Absorption of CO_2 and N_2O into Aqueous Solutions of Methyldiethanolamine

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The absorption of CO_2 in aqueous methyldiethanolamine (MDEA) solutions is a mass-transfer process accompanied by chemical reaction in the liquid phase. Since the rate of CO_2 absorption governs the selectivity of an amine absorption process for H_2S, it is desirable to have accurate values of the kinetic rate parameters that characterize CO_2 absorption. The existing experimental data for diffusion coefficients and the reaction rate constant in MDEA solutions do not cover the full range of industrial interest.

In this investigation, experimental measurements of the rate of absorption of N_2O and CO_2 into aqueous solutions of MDEA were taken, using a single sphere absorber. Diffusion coefficients and kinetic rate constants were calculated from the absorption rate data by allowing for resistance to mass transfer in the gas and liquid phases. The N_2O data were used to infer the diffusivity of CO_2 in MDEA solutions. As discussed by Tomcej et al. (1987), these fundamental parameters are required by nonequilibrium stage models used to predict the performance of industrial contactors that use MDEA as the chemical solvent for the selective removal of H_2S from gaseous streams containing H_2S and CO_2.

Theory

The reactions of H_2S and CO_2 with primary, secondary, and tertiary amines are discussed in detail by Astarita (1967), Danckwerts (1970), Astarita et al. (1983), and Kohl and Riesenfeld (1985). Carbon dioxide undergoes the following two reactions in aqueous solution:

$$CO_2 + H_2O \overset{k_{H_2O}}{\rightleftharpoons} HCO_3^- + H^+ \tag{1}$$

$$CO_2 + OH^- \overset{k_{OH^-}}{\rightleftharpoons} HCO_3^- \tag{2}$$

Measured rates of CO_2 absorption in aqueous tertiary amine solutions are well in excess of the rate predicted by theory, assuming that the two parallel reactions, Eq. 1 and 2, occur as indicated. It is generally accepted that MDEA acts as a catalyst for the CO_2 hydrolysis reaction, Eq. 1; however, there is no general agreement on the catalytic mechanism.

The rate of reaction of CO_2 in aqueous MDEA solutions may be expressed as the sum of three terms,

$$r_{CO_2} = \{k_{H_2O} + k_{OH^-}[OH^-] + k_2[MDEA]\}[CO_2] \tag{3}$$

where k_2 is the second-order rate constant for the increase in the CO_2 reaction rate, which is a result of MDEA base catalysis. When measured using a laboratory absorber, an overall reaction rate constant, k_{ov}, is obtained from the raw absorption data such that

$$r_{CO_2} = k_{ov}[CO_2] \tag{4}$$

Pinsent et al. (1956) and Astarita et al. (1983) present correlations for k_{H_2O} and k_{OH^-}, respectively. The values of $[OH^-]$ and $[MDEA]$ can be estimated using a suitable equilibrium model.

The analytical method used to obtain molecular diffusion coefficients and reaction rate constants from absorption data, measured using a sphere absorber, is presented by Tomcej (1987). For steady-state physical absorption of a single-solute gas into a spherical liquid film, Davidson and Cullen (1957) derived the following solution to the continuity equation:

$$G_S = L(C_i - C_O)\left[1 - \sum_i \beta_i e^{-\gamma_i \alpha}\right] \tag{5}$$

where

$$\alpha = 3.3653\pi\left\{\frac{2\pi g}{3\upsilon}\right\}^{1/3} D\, R^{7/3}\, L^{-4/3} \tag{6}$$

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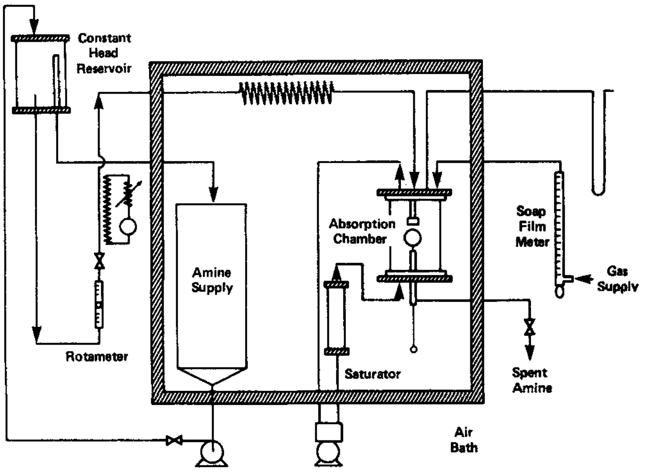

Figure 1. Single-sphere absorber.

The coefficients, β_i and γ_i are constants that were later modified by Olbrich and Wild (1969).

For steady-state absorption of a single-solute gas into a spherical liquid film, accompanied by simultaneous chemical reaction in the liquid phase, the rate of absorption can be shown to be:

$$G_s = 4\pi R^2 \{k_{ov} D\}^{1/2} (C_i - C_{eq}) \qquad (7)$$

provided that the reaction occurs under pseudo first-order fast reaction conditions. The nitrous oxide analogy can be used to infer the effect of amine concentration on the molecular diffusion coefficient, and the physical solubility of CO_2 in MDEA solutions from corresponding measurements taken with N_2O.

Experimental

A detailed description of the single-sphere absorber apparatus, and the procedure used to bring the absorber to a steady state may be found in Tomcej (1987). A simplified schematic diagram of the equipment is given in Figure 1. A 50.8 mm sphere was used, with amine solution flow rates ranging from 0.4 mL/s to 2.0 mL/s. To avoid surface rippling, liquid flow rates were restricted to less than 2.0 mL/s. In operation, the laminar jet length and liquid take-off length were maintained at 2.0 mm and 20 mm, respectively. The total pressure in the absorption chamber was maintained at 96 kPa for all the experiments.

The aqueous MDEA solutions were prepared from distilled water and *N*-methyldiethanolamine, supplied by Aldrich Chemical Co. The MDEA had a minimum purity of 99% and was used without further purification. The CO_2 and N_2O were supplied by Linde and had minimum purities of 99.9% and 98.5%, respectively. The N_2O was analyzed by gas chromatography and found to have a purity of 99.4%.

Table 1. Diffusion Coefficient for CO_2 in Water at 25°C

$D \times 10^9$ m^2/s	Reference
1.92	Davidson and Cullen (1957)
1.92	Ratcliff and Holdcroft (1961)
2.00	Vivian and King (1964)
1.95	Thomas and Adams (1965)
1.93	Khalil (1984)
1.97	This Work

Table 2. Diffusion Coefficient for N_2O in MDEA Solutions

MDEA wt. %	T °C	$\mu \times 10^3$ kg/m · s	$D \times 10^9$ m^2/s
20	25.0	1.94	0.934
20	49.6	1.02	1.87
20	74.7	0.642	2.82
40	25.0	5.31	0.629
40	49.6	2.30	1.40
40	74.8	1.23	2.28

Sodium lauryl sulfate (Teepol) was added to the liquid to promote uniform wetting of the sphere surface. It was determined by successive addition that 0.01 wt.% Teepol was required to maintain a stable film under all conditions encountered in the experiment. Measurements of the rate of absorption of N_2O in 20 wt.% MDEA solution were taken at 25°C before and after the addition of surfactant. The absorption rates were identical, and the effect of Teepol was assumed to be negligible.

Using the sphere absorber, the diffusion coefficient of CO_2 in water at 25°C was determined to be 1.97×10^{-9} m^2/s. Table 1 contains a comparison of experimental values of D_{CO_2} at 25°C, as reported by several authors.

Following the CO_2-water study, the apparatus was used to measure the rates of absorption of N_2O and CO_2 into MDEA solutions. Tables 2 and 3 contain summaries of the pertinent results. The solubility data for N_2O in MDEA solutions as reported by Jou et al. (1986) were used to interpret the experimental physical-absorption measurements. Gas-phase resistance was accounted for by using the correlation of Froessling (1938) for the gas-phase mass-transfer coefficient.

Discussion

Physical absorption studies

The results of the analysis of the N_2O absorption studies, along with data from other sources, are shown in Figure 2. This

Table 3. Reaction Rate Constant for CO_2 Absorption in MDEA Solutions

T °C	[MDEA] $kmol/m^3$	k_{ov} s^{-1}	k_2 [MDEA] s^{-1}	k_2 $m^3/kmol \cdot s$
20 wt. % MDEA Solution				
25.1	1.64	9.7	9.0	5.5
49.7	1.61	44.9	39.0	24.2
59.9	1.59	65.4	53.8	33.7
74.8	1.58	130.3	99.1	62.8
40 wt. % MDEA Solution				
25.3	3.35	19.3	18.5	5.5
40.2	3.32	43.5	40.2	12.1
49.9	3.30	71.4	64.1	19.4
74.9	3.23	246.7	207.2	64.1

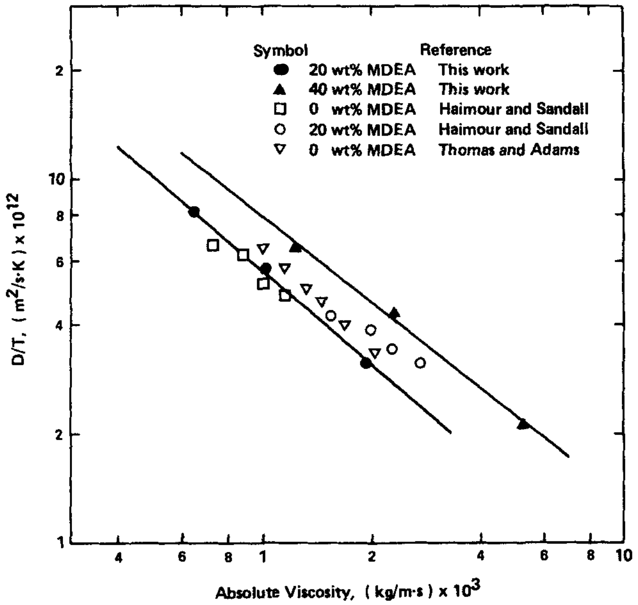

Figure 2. Stokes-Einstein relationship for N_2O diffusivity.

plot illustrates the combined influence of temperature and liquid viscosity on the N_2O diffusion coefficient. The data of Thomas and Adams (1965) are for N_2O absorption in water-glycerol solutions at 20°C. The data of Haimour and Sandall (1984) are for N_2O absorption in water and 20 wt.% MDEA solutions at temperatures ranging from 15° to 35°C. All the experimental data points display the same general trend. Diffusivity is seen to increase with temperature and to decrease with increasing liquid viscosity.

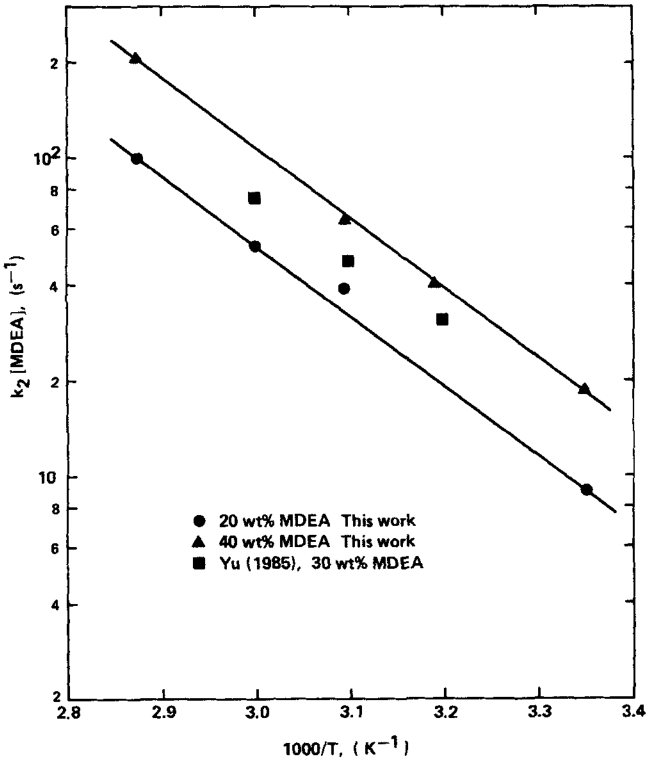

Figure 3. Effect of temperature on pseudo first-order rate constant.

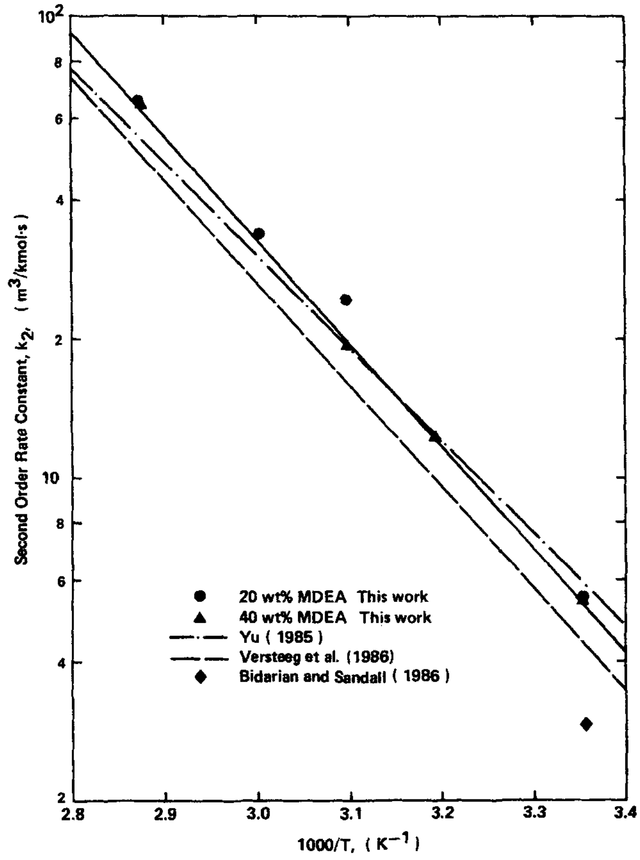

Figure 4. Effect of temperature on second-order rate constant.

The data for the 20 wt.% and 40 wt.% solutions were correlated with the following expressions:

20 wt.% MDEA

$$\ln D_{N_2O}/T = -31.8133 - 0.8558 \ln \mu \tag{8}$$

40 wt.% MDEA

$$\ln D_{N_2O}/T = -30.9420 - 0.7785 \ln \mu \tag{9}$$

which are shown as the solid lines in Figure 2. These correlations are of the form $D\mu^{C_1}/T = C_2$, and the calculated values of C_1 (0.8558 and 0.7785) compare favorably with the value of 0.80 reported by Versteeg and van Swaaij (1988b), but differ from the value of 0.5 reported by Diaz et al. (1988).

Chemical absorption studies

The pseudo first-order reaction-rate constant for the CO_2 hydrolysis reaction, k_2 [MDEA], is plotted in Figure 3 as a function of reciprocal temperature and amine concentration. The data of Yu (1985) for 30 wt.% MDEA (2.5 kmol/m³) are included for comparison. The rate constant ranges from 9 to 210 s^{-1}, and increases with temperature and free amine concentration.

The pseudo first-order reaction-rate constants were divided by the free amine concentration to calculate the second-order rate constant, k_2, which is independent of concentration. The values of k_2 derived from the experimental data are plotted in Figure 4 as a function of reciprocal temperature. The values reported by Yu (1985), Versteeg et al. (1986), and Bidarian and Sandall (1986) are included for comparison. The experimental data for k_2 were correlated with the following expression:

$$k_2 = 1.615 \times 10^8 \exp\left(\frac{-5134}{T}\right) \tag{10}$$

The activation energy was calculated to be 42.7 kJ/mol (10.2 kcal/mol). This compares with the values of 38.5 kJ/mol and 42.4 kJ/mol as determined by Yu (1985), and Versteeg and van Swaaij (1988a), respectively.

Acknowledgment

Funding for this work was provided by the Natural Sciences and Engineering Research Council of Canada and the University of Alberta. The assistance given by Mr. D. Lal in operating the equipment is greatly appreciated.

Notation

C = concentration of solute gas, kmol/m^3
C_i = concentration of solute gas at gas-liquid interface, kmol/m^3
C_{eq} = concentration of solute gas in bulk liquid at equilibrium, kmol/m^3
C_o = concentration of solute gas in bulk liquid, kmol/m^3
D = molecular diffusion coefficient, m^2/s
G_s = rate of absorption of solute gas in liquid over sphere, kmol/s
g = acceleration due to gravity, 9.80665 m/s^2
k_2 = second-order rate constant, m^3/kmol · s
k_{H_2O} = pseudo first-order rate constant for CO_2 hydrolysis, s^{-1}
k_{OH^-} = second-order rate constant for reaction of CO_2 with OH^-, m^3/kmol · s
k_{ov} = pseudo first-order overall rate constant, s^{-1}
L = volumetric liquid flow rate, m^3/s
R = radius of sphere, m
r = rate of reaction of solute gas, kmol/m^3 · s
T = temperature, K

Greek letters

α = parameter, Eq. 6
β = constant coefficient, Eq. 5
γ = constant coefficient, Eq. 5
μ = absolute viscosity of liquid phase, kg/m · s
ν = kinematic viscosity of liquid phase, m^2/s
[ ] = concentration in liquid phase, kmol/m^3

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Manuscript received July 22, 1988, and revision received Jan. 10, 1989.