Approximate Simulation of CO_2 and H_2S Absorption into Aqueous Alkanolamines

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Rigorous and approximate methods are compared for the simulation of CO_2 absorption into aqueous alkanolamine mixtures of methyldiethanolamine and diethanolamine. In addition, data for the mixtures containing monoethanolamine and the simultaneous absorption of CO_2 and H_2S are presented. For the rigorous approach, the simplified eddy diffusivity theory is used to simulate the liquid-phase hydrodynamic characteristics. The approximation methods examined are the pseudo-first-order approximation, the interpolation approximation of Wellek et al. (1978), the algebraic combined flux (ACFLUX) approximation and the modified combined flux (MCFLUX) approximation. The latter approximation utilizes the reaction zone concept to determine the kinetic preference of the absorbing gas at the gas-liquid interface. Under the range of conditions studied, the MCFLUX approximation predicts very accurately the CO_2 and H_2S flux rates in mixed amine systems, as compared with the rigorous solution of the differential equations.

Introduction

An exact solution of the problem of mass transfer with reaction at a gas-liquid interface is impossible. A number of theories have been proposed, however, to simulate the liquid-phase behavior at the gas-liquid interface by means of idealized models. These theories include the film, penetration and surface renewal theories, and usually require the solution of ordinary or partial differential equations describing the concentration profiles in the boundary layer at the gas-liquid interface. The performance of these theories has been compared by Glasscock and Rochelle (1989).

Much effort has been put into the development of approximations which can be used instead of the exact solution of the differential equations. These approximations are subject to possible severe error, especially with complex reaction schemes. Therefore, our general approach has been to simulate the reactions rigorously using an eddy diffusivity model for the liquid phase (Glasscock and Rochelle, 1989; Glasscock, 1990). However, the computation time, complexity, and numerical difficulties encountered in a rigorous solution of the differential equations can be formidable.

Rate-based models of acid gas absorption/stripping systems can require numerous solutions of this mass-transfer problem at every point in the absorber and stripper. Each rigorous calculation of the mass-transfer problem typically requires 0.5 to 4 s on a Cray X-MP/24 vector processor. A single solution of an absorber/stripper model may require thousands of calls to the mass-transfer routine. Use of parameter estimation with ten data sets and three parameters would require hundreds of solutions of an absorber/stripper model and on the order of 100,000 calls to the mass-transfer calculation. Even with faster computers, it is not computationally efficient to solve a set of partial differential equations at every point in the absorber and stripper for every iterative pass through the system, especially in combination with parameter estimation. Therefore, it is imperative that simplified, algebraic approximations be developed for the prediction of absorption rates during reactive absorption. Such algebraic approximations should reduce computation time by a factor of ten to a hundred.

In this article, a combined mass-transfer/equilibrium model is presented for the absorption of acid gases into alkanolamines. In this model, the equilibria are rigorously taken into account using the Electrolyte-NRTL model for the activity coefficients of ionic species. Reversible kinetic expressions take into account the complex kinetic mechanisms of the reaction of CO_2 with alkanolamines. The eddy diffusivity theory is used to simulate the liquid-phase hydrodynamic characteristics. The

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model will be described briefly here, since it was detailed by Glasscock and Rochelle (1989), Glasscock et al. (1991), and Glasscock (1990).

Several approaches for approximating the flux rate of CO_2 are presented, including the pseudo-first-order approximation and the approximation of Wellek et al. (1978). Both of these approximations have been used in acid gas simulators (Tomcej et al., 1987; Sivasubramanian, 1985). Numerical results show both of these methods contain serious error under some typical conditions. In addition, they do not take into account the interaction between CO_2 and H_2S during simultaneous absorption. Therefore, the algebraic combined flux (ACFLUX) and modified combined flux (MCFLUX) approximations are developed in this work.

The ACFLUX approximation is based on the assumption of equilibrium between all species at the gas-liquid interface, except for the absorbing gas. The ACFLUX approximation utilizes the principles of Van Krevelen and Hoftjizer (1948) and with tertiary amines is essentially identical to the approximations used by Carey et al. (1991) and Yu and Astarita (1987). With the addition of primary or secondary amines, the ACFLUX approximation includes an equilibrium assumption to account for the simultaneous formation of carbamate and bicarbonate and is identical to that used by Critchfield (1988).

The MCFLUX approximation uses the reaction zone concept to determine the kinetic preference of CO_2 toward various chemically combined forms, removing the unnecessary equilibrium assumption. Both of the flux approximations use DeCoursey's (1982) approximation for the enhancement factor for reversible reactions. Results indicate that the MCFLUX approximation performs remarkably well for the systems studied: CO_2 and H_2S absorption into methyldiethanolamine (MDEA), diethanolamine (DEA), and the mixtures DEA/MDEA and monoethanolamine MEA/MDEA. The model also predicts the simultaneous desorption of H_2S with CO_2 absorption. In all cases, the error is less than 20%, and most of the time within 10%.

Rigorous Model

The nonstoichiometric algorithm of Smith and Missen (1988) is used to determine the equilibrium composition. The Electrolyte-NRTL model (Chen and Evans, 1986) is used for the activity coefficients—the acid gas systems are characterized by highly nonideal solutions of electrolytes. The use of the Electrolyte-NRTL model for acid gas/alkanolamine systems has been studied in detail by Austgen (1989) and Austgen et al. (1991). Having obtained the solution to the equilibrium problem, we can now proceed to the rate simulation.

A steady-state form of eddy diffusivity theory for simulating gas absorption with chemical reaction is used. It has been shown that this theory provides results comparable to the unsteady-state surface renewal and penetration theories for the systems under consideration (Glasscock and Rochelle, 1989). This is important since the unsteady-state theories are considered to be more accurate for gas absorption into a turbulent liquid phase (Danckwerts, 1970). Therefore, we have used a steady-state theory that provides results comparable to an unsteady-state theory, resulting in a large reduction in computation time for such time-intensive tasks as kinetic parameter estimation.

In the general context, we can write a material balance equation for each species in solution:

$$-\nabla J_i + \mathcal{R}_i = 0 \quad i = 1,\ldots,N \tag{1}$$

In this case, $\mathcal{R}_i$ represents the net rate of production of species i, ∇ is the one-dimensional differentiation operator, and J_i represents the flux of a species, which for eddy diffusivity theory is:

$$J_i = -(D_i + \epsilon x^2)\nabla C_i \tag{2}$$

It is assumed that the electrical potential gradient has no effect on the diffusion of ions (true if all ions have the same diffusion coefficient). For a discussion of the effect of electrical potential gradients and the diffusion of ions in nonideal systems, see Glasscock (1990).

The eddy diffusivity parameter ϵ is obtained from the mass-transfer coefficient by the following relationship:

$$k_1^o = \frac{2}{\pi}\sqrt{\epsilon D_1} \tag{3}$$

D_1 is the diffusion coefficient of the absorbing gas.

We briefly summarize the complete set of reactions that must be simulated in the mass-transfer model. For the absorption of CO_2 and H_2S into mixed amines, the entire reaction scheme considered is shown below. For simplicity, we will take the example of the DEA/MDEA mixed amine system—for the MEA/MDEA system, DEA can be replaced by MEA in all reaction terms.

For the secondary amine, the reaction of CO_2 occurs by means of a zwitterion mechanism:

$$\begin{gathered} CO_2 + DEA \Longleftrightarrow DEA + COO^- \\ DEA + COO^- + H_2O \Longleftrightarrow H_3O^+ + DEACOO^- \\ DEA^+COO^- + DEA \Longleftrightarrow DEAH^+ + DEACOO^- \end{gathered} \tag{4}$$

In addition, for mixed amines, the interaction between primary (or secondary) amine and tertiary amine must be considered:

$$DEA^+COO^- + MDEA \Longleftrightarrow MDEAH^+ + DEACOO^- \tag{5}$$

Assuming a pseudo-steady-state approximation for the zwitterion intermediate and the deprotonation step in the zwitterion mechanism is rate-controlling, these equations yield the net rate of formation of carbamate:

$$\mathcal{R}_{DEACOO} = [C_{CO2} - C_{CO2,eq}]C_{DEA}[k_1' C_{H2O} + k_2' C_{DEA} + k_3' C_{MDEA}] \tag{6}$$

$C_{CO2,eq}$ is the concentration of CO_2 in equilibrium with the mixture. For the MEA/MDEA system, the first step in the zwitterion is assumed to be controlling, and the rate expression is of the form:

$$\mathcal{R}_{MEACOO} = [C_{CO2} - C_{CO2,eq}]k_{MEA}' C_{MEA} \tag{7}$$

For the tertiary amine, the reactions involving both water and hydroxide are considered:

$$CO_2 + MDEA + H_2O \Longleftrightarrow MDEAH^+ + HCO_3^- \qquad (8a)$$

$$CO_2 + MDEA + OH^- \Longleftrightarrow MDEA + HCO_3^- \qquad (8b)$$

Equation 8a is the standard expression for the base catalysis of the CO_2 hydration reaction. It has been found, however, that the apparent reactivity of the MDEA solutions varies with the loading and CO_2 partial pressure in such a manner that reaction 8b reconciles much of the experimental data (see Glasscock, 1990). In addition, we include the direct reaction of hydroxide with CO_2:

$$CO_2 + OH^- \Longleftrightarrow HCO_3^- \qquad (9)$$

Using reaction mechanisms 8 and 9, we write an equation for the formation of bicarbonate:

$$\mathcal{R}_{HCO3} = [C_{CO2} - C_{CO2,eq}][k_4' C_{MDEA} C_{H2O} + k_5' C_{MDEA} C_{OH} + k_{OH}' C_{OH}] \qquad (10)$$

Of course, $\mathcal{R}_{CO2} = -\mathcal{R}_{DEACOO} - \mathcal{R}_{HCO3}$. In addition, the following buffer equilibria must be considered:

$$CO_3^{=} + H_2O \Longleftrightarrow HCO_3^- + OH^- \qquad (11a)$$

$$DEA + H_2O \Longleftrightarrow DEAH^+ + OH^- \qquad (11b)$$

$$MDEA + H_2O \Longleftrightarrow MDEAH^+ + OH^- \qquad (11c)$$

$$HS^- + H_2O \Longleftrightarrow H_2S + OH^- \qquad (11d)$$

$$S^{=} + H_2O \Longleftrightarrow HS^- + OH^- \qquad (11e)$$

$$OH^- + H_3O^+ \Longleftrightarrow 2H_2O \qquad (11f)$$

The rate equations are activity-based and take into account the reversibility of the reactions by use of equilibrium constants. The actual rate constants used are shown in Table 1, but these are activity-based rate constants which must be corrected using the activity coefficients. In addition, the forward rate constants are divided by the activity coefficients of the products, which in essence makes the reverse reaction rates independent of ionic strength:

$$k_j' = k_j \prod_{i=1}^{N} \gamma_i^{-\nu_{ij}} \qquad (12)$$

where ν_{ij} is the stoichiometric coefficient of the species i in reaction j. This correction was found to provide the best consistency between data at high and low ionic strengths, and the details and physicochemical parameters were presented by Glasscock (1990) and Glasscock et al. (1991).

For computation, the components are combined into buffer systems—those subsets of chemical components which interchange among one another *instantaneously*, and a material balance is formed for each buffer system. The equilibrium relationships and a charge balance are used for the remaining equations. This general approach is termed the combined flux method using the partial equilibrium approximation by Gallagher et al. (1986). Furthermore, this approach yields a system of differential/algebraic equations that must be integrated, as opposed to the ACFLUX approximation to be described later.

Table 1. Rate Parameters Used (Glasscock, 1990)

Rate Expression	Parameter Estimates k_{298} ($m^6/kmol^2 \cdot s$)	 E_a ($kcal/kmol \cdot K$)
Activity-Based Expressions		
DEA		
$k_1(DEA)(H_2O)(CO_2)$	30.0	11,000
$k_2(DEA)(DEA)(CO_2)$	18,500	9,314
DEA/MDEA		
$k_3(MDEA)(DEA)(CO_2)$	3,310	−105
MDEA		
$k_4(MDEA)(H_2O)(CO_2)$	0.0157	3,710
$k_5(MDEA)(OH^-)(CO_2)$	1.54×10^5	8,107
Concentration-Based Expressions	($m^3/kmol^2 \cdot s$)	
MEA (Hikita et al., 1977)		
k_6[MEA Conc.][CO_2]	5,868	9,848
Hydroxide (Astarita et al., 1983)		
$k_7^o[OH^-][CO_2]$	8,322	13,248
with $k_7 = k_7^o 10^{0.08 I_c}$ where $I_c = \sum_{i=1}^{N} z_i^2 C_i$		

For the $CO_2 - H_2S -$ mixed alkanolamine system, a total of six independent mass-transfer equations is obtained:

$$0 = -\nabla J_{CO_2} + \mathcal{R}_{CO_2} \qquad (13a)$$

$$0 = -\nabla J_{DEA} - \nabla J_{DEAH} - \mathcal{R}_{DEACOO} \qquad (13b)$$

$$0 = -\nabla J_{DEACOO} + \mathcal{R}_{DEACOO} \qquad (13c)$$

$$0 = -\nabla J_{MDEA} - \nabla J_{MDEAH} \qquad (13d)$$

$$0 = -\nabla J_{HCO_3} - \nabla J_{CO_3} + \mathcal{R}_{HCO_3} \qquad (13e)$$

$$0 = -\nabla J_{H2S} - \nabla J_{HS} - \nabla J_S \qquad (13f)$$

There are a total of 13 unknowns, CO_2, H_2S, DEA, $DEAH^+$, $DEACOO^-$, MDEA, $MDEAH^+$, HCO_3^-, $CO_3^=$, HS^-, $S^=$, H_3O^+, and OH^-. The composition of all of these species is obtained from the six material balance equations (Eqs. 13), the charge balance (Eq. 14), and the six buffer equilibria (Eqs. 11):

$$\sum_{i=1}^{N} z_i C_i = 0 \qquad (14)$$

Note that the carbamate species, $DEACOO^-$, is not considered part of the secondary amine buffer system, since its transition to the amine DEA is a finite rate reaction. For a similar reason, CO_2 is not included in the total carbonate buffer system. Note that Eqs. 13b, 13d and 13e can be obtained by linear combinations of the material balance equations for the individual species in the buffer system.

Numerical methods for the rigorous model

A set of coupled, nonlinear differential equations must be solved to determine the flux rates. This is accomplished first by using orthogonal collocation on finite elements (Villadsen and Michelson, 1978; Finlayson, 1980). The method is only briefly outlined here; the cited references contain all the necessary background information. We first divide the domain into elements, and within each element the concentration of each species is approximated by a polynomial. The criterion for choosing the coefficients of the approximating polynomials is that the residuals of the differential equations, shown in Eq. 15 as an example, are zero at certain points, known as collocation points:

$$\text{Res} = \nabla[(D_i + \epsilon x^2)\nabla C_i] + \mathcal{R}_i[\underline{C}(x)] = 0 \quad i = 1, \ldots, N \tag{15}$$

The residual for each component is satisfied at the collocation points, but not necessarily in between. Note that although the residual of the differential equation is satisfied at a collocation point, the solution, C, is not necessarily correct at that point. In our case, orthogonal collocation is being used, and the collocation points are the zeroes of a series of shifted Legendre polynomials on [0,1], mapped into each element. Several elements are usually used, with the condition that at each element boundary the flux is continuous:

$$J_i|_{x^+} = J_i|_{x^-} \tag{16}$$

where x^+ and x^- denote the approach to the element boundary from the right and left sides, respectively.

Collocation leads to a set of coupled nonlinear algebraic equations. The solution to these equations is not trivial. Therefore, the steady-state equations were also solved using a parametric continuation method. In this method, we vary a parameter continuously from a problem for which we know the solution to a problem for which we need the solution. Let us multiply each of the production terms by a parameter, t:

$$\nabla[(D_i + \epsilon x^2)\nabla C_i] + t\mathcal{R}_i[\underline{C}(x)] = 0 \quad i = 1, \ldots, N \tag{17}$$

When t is 0, the problem reduces to that of physical diffusion and the solution is trivial. As t is advanced to 1, the solution changes from the trivial problem to the problem that we wish to solve. DASSL (Petzold, 1983) is used to integrate the equations (see Glasscock, 1990).

Approximations

Pseudo-first-order approximation

The pseudo-first-order approximation neglects gradients of amine and reaction products in the mass-transfer boundary layer. The enhancement factor is defined as the ratio of the rate of absorption with reaction relative to that without reaction:

$$E = \frac{R}{R_{\text{phys}}} \tag{18}$$

In the limit of no reaction, the enhancement factor approaches unity. Under conditions in which the concentration of every species except the absorbing gas is constant throughout the boundary layer, one may approximate the enhancement factor by the following expression (Danckwerts, 1970):

$$E_{\text{first}} = \sqrt{1 + \frac{k_1 D_1}{k_1^{o2}}} \tag{19}$$

This expression was developed for surface renewal theory; however, it provides an excellent approximation to the eddy diffusivity theory (Glasscock and Rochelle, 1989). D_1 is the diffusion coefficient of the absorbing gas and k_1^o is the mass-transfer coefficient. The term k_1 is the first-order rate constant. For the case of multiple reactions, we may define k_1 as follows:

$$k_1 = \frac{\mathcal{R}_{CO2}}{C_{CO2} - C_{CO2,eq}} \tag{20}$$

$\mathcal{R}_{CO2}$ is calculated at the bulk solution composition.

Interpolation approximation of Wellek et al.

Wellek et al. (1978) found that the following expression could be used as an interpolation between the pseudo-first-order enhancement factor and the instantaneous upper limit:

$$\frac{1}{(E-1)^{1.35}} = \frac{1}{(E_{\text{inst}}-1)^{1.35}} + \frac{1}{(E_{\text{first}}-1)^{1.35}} \tag{21}$$

This approximation requires estimation of the instantaneous upper limit on the enhancement factor, which is the upper limit on the enhancement factor as all reactions become instantaneous with respect to the mass-transfer rate. This could be calculated rigorously; however, such a calculation would be iterative and have no potential advantage over the MCFLUX approximation. In addition, for the mixed amine system in which the kinetics of the primary or secondary amine dominate, it is not obvious that the true instantaneous upper limit is the proper value to be used in Eq. 21. We therefore use the instantaneous upper limit for an irreversible reaction as used by Sivasubramanian (1985):

$$E_{\text{inst}} = 1 + \frac{C_{\text{DEA,bulk}}}{\nu\, C_{\text{CO2,interface}}}\sqrt{\frac{D_{\text{DEA}}}{D_{\text{CO2}}}} \tag{22}$$

Equation 22 is for a reaction of the form shown in Eq. 23 and is corrected for unequal diffusion coefficients by the approximation of Chang and Rochelle (1982):

$$CO_2 + \nu\ \text{DEA} \Rightarrow \text{products} \tag{23}$$

In addition, however, we consider that the MDEA can participate in the DEA reaction kinetics; therefore, the stoichiometric coefficient should be closer to unity than 2 for mixed amine systems with only a small amount of promoter added. For this reason, we use the following expression for the stoichiometric coefficient:

$$\nu = 1 + \frac{C_{\text{DEA}}}{C_{\text{DEA}} + C_{\text{MDEA}}} \tag{24}$$

Combined flux approximations

For simplicity, the flux methods will be developed using the film theory. First, combine the differential equations for the total carbonate, CO_2, and carbamate (Eqs. 13a, 13c and 13e) to obtain an equation for the total CO_2 in both chemically combined and physical forms throughout the boundary layer:

$$-\nabla J_{CO_2}-\nabla J_{DEACOO}-\nabla J_{HCO_3}-\nabla J_{CO_3}=0 \tag{25}$$

Integrating once:

$$-D_{CO2}\nabla C_{CO_2}-D_{DEACOO}\nabla C_{DEACOO}-D_{HCO_3}\nabla C_{HCO_3}-D_{CO_3}\nabla C_{CO_3}=R_{CO2} \tag{26}$$

Equation 26 states that the total flux of CO_2 through the film is equivalent to the absorption rate, R_{CO2}. Equation 26 may be integrated again to yield the difference for total CO_2:

$$D_{CO2}\Delta C_{CO_2}+D_{DEACOO}\Delta C_{DEACOO}+D_{HCO_3}\Delta C_{HCO_3}+D_{CO_3}\Delta C_{CO_3}=R_{CO2}\delta \tag{27}$$

δ is the film thickness, and the term Δ is the difference between the interface and the bulk liquid-phase values:

$$\Delta C_i=C_{i,\text{interface}}-C_{i,\text{bulk}} \tag{28}$$

The concentrations in the bulk liquid phase are known *a priori* via the equilibrium model. Analogous expressions may be obtained for the total sulfur, MDEA, and DEA:

$$D_{H2S}\Delta C_{H2S}+D_{HS}\Delta C_{HS}+D_S\Delta C_S=R_{H2S}\delta \tag{29}$$

$$\begin{gathered}D_{DEA}\Delta C_{DEA}+D_{DEAH}\Delta C_{DEAH}+D_{DEACOO}\Delta C_{DEACOO}=0\\ D_{MDEA}\Delta C_{MDEA}+D_{MDEAH}\Delta C_{MDEAH}=0\end{gathered} \tag{30}$$

In addition, four more equations must be added to determine the absorption rate and the interfacial concentration of CO_2 and H_2S:

$$R_{H2S}=k_{g,H2S}(P_{H2S}-C^{*}_{H2S,int}H_{H2S}) \tag{31a}$$

$$R_{CO2}=k_{g,CO2}(P_{CO2}-C^{*}_{CO2,int}H_{CO2}) \tag{31b}$$

$$R_{CO2}=k^o_{1,CO2}E_{CO2}(C_{CO2,int}-C_{CO2,bulk}) \tag{31c}$$

$$R_{H2S}=k^o_{1,H2S}E_{H2S}(C_{H2S,int}-C_{H2S,bulk}) \tag{31d}$$

The enhancement factors appearing in Eqs. 31a-31d are assumed to be explicit functions of the interfacial concentration and will be discussed shortly. Equations 31d and 29 are redundant, so Eq. 31d can be eliminated (this is due to the analytical form of the enhancement factor for absorption with instantaneous reaction, see Astarita et al., 1983). Therefore, the problem posed consists of 15 unknowns: concentrations of CO_2, H_2S, DEA, $DEAH^+$, $DEACOO^-$, MDEA, $MDEAH^+$, HCO_3^-, $CO_3^=$, HS^-, $S^=$, H_3O^+, and OH^- at the interface, and R_{H2S} and R_{CO2}; and 14 equations (Eqs. 11a-11f, 14, 27, 29, 30, 2 and 31a-31c). The 15th equation used reflects the critical assumption made distinguishing the ACFLUX and MCFLUX approximations and will be discussed in the next section.

We make the film theory results look quantitatively like surface renewal theory by making the following substitution for the diffusion coefficients (Chang and Rochelle, 1982):

$$D_{i,corr}=D_i\sqrt{\frac{D_{CO2}}{D_i}} \tag{32}$$

It has been shown (Glasscock and Rochelle, 1990) that this approximation works quite well for finite rate reactions, although it was developed originally for instantaneous reactions. For CO_2, we determine the effective pseudo-first-order rate constant, and then Eq. 28 of DeCoursey (1982) is used as an interpolation from the first-order rate constant at the interface and the instantaneous upper limit. Carey et al. (1991) rearranged Decoursey's equation to get:

$$E_{CO_2}=1+(E_{int}-1)\left[1-\Theta-\frac{\Theta}{E_{int}+C_9}\right] \tag{33a}$$

where the enhancement factor at the interface, E_i, is based on the Hatta number, Ha_i, calculated with reaction rates at the interface solution composition:

$$E_{int}=\sqrt{1+Ha_{int}{}^2} \tag{33b}$$

$$Ha_{int}{}^2=\frac{D_{CO_2}}{k_1^{o2}}\frac{\Re_{CO2,int}}{C_{CO2,int}-C_{CO2,int,eq}} \tag{33c}$$

and the ratio, Θ, is a measure of the approach to the instantaneous upper limit:

$$\Theta=\frac{C_{CO2,e,int}-C_{CO2,bulk}}{C_{CO2,int}-C_{CO2,bulk}} \tag{33d}$$

$C_{CO2,e,int}$ is the CO_2 concentration at the interface under the limiting conditions of instantaneous reaction. For our calculations we have used a value of 1.1 for C_9. However, Decoursey showed that the results of this equation are independent of C_9 and the term containing it. Therefore, the effective equation is given by the simpler form:

$$E_{CO_2}=1+(E_{int}-1)(1-\Theta) \tag{34}$$

ACFLUX approximation

In the ACFLUX approximation as used by Critchfield (1988) for CO_2 absorption into amine mixtures, the following equilibrium equation is assumed to hold true at the interface:

$$DEACOO^-+H_2O\Longleftrightarrow HCO_3^-+DEA \tag{35}$$

In the rigorous model, this reaction cannot proceed instantaneously and, in fact, occurs only by means of carbamate reversion to CO_2, and then subsequent reaction to form bicarbonate. Under many conditions, this is not a bad assumption; however, it can lead to misleading results, and by taking into account the kinetic preference of CO_2 toward $DEACOO^-$ or HCO_3^-, one can arrive at a much better approximation of the enhancement factor.

MCFLUX approximation

Consider Eq. 13d rewritten as follows:

$$\nabla J_{DEACOO} = \mathcal{R}_{DEACOO} \tag{36}$$

Integrating twice:

$$D_{DEACOO}\Delta C_{DEACOO} = \delta^2 \int_0^1 \int_0^{\zeta'} \mathcal{R}_{DEACOO}\, d\zeta''\, d\zeta'$$

$$= G(\mathcal{R}_{DEACOO}) \tag{37}$$

ζ' and ζ'' are dummy variables of integration. The notation G has been used for brevity. A similar equation may be written for the formation of bicarbonate and carbonate:

$$D_{HCO3}\Delta C_{HCO3} + D_{CO3}\Delta C_{CO3} = G(\mathcal{R}_{HCO3}) \tag{38}$$

From Eqs. 37 and 38, the ratio of carbamate formation to the total reaction rate of CO_2 is obtained:

$$f = \frac{D_{DEACOO}\Delta C_{DEACOO}}{D_{DEACOO}\Delta C_{DEACO} + D_{HCO3}\Delta C_{HCO3} + D_{CO3}\Delta C_{CO3}}$$

$$= \frac{G(\mathcal{R}_{DEACOO})}{G(\mathcal{R}_{DEACOO}) + G(\mathcal{R}_{HCO3})} \tag{39}$$

Let us assume that all of the reaction occurs in a reaction zone of width r, and the reaction rate throughout this reaction zone is constant and equal to the value based on interfacial conditions multiplied by a constant α. In this case, the integration in Eq. 37 may be performed analytically:

$$G(\mathcal{R}) = \delta^2 \alpha \mathcal{R}_{int} \int_0^1 \int_0^{\max(\zeta', r)} d\zeta''\, d\zeta'$$

$$= \delta^2 \alpha \left(r - \frac{1}{2} r^2 \right) \mathcal{R}_{int} \tag{40}$$

Equation 40 makes intuitive sense, since, as $r \Rightarrow 0$, $G(\mathcal{R})$, and the accumulation of products at the interface, is zero. Also, $G(\mathcal{R})$ approaches a maximum as $r \Rightarrow 1$, that is, as the reaction zone contains the entire boundary layer. Fortunately, the values of r and α are not important. What is important is that the function G is a simple function of $\mathcal{R}_{int}$, and Eq. 39b may be simplified:

$$f = \frac{\mathcal{R}_{DEACOO,int}}{\mathcal{R}_{DEACOO,int} + \mathcal{R}_{HCO3,int}} \tag{41}$$

The use of Eq. 41 in place of assuming equilibrium for Eq. 35 constitutes the MCFLUX approximation. By use of Eq. 41, the distribution of CO_2 among its chemically combined forms is governed by the kinetic rate expressions at the interface conditions, rather than the equilibrium condition.

For purposes of numerical computation, all diffusion coefficients are assumed to be the same, except for CO_2. This is an assumption of convenience made for purposes of calculation, but does not restrict the validity of the results. In addition, gas-phase resistance has been neglected for CO_2, since the absorption of CO_2 is a liquid-phase limited phenomenon. Therefore, the interfacial concentration is known, and Eq. 31b can be eliminated. However, with H_2S, gas-phase resistance plays a much larger role, and a gas-phase resistance is considered. The actual composition at the gas-liquid interface is calculated using the same equilibrium algorithm that determines the bulk liquid-phase composition. This is done by iteratively modifying the equilibrium constant for Eq. 35 until Eq. 41 is satisfied. This assumption involves a slight error since the equilibrium model considered free CO_2, as well as chemically combined CO_2; so, some free CO_2 is formed in the equilibrium calculation. However, the free CO_2 is much smaller than the chemically combined CO_2, making this error negligible. This procedure also results in estimating the effective equilibrium CO_2 concentration at the interface, $C_{CO2,int,eq}$ from the bicarbonate equilibrium (reaction 9). A more accurate approximation would use a weighted average of the CO_2 concentration calculated from the bicarbonate equilibrium and the carbamate equilibrium (reaction 4).

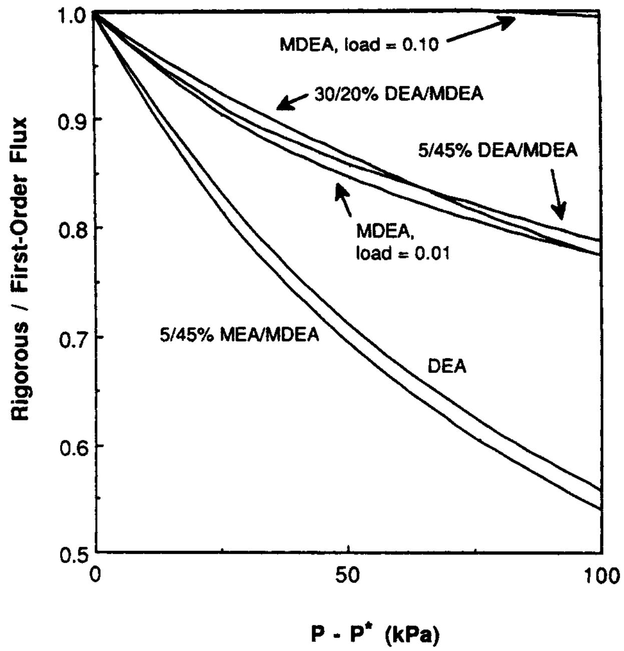

Figure 1. Rigorous method vs. the pseudo-first-order approximation for various amine solutions.

Base conditions: 313 K, $k_l^o = 10^{-4}$ m/s; CO_2 loading = 0.01.

Results

The results comparing the pseudo-first-order approximation to the rigorous model are shown in Figure 1. The results are shown as a function of the driving force, P-P^*, where P^* is the equilibrium partial pressure corresponding to the loading. As can be seen, when the driving force is less than 10 kPa, the first-order approximation is accurate to within 10%. In some cases of interest, such as pressures above 10 kPa for the faster reacting amines, this approximation is quite invalid and can cause an overestimation of stage efficiencies (this has been noted by Rangwala et al., 1989, who modified the AMSIM simulator to account for depletion of the amine at the gas-liquid interface).

The range of conditions under which the combined flux and Wellek approximations have been compared are shown in Ta-

Table 2. Range of Conditions Studied

MDEA (wt. %)	DEA (wt. %)	T (K)	k^o_{lCO2} (m/s)	P_{CO2} (kPa)	CO_2 Loading (mol/mol Amine)	P_{H2S}* (kPa)	H_2S Loading (mol/mol Amine)
50	0	313.	$10^{-5} - 10^{-4}$	10–100	0.01–0.1		
0	30						
40	10						
30	20						
45	5	313.	10^{-4}	10–100	0.01–0.1	1–10	0.01–0.1
20	30						
45	5 (MEA)	313.	10^{-4}	10–100	0.01–0.1	1–10	0.01–0.1

*For H_2S, $k_g = 10^{-5}$ kmol/m²/s/kPa

ble 2. Figures 2 and 3 compare the case of CO_2 absorption only into 50 wt. % MDEA, 5/45 wt. % DEA/MDEA, and 30/20 wt. % DEA/MDEA. The results in Figure 2 are for a mass-transfer coefficient of 10^{-4} m/s, typical of a packed bed column. Under these conditions, all of the approximations perform quite well. At a lower mass-transfer coefficient (results shown in Figure 3), however, we see that the Wellek approximation and the ACFLUX approximation are in significant error. The MCFLUX approximation performs quite well, however, with no deviations greater than 20%. Based on the results in Figures 2 and 3, it is clear that the MCFLUX approximation is superior to other approximations. Note that for MDEA solutions the MCFLUX and ACFLUX approximations give identical results.

Because of the importance of simultaneous absorption of CO_2 and H_2S, the MCFLUX approximation was tested over a range of conditions including simultaneous CO_2 absorption with H_2S desorption. The results are shown in Figure 4 for the CO_2 flux and Figure 5 for the H_2S flux for the same conditions. Figure 4 shows that all of the absorption rates for CO_2 are predicted extremely well, with the maximum deviation being approximately 15% for MDEA. Figure 5 shows that the MCFLUX approximation does an excellent job of predicting the H_2S flux rate. Figure 6 shows that the Wellek approximation does a poor job of representing the CO_2 flux rate for the mixed amine systems during simultaneous H_2S and CO_2 absorption.

An interesting observation obtained from the results is that the H_2S/CO_2 flux ratio takes on extremely high values. This is, of course, due to the instantaneous reaction rate of H_2S, as compared to CO_2, and is especially pronounced for MDEA, which can be used for selective H_2S removal.

In Figure 7, concentration profiles are shown for a typical case that has been solved by the rigorous mass-transfer model and the approximation models. The concentration of each species is shown as a function of the dimensionless distance

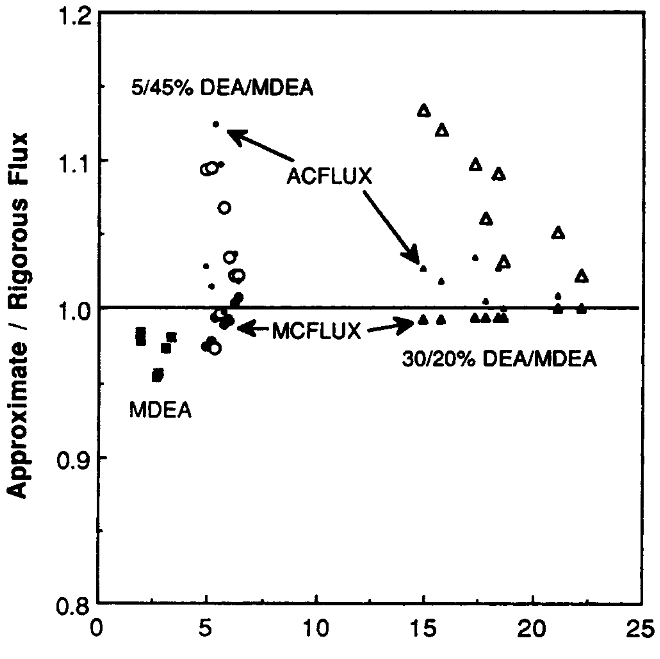

Figure 2. Comparison of the Wellek (large open symbols), ACFLUX (small filled), and MCFLUX (large filled) approximations for 50% MDEA (squares), 5/45% DEA/MDEA (circles), and 30/20% DEA/MDEA (triangles) at 313 K.

$k^o_l = 10^{-4}$ m/s; CO_2 loading = 0.01 & 0.10.

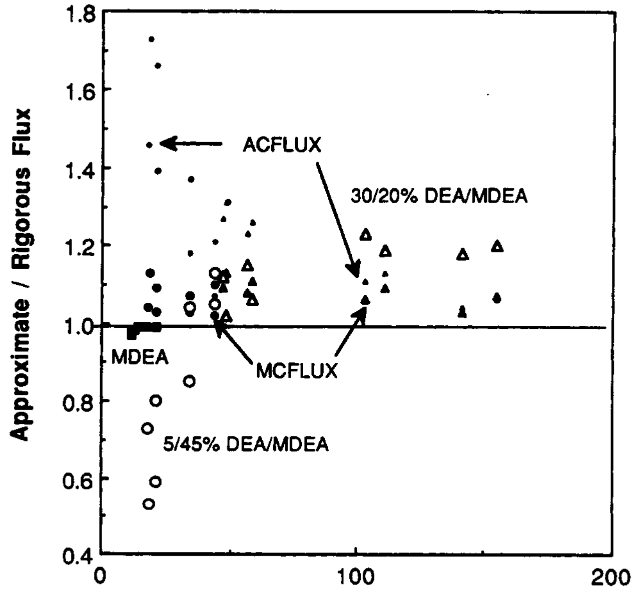

Figure 3. Comparison of the Wellek (large open symbols), ACFLUX (small filled), and MCFLUX (large filled) approximations for 50% MDEA (squares), 5/45% DEA/MDEA (circles), and 30/20% DEA/MDEA (triangles) at 313 K.

$k^o_l = 10^{-5}$ m/s; loading = 0.01, 0.10.

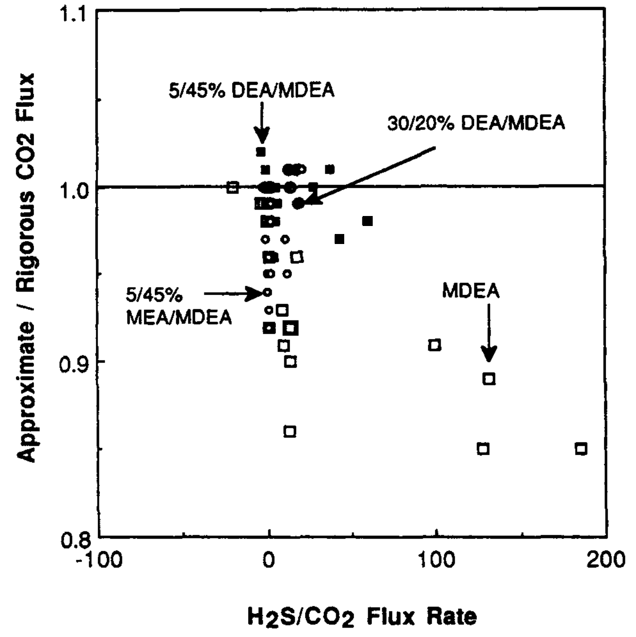

Figure 4. Accuracy of the MCFLUX approximation for prediction of CO$_2$ flux in 50% MDEA, 5/45% DEA/MDEA, 30/20% DEA/MDEA, and 5/45% MEA/MDEA at 313 K.

$k_l^o = 10^{-4}$ m/s; loading = 0.01, 0.10.

from the interface, defined as shown:

$$r = \frac{2}{\pi} \tan^{-1} \left(x \sqrt{\frac{\epsilon}{D}} \right) \tag{42}$$

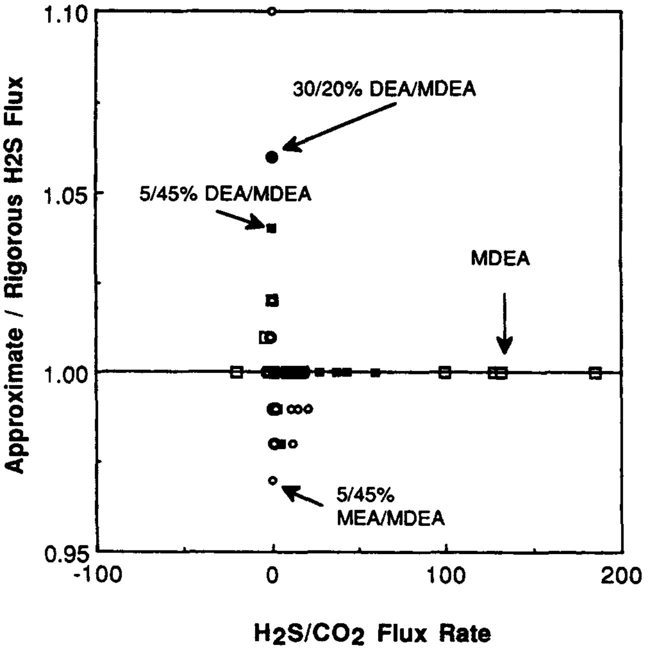

Figure 5. Accuracy of the MCFLUX approximation for prediction of H$_2$S flux in 50% MDEA, 5/45% DEA/MDEA, 30/20% DEA/MDEA, and 5/45% MEA/MDEA at 313 K.

$k_l^o = 10^{-4}$ m/s; loading = 0.01, 0.10.

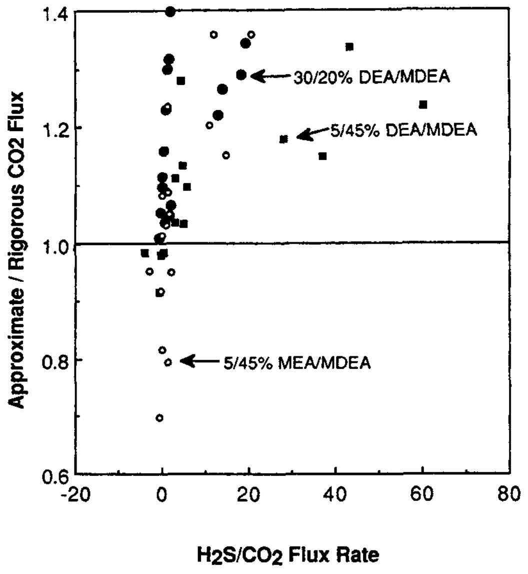

Figure 6. Accuracy of the Wellek approximation for prediction of CO$_2$ flux in 50% MDEA, 5/45% DEA/MDEA, 30/20% DEA/MDEA, and 5/45% MEA/MDEA at 313 K.

$k_l^o = 10^{-4}$ m/s; loading = 0.01, 0.10.

(D is a reference diffusion coefficient, usually set to that of CO$_2$.) Even with the rather large gradients of HS$^-$ and carbamate, the MCFLUX approximation predicts within 2% both the H$_2$S and CO$_2$ fluxes at the conditions corresponding to this figure. Note that the gradient of carbamate at the interface is much greater than the gradient of bicarbonate. The accumulation of carbamate is much greater than would be predicted by equilibrium considerations and is properly accounted for by the MCFLUX approximation.

Conclusions

A general methodology has been presented for the approximate solution of multiple gas absorption with chemical reaction. The critical assumption of the MCFLUX approximation is the use of interfacial compositions to determine the enhancement factor and nonequilibrium reaction selectivity. It has been shown that the approximation works quite well for a wide range of conditions including simultaneous H$_2$S and CO$_2$ absorption into single and mixed amine systems.

Notation

C = concentration, kmol/m^3
D = diffusion coefficient, m^2/s
E = enhancement factor, rate of absorption with to that without reaction
E_a = activation energy, kcal/kmol
E_{int} = enhancement factor at interface composition
H = Henry's constant
Ha = Hatta number (Eq. 33c)
J = flux, kmol/m^2/s
k = rate constant
k_l^o = mass-transfer coefficient, m/s
N = number of chemical components
P = pressure, kPa
$\mathcal{R}$ = net production rate of a species
R = absorption flux rate, kmol/m^2/s

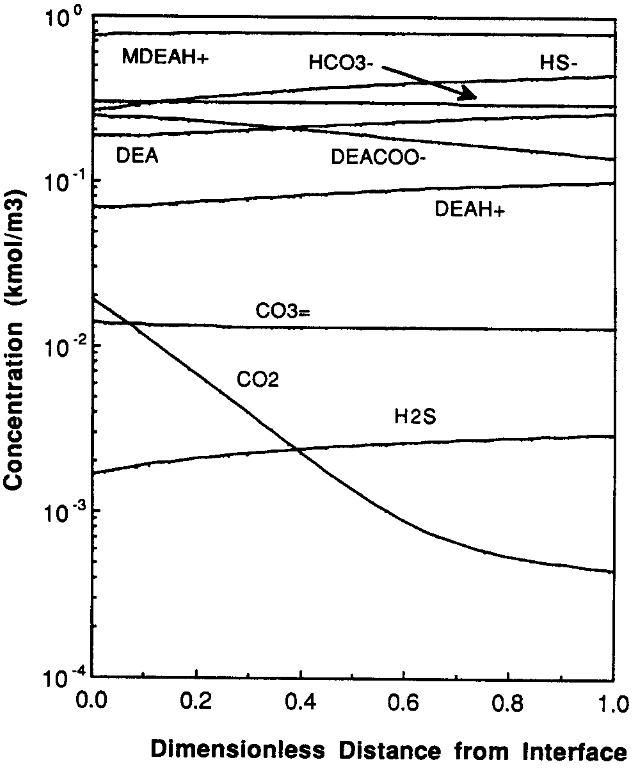

Figure 7. Concentration profiles for simultaneous CO_2 absorption and H_2S desorption with 5/45% DEA/MDEA calculated by the rigorous model at 313 K.

CO_2 and H_2S loadings = 0.1; P_{CO2} = 101 kPa, P_{H2S} = 1.01 kPa; $k_l^o = 10^{-4}$ m/s.

T = temperature, K
x = distance from interface, m
z = charge number of a species

Greek letters

γ = activity coefficient
∇ = differentiation operator, $\partial/\partial x$
ϵ = eddy diffusivity parameter, Eq. 2
ζ = dimensionless distance from interface
Θ = parameter defined by Eq. 33d

Subscripts

bulk = bulk value of concentration
corr = corrected value of diffusion coefficient
e = equilibrium value of concentration
i = component i
int = interface value of concentration
phys = physical conditions, mass transfer without reaction

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Manuscript received Oct. 17, 1990, and revision received Dec. 14, 1992.