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Selective Removal of Hydrogen Sulfide from Gases Containing Hydrogen Sulfide and Carbon Dioxide Using Diethanolamine

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ABSTRACT

It is sometimes necessary to selectively remove hydrogen sulfide from gases containing carbon dioxide. This may be the case for example in the production of sulfur using the Claus process. When two gases are simultaneously absorbed into a solution containing a reactant with which each gas can react, the rate of absorption of each component is affected by the presence of the other gas. For the absorption of hydrogen sulfide into primary and secondary amines, the reaction which occurs can usually be considered to be instantaneous. An instantaneous reaction is diffusion-limited since the reaction occurs so rapidly that the liquid phase reactant and the absorbed gas cannot coexist in the same region of the liquid. For primary and secondary amines used for gas treatment, the reaction with carbon dioxide is much slower than for hydrogen sulfide and can often be considered to be second order.

In this work the simultaneous absorption of two gases into a liquid containing a reactant with which both gases can react is modeled using penetration theory. It is assumed that one gas reacts instantaneously and the other gas undergoes a second order reaction. Parameters used in the calculations are those available in the literature corresponding to the absorption of hydrogen sulfide and carbon dioxide in diethanolamine.

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INTRODUCTION

In this work the simultaneous absorption of two gases into a reactive liquid with which both gases can react is modeled according to the penetration theory. One gas is assumed to undergo an instantaneous reaction while the other gas reacts with second order kinetics. Hydrogen sulfide and carbon dioxide absorption into aqueous diethanolamine solution is the specific system studied in this research. For this system all of the physicochemical parameters such as free gas solubilities, diffusion coefficients, and kinetic rate parameters are available in the literature. Aqueous diethanolamine is a common chemical absorbent used in refineries to remove hydrogen sulfide (Kohl and Riesenfeld (1)).

It is sometimes required to remove hydrogen sulfide selectively while the absorption of carbon dioxide is undesireable. This may be the case for example in order to obtain a high concentration of hydrogen sulfide for subsequent treatment in a Claus process to obtain pure sulfur. In other circumstances carbon dioxide left in the gas may not be harmful and has the advantage of requiring a lower solvent circulation rate. The work described here addresses the question of the selectivity of diethanolamine for the absorption of hydrogen sulfide in the presence of carbon dioxide.

For the absorption of hydrogen sulfide into amine solutions, the reaction which occurs can usually be considered to be instantaneous since the reaction only involves a proton transfer. An instantaneous reaction is diffusion limited since the reaction occurs so rapidly that the liquid phase reactant and the absorbed gas cannot coexist in the same region of the liquid. For primary amines usually used for gas treatment the reaction with carbon dioxide can be considered to be second order. For secondary and tertiary amines, there is some disagreement in the literature regarding the kinetics of the reaction with carbon dioxide (Danckwerts (2)). As discussed in a later section, the kinetics of the carbon dioxide/diethanolamine reaction are taken to be second order in this study.

Under most conditions for gas absorption in packed columns, the mass transfer will be liquid phase controlled. In this work liquid phase mass transfer coefficients for both gases are determined as a function of contact time and gas partial pressures. Results are obtained for contact times up to 0.7 seconds. According to Danckwerts and Sharma (3) a liquid contact time of 1.5 seconds is the maximum to be expected in packed columns. The calculations cover a range in partial pressures of approximately 0.15 to 15 atmospheres for hydrogen sulfide and 0.25 to 25 atmospheres for carbon dioxide. The physical properties used for the calculations correspond to a 15 weight % solution of diethanolamine in water at 25°C.

PREVIOUS WORK

Simultaneous absorption of two gases in a reactive liquid was first studied by Roper et al. (4). These authors gave an analytical solution using the penetration theory model for the case where both gases react instantaneously with a reactive liquid. Astarita and Gioia (5) modeled the case of simultaneous absorption of hydrogen sulfide and carbon dioxide into sodium hydroxide solution according to the film theory model assuming that both gases (CO_2 and H_2S) react instantaneously with NaOH.

Goettler and Pigford (6) used the penetration theory to consider the case of simultaneous absorption of carbon dioxide and sulfur dioxide in a sodium hydroxide solution where they react with a finite reaction rate. The resulting partial differential equations were solved numerically. Goettler and Pigford extended their analysis and used the film theory model for the case when one of the gases reacts instantaneously with the liquid reactant. A numerical solution was again required to solve the resulting non-linear differential equations.

Many later authors (Goettler and Pigford (7), Ouwerkerk (8), Onda et al. (9), Ramachandran and Sharma (10), Cornelisse et al. (11), Hikita et al. (12), and Barreto and Farina (13)) tried to find an approximate analytical solution for the case of simultaneous absorption into a reactive liquid with which one of the gases reacts instantaneously. These analyses were carried out following the film theory model. These studies, excluding Barreto and Farina (13), differ only on selecting a linearized form for the non-linear profiles using different boundary conditions. Barreto and Farina used a perturbation method to solve the problem. A summary of these methods is presented by Cornelisse et al. (11) and Barreto and Farina (13). Aiken (14) numerically solved the film theory model equations for this case where one gas reacts instantaneously. Cornelisse et al. (15) numerically solved the case of simultaneous absorption of two gases into a reactive liquid using the penetration theory model. These authors analyzed the situation where reversible reactions occur between the gases and the reactive liquid.

The issue of selectivity for the simultaneous absorption of two gases into a reactive liquid has been studied by Astarita and Gioia (5) Sada et al. (16) and Aiken (14).

REACTION KINETICS

Diethanolamine (DEA) has two active functional groups, the hydroxyl groups and the amine group. The kinetics of the reaction between DEA and CO_2 have been investigated by many researchers (Jensen et al. (17), Jørgensen (18), Nunge and Gill (19), Sharma (20), Coldrey and Harris (21), Sada et al. (16), Hikita et al. (22), Danckwerts (2), Alvarez-Fuster et al. (23), Laddha and Danckwerts (24), Hikita et al. (25)). A considerable disagreement exist among these authors regarding the kinetics of this reaction. Jensen et al. (17) and Sharma (20) assumed that the mechanism of the reaction proceeds as follows:

$$CO_2 + R_2NH \rightleftarrows R_2NCOOH \qquad (1)$$

$$R_2NCOOH + R_2\ NH \rightarrow R_2NCOO^- + R_2NH_2^+ \qquad (2)$$

Reaction (1) is assumed to have a second order kinetics and is the rate determining step while reaction (2) occurs instantaneously. Jensen et al. (17) obtained a second order rate constant of 5300 l/mol·s at 18°C, while Sharma (20) found that the reaction rate constant is 1000 l/mol·s at 18°C and 1470 l/mol·s at 25°C for 1 M aqueous DEA solution. Jørgensen (18) proposed that in addition to the reaction of CO_2 with DEA to form a carbamate, CO_2 reacts with the alcohol groups of DEA in strongly alkaline solutions (pH = 13) to form an alkyl carbonate according to the following mechanism.

$$R' - OH + OH^- \overset{\text{fast}}{\rightleftarrows} R' - O^- + H_2O \qquad (3)$$

$$R' - O' + CO_2 \rightleftarrows R' - O - COO^- \qquad (4)$$

where R′ is $OH(CH_2)_2 \cdot NH \cdot (CH_2)_2$.

Equation 4 is the rate determining step for this mechanism. Jørgensen found that the formation of the alkyl carbonate has a third order rate constant while the formation of carbamate is second order. The rate constant for the second order reaction agreed with the value obtained by Jensen. For pH values less than 11.7, it is usually assumed that carbamate formation is the only reaction occuring (Coldrey and Harris (21)).

Coldrey and Harris (21) used a rapid mixing method to study the kinetics of the reaction between CO_2 and DEA. The DEA concentration varied from 0.1 to 1.0 M. These authors assumed that a secondary reaction occurs in addition to the formation of carbamate. However, the overall reaction is that represented by the formation of carbamate and is considered to have second order kinetics. The second order rate constant for carbamate formation is given as 430 l/mol·s at 19°C.

Sada et al. (26) assumed that the reaction between CO_2 and DEA occurs in two consecutive steps. The first step is the formation of the carbamate followed by carbonate formation as follows:

$$CO_2 + 2R_2NH \rightarrow R_2NCOOR_2NH_2 \qquad (5)$$

$$CO_2 + R_2NCOOR_2NH_2 + 2H_2O \rightarrow 2HCO_3R_2NH_2 \qquad (6)$$

For absorption with short contact time similar to laminar liquid jets or wetted wall columns only reaction (5) is important. Reaction (6) becomes important for absorption at long times such as in quiescent liquid absorbers. The rate constant for reaction (5) was found to be of a second order and has the value of 1340 l/mole·s at 25°C. The DEA concentration varied from 0.249 to 1.922 M. Nunge and Gill (19) studied the kinetics of the reaction between CO_2 and pure DEA using a gas-liquid stirred reactor. They proposed that the reaction between CO_2 and DEA has third order kinetics. They assumed that the reaction mechanism is as follows:

$$CO_2 + R_2NH \rightleftarrows R_2NCOO^- + H^+ \qquad (7)$$

$$H^+ + R_2NH \rightarrow R_2NH_2^+ \qquad (8)$$

$$R_2NH_2^+ + R_2NCOO^- \rightarrow R_2NH_2NCOOR_2 \qquad (9)$$

with reaction (9) as the rate controlling step. According to Coldrey and Harris (21), this mechanism is invalid.

Hikita et al. (22) using a rapid mixing experimental method found that the reaction between CO_2 and DEA has third order kinetics in the range of DEA concentration from 0.174M to 0.719M and CO_2 concentration in the range 0.0047M to 0.0072M. The reaction mechanism was assumed to be:

$$2R_2NH \rightleftarrows (R_2NH)_2 \qquad (10)$$

$$CO_2 + (R_2NH)_2 \rightarrow R_2NH_2NCOO\ R_2 \qquad (11)$$

$$R_2NH_2NCOOR_2 \rightleftarrows R_2NH_2^+ + R_2NCOO^- \qquad (12)$$

in which the dimer formation (reaction 10) and the diethanolamine carbamate dissociation (reaction 12) reach equilibrium instantaneously while reaction (11) is the rate controlling step. The third order rate constant was correlated by the empirical equation:

$$\log k_3 = 12.41 - \frac{2775}{T} \tag{13}$$

Hikita et al. (25) used this rate constant for DEA concentrations up to 2 M. However, in order to reconcile the homogeneous kinetics with the observed rate of absorption these authors had to make assumptions about the solubilities of CO_2 in DEA solutions which appear to be anomolous (24). Danckwerts (2) has also discussed the mechanism of reactions between CO_2 and ethanolamines. In order to reconcile the discrepancies between the results of various authors, Danckwerts suggested that the reaction mechanism includes the formation of a zwitterion followed by the removal of a proton by a base B:

$$CO_2 + R_2NH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R_2N^+HCO_2^- \tag{14}$$

$$R_2N^+HCO_2^- + B \xrightarrow{k_B} R_2NCO_2^- + BH^+ \tag{15}$$

The second step (15) is the rate determining step. According to this mechanism, the rate of reaction between CO_2 and DEA is given by:

$$\frac{R}{[CO_2][DEA]} = \frac{k_1}{1 + \frac{k_{-1}}{\Sigma k_B[B]}} \tag{16}$$

where $\Sigma k_B[B]$ is the contribution of the various bases present to the rate of removal of protons. If the second term in the denominator is << 1, the rate will have second-order kinetics:

$$R = k_1[CO_2][DEA] \tag{17}$$

and the rate controlling step is the formation of zwitterion which is not subject to catalysis. However, if the second term in the denominator is >> 1, the rate is given by:

$$\frac{R}{[CO_2][DEA]} = \frac{k_1}{k_{-1}} \Sigma k_B[B] \qquad (18)$$

If the reaction is dominantly catalyzed by DEA, Equation (18) becomes:

$$R = \frac{k_1}{k_{-1}} k_B [CO_2][DEA]^2 \qquad (19)$$

which explains the third order kinetics. Danckwerts (2) concluded that if the concentration of DEA is much greater than 0.7M, the second term in the denominator of (16) might become comparable with unity, or even less, and the order of reaction with respect to DEA might become less than 2. This mechanism was supported by Laddha and Danckwerts (24) using a stirred cell absorber. Their results showed that the reaction tended to be second order with respect to amine at low amine concentrations and first-order at high concentrations. Laddha and Danckwerts found that third order kinetics were not attained for an amine concentration of 0.72M which contradicts the results of Hikita et al. (22). Alvarez-Fuster et al. (25) reported that third order kinetics was obtained for amine concentrations up to 0.8 M. Laddha and Danckwerts reported that a first order mechanism with respect to the amine was obtained by the British Gas Corporation for amine concentration in the range 0.01-0.03 M.

From the previous mechanisms, it can be seen that for aqueous DEA solutions with amine concentrations higher than 1 M, a second order reaction is predominant between CO_2 and DEA. For lower concentrations, the possibility of third order kinetics is more valid. This is in agreement with Danckwerts model.

When H_2S is absorbed into aqueous DEA, it reacts to form the acid sulfide. The reaction involves only the transfer of a proton. For all practical purposes, this reaction may be considered as infinitely rapid since the second order rate constant is greater than 10^9 l/gmol s (27). In this work, the DEA concentration studied is 15 wt% (1.43 M). With this amine concentration, the overall reaction involved can be considered as second order, i.e., first order with respect to each of CO_2 and DEA. The second order kinetics can be also applied to higher DEA concentrations which are used in industry (20-30 wt%) which extends the validity of the analysis in this work to higher amine concentrations. All of the physical properties necessary to predict absorption rates can be estimated from the literature for a 15% solution.

THEORY

Consider A and B to be two gases which are being simultaneously absorbed into a liquid containing reactant C. Assume that A reacts irreversibly with C under second order reaction conditions and B undergoes an irreversible instantaneous reaction with C. Both A and B are nonreactive toward each other. The reaction between A, B, and C can be represented by

$$A + \nu_A C \xrightarrow{k_r} \text{products} \qquad (20)$$

$$B + \nu_B C \rightarrow \text{products (instantaneous)} \qquad (21)$$

Since B and C react instantaneously, the liquid region where the reactions occur is divided into two regions as shown in Figure 1. In the first region which extends from $X = 0$ to $X = X_1$ only A and B exist. The second region extends from $X = X_1$ to $X \rightarrow \infty$. In this region only A and C exist and react according to a second order irreversible reaction. A material balance over a differential element of liquid in each region results in the following nondimensional unsteady state diffusion equations.

$0 < X \leq X_1$

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial X^2} \qquad (22)$$

$$\frac{\partial b}{\partial \theta} = r_B \frac{\partial^2 b}{\partial X^2} \tag{23}$$

$X \geq X_1$

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial X^2} - ac \tag{24}$$

$$\frac{\partial c}{\partial \theta} = r_C \frac{\partial^2 c}{\partial X^2} - M_A ac \tag{25}$$

where the nondimensional parameters are defined similar to Goettler and Pigford (7). The boundary conditions are:

$$\left.\begin{array}{lll} a(X, 0) = 0 & a(0, \theta) = 1 & a(\infty, \theta) = 0 \\ b(X, 0) = 0 & b(0, \theta) = 1 & b(X_1, \theta) = 0 \\ c(X, 0) = 1 & c(X_1, \theta) = 0 & c(\infty, \theta) = 1 \end{array}\right\} \tag{26}$$

$$M_B r \frac{\partial b}{\partial X} = -\frac{\partial c}{\partial X} \text{ at } X = X_1$$

Equations (22), (23), (24), (25) are coupled differential equations with nonlinear terms in both Equations (24) and (25) and having a moving boundary at $X = X_1$. These equations will be solved numerically except for some limiting cases.

Numerical Solution

A simple and useful technique in dealing with one dimensional diffusion problems having a moving boundary is to change the space variable in order to fix the position of the moving boundary. This technique was used by Landau (28), Crank (29), and Ferriss (30). By using a new variable $\eta = X/X_1(\theta)$ and replacing $X_1^2(\theta)$ by $\xi(\theta)$, Equations (22) to (26) become:

$$0 < \eta \leq 1$$

$$\frac{\partial^2 a}{\partial \eta^2} = \xi \frac{\partial a}{\partial \theta} - \frac{\eta}{2} \frac{d\xi}{d\theta} \frac{\partial a}{\partial \eta} \tag{27}$$

$$r_B \frac{\partial^2 b}{\partial \eta^2} = \xi \frac{\partial b}{\partial \theta} - \frac{\eta}{2} \frac{d\xi}{d\theta} \frac{\partial b}{\partial \eta} \tag{28}$$

$$\eta \geq 1$$

$$\frac{\partial^2 a}{\partial \eta^2} = \xi \frac{\partial a}{\partial \theta} - \frac{\eta}{2} \frac{d\xi}{d\theta} \frac{\partial a}{\partial \eta} + \xi ac \tag{29}$$

$$\frac{\partial^2 c}{\partial \eta^2} = \xi \frac{\partial c}{\partial \theta} - \frac{\eta}{2} \frac{d\xi}{d\theta} \frac{\partial c}{\partial \eta} + M_A \xi ac \tag{30}$$

with the boundary conditions:

$$\left.\begin{array}{l} \left.\begin{array}{ll} a(0, \theta) = 1, & b(0, \theta) = 1 \\ b(1, \theta) = 0, & c(1, \theta) = 0 \\ a(\infty, \theta) = 0, & c(\infty, \theta) = 1 \end{array}\right\} \quad \theta > 0 \\ a(\eta, 0) = 0, \quad b(\eta, 0) = 0, \quad c(\eta, 0) = 1; \quad \eta > 0 \end{array}\right\} \tag{31}$$

$$M_B r \left.\frac{\partial b}{\partial \eta}\right|_{\eta=1} = - \left.\frac{\partial c}{\partial \eta}\right|_{\eta = 1} \tag{32}$$

Equations (27), (28), (29), and (30) subjected to the boundary and initial conditions given by Equations (31) and (32) were solved numerically using a finite difference method.

The derivatives were approximated by the Crank-Nicolson implicit finite difference scheme. The resulting finite difference equations were linear except the term (ac) which can be linearized by taking the value of c to be the same as in previous time step in Equation (29).

Equations (27), (28), (29), and (30) after linearization can be solved simultaneously using the Thomas algorithm if the position of the moving boundary is known. The procedure used is to assume the position of the moving boundary and iterate on this position until boundary condition, Equation (32), is satisfied.

Another problem which arises in using this numerical method is that due to singularities for a(0, 0), b(0, 0) and c(1, 0), the solution for the first few steps is not accurate and gives unacceptable values for the position of the moving boundary. This problem was solved by finding an approximate analytical solution for the small time region. Small time was taken to be $\theta_s = 0.1$ compared with a total time of $\theta = 1500$.

The numerical results were checked by comparing the results for large time with an approximate analytical solution valid large times. Large time is defined as the time when each of the enhancement factors, E_A and E_B, asymptotically approach constant values.

Small Time Solution

The starting equations are Equations (22), (23), (24), and (25) with the boundary conditions given by (26). By using a new variable defined by $Z = X/\theta^{\frac{1}{2}}$ the system of equations become:

$0 < Z \leq Z_1$

$$\frac{d^2a}{dZ^2} + \frac{Z}{2}\frac{da}{dZ} = 0 \tag{33}$$

$$\frac{d^2b}{dZ^2} + \frac{Z}{2r_B}\frac{db}{dZ} = 0 \tag{34}$$

$Z \geq Z_1$

$$\frac{d^2a}{dZ^2} + \frac{Z}{2}\frac{da}{dZ} = \theta ac \qquad (35)$$

$$\frac{d^2c}{dZ^2} + \frac{Z}{2r_c}\frac{dc}{dZ} = \frac{M_A}{r_c}\theta ac \qquad (36)$$

$$\left.\begin{array}{ll} a(0) = 1, & b(0) = 1 \\ b(Z_1) = 0, & c(Z_1) = 0 \\ a(\infty) = 0, & c(\infty) = 1 \end{array}\right\} \qquad (37)$$

$$M_B r \left.\frac{db}{dZ}\right|_{Z_1} = -\left.\frac{dc}{dZ}\right|_{Z_1} \qquad (38)$$

For small times, Equations (35) and (36) become:

$$\frac{d^2a}{dZ^2} + \frac{Z}{2}\frac{da}{dZ} \simeq 0 \qquad (39)$$

$$\frac{d^2c}{dZ^2} + \frac{Z}{2r_c}\frac{dc}{dZ} \simeq 0 \qquad (40)$$

In this form 'a' is independent of 'b' and 'c' and undergoes a physical absorption where the solution is given by:

$$a = \text{erfc}\ (\frac{Z}{2}) \qquad (41)$$

Also 'b' and 'c' react instantaneously without any effect of the presence of 'a'. The solution for this case as given by Danckwerts (31) is:

$$b = 1 - \frac{\text{erf}\ (Z/2\sqrt{r_B})}{\text{erf}\ (Z_1/2\sqrt{r_B})} \qquad (42)$$

$$c = 1 - \frac{1 - \mathrm{erf}\,(Z/2\sqrt{r_c})}{1 - \mathrm{erf}\,(Z_1/2\sqrt{r_c})} \qquad (43)$$

where Z_1 is given by:

$$1 - \mathrm{erf}\,(\frac{Z_1}{2\sqrt{r_c}}) = \mathrm{erf}\,(\frac{Z_1}{2\sqrt{r_B}})\ \exp\,\{\frac{Z_1^2}{4}\ (\frac{1}{r_B} - \frac{1}{r_C})\} \cdot \frac{1}{M_B\sqrt{r}} \qquad (44)$$

The error introduced by using this analytical approximation can become negligible if θ is chosen small enough compared to the final contact time.

Large Time Solution

For large time, the dimensionless variable θ becomes large. The solution in this case is similar to the case where $k_r \rightarrow \infty$, i.e., an instantaneous reaction between C and A and C and B. A theoretical solution was obtained for this case by Roper et al. (4).

Enhancement Factor Calculation

The enhancement factors for gases A and B according to penetration theory are given by:

$$E_A = \sqrt{\frac{\theta_s}{\theta}} - \frac{1}{2}\sqrt{\frac{\pi}{\theta}} \int_{\theta_s}^{\theta} \frac{1}{\sqrt{\xi_1(\theta)}} \left.\frac{da}{d\eta}\right|_{\eta=0} d\theta \qquad (45)$$

and

$$E_B = \sqrt{\frac{\theta s}{\theta}} \left(\mathrm{erf} \sqrt{\frac{\xi(\theta)}{4r_B\theta}}\right)^{-1} - \frac{1}{2}\sqrt{\frac{\pi r_B}{\theta}} \int_{\theta_s}^{\theta} \frac{1}{\sqrt{\xi_1(\theta)}} \left.\frac{db}{d\eta}\right|_{\eta=0} d\theta \qquad (46)$$

In Equations (45) and (46) the first term represents the small time approximation with θ_s being the dimensionless contact time over which the approximation is made. Equations (45) and (46) are for the case where there is no change in diffusion coefficients for the gases between pure water and the amine solution. Thus, in practice and in the results presented here, E_A and E_B as determined from Equations (45) and (46) are multiplied by the factors $(D_A/D_A^o)^{\frac{1}{2}}$ and $(D_B/D_B^o)^{\frac{1}{2}}$, respectively. D_A^o and D_B^o are the diffusivities in pure water.

PHYSICAL PROPERTIES

The numerical calculations require knowledge of the molecular diffusivities. The experimental results of Hikita et al. (32) are the most recent for the diffusivity of DEA at different concentrations. The value of the diffusivity of DEA in a 15% by weight solution at 25°C is given as 5.68×10^{-6} cm^2/s.

The diffusivity of CO_2 in DEA solutions was obtained from the corresponding value for the diffusivity of N_2O into DEA. The ratio of D_{CO_2}/D_{N_2O} in water and in solutions having different DEA concentrations is assumed to be constant. This method was first suggested by Clarke (33) and was later used by Weiland and Trass (34), Joosten and Danckwerts (35), Sada et al. (36, 37), Alvarez-Fuster (23, 38), and Laddha and Danckwerts (24). The values of D_{N_2O} in water and different amine concentrations at 25°C were obtained from the experimental results of Sada et al. (37). In this way the diffusivity of CO_2 in 15 wt% DEA solution was estimated to be 1.66×10^{-5} cm^2/s at 25°C.

The effect of the amine on the diffusivity of H_2S is assumed to be the same as for CO_2. The diffusivity of H_2S in pure water was obtained experimentally using a laminar jet. At 25°C, D_{H_2S} in pure water was found to be 1.89×10^{-5} cm^2/s. D_{H_2S} in 15 wt% DEA was thus calculated to be 1.60×10^{-5} cm^2/s at 25°C.

Interpretation of the numerical results requires knowledge of the solubilities for CO_2 and H_2S in aqueous DEA. It is the free gas solubility and not the total solubility that is required. The solubility of CO_2 in 15 wt% DEA at 25°C and 1 atm. was taken as 2.77×10^{-5} $gmole/cm^3$ by interpolation form the values of Laddha et al. (39). The effect of amine on the solubility of H_2S is assumed to be the same as for CO_2. The solubility of CO_2 in pure water is taken to be 3.295×10^{-5} gmole/cm^3 at 25°C and 1 atm. (Danckwerts and Sharma (3)), and the solubility of H_2S in pure water is taken as 1.027×10^{-4} gmole/cm^3 at 25°C and 1 atm. (Arnold (40)). The solubility of H_2S in 15 wt% DEA was thus calculated to be 8.63×10^{-5} gmole/cm^3 at 1 atm. Table 1 summarizes the physico-chemical properties for a 15 wt % solution of diethanolamine at 25°C.

RESULTS

Figure 1 shows the computed concentration profiles for two different contact times, $\theta = 225$ and $\theta = 750$, for gas partial pressures corresponding to $M_A = 0.5$ and $M_B = 0.1$. Figure 1 shows how the instantaneous reaction plane moves into the liquid as contact time increases. In the region from the free surface to the reaction plane, A and B diffuse without reaction. Gas B reacts at the reaction plane. Gas A reacts with reactant C at distances beyond the reaction plane. The effect of the reaction

TABLE 1

Physico-Chemical Properties of 15 Weight Percent Diethanolamine Solution at 25°C

$D_A = 1.66 \times 10^{-5}$ cm^2/s

$D_B = 1.60 \times 10^{-5}$ cm^2/s

$D_c = 5.68 \times 10^{-6}$ cm^2/s

$A_i/p_A = 2.77 \times 10^{-5}$ g moles /cm^3 atm

$B_i/p_B = 8.63 \times 10^{-5}$ g moles/cm^3 atm

$C_o = 1.43 \times 10^{-3}$ g moles/cm^3

$k_r = 1500$ g moles/l s

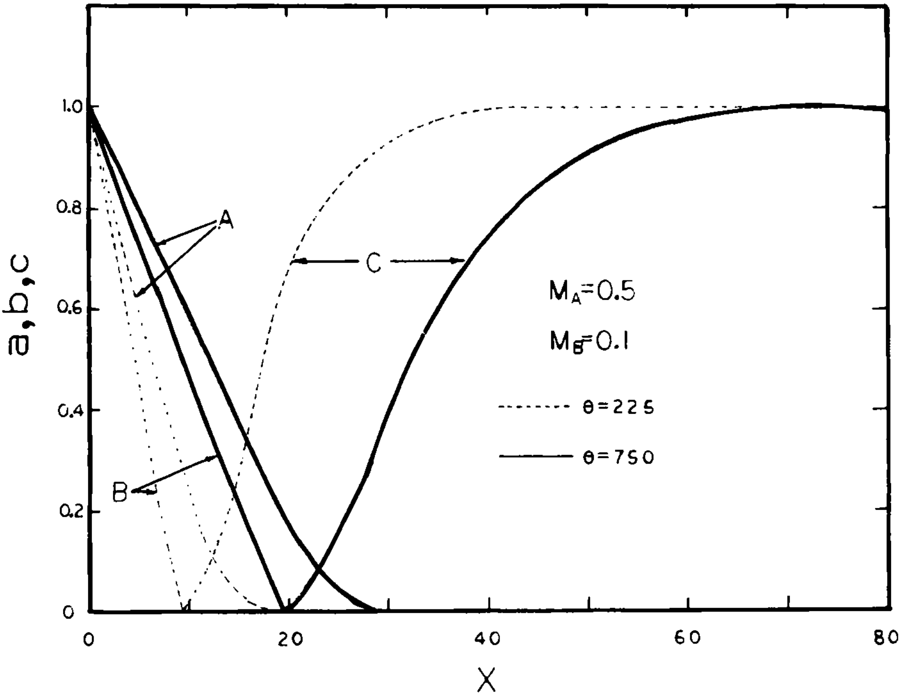

Figure 1: Concentration Profiles for Gases A and B and Reactant C at θ = 225 and θ = 750.

on the concentration profile of A can be seen by the curvature in the profile.

Figures 2 through 7 show the enhancement factors for A and B as a function of contact time with M_A and M_B as parameters. The calculations are for $D_B/D_A = 0.964$, $D_C/D_A = 0.342$, and $D_B/D_C = 2.818$, corresponding to absorption of hydrogen sulfide and carbon dioxide into 15 weight percent DEA solution at 25°C. The calculations were carried out to a dimensionless contact time of θ = 1500. This corresponds to an actual contact time of 0.7 seconds. It is seen in these figures that as M_A and M_B decrease both E_A and E_B increase. However, E_A is less sensitive towards the change of M_A and M_B than E_B. The sensitivity of E_A and E_B towards the

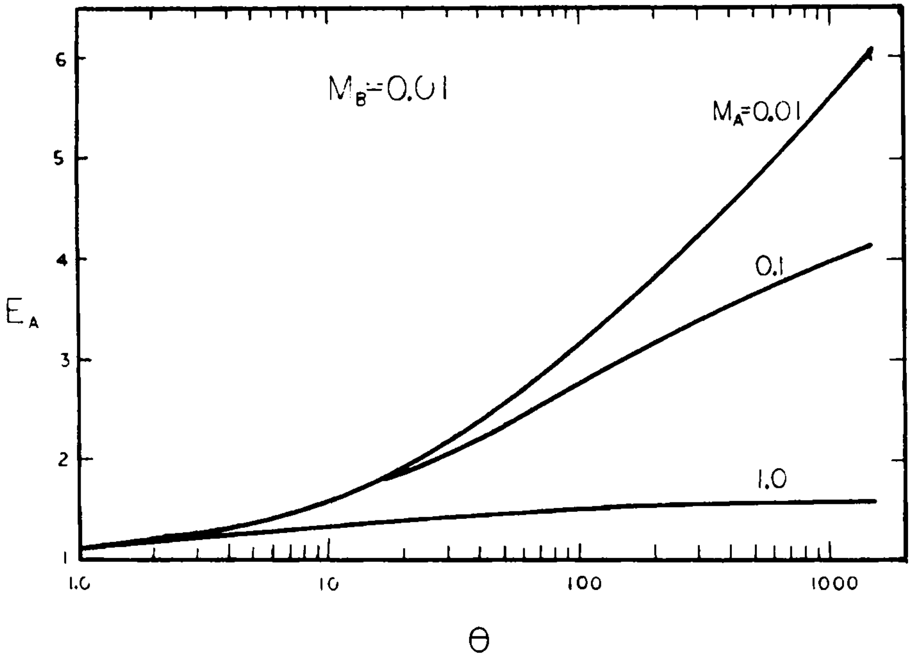

Figure 2: Enhancement Factor for Gas A as a Function of Contact Time for M_B = 0.01.

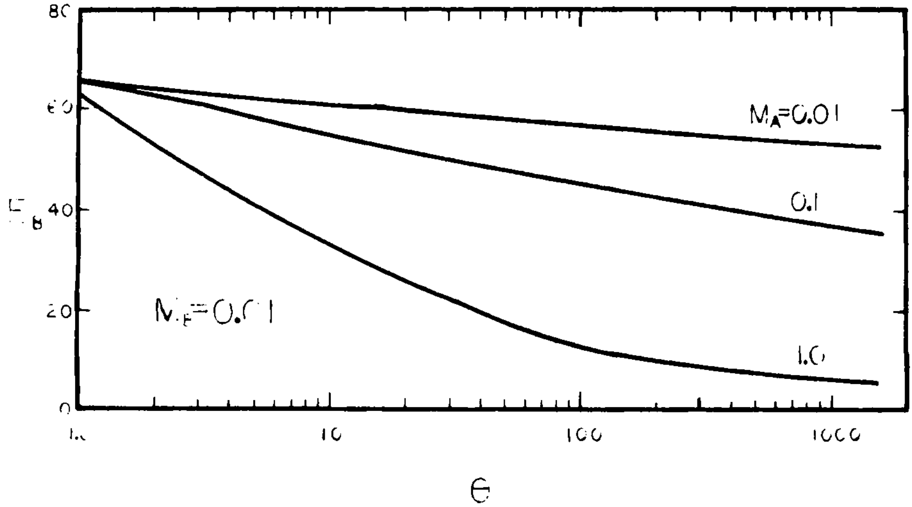

Figure 3: Enhancement Factor for Gas B as a Function of Contact Time for M_B = 0.01.

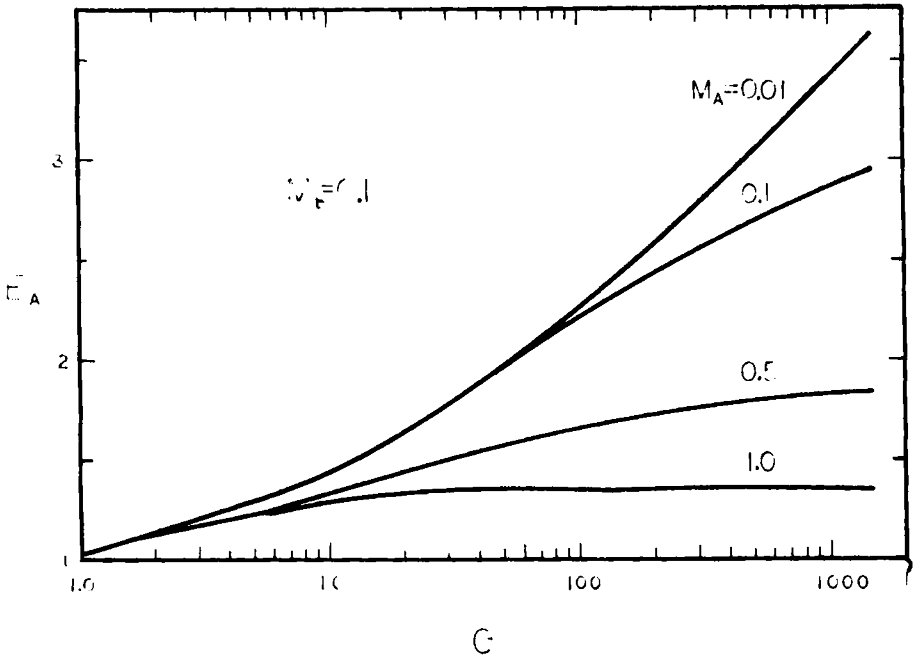

Figure 4: Enhancement Factor for Gas A as a Function of Contact Time for $M_B = 0.1$.

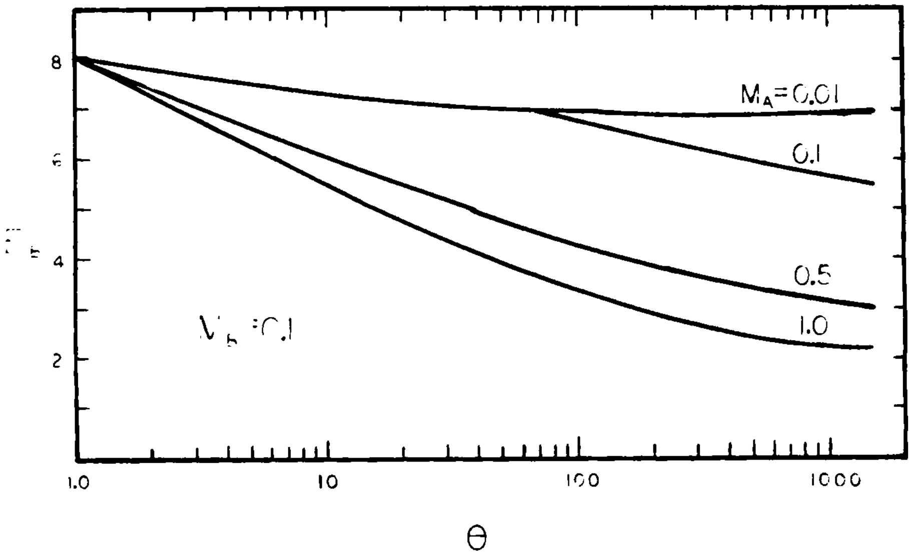

Figure 5: Enhancement Factor for Gas B as a Function of Contact Time for $M_B = 0.1$.

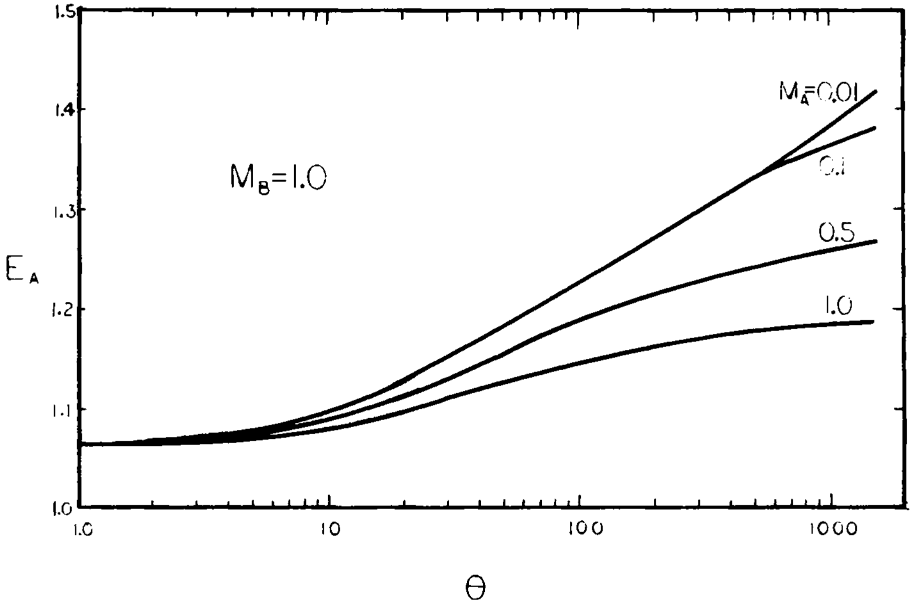

Figure 6: Enhancement Factor for Gas A as a Function of Contact Time for $M_B = 1.0$.

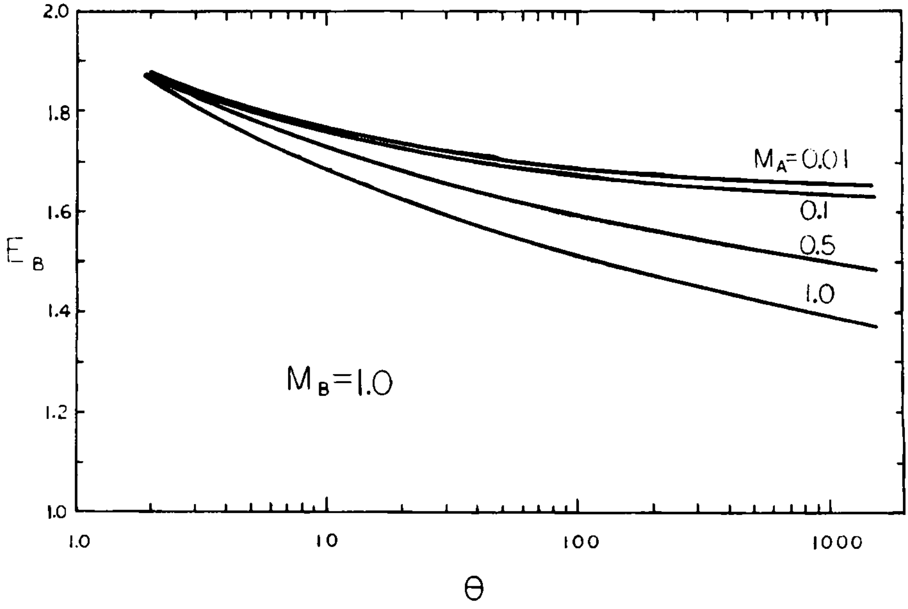

Figure 7: Enhancement Factor for Gas B as a Function of Contact Time for $M_B = 1.0$.

change of M_A and M_B increases with increasing θ. At small values of M_A, E_B becomes less sensitive towards M_A.

Figures 8, 9, and 10 show the selectivity, σ, plotted as a function of M_B with M_A and θ parameters. The selectivity of the absorbent for hydrogen sulfide is defined as

$$\sigma = E_B/E_A \tag{47}$$

In general, the selectivity σ increases with decreasing θ, and it changes rapidly at low θ. For $\theta > 1000$, σ is not very sensitive to changes in M_A or M_B. For lower θ values, σ is very sensitive towards the change of M_B while it is less sensitive to the change of M_A. For the parameters investigated in this study, it is observed that σ is independent of M_A for $M_A < 0.1$.

To obtain high selectivity, it is preferred to use absorbers with short contact times and low temperatures. Lower temperatures

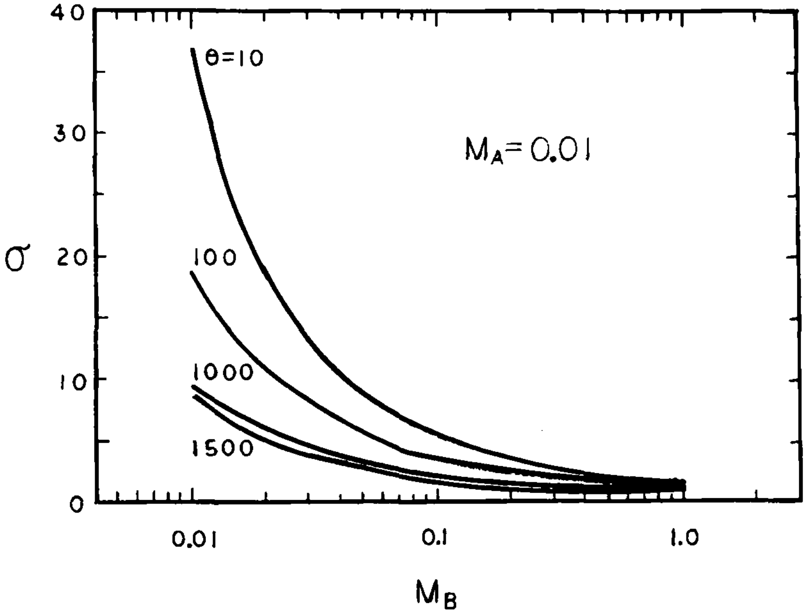

Figure 8: Selectivity for Gas B as a Function of M_B for M_A = 0.01.

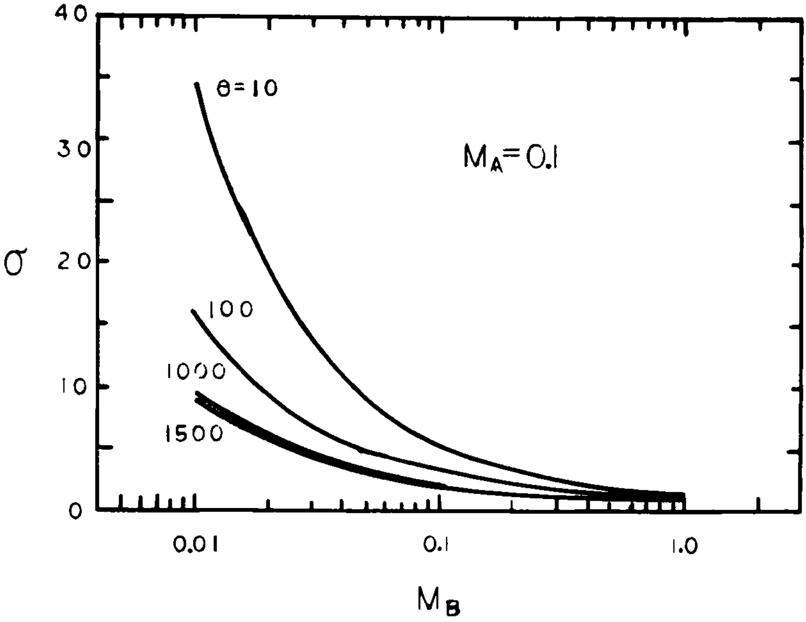

Figure 9: Selectivity for Gas B as a Function of M_B for M_A = 0.01.

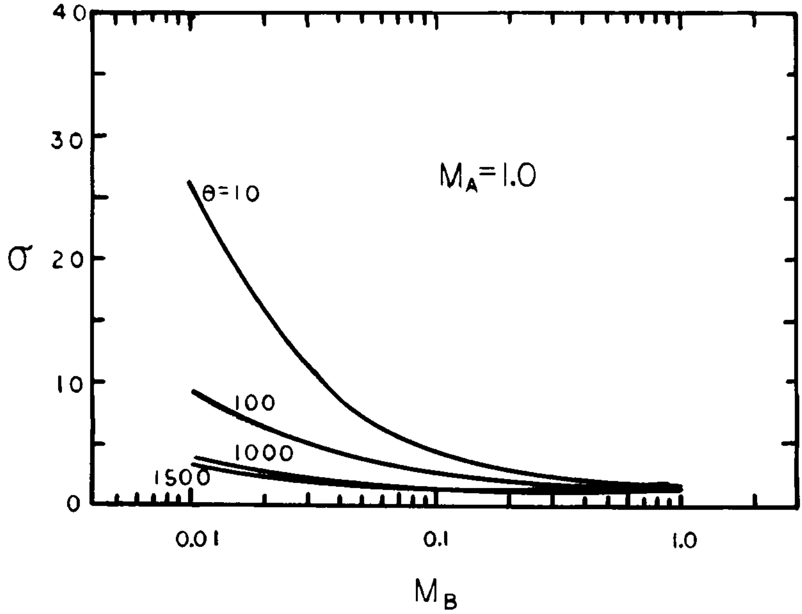

Figure 10: Selectivity for Gas B as a Function of M_B for M_A = 1.0.

decrease the value of the rate constant, which leads to a decrease in the value of θ. To get high selectivity, it is better to have low values of M_A and M_B which means low partial pressures of gases A and B or high concentration of amine. High gas phase resistance decreases the equilibrium concentration of gases A and B which improves the selectivity. Conversely, increasing the pressure in the absorber increases the equilibrium concentrations of A and B which decreases the selectivity.

As pointed out by Aiken (14) the maximum value of the selectivity for hydrogen sulfide would correspond to E_B at its maximum value and $E_A = 1.0$ for pure physical absorption. For no interference from carbon dioxide, the enhancement factor for hydrogen sulfide with an instantaneous reaction is given by a solution due Pearson (41).

$$E_B = 1/\mathrm{erf}\,\frac{\beta}{\sqrt{D_B}} \tag{48}$$

where β is given by the solution of the non-linear equation:

$$\frac{1}{M_B}\left(\frac{D_C}{D_B}\right)^{\frac{1}{2}} \exp\,(\beta^2/D_B)\cdot\mathrm{erf}\,(\beta/\sqrt{D_B}) = \exp\,(\beta^2/D_C)\cdot\mathrm{erf}\,(\beta/\sqrt{D_B}) \tag{49}$$

Equation (48) for the maximum enhancement factor for B assumes equal diffusivities for B for both physical absorption and chemical absorption. Thus, if the change in diffusion coefficient for B in the presence of liquid phase reactant is taken into account, the limiting (maximum) value of the selectivity for hydrogen sulfide is given by

$$\sigma_{max} = (D_B/D_B^o)^{\frac{1}{2}}/\mathrm{erf}\,(\beta/\sqrt{D_B}) \tag{50}$$

Figure 11 gives a plot of σ_{max} versus M_B as determined from Equations (49) and (50).

The analysis presented here can be applied to solutions of higher concentrations such as those used in industry (20-30 wt%) since the fixed parameters used in the theoretical analysis corresponding to 15 wt% DEA solution are r, r_B, and r_C. These para-

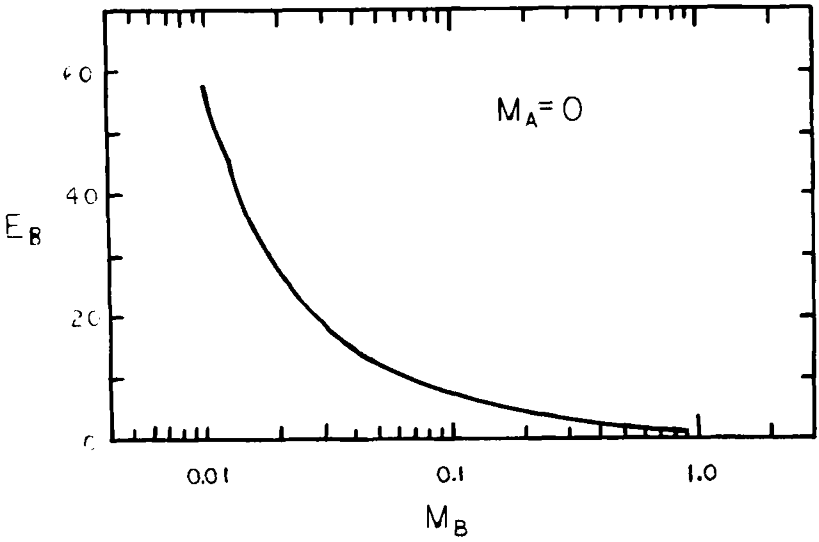

Figure 11: Maximum Value of Selectivity for B as a Function of M_B.

meters are not very sensitive to the change of DEA concentration since it represents the ratios of D_A, D_B, and D_C. For 30 wt% solution, the values of r and r_c change only by about 10% from that of 15 wt% DEA solution while the value of r_B is almost constant.

NOMENCLATURE

a dimensionless concentration for gas A (carbon dioxide) = A/A_i

A concentration of gas A, g moles/l

A_i interfacial concentration of gas A, g moles/ l

b dimensionless concentration of gas B (hydrogen sulfide) = B/B_i

B concentration of gas B, g moles/l

B_i interfacial concentration of gas B, g moles/l

c	dimensionless concentration of liquid reactant C (diethanolamine) = C/C_o
C	concentration of liquid reactant, g moles/l
C_o	bulk concentration of reactant C, g moles/l
D_A	diffusion coefficient for A in amine solution, cm^2/s
D_A^o	diffusion coefficient for A in pure water, cm^2/s
D_B	diffusion coefficient for B in amine solution, cm^2/s
D_B^o	diffusion coefficient for B in pure water, cm^2/s
D_c	diffusion coefficient for C, cm^2/s
erf(t)	error function = $\frac{2}{\sqrt{\pi}} \int_o^t e^{-u^2} du$
erfc(t)	error cofunction = 1-erf(t)
E_A	enhancement factor for gas A = k_{LA}/k_{LA}^o
E_B	enhancement factor for gas B = k_{LB}/k_{LB}^o
k_1	second order forward reaction rate constant, l/g mole s
k_{-1}	second order reverse reaction rate constant, l/g mole s
k_3	third order reaction rate constant, $l^2/g\ mole^2 s$
k_B	first order reaction rate constant, s^{-1}
k_{LA}	mass transfer coefficient for A (with reaction), cm/s
k_{LA}^o	mass transfer coefficient for A (without reaction) = $2\sqrt{\frac{D_A^o}{\pi t}}$, cm/s
k_{LB}	mass transfer coefficient for B (with reaction), cm/s
k_{LB}^o	mass transfer coefficient for B (without reaction) = $2\sqrt{\frac{D_B^o}{\pi t}}$, cm/s

k_r	second order reaction rate constant, 1/g mole s
M_A	$= \nu_A A_i/C_o$
M_B	$= \nu_B B_i/C_o$
p_A	partial pressure of gas A (carbon dioxide), atm
p_B	partial pressure of gas B (hydrogen sulfide), atm
r	$= D_B/D_C$
r_B	$= D_B/D_A$
r_C	$= D_C/D_A$
R	rate of reaction per unit volume, g moles/ls
t	contact time, s
T	temperature, °K
x	distance from free surface, cm
x_1	distance from free surface to reaction plane, cm
X	dimensionless distance from free surface = $(k_r C_o/D_A)^{\frac{1}{2}} x$
X_1	dimensionless distance to reaction plane
Z	$= X/\theta^{\frac{1}{2}}$
Z_1	$= X_1/\theta^{\frac{1}{2}}$
η	$= X/X_1$
θ	dimensionless contact time = $k_r C_o t$
θ_s	dimensionless contact time for which small time approximate solution applies
ν_A	stoichiometric coefficient in Equation 20
ν_B	stoichiometric coefficient in Equation 21
ξ	$= x_1^2$
π	$= 3.14159$
σ	selectivity for B = E_B/E_A

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