. The pump was automated to inject the right amount of solvent, positioning the gas−liquid interface about 7 cm from the top of the cell. The injection rate was 5.0 cm^3/min, and the total injection time was 4 s. During the injection process, the valve to the ballast cylinder (150 cm^3) was left open so that the injection caused little change in pressure. Even so, the reference side of the pressure transducer was also open so that any change in pressue due to injection would not affect the pressure-drop measurements. Immediately when the pump shut off, the valves to the reference side of the transducer and to the ballast cylinder were closed. This minimized the dead volume and maximized the pressure-drop values. The zero of time was recorded by the computer as the time when the pump was shut off, and so there is an ambiguity

Table 4. Diffusion Coefficients of CO_2 in Pure Water at 298 K Measured in the Inverted Tube Absorption Apparatus and Compared to Previously Reported Values

source	$D/10^{-9}$ m^2·s^{-1}
this work	2.03 ± 0.10
Al-Ghawas *et al.* (1989)	1.95 ± 0.05
Tang and Sandall (1985)	1.98
Vivian and King (1964)	2.00 ± 0.07
Perez and Sandall (1973)	1.98
Himmelblau (1964)	from 1.74 to 1.94
Takahashi *et al.* (1982)	1.97
Perry and Green (1984)	1.96
Clarke (1964)	2.05, 1.96

in the starting time of 4−6 s during which time the gas was in contact with the liquid while the valve to the pressure detector was still open.

The differential pressure was recorded at preset intervals, usually every 15 s, for at least 1 h. The Redlich−Kwong−Soave equation of state in conjunction with the precisely known dead volume was used to convert the pressure measurements to molar uptake as a function of time. Generally, four to six replicates were performed at each desired temperature and composition in order to monitor reproducibility of the data.

Testing of the Apparatus. The apparatus was tested by measuring the diffusion coefficient of CO_2 in pure water. The bicarbonate equilibrium constant is small, and so the rate of CO_2 absorption in water can be modeled as a diffusion-controlled process by assuming no mass transfer resistance at the interface (i.e., assuming the interface is always saturated with CO_2). The following boundary value problem models the diffusion process:

$$\left(\frac{\partial C}{\partial t}\right) = D\left(\frac{\partial^2 C}{\partial z^2}\right)$$

$$\begin{aligned}&\text{initial condition:} && C = 0 \text{ at } t = 0\\ &\text{boundary condition:} && C = C_0 \text{ at } z = 0\\ &\text{boundary condition:} && C = 0 \text{ at } z = \infty\end{aligned} \qquad (6)$$

where C is the concentration of CO_2 in solution, C_0 is the equilibrium solubility of CO_2 in water, and z is the distance from the interface upward into the solution. In writing this equation, we have assumed that the concentration of CO_2 is adequately small that the diffusion coefficient is constant and that there is no movement of the center of mass. The equilibrium solubility was obtained from the CO_2 pressure using the Henry's law constant of Hagewiesche *et al.* (1995).

The boundary value problem posed in eqs 6, when solved explicitly and solved for the molar uptake (Δn) of CO_2 as a function of time, yields

$$\Delta n = 2C_0A\sqrt{\frac{Dt}{\pi}} \qquad (7)$$

where A is the cross-sectional area of the diffusion tube. This equation can be conveniently linearized by plotting Δn versus the square root of t. The diffusion coefficient was calculated from the measured uptake in this manner using linear least squares regression. Results for the measurements are reported in Table 4, as are the standard deviations obtained from the replicate runs. Agreement with literature values is within the precision of the measurements. It should be noted that standard deviations on the measurements made here are larger than those obtained from diffusiometers designed to measure very small uptakes. In our case, the pressure transducer was calibrated for the range expected for the amine solutions, and so it was operating at its lower sensitivity limit for the pure-water calibration runs. Total uptake for an hour run was only about 0.3 to 0.35 μmol.

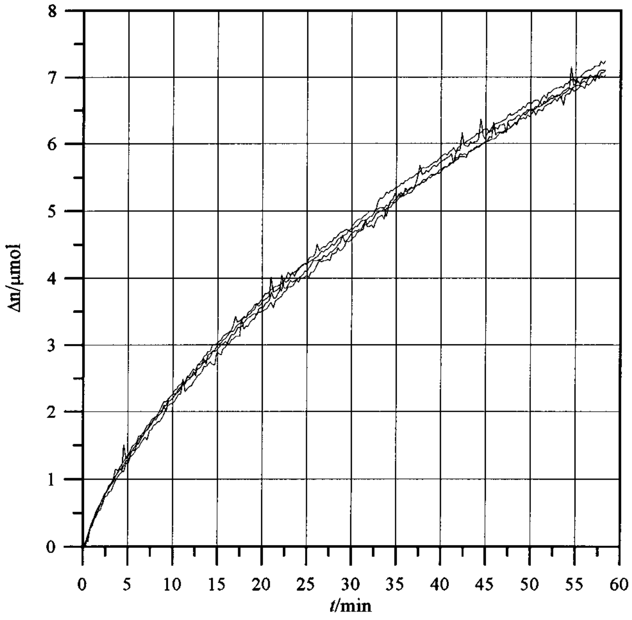

Figure 3. Reproducibility of CO_2 absorption runs for 35 mass % MDEA and 65 mass % water at 298.2 K.

Measurement of CO_2 Absorption in MDEA + Water Solutions. Absorption measurements made with the aqueous amine solutions had 25 to 30 times as much uptake during the hour-long experiment than the pure-water measurements because of the reactions involved. The noise in the pressure measurements was much less than for the pure-water experiments because the pressure drops were a substantial fraction of the full-scale range of the pressure transducer. Figure 3 illustrates the consistency of raw data obtained from some of the better replicate measurements made at the same condition. The raw data would not be expected to align exactly because the pressure, hence the CO_2 solubility, is slightly different for each run.

Analysis of Absorption Data

Often diffusion in reacting systems has been modeled as diffusion with a first-order irreversible reaction (Clarke, 1964). This model is applicable if there is reaction occurring in the system that acts as a sink to the diffusing species. Even if the actual kinetics are not first-order, often the reaction can be modeled as a first-order reaction with an effective first-order rate constant, k. For this model, the concentration of CO_2 is governed by

$$\left(\frac{\partial C}{\partial t}\right) = D\left(\frac{\partial^2 C}{\partial z^2}\right) - kC \qquad (8)$$

using the same initial and boundary conditions as before. The problem can be solved for the molar rate of uptake and integrated to obtain

$$\Delta n = C_0A\sqrt{\frac{D}{k}}\left[\left(kt + \frac{1}{2}\right)\operatorname{erf}\sqrt{kt} + \sqrt{\frac{kt}{\pi}}e^{-kt}\right] \qquad (9)$$

for the cumulative moles of CO_2 absorbed as a function of time.

A sensitivity analysis of the above equation indicated that at short times, the sensitivity coefficients were different enough that both D and k could be simultaneously regressed from a single data set, provided the value of k is adequately large. Figure 4 is a plot of $\Delta n/C_0AD^{1/2}$ versus

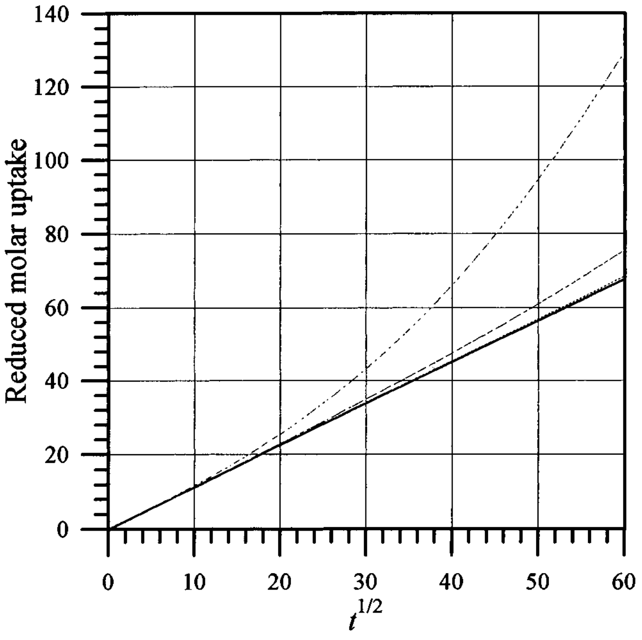

Figure 4. Deviation from diffusion-contolled regime due to first-order irreversible reaction for $k = 10^{-6}$ s^{-1} (—), $k = 10^{-5}$ s^{-1} (···), $k = 10^{-4}$ s^{-1} (— — —), and $k = 10^{-3}$ s^{-1} (—·—).

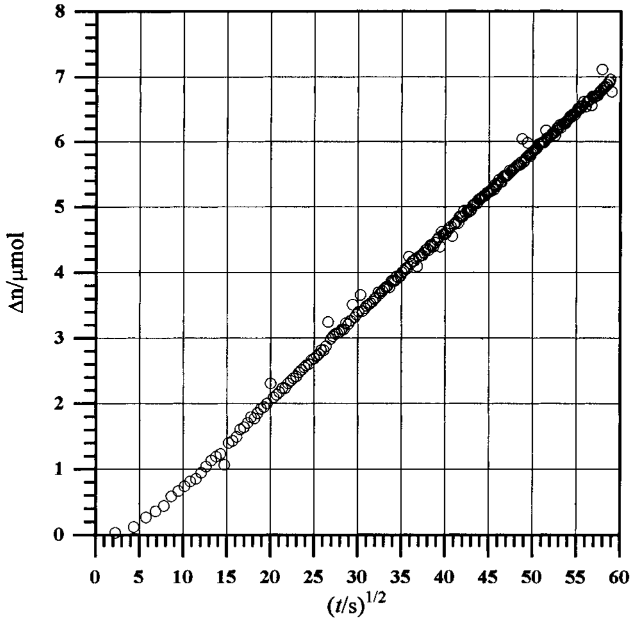

Figure 5. Typical raw absorption data from experiment exhibiting diffusion-controlled linearity when plotted versus square root of time.

t using eq 9 and various values of k. For k less than about 5×10^{-4} s^{-1} the molar uptake is linear with the square root of time, indicating diffusion-controlled absorption (as in eq 7). Larger rate constants give ever increasing deviations from the dependence on the square root of time. However, all of our measured absorption rates were linear with respect to $t^{1/2}$, as shown in Figure 5. This is not an indication that the k values are small because large amounts of absorption occurred, but rather that the irreversible-reaction model is incorrect. We infer, therefore, that the reactions given in eq 1 equilibrate rapidly relative to the diffusion of species in solution.

To analyze the absorption data using the equilibrium reaction model of eq 1, a numerical algorithm was devised on the basis of the assumptions that (a) the concentrations of all species satisfy the equilibrium constants for eqs 1−4 at all times and positions in the cell, (b) there is no resistance to mass transfer at the interface, (c) the Henry's law constant given by Chakma and Meisen (1987) applies, (d) the diffusion coefficients are independent of composition, (e) binary mutual diffusion coefficients can be used in place of the diffusion coefficients in the actual mixture, and (f) electroneutrality exists locally. The equilibrium and Henry's law constants for eq 1 were used directly as obtained from Chakma and Meisen (1987); namely,

$$K_1 = \exp\{\sum_{i=1}^{3} A_{1i}T^{i-2} + A_{14}\ln(T) + B\}$$

$$B = B_1[\mathrm{CO_2}] + B_2\ln[\mathrm{CO_2}] + B_3[\mathrm{MDEA}] + B_4\ln[\mathrm{MDEA}]$$

$$K_j = \exp(\sum_{i=1}^{5} A_{ji}T^{1-i}) \quad j = 2, ..., 4 \qquad (10)$$

$$H = \frac{1}{7.50061}\exp(\sum_{i=1}^{5} A_{Hi}T^{1-i})$$

with the constants given in Table 5. The equilibrium constants are K_c, not K_a, values, and they are functions of composition because mixture nonidealities are lumped into the K_c's. We checked this against a model in which activity coefficients were computed directly and K_a values were used; similar results were obtained with both models.

To apply the model to the analysis of the absorption measurements, the area representing the diffusion cell was discretized in the z direction (direction of diffusion) into equally spaced nodes beginning at the liquid−vapor interface. Each node, j, therefore had a volume of $V_j = \pi r^2 \Delta z$ associated with it, except for the first node. The first node was located at the interface, rather than at the center of its corresponding volume element, and therefore had only half the regular nodal volume associated with it. The initial compositions for H^+, OH^-, $MDEAH^+$, and MDEA were set to their equilibrium values on the basis of the nominal MDEA composition and eqs 1−4 and 10; the initial compositions for CO_2, HCO_3^-, and CO_3^{2-} were all 0.0 mol·L^{-1}. Using the experimental CO_2 pressure and the Henry's law expression in eq 10, the saturation concentration of CO_2 was obtained. An accumulator was initialized to the amount of CO_2 absorbed (volume of surface node times the saturation molarity). Computations for each time step then proceeded in the following order:

1. On the basis of the current concentrations at a node, j, mass was transferred to the next node (away from the interface) using the forward finite difference representation of the flux equation for that component; i.e.,

$$\Delta C_{j+1} = -\frac{DA(C_{j+1} - C_j)\Delta t}{V_j \Delta z} \qquad (11)$$

where t is time, A is the cross-sectional area of the diffusion tube, D is the binary mutual diffusion coefficient for the species in question, and C_j is the molarity of that species at node j.

2. Chemical equilibrium was then established at nodes j and $j + 1$ by solving eqs 1−4 and 10 using a series-reactor method. In this way, chemical equilibrium was represented as occurring instantaneously with diffusion as the rate controlling step.

3. Steps 1 and 2 were repeated for each node until there was no appreciable gradient between neighboring nodes.

4. The concentration of CO_2 at the interfacial node was again set to the saturation value and the equilibrium

Table 5. Constants from Chakma and Meisen (1987) Used in Eqs 10

	j				
coeff	1	2	3	4	5
A_{1j}	40.847708	92.421453	−0.0149081486	−14.031652	
A_{2j}	−241.818	298253.0	-1.48528×10^8	3.32648×10^{10}	-2.82394×10^{12}
A_{3j}	39.554	−98790.0	5.68828×10^7	-1.46451×10^{10}	1.36146×10^{12}
A_{4j}	−294.74	364385.0	-1.84158×10^8	4.15793×10^{10}	-3.54291×10^{12}
A_{Hj}	22.2819	−13830.6	6.91346×10^6	-1.55895×10^9	1.20037×10^{11}
B	0.098778738	0.18275505	3.9862282	−12.715421	

Table 6. Diffusion Coefficients for HCO_3^- and $MDEAH^+$ Obtained from CO_2 Absorption Rate Data and the Model Developed in This Work

	$D/10^{-10}\ m^2 \cdot s^{-1}$	
mass % MDEA	$T = 298$ K	$T = 318$ K
20	2.35 ± 0.49	5.03 ± 0.15
35	1.46 ± 0.08	3.39 ± 0.73
50	0.55 ± 0.09	0.98 ± 0.09

expressions again solved for the interfacial node. The amount of CO_2 absorbed during that time step was taken as the difference between α at this time step and its previous value, where α, the total amount of CO_2 in solution in its various forms, is given by

$$\alpha = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \qquad (12)$$

The amount of CO_2 absorbed during each time step was then added to the accumulator.

According to the model shown as eqs 1−4, there are eight species in solution: H^+, OH^-, H_2O, MDEA, $MDEAH^+$, CO_2, HCO_3^-, and CO_3^{2-}. The concentrations of H^+, OH^-, and CO_3^{2-} are everywhere so small that the CO_2 absorption rate is independent of the diffusion coefficients for these species. Without loss of generality, the diffusion coefficients for these ions were set to 1.0×10^{-9} m²/s. The mutual diffusion coefficient for MDEA in water was measured as part of this work, and the correlation given in eq 5 was used in the analysis. The diffusion coefficient of CO_2 in amine solutions was used instead of the value in pure water. The values used were obtained from the N_2O-analogy measurements by Al-Ghawas *et al.* (1989) and Tamimi *et al.* (1994). This left only the diffusion coefficients for $MDEAH^+$ and HCO_3^- yet undefined in the model. It is easily shown that local electroneutrality requires that these two species diffuse at the same rate. Therefore, the diffusion coefficient for the protonated amine and the bicarbonate ion were set equal and treated as a single parameter adjusted to give the best fit of the model to the experimental absorption rates.

The model was checked for convergence by varying the time step size and the spacial grid size over approximately 2 orders of magnitude. Variations in temporal and spatial grid sizes were not independent, but for any sufficiently small spatial grid, a corresponding time step was found that had both converged and produced equivalent results to the converged time step values for the other spatial grids. Any of these converged temporal and spatial grid pairs produced equivalent results.

Results and Discussion

The value of the diffusion coefficient for $MDEAH^+$ and HCO_3^- obtained from the absorption measurements are given in Table 6 along with the uncertainties obtained from replicate runs at each condition. Because these values are inferred from a model, it is difficult to assess the absolute accuracy of the data, but sensitivity analysis and the reproducibility of the measurements suggest a relative uncertainty of approximately 12% for the reported diffusion coefficients. The model represents the absorption data quite well in every case, as illustrated in Figure 6. As one would expect, the values at 318.2 K are larger than those at 298.2 K. Figure 7 shows that the diffusion coefficient decreases linearly with increasing amine concentration which is consistent with the corresponding increase in

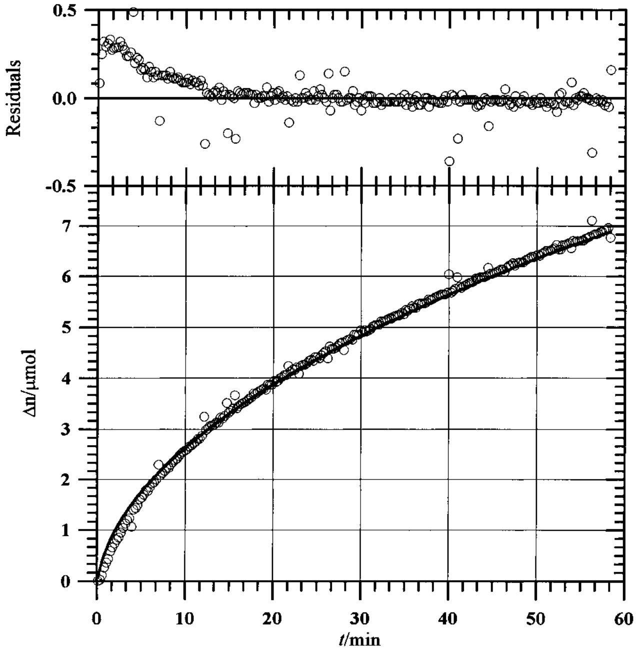

Figure 6. Absorption of CO_2 in 35 mass % MDEA in water at 298.2 K showing the measured values (○), values calculated from the numerical model (—), and the residual (top graph) error of the calculated from the experimental value.

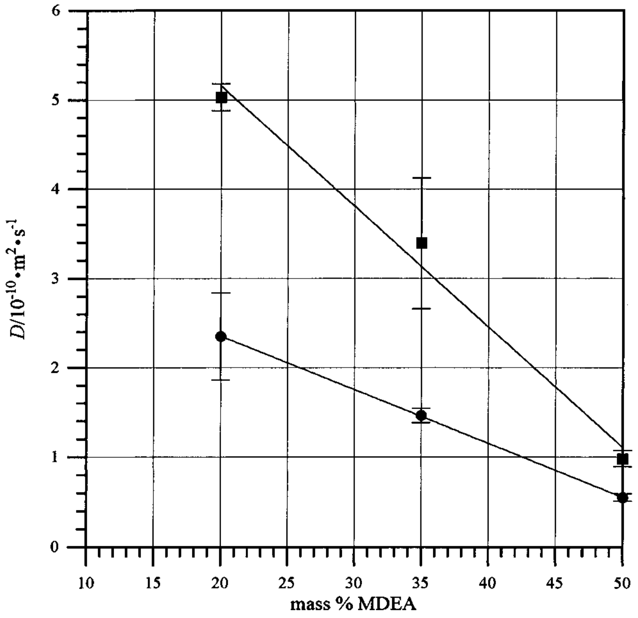

Figure 7. Concentration dependence of the $MDEA^+/HCO_3^-$ diffusion coefficients at 298.2 K (●) and at 318.2 K (■).

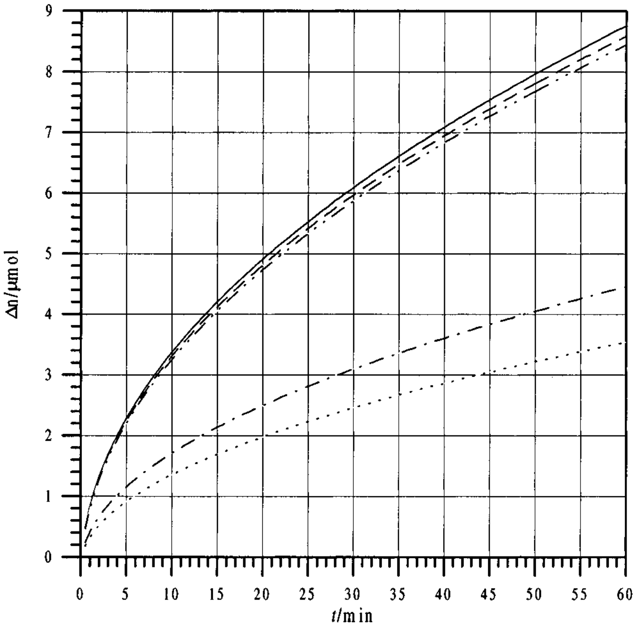

Figure 8. Relative changes in CO_2 uptake rate predicted by model as diffusion coefficients are varied from $D_0 = 1.0 \times 10^{-10}$ m^2 s^{-1} for CO_2 (top set of curves: —, $D_{CO_2}/D_0 = 10$; — — —, $D_{CO_2}/D_0 = 5$; —••—, $D_{CO_2}/D_0 = 1$) and for HCO_3^- (bottom two curves: —•—, $D_{CO_2}/D_0 = 1$; •••, $D_{CO_2}/D_0 = 0.5$).

solution viscosity. A comparison of Tables 2 and 6 reveals that the diffusion coefficient for the $MDEAH^+-HCO_3^-$ complex is smaller than that for MDEA in water. This is explicable in terms of the much larger size and weight of the complex (than the MDEA molecule itself) that must diffuse together to maintain local electroneutrality.

The results obtained have significant implications in modeling absorption in diffusing−reacting systems. The premise that the rate of CO_2 diffusion away from the interface controls the rate of CO_2 absorption into aqueous MDEA solutions is wrong. The CO_2 absorption rate is much more sensitive to the rate of HCO_3^- and $MDEAH^+$ diffusion than to CO_2, as shown in Figure 8. This is because most of the absorbed CO_2 is rapidly converted to bicarbonate so that the concentration of aqueous CO_2 is very small. Concentration profiles of the various species, as calculated from the model, are shown as a function of spatial position in Figure 9. Figure 10 shows the predicted pH in the diffusion cell as a function of time and position. While we have no way to measure a spatially- and time-resolved pH in our diffusion cell, it is interesting to compare the short- and long-time predicted pH values to measured values. Before contact with CO_2, the measured pH of a 20 mass % MDEA solution was 11.8, in excellent agreement with the predicted value of 11.88. The pH of this solution after saturation with CO_2 was 8.55, which is close to the value of 7.97 that is predicted by the model at the interface of our absorption experiment.

Conclusions

A quiescent, inverted-tube diffusiometer was used to measure absorption rates of CO_2 in aqueous MDEA solutions. The diffusiometer was tested by measuring the diffusion coefficient of CO_2 in water. The value obtained agreed well with values reported in the literature. The apparatus was then used to measure absorption rates of CO_2 into aqueous solutions of MDEA at 298.2 and 318.2 K as a function of MDEA concentration. It was found that CO_2 absorption was diffusion controlled and that it cannot be modeled with irreversible reactions. This supports a model in which reversible reactions equilibrate rapidly relative to diffusion.

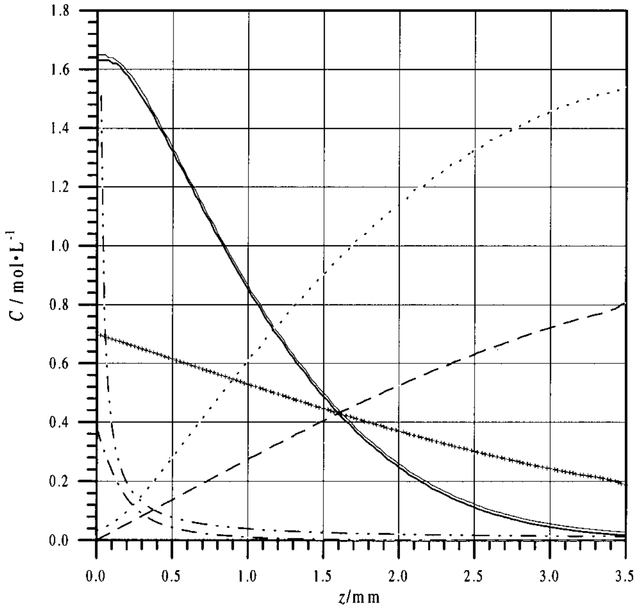

Figure 9. Predicted molar concentrations of species in the absorption cell after 1 h (at 298.2 K in 20 mass % MDEA solution) for $[MDEAH^+]$ and $[HCO_3^-]$ (—), [MDEA] (•••), $100[OH^-]$ (— — —); $10^{10}[H^+]$ (—••—); $10[CO_2]_{aq}$ (—•—), and $100[CO_32^-]$ (+++).

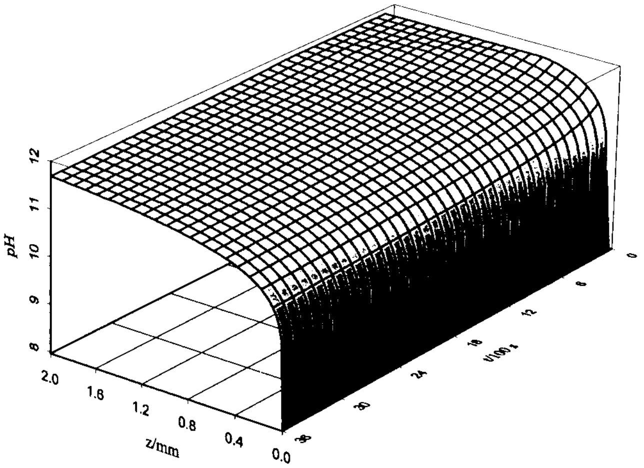

Figure 10. Predicted pH in absorption cell as a function of distance from interface (*z*) and time (*t*).

Using a numerical model based on the above findings, we were able to reduce the absorption data in terms of a single diffusion coefficient for the $MDEAH^+$ and HCO_3^- ions. The diffusion coefficient of MDEA in water was measured with a Taylor dispersion apparatus as a function of temperature and MDEA concentration for inclusion in the model. The model for absorption, reaction, and diffusion correlated the measured CO_2 absorption rates well. Values of the diffusion coefficient for $MDEAH^+$ and HCO_3^- regressed from the measurements were of appropriate magnitude, exhibited the correct temperature and concentration dependence, and were consistent with expectations based on molecular size.

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