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Kinetics of Absorption of CO_2 in Concentrated Aqueous Methyldiethanolamine Solutions in the Range 296 K to 343 K

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The kinetics of CO_2 absorption by aqueous solutions of methyl diethanol amine (MDEA) were measured in the temperature range (296−343) K and MDEA concentration range (830−4380) mol·m^{-3} (10−50 mass %). A thermoregulated constant interfacial area Lewis-type cell was operated by recording the pressure drop during batch absorption. The kinetic results are in agreement with a fast regime of absorption according to film theory. MDEA depletion at the interface has a significant effect on the kinetics at the CO_2 pressures (100 to 200 kPa) studied in this work, especially at low temperatures and low MDEA concentrations. Considering only the reaction between CO_2 and MDEA, the CO_2 absorption appears as a first-order reaction with respect to MDEA. The activation energy found for the reaction between CO_2 and MDEA is 45 kJ·mol^{-1}, but this value depends significantly (by about 10% in the worst case) on the vapor−liquid equilibrium data used.

Introduction

Absorption by aqueous solutions of alkanolamines is the dominant industrial process for removing acid gases, mainly CO_2 and H_2S, from natural gas. Such washing processes are also used in petroleum refining, coal gasification, and hydrogen production. Instead of ethanolamine (MEA) and diethanolamine (DEA) solutions, industry would prefer to use less corrosive and more advanced solvent systems which could be formulated along with the plant design and operation, according to the feed and exit stream specifications of plants. Methyldiethanolamine (MDEA) and blends with primary or/and secondary amines and sterically hindered amines are new systems that have been studied in the laboratory and sometimes used on industrial scale. In spite of an abundance of literature (Barth et al., 1981, 1984; Blauwhoff et al., 1984; Yu et al., 1985; Critchfield, 1988; Haimour et al., 1987; Versteeg and van Swaaij, 1988a; Littel et al., 1990; Rinker et al., 1995), only a few works (Tomcej and Otto, 1989; Toman and Rochelle, 1989; Xu et al., 1992) deal with absorption kinetics for CO_2 + MDEA + H_2O with solutions more concentrated than 3×10^{-3} mol·m^{-3} MDEA in water. High MDEA concentrations seem advantageous for absorption kinetics, in spite of the increasing viscosities which lead to decreasing diffusivities and physical transfer. Only Tomcej and Otto (1989) and Xu et al. (1992) investigated absorption of carbon dioxide in aqueous MDEA solution with MDEA concentrations higher than 3400 mol·m^{-3} solutions and temperatures higher than 340 K.

Rate expressions generally accepted (Yu et al., 1985; Critchfield, 1988; Haimour et al., 1987; Versteeg and van Swaaij, 1988a; Littel et al., 1990; Rinker et al., 1995; Tomcej and Otto, 1989; Toman and Rochelle, 1989) for the forward chemical reaction between CO_2 and MDEA are first order with respect to the concentrations of each of these species, while the estimated energies of activation lie between (33.1 and 71.6) kJ.mol^{-1}.

This paper describes the very efficient apparatus developed to measure absorption kinetics of acid gases into amines solutions. Experiments of CO_2 absorption by aqueous MDEA solutions, starting with CO_2 pressures ranging from (100 to 200) kPa, and in an extended range of MDEA concentrations and temperatures have been made with this apparatus.

Experimental Section

Chemicals. Twice-distilled water and reagent-grade MDEA are used. MDEA is from different origins: from Aldrich, with a certified minimum purity of 99 mass %, from Merck, with a certified minimum purity of 98 mass %, and from Alfa with a certified minimum purity of 98 mass %. Carbon dioxide is from L'Air Liquide, with a certified purity of 99.995 vol %.

Experimental Setup and Mode of Operation. The $(6.00 \pm 0.02) \times 10^{-2}$ m internal diameter thermostated glass reactor (Lewis type, Lewis 1954) shown in Figure 1 is provided with a six-bladed Rushton turbine, $(4.25 \pm 0.02) \times 10^{-2}$ m, in its lower part, a $(4.00 \pm 0.02) \times 10^{-2}$ m diameter propeller in its upper part, and four equally spaced vertical PTFE baffles to prevent vortexing. A horizontal PTFE plate and a ring are put midway between the bottom and the top of the cell to set both the level and area of the gas−liquid interface and to make sure of its stability during stirring. The shafts are maintained vertically between two pivots supported by two sapphire bearings fixed in the seats machined on the inside parts of the two stainless steel flanges on the flanges of the cell and the horizontal PTFE plate; they are driven magnetically by adjustable speed motors. This technique avoids leaking, friction, and heat generation due to shafts passing through the envelope of the cell by means of packings. The impeller speed is checked with a stroboscope, it remains constant within 1 rpm during each test. The temperature in the reactor is known within ±0.05 K through a 100 Ω platinum probe, calibrated against a 25 Ω STHPB platinum probe from LYON ALEMAND LOUYOT. The temperature is controlled by circulating a thermostatic fluid through the glass double jacket. The whole cell is placed inside a thermoregulated air bath. A tube allows us either to evacuate the cell or to introduce CO_2 into the cell. The total volume available for gas and liquid is $(0.3504 \pm 0.0005) \times 10^{-3}$ m^3 and the gas−liquid interfacial area A is $(11.72 \pm 0.05) \times 10^{-4}$ m^2. Uncertainties are geometrically estimated.

Kinetics of gas absorption are measured by recording the absolute pressure drop through a SEDEME pressure transducer, working in the range (0 to 200) kPa. This transducer is thermostated at a temperature slightly higher than the experiment temperature to avoid liquid condensation in its measuring chamber. For each temper-

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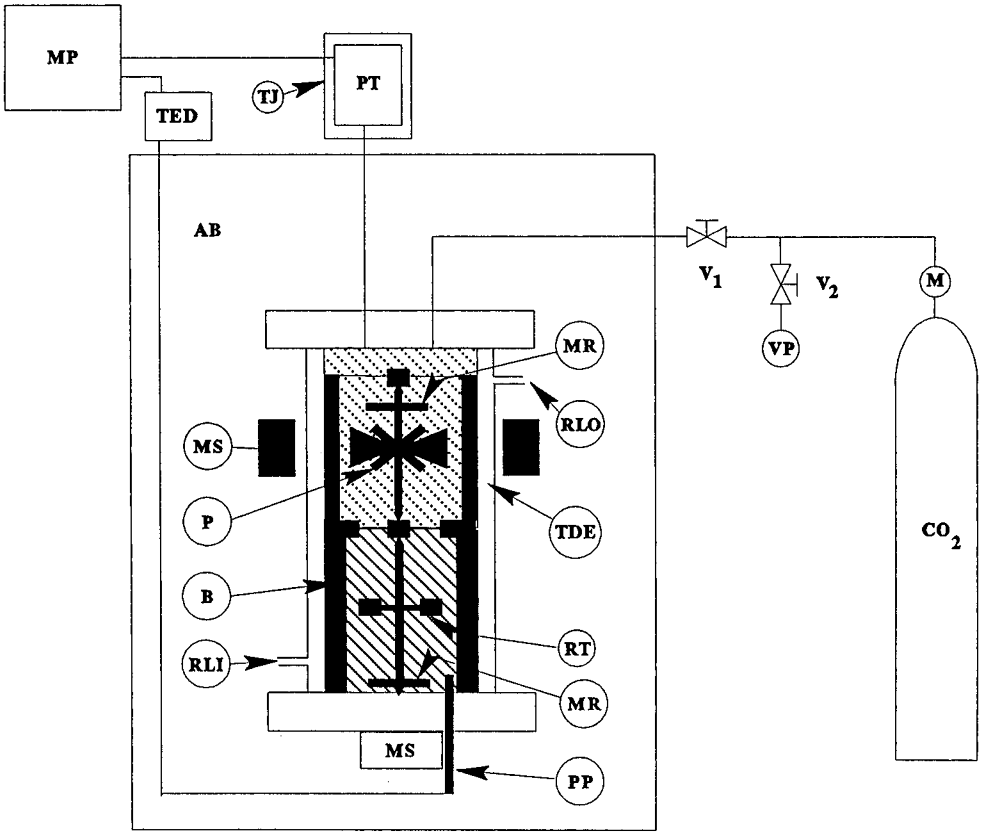

Figure 1. Lewis-type stirred reactor and its flow diagram: (AB) air bath, (B) baffles, (MP) microcomputer, (MR) magnetic rod, (MS) magnetic stirrer, (P) propeller, (PP) platinum probe, (PT) pressure transducer, (RLI) temperature control liquid inlet, (RLO) thermostatic-liquid outlet, (RT) Rushton turbine, (TED) thermal electronic display, (TDE) transparent thermostated double envelope, (TJ) thermostated jacket, (Vi) shut-off valve i, (VP) vacuum pump.

ature investigated, it is calibrated within 200 Pa against a mercury manometer. A microcomputer fitted with a data acquisition card is used to convert the pressure transducer signal directly into pressure units (Pa), using calibration constants previously determined, and record it as a function of time.

Water and MDEA are degassed independently, and aqueous solutions are prepared under a vacuum. The mass of water and MDEA are known by differential weighings to within 10^{-2} g. In the worst cases, uncertainties on masses lead to uncertainties on concentrations of 0.05%. The flask containing the solution is connected to the reactor to allow the solution to transfer by gravity under vacuum. Accurate weighings of the flask before and after transfer yield the mass of solution actually present in the cell, and the liquid phase volume was calculated using the density measurements from Al-Ghawas et al. (1989) for MDEA aqueous solutions. At a given temperature, and under solution vapor pressure P_I, pure CO_2 is introduced during a very short time (about 2 s) in the upper part of the cell, the volume of which is noted as V_G. The resulting pressure P_0 is between 100 and 200 kPa. Then stirring is started, and the pressure drop resulting from absorption is recorded. The kinetics of CO_2 absorption into MDEA + water solutions with no initial CO_2 loading are adequately measured within 1 h.

Results

Measurements have been carried out at three temperatures: 296, 318, and 343 K, for six MDEA compositions. All rough results of "pressure-time" absorption data (33 tables) are compiled as Supporting Information. The first table is given in Appendix A. Table 1 gives in column 1 the reference number of the experiment, column 2 the temperature of the experiment, column 3 the concentration of MDEA, column 4 the initial pressure, column 5 the inert pressure, column 6 the CO_2 partial pressure, column 7 the vapor phase volume inside the Lewis cell, column 8 the mass transfer coefficient in the liquid side, column 9 the slope *b*, and column 10 the flux.

The influence on absorption kinetics of all chemical reactions between dissolved CO_2 and reactants in solution is usually expressed by an "enhancement factor" *E* over physical absorption:

$$\frac{\mathrm{d}P_{CO_2}}{\mathrm{d}t} = -\frac{RT}{V_G} k_L A E C_{CO_2,i} \qquad (1)$$

where k_L is the liquid-side mass transfer coefficient of unreacted CO_2, *R* is the gas constant 8.3143 $J\cdot K^{-1}\cdot mol^{-1}$, *T* is the absolute temperature. V_G is the volume of gas. The gas phase is assumed ideal, and the concentration of CO_2 is very small in the bulk liquid compared to its concentration $C_{CO_2,i}$ at the interface.

At the interface, vapor–liquid equilibrium is assumed. The partial pressure P_{CO_2} is related to the concentration of unreacted dissolved CO_2 by Henry's law:

$$P_{CO_2} = HC_{CO_2,i} \qquad (2)$$

where *H* is the molar scale Henry's law constant. P_{CO_2} is obtained from the measured pressures:

$$P_{CO_2} = P - P_I \qquad (3)$$

where *P* is the total pressure. P_I is the total vapor pressure

Table 1. Conditions of CO_2 Absorption Kinetics by MDEA Aqueous Solutions in the Lewis Cell

ref no.	T/K	$C_{MDEA,T}$/mol·m^{-3}	P_0/Pa	P_I/Pa	$P_{CO_2,i}$/Pa	$V_{g/10}{}^{-6}$ m^3	k_L/10^{-5} m.s^{-1}	b/10^{-4} s^{-1}
1	295.95	844.4	177608	2790	174818	181.73	1.319	3.19
2[d]	295.85	1272.6	178836	2840	175996	180.35	1.102	3.39
3	296.15	1984.1	188084	2730	185354	179.00	0.804	3.58
4	295.95	1984.2	158324	2720	155604	179.27	0.799	3.89
5[d]	295.75	2583.2	190252	2660	187592	182.22	0.591	3.36
6[d]	295.25	3477.4	175169	2710	172459	181.30	0.365	2.8
7	296.45	4379.1	114916	2830	112086	177.84	0.238	2.66
8	296.45	4379.1	135463	2424	133039	181.12	0.238	2.84
9	296.45	4379.1	134244	5730	128514	179.00	0.238	2.59
10	296.45	4379.1	127511	5890	121332	179.00	0.238	2.6
11[g]	296.45	4379.1	133356	4690	128666	179.00	0.238	2.47
12[a]	296.45	4379.1	198841	2820	196021	181.49	0.238	2.22
13[a]	296.45	4379.1	178580	2816	175764	181.29	0.238	2.36
14[b]	296.45	4379.1	118458	2500	116048	179.65	0.150	2.28
15[c]	296.45	4379.1	167527	2300	165227	181.61	0.312	2.3
16[d]	317.75	838.0	173484	9650	163834	183.30	2.168	5.36
17[d]	318.25	1262.1	183039	9600	173439	180.21	1.985	5.84
18	317.55	1966.6	166516	9415	157101	177.48	1.493	6.6
19	318.35	2556.7	176797	9460	167337	179.52	1.197	6.28
20	318.15	3435.8	172549	9440	163109	179.60	0.816	5.75
21	317.65	4324.1	113864	8942	104922	179.83	0.543	5.22
22[d]	343.45	826.7	178912	31800	147112	178.25	3.619	9.62
23[e,f]	343.45	826.7	191684	32630	159054	168.83	3.619	9.74
24[d]	343.55	1245.0	181652	32000	149652	179.04	3.205	10.65
25	342.55	1939.2	173218	33950	139268	176.87	2.527	12.32
26	342.65	1939.0	175590	33660	141930	178.88	2.531	11.86
27	342.65	1939.0	176608	34550	142058	174.32	2.531	11.89
28	342.65	1939.0	172657	31250	141407	177.33	2.531	11.13
29	342.55	1939.2	172043	33750	138293	176.61	2.527	11.46
30[e,f]	343.55	1937.9	182505	31745	150760	170.27	2.571	12.34
31[e,f]	343.55	1937.9	182365	31800	150565	168.38	2.571	12.49
32[d]	342.75	2519.8	182503	29220	153283	180.31	2.080	10.93
33[d]	342.95	3381.4	188045	29060	158985	180.22	1.534	10.56
34	342.25	4251.2	127278	28520	100070	179.76	1.098	10.25

[a] MDEA from Alfa. [b] Liquid-side stirring speed = 50 rpm. [c] Liquid-side stirring speed = 150 rpm. [d] Volume of cell $V_g + V_l = 350.8$ cm^3. [e] Volume of cell $V_g + V_l = 351.4$ cm^3; others with $V_g + V_l = 350.4$ cm^3. [f] Gas phase stirred at 680 rpm. [g] MDEA from Merck.

over the MDEA + water solution before CO_2 loading; it is assumed constant during an experiment (the absence of leak was verified by checking for pressure stability before pure CO_2 was introduced in the cell).

Initial absorption rates are measured for a pressure range of 10 kPa from the initial total pressure P_0: for this small pressure drop, the concentration of CO_2 resulting from absorption does not change much the composition of the solution, so that k_L, H, and E remain constant with time, and integration of eq 1 yields

$$\ln \frac{P - P_I}{P_0 - P_I} = -bt \tag{4}$$

where

$$b = \frac{RT}{V_G H} k_L A E \tag{5}$$

The regression of experimental data shows that eq 4 is verified with a root mean square average error on the left member lower than 0.01. Slopes b are given for each experiment in Table 1. MDEA is from Aldrich except for some experiments pointed out in the footnotes of Table 1.

For 4380 mol·m^{-3} MDEA solutions, at $T = 296.45$ K and $N = 100$ rpm, reproducibility tests have been performed (experiments 8−13). The relative standard deviation on slope b for the six experiments is less than 8%, within the reproducibility range, which shows that no significant difference can be found when solutions are prepared with MDEA supplied by either Alfa, Aldrich, or Merck, despite their slight differences in purity. For 1980 mol·m^{-3} MDEA solutions, at $T = 296.45$ K and $N = 100$ rpm, and widely varying initial pressures P_0, a reproducibility of 8% is obtained (experiments 3 and 4). For 1980 mol·m^{-3} MDEA solutions, at $T = 342.6$ K and $N = 100$ rpm, a reproducibility of b better than 3.5% is obtained (experiments 25−29). Therefore, all chemical reactions between dissolved CO_2 and reactants in solution are first order with respect to the amount of dissolved CO_2.

With a 4380 mol·m^{-3} MDEA solution, at 296.45 K, changing the liquid-side stirring speed N from 50 (experiment 14) to 100 rpm (experiments 7−9) leads to an increase in CO_2 absorption rate values of about 15%, but no increase is found between $N = 100$ rpm and $N = 150$ rpm (experiment 15). In conditions of faster absorption kinetics, and higher vapor pressure of the inert components, for example at 343.45 K, 1940 mol·m^{-3} MDEA, and $N = 100$ rpm, where gas-side mass transfer resistance may appear, two experiments (nos. 30 and 31) have been made with the gas phase stirred at 680 rpm. For these two experiments, slopes b are similar within 1.2%. Another test of the influence of gas phase stirring was done with an 830 mol·m^{-3} MDEA solution (experiment 23). The differences between slopes b from experiments with and without gas-side stirring are found to be within the reproducibility range.

At a given temperature, the slopes b show that absorption kinetics become faster when the MDEA concentration increases from 840 to 1900 mol·m^{-3}, but decrease again for MDEA concentrations from 1900 to 4300 mol·m^{-3} (Figure 2). This behavior comes from opposite influences of MDEA concentration upon chemical kinetics, CO_2 diffusion, and CO_2 solubility. Additionaly, for given a MDEA concentration, the absorption kinetics always increases with temperature in the range 296 K to 343 K.

Interpretation of Results in Terms of Reaction Kinetics. For each experiment, the enhancement factor

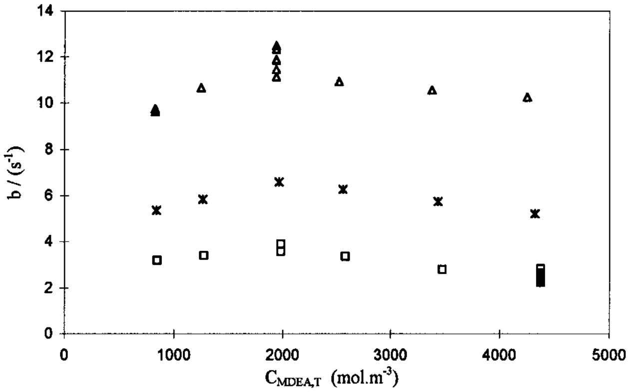

Figure 2. Initial slopes *b* as a function of the total MDEA concentration at 296 K, 318 K, and 343 K from experiments present in Table 1.

E is obtained from *b* using eq 5 and estimates of data for the molar-based Henry's law constant *H* and the liquid-side mass transfer coefficient k_L of dissolved CO_2.

The data and correlations of Al-Ghawas et al. (1989) are used to estimate the CO_2 Henry's constant *H*.

The mass transfer coefficient k_L is calculated using the correlation between dimensionless numbers presented in Appendix B. This correlation has been established for our apparatus from N_2O absorption experiments by similar MDEA + water solutions and correlations of density, viscosity, and diffusion coefficients from previous studies cited.

At a given temperature and stirring speed, because of both the increase of the molar-based CO_2 Henry's constant *H* and decrease of the mass transfer coefficient k_L with the concentration of MDEA, the enhancement factor increases with the concentration of MDEA. The values of *E* are always higher than 3, indicating a fast regime of absorption.

Kinetics of the Reaction between CO_2 and MDEA. Most previous works on CO_2 absorption by solutions of tertiary amines $R_1R_2R_3N$ consider base catalysis for the reaction of CO_2 with water, as initially proposed by Donaldson and Nguyen (1980). Fast hydrogen bonding between the nitrogen electron pair of the tertiary amine and a water molecule would increase the reactivity of water with dissolved CO_2 according to the mechanism

$$R_1R_2R_3N + H_2O = R_1R_2R_3N,HOH \qquad (I)$$

$$CO_2 + R_1R_2R_3N,HOH \rightarrow R_1R_2R_3NH^+ + HCO_3^- \qquad (II)$$

Equation I is assumed to be at equilibrium. Such a mechanism, for water concentrations far higher than the MDEA concentration, leads to the generally accepted rate expression

$$r = kC_{MDEA}C_{CO_2} \qquad (6)$$

Hereafter, the first order with respect to the MDEA concentration is tested and the Arrhenius law for the kinetic constant *k* is obtained.

For the fast regime of absorption found, whatever the hydrodynamics at the interface and the mass transfer model chosen, the enhancement factor *E* is expressed as a function of chemical kinetics at the interface:

$$E = \frac{1}{k_L}(k_{ov}D_{CO_2})^{1/2} \qquad (7)$$

where

$$k_{ov} = kC_{MDEA,i} \qquad (8)$$

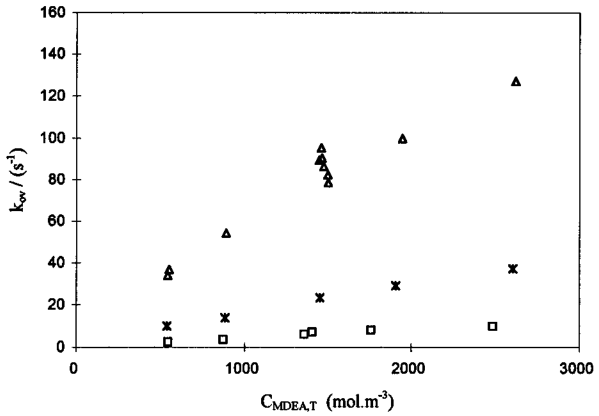

Figure 3. Influence of the interfacial MDEA concentration on k_{ov} at 296 K, 318 K, and 343 K.

if it is assumed that CO_2 only reacts with MDEA according to the rate, eq 7. Subscript i indicates the interfacial concentration of MDEA.

Using Brian's approximate film theory (Brian et al., 1961), which assumes that a single irreversible reaction between CO_2 and MDEA is responsible for the enhancement of absorption, leads to

$$C_{MDEA,i} = C_{MDEA,T}\left(1 - \frac{p_{CO_2}}{HC_{MDEA,T}}\left(\frac{D_{CO_2}}{D_{MDEA}}\right)^{1/2}(E - 1)\right) \qquad (9)$$

$C_{MDEA,T}$ is the total MDEA concentration. The estimation of the diffusion coefficient D_{CO_2} of CO_2 is based on the work of Versteeg and van Swaaij (1988b), also used by Glasscock et al. (1991), for temperatures between (293 and 333) K, and MDEA concentrations between (240 and 2900) $mol \cdot m^{-3}$. These authors also give a correlation to estimate the ratio of diffusion coefficients of CO_2 and MDEA (see Appendix B). Significant discrepancies appear between diffusion coefficient data sets, here between those from Versteeg and van Swaaij (1988b) and those from Al-Ghawas et al. (1989). Both values are based on experiments with N_2O and the analogy between N_2O and CO_2, but Versteeg and van Swaaij (1988b) use a Lewis-type cell, similar to ours, while Al-Ghawas et al. (1989) use a wetted sphere and a laminar-jet apparatus. We chose the correlation given by Versteeg and van Swaaij (1988b).

For each experiment, the interfacial MDEA concentration is calculated using eq 9, for the partial pressure of CO_2 after a decrease of 5 kPa, and the initial MDEA concentration. For the lowest concentrations of MDEA used in this work, at all temperatures, the MDEA depletion reached 36%.

With *H* from Al-Ghawas at al. (1989) and by assuming that the kinetic constant *k* varies with temperature according to an Arrhenius law, a multiple regression of ln k_{ov} upon ln($C_{MDEA,i}$) and 1/*T* yields for our results in the range (293 to 343) K and (840 to 2900) $mol \cdot m^{-3}$ MDEA (Figure 3)

$$\ln k_{ov} = 13.5 + 0.934 \ln(C_{MDEA,i}/mol \cdot cm^{-3}) - \frac{5454}{(T/K)} \qquad (10)$$

With eq 10, the relative root mean square average error on the estimate of slopes *b* is 3.6%. Using the regression of ln[$k_{ov}/C_{MDEA,i}$] upon 1/*T*, leads to the Arrhenius expression for the kinetic constant (Figure 4):

Table 2. Predicted Kinetic Constants at 296 K, 318 K, and 343 K from Literature Constants and Energies of Activation (Comparison to Values from Equation 11)

					$k/10^{-3}$ $m^3 \cdot mol^{-1} \cdot s^{-1}$		
ref	T/K	$C_{MDEA}/10^3$ $mol \cdot m^{-3}$	$P_{CO_2}/10^5$ Pa	E_a/kJ·mol^{-1}	296 K	318 K	343 K
Yu et al. (1985)	313−333	0.2−2.5	1	38.5	15.4		
Haimour et al. (1987)	288−308	0.85−1.7	1	71.6	2.02	14.6	
Critchfield (1988)	282−350	1.7	1	56.9	2.24	11.0	51.6
Versteeg and van Swaaij (1988a)	293−333	0.17−2.7	<1	42.3	4.02	13.0	
Toman and Rochelle (1989)	298−308	4.3	0.02−0.12				
Tomcej et al. (1989)	298−308	1.7−3.47	0.95	42.7	4.91	16.0	
Littel et al. (1990)	293−333	0.17−2.7	<1	48.1	4.70	17.8	
Rinker et al. (1995)	293−342	0.85	1	37.8	5.57	16.2	46.4
this work	296−343	0.84−4.4	1−1.7	44.3	4.55	16.3	57.0

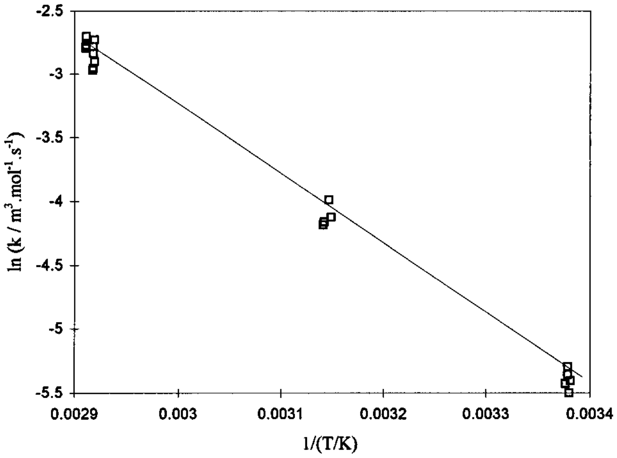

Figure 4. Arrhenius plot.

$$k = 4.68 \times 10^5 \exp\left\{-\frac{5461}{(T/\mathrm{K})}\right\} \qquad (11)$$

with 3.9% as the relative root mean square average error on the estimate of b, very close to the previous one.

Using for H the work of Versteeg and van Swaaij (1988b), the multiple regression of ln k_{OV} upon ln($C_{MDEA,i}$) and $1/T$ yields for our results in the range 293 to 323 K and 840 to 2960 mol·m^{-3} MDEA

$$\ln k_{ov} = 12.2 + 0.879 \ln(C_{MDEA,i}/\mathrm{mol \cdot m^{-3}}) - \frac{4957}{(T/\mathrm{K})} \qquad (12)$$

with 3.8% for the relative root mean square average error on the estimate of slopes b. The slight difference between the temperatures of activation in eqs 10 and 12 shows the significant influence of the thermodynamic data chosen on the Arrhenius equation for the CO_2 + MDEA reaction and how important is the reliability of both diffusion and equilibrium data. The two sets of Henry's constants lead to k_{ov} values different by a maximum of 22%.

Comparison with Previous Data and Analysis

Versteeg and van Swaaij (1988a), Haimour et al. (1987), Yu et al. (1985), and Critchfield (1988) have already studied CO_2 absorption by MDEA solutions in stirred cells with a known flat interface similar to our own. Tomcej and Otto (1989) used a single-sphere absorber. Yu et al. used pure CO_2 at 1 atm, and Versteeg used CO_2 pressures lower than 1 atm. The ranges of temperatures and MDEA concentrations, as well as partial pressures of CO_2 investigated, are presented in Table 2.

The values of k of eq 11 for the temperatures investigated are in very good agreement with those of recent work (Tomcej and Otto (1989) and Littel et al. (1990)) (Table 2). But, because the MDEA depletion at the interface has been taken into account in this work, they are higher than those calculated by the first authors cited, whose data are limited to less concentrated MDEA solutions and low temperatures. Table 2 also shows that there is a very good agreement with the recent work for the activation energy from eq 11.

Conclusions

Kinetics of CO_2 absorption by aqueous solutions of MDEA have been studied in the extended ranges of temperatures from 296 K to 343 K and of MDEA concentrations from 10 to 50 mass % and compared with previous studies. They were measured by recording the pressure drop during absorption in a batch thermoregulated Lewis-type cell. Mass transfer properties corresponding to this cell have been characterized by considering absorption measurements with the MDEA + water + N_2O system, leading to a correlation between the classical dimensionless criteria.

Kinetics constants are in good agreement with the Tomcej and Otto (1989) and Littel et al. (1990) data as well as for activation energy. Data treatment which involves additional data is very dependent on the Henry's constants and diffusion coefficients for which careful and accurate measurements would be of the utmost interest.

Supporting Information Available:

Tables 2−34 for Appendix A are available via the Internet. Accessing information is given on any current masthead page.

Appendix A. Rough Results

Just Table A1 is enclosed for information (Tables 2−34 are available as Supporting Information).

Appendix B. Lewis Cell Correlation for Mass Transfer

A mass transfer correlation between dimensionless numbers has been established for our apparatus from N_2O absorption experiments by the same MDEA−water solutions:

$$\mathrm{Sh} = 0.340\mathrm{Re}^{2/3}\mathrm{Sc}^{1/3} \qquad (B1)$$

$\mathrm{Re} = dND_{Ag}^2/\mu$ is the stirrer Reynolds number, $\mathrm{Sc} = \mu/dD_j$ is the Schmidt number, $\mathrm{Sh} = k_{L_j}D_T/D_j$ is the Sherwood number.

The mass transfer correlation (B1) is established for ranges of Re and Sc similar to those for experiments of CO_2 absorption by MDEA. D_{Ag} (m) is the stirrer diameter, D_T (m) is the internal diameter of the Lewis cell. k_{L_j} (m·s^{-1}) and D_j (m^2·s^{-1}) are the mass transfer and the diffusion coefficient of a species j.

The viscosity μ (Pa.s) and the density d of the mixture are estimated using the correlations of Al-Ghawas et al. (1989).

Table A1. CO_2 Absorption Kinetics[a]

t/s	*P*/Pa	*t*/s	*P*/Pa	*t*/s	*P*/Pa	*t*/s	*P*/Pa
0.00	177608.0	670.48	144025.0	1339.97	116976.0	2010.17	94728.9
10.49	176473.0	680.42	143540.0	1350.40	116590.0	2020.11	94417.2
20.38	175863.0	690.31	143148.0	1360.29	116226.0	2029.99	94119.0
30.32	175194.0	700.19	142682.0	1370.23	115851.0	2039.94	93827.0
40.21	174673.0	710.08	142288.0	1380.12	115446.0	2050.43	93505.7
50.15	174134.0	720.02	141850.0	1390.00	115117.0	2060.37	93255.1
60.04	173628.0	730.51	141414.0	1399.94	114783.0	2070.25	92979.3
69.98	173022.0	740.40	140983.0	1410.43	114431.0	2080.20	92668.3
80.47	172471.0	750.29	140513.0	1420.32	114094.0	2090.08	92364.8
90.36	171892.0	760.17	140139.0	1430.21	113802.0	2100.02	92127.0
100.24	171371.0	770.00	139756.0	1440.15	113400.0	2109.97	91752.4
110.18	170906.0	780.49	139285.0	1450.04	113086.0	2120.46	91469.0
120.07	170407.0	790.33	138901.0	1460.53	112632.0	2130.34	91176.7
130.01	169826.0	800.21	138412.0	1470.41	112308.0	2140.28	90922.3
140.01	169282.0	810.10	138010.0	1480.30	112001.0	2150.17	90623.6
150.44	168783.0	819.99	137684.0	1490.24	111572.0	2160.11	90325.1
160.33	168262.0	830.48	137117.0	1500.13	111263.0	2170.05	90018.9
170.27	167681.0	840.36	136668.0	1510.07	110897.0	2179.94	89796.2
180.16	167246.0	850.19	136240.0	1519.96	110589.0	2190.43	89363.9
190.10	166718.0	860.08	135964.0	1530.45	110174.0	2200.32	89105.8
199.99	166223.0	869.97	135496.0	1540.33	109879.0	2210.31	88838.9
210.48	165684.0	880.46	135038.0	1550.28	109557.0	2220.20	88524.6
220.36	165259.0	890.35	134669.0	1560.16	109104.0	2230.09	88216.6
230.31	164704.0	900.23	134137.0	1570.10	108848.0	2240.03	87987.9
240.19	164189.0	910.12	133761.0	1579.99	108510.0	2250.52	87661.4
250.13	163727.0	920.01	133474.0	1590.48	108135.0	2260.41	87401.8
260.08	163209.0	930.44	132924.0	1600.37	107828.0	2270.35	87127.9
269.96	162733.0	940.33	132570.0	1610.25	107463.0	2280.23	86889.1
280.40	162220.0	950.21	132087.0	1620.20	107138.0	2290.18	86598.3
290.34	161659.0	960.10	131757.0	1630.14	106828.0	2300.06	86354.0
300.28	161277.0	969.99	131237.0	1640.08	106496.0	2310.00	86059.8
310.17	160751.0	980.48	130862.0	1649.96	106197.0	2320.50	85761.3
320.11	160235.0	990.36	130456.0	1660.40	105872.0	2330.38	85451.4
330.00	159743.0	1000.20	130141.0	1670.34	105473.0	2340.32	85185.9
340.49	159310.0	1010.08	129643.0	1680.23	105153.0	2350.21	84912.4
350.43	158847.0	1019.97	129314.0	1690.17	104822.0	2360.15	84639.6
360.31	158309.0	1030.46	128874.0	1700.06	104482.0	2370.09	84392.3
370.26	157872.0	1040.46	128446.0	1709.94	104168.0	2379.98	84070.7
380.14	157392.0	1050.29	128036.0	1720.43	103834.0	2390.47	83823.4
390.08	156862.0	1060.18	127687.0	1730.38	103492.0	2400.36	83565.4
399.97	156365.0	1070.06	127312.0	1740.26	103232.0	2410.30	83327.4
410.46	155965.0	1079.95	126986.0	1750.15	102890.0	2420.24	83086.7
420.40	155454.0	1090.49	126430.0	1760.09	102585.0	2430.13	82731.6
430.29	154996.0	1100.38	126074.0	1769.98	102231.0	2440.07	82414.4
440.23	154523.0	1110.27	125699.0	1780.47	101898.0	2449.95	82252.8
450.12	154050.0	1120.10	125359.0	1790.35	101580.0	2460.45	81998.4
460.06	153625.0	1130.04	124945.0	1800.24	101328.0	2470.39	81721.1
469.95	153196.0	1140.48	124553.0	1810.18	100949.0	2480.27	81430.0
480.44	152614.0	1150.36	124103.0	1820.07	100721.0	2490.22	81170.8
490.38	152195.0	1160.25	123737.0	1829.96	100331.0	2500.10	80931.1
500.26	151647.0	1170.14	123439.0	1840.45	99996.7	2509.99	80680.9
510.21	151256.0	1180.02	123012.0	1850.39	99708.2	2520.48	80378.6
520.09	150819.0	1190.51	122580.0	1860.33	99242.7	2530.42	80136.2
530.03	150348.0	1200.40	122212.0	1870.22	99103.9	2540.31	79926.3
540.52	149834.0	1210.29	121716.0	1880.10	98698.8	2550.25	79618.6
550.41	149508.0	1220.17	121443.0	1890.04	98499.0	2560.14	79394.5
560.35	149025.0	1230.06	121001.0	1900.54	98144.4	2570.02	79160.8
570.24	148557.0	1239.95	120737.0	1910.48	97817.8	2579.96	78844.7
580.13	148091.0	1250.44	120334.0	1920.36	97478.7	2590.45	78607.4
590.01	147633.0	1260.27	119940.0	1930.25	97164.5	2600.34	78366.5
599.95	147202.0	1270.16	119499.0	1940.19	96920.9	2610.28	78093.9
610.45	146674.0	1280.04	119205.0	1950.08	96554.5	2620.17	77930.6
620.39	146366.0	1290.53	118784.0	1960.02	96304.5	2630.11	77618.1
630.27	145765.0	1300.42	118467.0	1970.51	95916.2	2640.00	77286.1
640.16	145386.0	1310.31	118094.0	1980.40	95626.8		
650.05	145035.0	1320.19	117685.0	1990.28	95379.6		
659.99	144524.0	1330.08	117334.0	2000.28	95070.3		

[a] $T = 295.95$ K, solvent = MDEA + H_2O. Initial concentration of MDEA = 0.8444 mol/L. Initial CO_2 loading: 0 mol of CO_2/mol of MDEA. Final CO_2 loading: 0.0522 mol of CO_2/mol of MDEA.

As did Glasscock et al. (1991), the work and correlations of Versteeg and van Swaaij (1988b), based on the analogy between CO_2 and N_2O, were used to estimate the diffusion coefficient D_{CO_2} ($m^2 \cdot s^{-1}$) of CO_2, although their study is limited to temperatures between (293 and 333) K and MDEA concentrations between (840 and 2960) $mol \cdot m^{-3}$. Their measurements were achieved in a stirred vessel with a horizontal gas−liquid interface, similar to our apparatus, and not a wetted sphere or a laminar-jet apparatus like in Al-Ghawas et al. (1989). The latter study, achieved with MDEA concentrations between (0 and 4400) $mol \cdot m^{-3}$, is limited to temperatures between (288 and 323) K. It must be pointed out that, for the maximum temperatures and concentrations in our study for which Versteeg and Al-Ghawas works are both available, i.e. 2600 mol·m^{-3} MDEA and 296 K or 318 K, diffusion coefficients from Versteeg are half the values of Al-Ghawas et al. (1989).

The work of Versteeg and van Swaaij (1988b) also allows an estimate of the ratio of CO_2 to MDEA diffusion coefficients, used to calculate the MDEA depletion in the interfacial boundary layer:

$$\left(\frac{D_{CO_2}}{D_{MDEA}}\right)_{aq\ sol} = \left(\frac{D_{CO_2}}{D_{MDEA}}\right)_{water}\left(\frac{\mu_{water}}{\mu_{aq\ sol}}\right)^{0.2} \tag{B2}$$

As did Bosch et al. (1989), in agreement with the Wilke and Chang (1955) correlation, the ratio of diffusion coefficients at T in water (subscript w) is related to the ratio of molal volumes of species at their normal boiling points:

$$\left(\frac{D_{CO_2}}{D_{MDEA}}\right)_{water} = \left(\frac{v_{MDEA}}{v_{CO_2}}\right)^{0.6} \tag{B3}$$

From Le Bas tables in Reid et al. (1977), $v_{CO_2} = 34 \times 10^{-6}$ m^3·mol^{-1} and $v_{MDEA} = 148.9 \times 10^{-6}$ m^3·mol^{-1}. Thence

$$\left(\frac{D_{CO_2}}{D_{MDEA}}\right)_{water} = 2.43$$

Literature Cited

Al-Ghawas, H. A.; Hagewiesche, D. P.; Ruiz-Ibanez, G.; Sandall, O. C. Physicochemical properties important for carbon dioxide absorption in aqueous methyldiethanolamine. *J. Chem. Eng. Data* **1989**, *34*, 385−391.

Barth, D.; Tondre C.; Lappai, G.; Delpuech, J. J. Kinetic study of carbon dioxide reaction with tertiary amines in aqueous solutions. *J. Phys. Chem.* **1981**, *85*, 3660−3667.

Barth, D.; Tondre, C.; Delpuech, J. J. Kinetics and mechanisms of the reactions of carbon dioxide with alkanolamines: a discussion concerning the cases of MDEA and DEA. *Chem. Eng. Sci.* **1984**, *39*, 1753−1757.

Blauwhoff, P. M. M.; Versteeg, G. F.; van Swaaij, W. P. M. A study on the reaction between CO_2 and alkanolamines in aqueous solutions. *Chem. Eng Sci.* **1984**, *39*, 207−225.

Bosch, H.; Versteeg, G. F.; van Swaaij, W. P. M. Gas-liquid mass transfer with parallel reversible reactions-I. Absorption of CO_2 into solutions of sterically hindered amines. *Chem. Eng. Sci.* **1989**, *44*, 2732−2734.

Brian, P. L. T.; Hurley, J. F.; Hasseltine, E. H. Penetration theory for gas absorption accompanied by a second order chemical reaction. *AIChE J.* **1961**, *7*, 226.

Critchfield, J. E. CO_2 absorption/desorption in methyldiethanolamine solutions promoted with monoethanolamine and diethanolamine: mass transfer and reaction kinetics. Ph.D. dissertation, The University of Texas at Austin, 1988.

Donaldson, T. L.; Nguyen, Y. N. Carbon dioxide reaction and transport into aqueous amine membranes. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 260−266.

Glasscock, D. A.; Critchfield, J. E.; Rochelle, G. T. CO_2 absorption/desorption in mixtures of methyldiethanolamine with monoethanolamine or diethanolamine. *Chem. Eng Sci.* **1991**, *46*, 2829−2845.

Haimour, N.; Bidarian, A.; Sandall, O. Kinetics of the reaction between carbon dioxide and methyldiethanolamine. *Chem. Eng. Sci.* **1987**, *42*, 1393−1398.

Lewis, J. B. The mechanism of mass-transfer of solutes across liquid-liquid interfaces-I. *Chem. Eng. Sci.* **1954**, *3*, 248−259.

Littel, R. J.; van Swaaij, W. P. M.; Versteeg, G. F. Kinetics of carbon dioxide with tertiary amines in aqueous solution. *AIChE J.* **1990**, *36*, 1633−1640.

Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The properties of gases and liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

Rinker E. B.; Ashour S. S.; Sandall O. C. Kinetics and modelling of carbon dioxide absorption into aqueous solutions of N-methyldiethanolamine. *Chem. Eng. Sci.* **1995**, *50*, 755−768.

Toman, J. J.; Rochelle, G. T. Carbon dioxide absorption rates and physical solubility in 50% aqueous methyldiethanolamine partially neutralized with sulfuric acid. Paper No. 56c, AIChE National Meeting, Houston, TX, 1989.

Tomcej, R. A.; Otto, F. D. Absorption of CO_2 and N_2O into aqueous solutions of methyldiethanolamine. *AIChE J.* **1989**, *35*, 861−864.

Versteeg, G. F.; van Swaaij, W. P. M. On the kinetics between CO_2 and alkanolamines both in aqueous and non-aqueous solutions-II. Tertiary amines. *Chem. Eng. Sci.* **1988a**, *43*, 587−591.

Versteeg, G. F.; van Swaaij, W. P. M. Solubility and diffusivity of acid gases (CO_2, N_2O) in aqueous alkanolamine solutions. *J. Chem. Eng. Data* **1988b**, *33*, 29−34.

Wilke, C. R.; Chang, P. Correlation of diffusion coefficients in dilute solutions. *Am. Inst. Chem. Eng. J.* **1955**, *1*, 264−270.

Xu, G-W.; Zhang, C-F.; Qin, S-J.; Wang, Y-W. Kinetics study on absorption of carbon dioxide into solutions of activated methyldiethanolamine. *Ind. Eng. Chem. Res.* **1992**, *31*, 921−927.

Yu, W. C.; Astarita, G.; Savage, D. W. Kinetics of carbon dioxide absorption in solutions of methyldiethanolamine. *Chem. Eng. Sci.* **1985**, *40* (8), 1585−1590.

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