Kinetics of Carbon Dioxide and Methyldiethanolamine with Phosphoric Acid

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The kinetics of the reaction between carbon dioxide and methyldiethanolamine (MDEA) were studied in the presence of various amounts of phosphoric acid at 298 K, 308 K, and 318 K. A stirred cell with a known interfacial area was used at atmospheric pressure to measure the volumetric absorption rate of CO_2 flowing through the vessel.

The addition of phosphoric acid to an aqueous solution of MDEA resulted in a Bronsted acid-base neutralization reaction. While virtually all of the acid was consumed by the neutralization reaction, a large part of the MDEA remained in its free form. The absorption of carbon dioxide in these solutions was slower than expected, given the amount of free MDEA present. The rate depression in the presence of hydrogen phosphate anions was attributed to the stabilization of the reaction transition state between MDEA, water, and carbon dioxide through charge dispersal.

Introduction

The technology used in the treatment of gas streams containing acidic impurities, such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S), has continued to evolve over several decades. Through careful process selection and choice of aqueous absorbing solutions, engineers continue to optimize gas treating systems based on the source of the acidic impurities. Alkanolamines, including monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), triethanolamine (TEA), and methyldiethanolamine (MDEA), are generally preferred over other types of chemical solvents because of their solubility in water, low volatility, and their ability to selectively remove acid gases from a hydrocarbon stream such as natural gas.

The selectivity of MDEA, a tertiary amine, for absorbing H_2S over CO_2 was first noted by Frazier and Kohl (1950). Since that time, the MDEA process has become a primary choice among gas cleaning systems due to increased energy efficiency and ease of sulfur recovery. The absorption of carbon dioxide into aqueous MDEA solutions is a mass-transfer process from the gas phase to the liquid phase followed by a chemical reaction. Several researchers have determined the kinetic parameters associated with the reaction between aqueous MDEA and carbon dioxide (Alper and Al-Ramadhan, 1987; Brabson, 1985; Haimour et al., 1984a; Tomcej and Otto, 1989; Versteeg et al., 1986; Yu et al., 1985). However, none have suggested that the selectivity of the MDEA process could be enhanced by the addition of a secondary chemical species to inhibit the reaction of carbon dioxide in solution. The objective of this study was to measure the reduction of CO_2 absorption into MDEA solutions containing small amounts of phosphoric acid.

Experiments were carried out at atmospheric pressure and 298 K, 308 K, and 318 K in a stirred-cell reactor, while the total MDEA concentration ranged from 1.69×10^3 to 3.40×10^3 $mol \cdot m^{-3}$. Phosphoric acid was added in amounts of 0.05, 0.10, and 0.15 moles per mole of MDEA. Pure aqueous solutions of MDEA were also tested for comparison.

Kinetics

Each of the researchers who have studied the reaction between carbon dioxide and MDEA have proposed mechanisms for the reaction, but there is no general agreement among them. It, however, has been established numerous times that the reaction is second-order overall: first-order in MDEA and first-order in CO_2. The overall reaction is:

$$R_2NCH_3 + CO_2 + H_2O = R_2N^+HCH_3 + HCO_3^- \qquad (1)$$

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where $R = CH_2CH_2OH$. The forward rate equation for this reaction is:

$$r_{CO_2} = k_2[\mathrm{MDEA}][CO_2] \tag{2}$$

The rate law may be reduced to a pseudo-first-order equation by lumping the k_2 [MDEA] term into an overall kinetic constant, k_{ov}.

$$r_{CO_2} = k_{ov}[CO_2] \tag{3}$$

Additionally, carbon dioxide is hydrolyzed in an aqueous solution.

$$CO_2 + H_2O = HCO_3^- + H^+ \tag{4}$$

$$CO_2 + OH^- = HCO_3^- \tag{5}$$

Reaction 4, however, is very slow (less than 0.026 s^{-1} at 298 K) relative to the rate of reaction in the presence of MDEA, and reaction 5 is insignificant since there is a depletion of OH^- at the free surface due to reaction; therefore, both have been disregarded in this study. Haimour et al. (1984a) also disregarded these reactions when they used a similar stirred-cell apparatus to study MDEA kinetics.

Acids, such as phosphoric acid (H_3PO_4), which have more than one dissociable proton are known as polyprotic acids. One mole of H_3PO_4 is capable of neutralizing three moles of a strong base. The three dissociation constants of phosphoric acid at 298 K are given below (McQuarrie and Rock, 1984).

$$H_3PO_4(aq) = H^+(aq) + H_2PO_4^-(aq)$$
$$K_{a1} = [H^+][H_2PO_4^-]/[H_3PO_4] = 7.1 \ \mathrm{mol \cdot m^{-3}} \tag{6}$$

$$H_2PO_4^-(aq) = H^+(aq) + HPO_4^{2-}(aq)$$
$$K_{a2} = [H^+][HPO_4^{2-}]/[H_2PO_4^-] = 6.2 * 10^{-5} \ \mathrm{mol \cdot m^{-3}} \tag{7}$$

$$HPO_4^{2-}(aq) = H^+(aq) + PO_4^{3-}(aq)$$
$$K_{a3} = [H^+][PO_4^{3-}]/[HPO_4^{2-}] = 4.4 * 10^{-10} \ \mathrm{mol \cdot m^{-3}} \tag{8}$$

Experimental Study

The experiments of this study were performed using a constant-pressure stirred-cell reactor system. This system is shown in Figure 1 and is described in detail by Cordi (1991). Amine solutions were prepared using distilled, deionized water and 99% MDEA obtained from Texaco Chemical Company. The phosphoric acid added to these solutions was purchased from J. T. Baker Inc. and was 86% pure; the balance consisted of water and trace impurities. All solutions were 500 mL in total volume. The carbon dioxide and nitrous oxide supplied by Airco had purities of 99.8% and 99%, respectively.

The absorption rates of carbon dioxide and nitrous oxide in the stirred cell shown in Figure 2 were measured volumetrically from the difference between inlet and outlet flow rates. The solution was stirred by a two-bladed turbine near the surface and a three-bladed propeller in the bulk. The stirring rate was limited to 45 rpm to keep the liquid surface planar and free of turbulence. Physical mass transfer and solubility of N_2O were also determined with the stirred-cell apparatus.

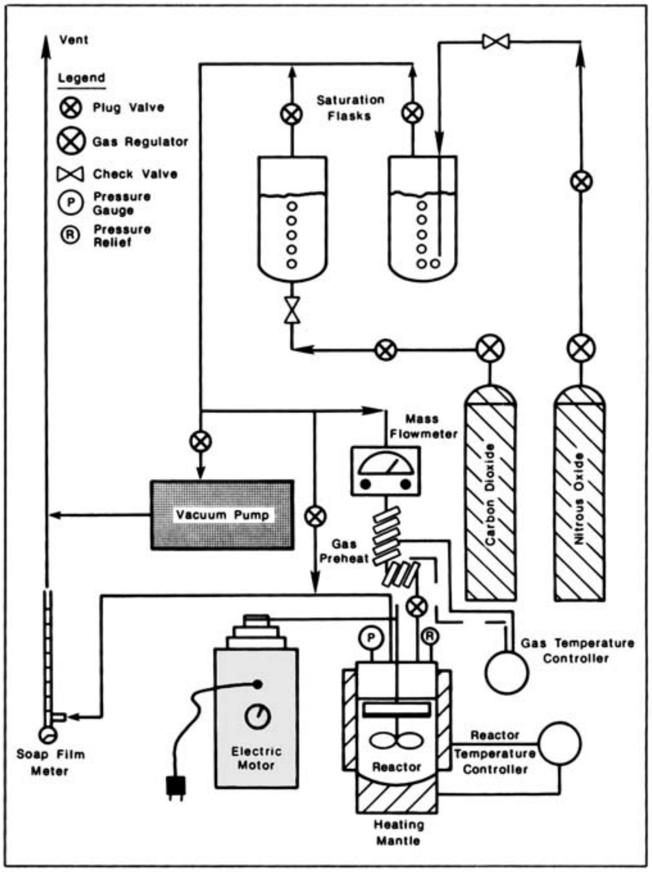


Figure 1. Stirred-cell reactor system.

Results and Discussion

Determination of kinetic constants

The two-film theory of Lewis and Whitman (1924) was used to model mass transfer of gas across a known interfacial area, followed by a chemical reaction. Using material balances for each phase and Henry's law to calculate the gas concentration at the interface, the two-film equation was solved for the pseudo-first-order rate constant, k_{ov}.

$$k_{ov} = \frac{\left(\frac{(p_{CO_{2,m}}/p_{CO_{2,B}}) V H_{CO_2}}{Z R T_G A_i} \right)^2}{D_{CO_2}} \tag{9}$$

The partial pressure ratio in the above equation is needed to correct for the differences in the CO_2 partial pressures in the meter and the reactor. Equation 9 is valid for fast first-order reactions. Calculations showed that this condition was satisfied for the present study. Gas-phase mass-transfer resistance was disregarded since pure gases were used with only small amounts of water vapor. In the absence of a reaction, the physical mass-transfer coefficient of a gas in a liquid was also calculated from the two-film theory.

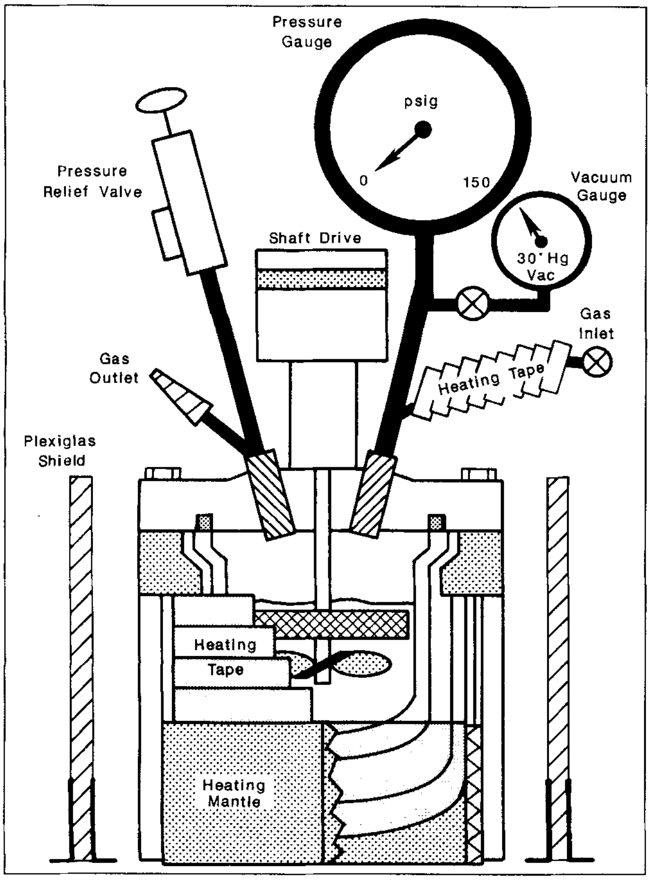


Figure 2. Stirred-cell reactor.

$$k_L = \left(\frac{VH_{N_2O}}{ZRT_GA_i}\right) \tag{10}$$

The compressibility factor, Z, of each gas was calculated from the Benedict-Webb-Rubin (BWR) equation. The interfacial area, A_i, was 8.09×10^{-3} m^2 inside the stirred-cell reactor.

Since CO_2 reacts directly in MDEA solutions, it is impossible to measure the Henry's law constant of diffusivity for carbon dioxide directly. The nitrous oxide analogy, developed by Clarke (1964) and used by many others in kinetic studies with CO_2, allows the Henry's law constant and diffusivity of carbon dioxide in alkanolamines to be estimated from measurements using N_2O and pure water ratios at the same temperature.

$$H_{CO_2} = H_{N_2O}\left(\frac{H^o_{CO_2}}{H^o_{N_2O}}\right) \tag{11}$$

$$D_{CO_2} = D_{N_2O}\left(\frac{D^o_{CO_2}}{D^o_{N_2O}}\right) \tag{12}$$

Haimour and Sandall (1984) report that the N_2O analogy has been experimentally verified as a method of parameter estimation in the case of aqueous MDEA. The results of the solubility experiments using pure aqueous MDEA were in agreement with those of Al-Ghawas et al. (1989). Solutions containing small amounts of phosphoric acid were found to have N_2O Henry's law constants equal to those of aqueous solutions with the same total MDEA concentration. Similar results were reported by Abu-Arabi (1988), who studied the solubility of N_2O in DEA fully protonated with hydrochloric acid, and found N_2O solubility to be independent of acid content. The diffusivity of N_2O in the MDEA was assumed to be independent of phosphoric acid content in the range of concentrations studied. Diffusivity and Henry's law constants, therefore, were taken from the work of Al-Ghawas et al. (1989) on the basis of total MDEA content alone.

Table 1. Pseudo-First-Order Rate Constants at 298 K

[MDEA] (mol·m^{-3})	[H_3PO_4] (mol·m^{-3})	[H_3PO_4]/[MDEA] (mol/mol)	k_{ov} (s^{-1})
1.69×10^3	0.000	0.00	3.7 ± 0.3
1.69×10^3	0.084×10^3	0.05	2.9 ± 0.4
1.69×10^3	0.169×10^3	0.10	2.4 ± 0.2
1.69×10^3	0.254×10^3	0.15	1.9 ± 0.3
2.54×10^3	0.000	0.00	4.9 ± 0.6
2.54×10^3	0.127×10^3	0.05	3.7 ± 0.4
2.54×10^3	0.254×10^3	0.10	3.2 ± 0.3
2.54×10^3	0.381×10^3	0.15	2.6 ± 0.5
3.40×10^3	0.000	0.00	7.3 ± 1.0
3.40×10^3	0.170×10^3	0.05	4.2 ± 0.8
3.40×10^3	0.340×10^3	0.10	3.7 ± 0.4
3.40×10^3	0.510×10^3	0.15	2.9 ± 0.5

Carbon dioxide absorption was measured at 298 K with 20, 30 and 40 wt. % MDEA (1.69×10^3, 2.54×10^3 and 3.40×10^3 mol·m^{-3}) containing pure water plus 0.05, 0.10 and 0.15 mol of phosphoric acid per mole of MDEA. At 308 K and 318 K, 40 wt. % MDEA was tested in pure water and in solutions containing 0.05 and 0.15 mol of phosphoric acid per mole of MDEA. The pseudo-first-order rate constants are reported in Tables 1, 2 and 3. All experiments satisfied the conditions for a pseudo-first-order reaction in the fast regime as given by Froment and Bischoff (1990) and Versteeg et al. (1986).

$$3 < Ha < E_{CO_2,i} \tag{13}$$

$$Ha = \frac{\sqrt{k_{ov}D_{CO_2}}}{k_{L,CO_2}} \tag{14}$$

Table 2. Pseudo-First-Order Rate Constants at 308 K

[MDEA] (mol·m^{-3})	[H_3PO_4] (mol·m^{-3})	[H_3PO_4]/[MDEA] (mol/mol)	k_{ov} (s^{-1})
3.40×10^3	0.000	0.00	15 ± 1
3.40×10^3	0.170×10^3	0.05	10 ± 1
3.40×10^3	0.510×10^3	0.15	7.6 ± 0.7

Table 3. Pseudo-First-Order Rate Constants at 318 K

[MDEA] (mol·m^{-3})	[H_3PO_4] (mol·m^{-3})	[H_3PO_4]/[MDEA] (mol/mol)	k_{ov} (s^{-1})
3.40×10^3	0.000	0.00	38 ± 2
3.40×10^3	0.170×10^3	0.05	27 ± 1
3.40×10^3	0.510×10^3	0.15	12 ± 1

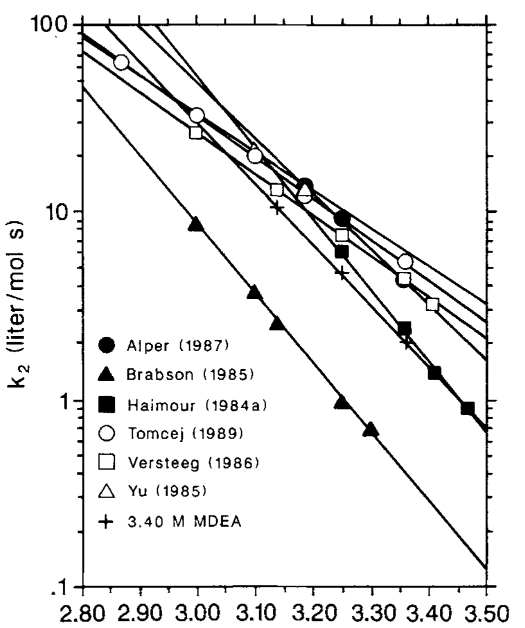


Figure 3. Comparative Arrhenius plot of significant CO_2/MDEA research.

$$E_{CO_2,i}=\sqrt{\frac{D_{CO_2}}{D_{MDEA}}}+\sqrt{\frac{D_{MDEA}}{D_{CO_2}}}\,\frac{[MDEA]RT_G}{\beta_{MDEA}p_{CO_2,B}} \tag{15}$$

Analysis of results

The second-order rate constant, k_2, determined from the data was:

$$(2.1\pm0.3)\times10^{-3}\ m^3\cdot mol^{-1}\cdot s^{-1}\ \text{at 298 K}$$
$$(4.4\pm0.2)\times10^{-3}\ m^3\cdot mol^{-1}\cdot s^{-1}\ \text{at 308 K}$$
$$(11\pm0.6)\times10^{-3}\ m^3\cdot mol^{-1}\cdot s^{-1}\ \text{at 318 K}$$

for the MDEA-water solutions. Figure 3 is an Arrhenius plot of these data and those of previous studies. These results are in closest agreement with Haimour et al. (1984), who also used a stirred-cell reactor. The value of k_2 is correlated by the following expression:

$$k_2=6.170\times10^8\times\exp\left(\frac{-7{,}884.54}{T}\right) \tag{16}$$

Table 4. Comparative Arrhenius Parameters for the Second-Order Rate Constant

Authors	Freq. Factor ($m^3\cdot mol^{-1}\cdot s^{-1}$)	E_a ($kJ\cdot mol^{-1}$)
Alper and Al-Ramadhan (1987)	1.417×10^8	60.2
Brabson (1985)	1.30×10^9	71.1
Haimour et al. (1984a)	8.741×10^9	71.5
Tomcej et al. (1989)	1.615×10^5	42.7
Versteeg et al. (1986)	1.19×10^5	42.3
Yu et al. (1985)	3.63×10^4	38.5
Present Work	6.170×10^8	65.6

The activation energy is 65.6 $kJ\cdot mol^{-1}$ for the reaction between MDEA and CO_2. Table 4 compares this result with those of previous studies. All previous research supports the conclusion that the reaction between aqueous MDEA and CO_2 is second-order overall. The wide variety of Arrhenius trends has not been addressed and may be a result of differing carbon dioxide solubility and diffusivity estimates or errors in experimental procedure.

The first step in determining why phosphoric acid reduces the rate of carbon dioxide absorption in aqueous MDEA solutions was to study the chemical make-up of each solution. When MDEA and phosphoric acid were mixed together in this study, two protons (H^+) were transferred from H_3PO_4 to the MDEA. The dissociation constant of protonated MDEA at 298 K is measured by the following equilibrium (Perrin, 1965):

$$(HOCH_2CH_2)_2N^+HCH_3=(HOCH_2CH_2)_2NCH_3+H^+$$

$$K_{am}=[H^+][R_2NCH_3]/[R_2N^+HCH_3]$$
$$=3.16\times10^{-6}\ mol\cdot m^{-3} \tag{17}$$

Mathematical analysis of MDEA-H_3PO_4 solution equilibrium shows that nearly 100% of H_3PO_4 donates two H^+ ions to two molecules of MDEA. Assuming 100% of the H_3PO_4 is converted to HPO_4^{2-} at equilibrium, the values of k_{ov} were correlated as a function of free amine concentration ([MDEA]) and hydrogen phosphate concentration ($[HPO_4^{2-}]$).

Multiple linear regression testing of several semi-empirical models led to the most statistically significant model for k_{ov} at 298 K.

$$k_{ov}=(k_2-k_3[HPO_4^{2-}]^{0.6})[MDEA]+k_4[HPO_4^{2-}] \tag{18}$$

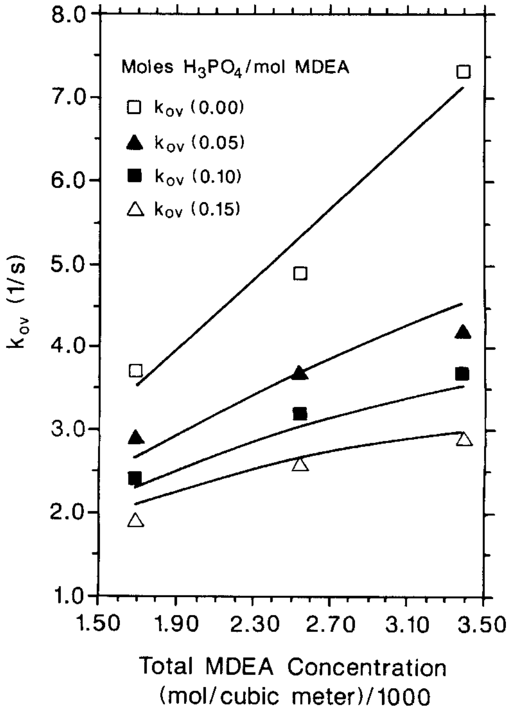


Figure 4. Pseudo-first-order rate constants at 298 K.

$$r_{CO_2} = k_{ov}[CO_2] \quad (3)$$

where

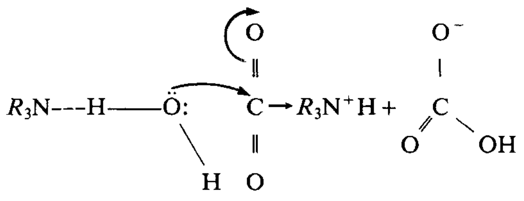
$$k_2 = 2.086 \pm 0.035$$

$$k_3 = 2.236 \pm 0.249$$

$$k_4 = 3.052 \pm 0.765$$

Figure 4 is a plot of k_{ov} vs. total MDEA concentration. To assess the reduction in k_{ov} beyond the point of simple neutralization, a plot of k_{ov} vs. free MDEA concentration calculated from Eq. 18 is shown in Figure 5. An Arrhenius plot for k_{ov} is shown in Figure 6 for 3.40×10^3 mol·m^{-3} MDEA solutions. Presently there are not enough data available to correlate k_{ov} as a function of temperature for solutions containing phosphoric acid.

Equation 18 is an expansion of k_{ov} for aqueous MDEA solutions, and it shows that the pseudo-first-order rate constant can be correlated with the concentration of hydrogen phosphate in the solution. The last term on the right accounts for the reaction between CO_2 and HPO_4^{2-} in these aqueous solutions. Any protons absorbed by the anion would be quickly transferred to an MDEA molecule, which is a more powerful base. Water molecules solvate MDEA through hydrogen bonding, and this association allows MDEA to catalyze the hydration of CO_2 as proposed by Barth et al. (1981).



The association of water with the MDEA molecule appears to be the crucial role of the tertiary amine, since Alper and Al-Ramadhan (1987) and Versteeg et al. (1986) have shown that CO_2 does not react with MDEA in the absence of water. It is thought that the rate depression results from the interference of the polyvalent hydrogen phosphate ion in the transition state involving MDEA, water, and carbon dioxide. During ion catalysis, any reorganization that disperses charge within a transmission state will reduce the rate of reaction, according to Gordon (1975). With a double negative charge, the HPO_4^{2-} ion may hinder the transfer of electrons and protons during the transition phase of the reaction by dispersing atomic charges.

In industrial practice, the absorption of H_2S in MDEA solutions is gas-phase mass-transfer-controlled, while the absorption of CO_2 is kinetically-controlled. The aim of reducing k_{ov} with the addition of phosphoric acid is to make MDEA solutions more selective toward H_2S. Dilute solutions of MDEA could be used to achieve the same effect, but this reduces the acid-gas-carrying capacity of the solvent. Since phosphoric acid reduces k_{ov} in MDEA solutions beyond the neutralization point, an MDEA-water-phosphoric acid solution is more selective than an aqueous solution with an equivalent amount of free MDEA.

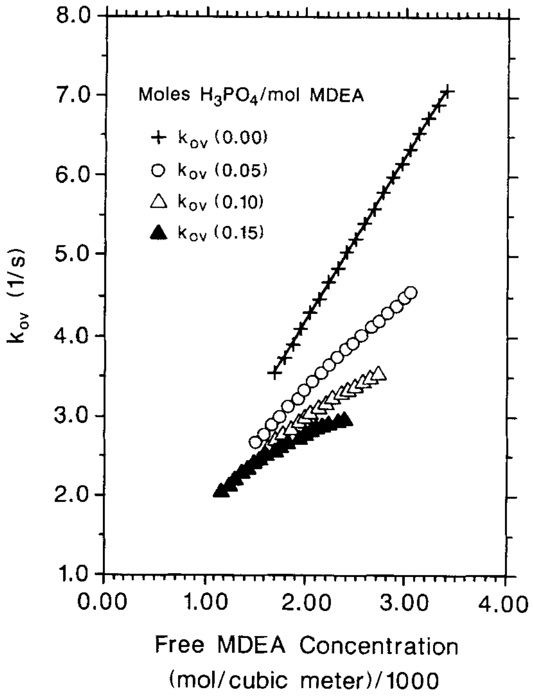


Figure 5. Free MDEA plot for pseudo-first-order rate constants at 298 K.

Conclusions

The effect of phosphoric acid on the absorption of carbon dioxide into solutions of MDEA was investigated using a stirred-cell batch reactor at atmospheric pressure and 298 K, 308 K, and 318 K. The two-film theory was chosen to model mass transfer followed by chemical reaction.

The reaction between MDEA and CO_2 was confirmed to be

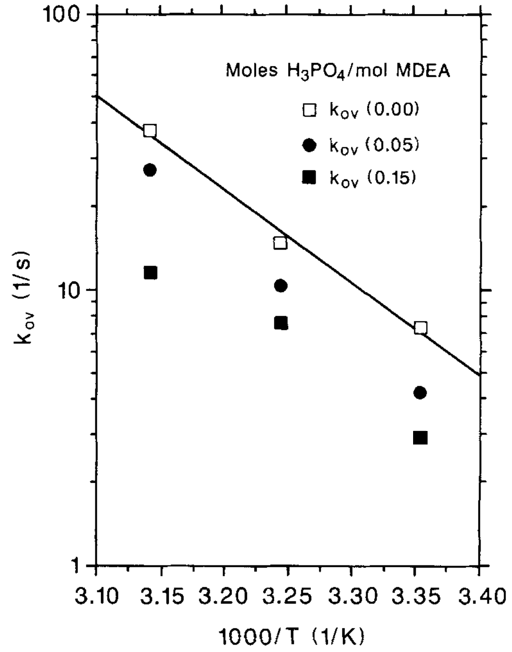


Figure 6. Arrhenius plot of pseudo-first-order rate constants for 3.40 M MDEA.

second-order overall, and the addition of phosphoric acid resulted in an absorption rate lower than expected for the remaining free MDEA in the solution after the neutralization reaction had occurred. The catalytic effect of MDEA on the absorption of CO_2 into aqueous solutions was attributed to the association between MDEA and water molecules that assists in the transfer of the OH^- nucleophile to the CO_2 molecule. The presence of hydrogen phosphate anions may reduce the rate of CO_2 absorption by interfering with the transition state that occurs during the MDEA-H_2O-CO_2 reaction.

The rate-depressing effects caused by salts dissolved in solution are very ion-specific; consequently, the effects observed in this study are limited to the presence of the dimethyldiethanolammonium hydrogen phosphate salt until further study establishes an exact mechanism for this phenomenon.

Acknowledgment

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Notation

A_i = interfacial area, m^2
D_{CO_2} = diffusivity of CO_2, m^2/s
D_{N_2O} = diffusivity of N_2O, m^2/s
E_a = activation energy, kJ/mol
Ha = Hatta number
H_{CO_2} = Henry's law constant for carbon dioxide, $m^3 \cdot atm \cdot mol^{-1}$
H_{N_2O} = Henry's law constant for nitrous oxide, $m^3 \cdot atm \cdot mol^{-1}$
K_{a1} = first phosphoric acid dissociation constant, $mol \cdot m^{-3}$
K_{a2} = second phosphoric acid dissociation constant, $mol \cdot m^{-3}$
K_{a3} = third phosphoric acid dissociation constant, $mol \cdot m^{-3}$
K_{am} = MDEA equilibrium constant, $mol \cdot m^{-3}$
k_2 = second-order MDEA reaction rate constant, $m^3 \cdot mol^{-1} \cdot s^{-1}$
k_3 = empirical rate coefficient
k_4 = empirical rate coefficient
k_L = physical mass-transfer coefficient, $m \cdot s^{-1}$
k_{ov} = pseudo-first-order reaction rate constant, s^{-1}
p_{CO_2} = partial pressure of CO_2, atm
$p_{CO_2,B}$ = bulk CO_2 partial pressure, atm
$p_{CO_2,m}$ = measured CO_2 partial pressure, atm
R = universal gas constant, $m^3 \cdot atm \cdot mol^{-1} \cdot K^{-1}$
r_{CO_2} = reaction rate of CO_2, $mol \cdot m^{-3} \cdot s^{-1}$
T = temperature, K
T_G = gas temperature, K
V = volumetric absorption rate, $m^3 \cdot s^{-1}$
Z = compressibility factor
β_{MDEA} = stoichiometric coefficient of MDEA in CO_2 reaction
$[\,]$ = concentration, $mol \cdot m^{-3}$

Superscript

$^\circ$ = pure-water parameter value

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