Asymptotic Models for H_2S Absorption into Single and Blended Aqueous Amines

Edward B. Rinker, Owen T. Hanna, and Orville C. Sandall
Dept. of Chemical Engineering, University of California, Santa Barbara, CA 93106

Asymptotic power series solutions for the mass-transfer enhancement factor for absorption of a gas component into a liquid where it undergoes irreversible instantaneous chemical reaction(s) with one and two liquid-phase reactants are developed in this work. The Padé technique is used to extend the region of applicability (accelerate the convergence) of the four-term asymptotic power series solutions. The resulting modified asymptotic expressions for the enhancement factor show excellent accuracy over a wide range and can be used to predict enhancement factors as low as 2 with an error of about 5% compared to the exact numerical solution. Predictions of these new asymptotic solutions are compared with experimental absorption data for H_2S absorption into aqueous methyldiethanolamine and H_2S absorption into aqueous mixtures of methyldiethanolamine and diethanolamine obtained in a laminar-jet absorber. The absolute mean deviations of the predictions from the experimental absorption data for the single and mixed amine solutions were 4.6% and 2.4%, respectively.

Introduction

The instantaneous reaction limit is a useful mass-transfer asymptote when a gas is absorbed into a liquid where it can undergo a fast irreversible chemical reaction. The partial differential equations for Higbie's penetration theory model for the case of absorption of a gas accompanied by the irreversible second-order reaction $A + mB \rightarrow$ Products (where m is a stoichiometric coefficient) have been solved numerically by Brian et al. (1961), Pearson (1963), and by Matheron and Sandall (1978). It is found from the numerical results that when $\sqrt{M} > 10E_i$, where $M = D_A k_2 B^o/(k_\ell^o)^2$ and E_i is the mass-transfer enhancement factor for an instantaneous reaction, then the mass-transfer enhancement factor E is given very closely by $E = E_i$. In the definition of M above, k_2 is the second-order kinetic rate constant (cm^3/gmol·s), B^o is the initial bulk liquid-phase concentration of species B (gmol/cm^3) and k_ℓ^o is the physical liquid-phase mass-transfer coefficient, cm/s. The enhancement factor for an instantaneous reaction is given by (Danckwerts, 1970)

$$E_i = \frac{1}{\operatorname{erf}\left(\sqrt{\frac{\beta}{D_A}}\right)} \tag{1}$$

where β is defined by the nonlinear equation (cm^2/s)

$$\frac{1}{\operatorname{erf}\left(\sqrt{\frac{\beta}{D_A}}\right)} = \frac{\frac{B^o}{mA^*}\sqrt{\frac{D_B}{D_A}}\exp\left(\frac{\beta}{D_A} - \frac{\beta}{D_B}\right)}{1 - \operatorname{erf}\left(\sqrt{\frac{\beta}{D_B}}\right)} \tag{2}$$

An approximate solution to Eqs. 1 and 2 for the limit of small β (or large E_i) is given by Danckwerts (1970) as

$$E_i = \sqrt{\frac{D_A}{D_B}} + \frac{B^o}{mA^*}\sqrt{\frac{D_B}{D_A}} \tag{3}$$

According to Danckwerts (1970), the error in E_i as predicted from this approximate equation is approximately $1/(2E_i)$. Thus, for small E_i (that is, $1 < E_i < 5$), Eq. 3 can be significantly in error. In the work presented here, a series with additional terms to Eq. 3, along with the series acceleration technique of Padé, are used to develop a better approximation for the instantaneous enhancement factor for the case of a gas component reacting instantaneously with a single liquid-phase reactant, and for the additional case of a gas component reacting instantaneously with two liquid-phase reactants. The predictive formulas developed here are compared to exact numerical calculations and also with experimental absorption data obtained for H_2S absorption into aqueous methyldiethanolamine (MDEA) and H_2S absorption into aqueous mixtures of MDEA and diethanolamine (DEA).

Asymptotic Analysis of Gas Absorption Accompanied by Instantaneous Reaction(s)

One liquid-phase reactant

For the case of a single gas component absorbing into a liquid where it undergoes an instantaneous chemical reaction with one liquid-phase reactant, Eq. 2 must be solved for $\sqrt{\beta/D_A}$ which is then substituted into Eq. 1 to obtain the instantaneous enhancement factor E_i. An approximate asymptotic solution for E_i from Eqs. 1 and 2 can be obtained for small values of β. For convenience, Eq. 2 can be written as

$$y = \frac{\operatorname{erf}(x)\exp[(1-b^2)x^2]}{1-\operatorname{erf}(bx)} \tag{4}$$

where

$$x = \sqrt{\frac{\beta}{D_A}} \quad y = \sqrt{\frac{D_A}{D_B}}\frac{mA^*}{B^o} \quad b = \sqrt{\frac{D_A}{D_B}}$$

and A^* is the interfacial concentration of species A (gmol/cm^3). Since y is small when x is small, we can expand $y = f(x)$ as a power series in x about $x = 0$. But since x is the unknown in this problem (because it is proportional to B), we want to get a series solution for x in terms of y. This is accomplished by reverting the series for $y = f(x)$ to obtain a new series for $x = g(y)$. The enhancement factor, the quantity for which we want to obtain an asymptotic series, is related to x by Eq. 1 which can be rewritten as

$$E_i = \frac{1}{\operatorname{erf}(x)} \tag{5}$$

We now expand $1/\operatorname{erf}(x)$ as a series in x and substitute for x the series $x = g(y)$. By expanding the series and collecting terms with different orders of y, we obtain an asymptotic series solution for E_i in terms of y for small values of y. This approach requires a great deal of complex and tedious series manipulations which are very difficult to perform by hand. Fortunately, by using the Mathematica system (Wolfram, 1991), the series manipulations can be performed symbolically and the series solution (with virtually any number of terms) is easily obtained. The following four-term series was derived by following the above procedure for the case of one gas absorbing and reacting instantaneously with one liquid-phase reactant

$$E_i = \frac{1}{y}\left[1 + by - \frac{\pi}{4}(b^2-1)y^2 + \frac{5\pi}{12}b(b^2-1)y^3 + O(y^4)\right] \tag{6}$$

Note that the first two terms of the series in Eq. 6 give the result reported by Danckwerts (1970), Eq. 3. Unfortunately, when we try to use Eq. 6 to predict E_i, we only get marginal improvements in the range of accuracy because the series diverges drastically from the exact numerical solution as y approaches unity. Therefore, Eq. 6 is not a significant improvement over Eq. 3. However, by "accelerating" the first four terms (up to y^3) of the series in Eq. 6 using the method of Padé (Hanna and Sandall, 1995), we obtain the following asymptotic solution

$$E_i = \frac{1}{y}\left[\frac{1 + \frac{8b}{3}y + \left(\frac{5b^2}{3} - \frac{\pi}{4}(b^2-1)\right)y^2}{1 + \frac{5b}{3}y}\right] \tag{7}$$

The formula for E_i given by Eq. 7 predicts values of E_i with greatly improved accuracy over a much larger range of E_i than Eq. 3. It was found that a (2,1)Padé expression (that is, a second-order polynomial in the numerator and a first-order polynomial in the denominator) showed the best agreement with the exact numerical solutions of Eqs. 4 and 5.

Two liquid-phase reactants

For the case of one gas component absorbing into a liquid where it undergoes irreversible instantaneous chemical reactions with two different liquid-phase reactants ($A + mB \rightarrow$ Products and $A + nC \rightarrow$ Products), B is defined by the following implicit equation

$$\frac{1}{\operatorname{erf}\left(\sqrt{\frac{\beta}{D_A}}\right)} = \frac{\frac{B^o}{mA^*}\sqrt{\frac{D_B}{D_A}}\exp\left(\frac{\beta}{D_A} - \frac{\beta}{D_B}\right)}{1-\operatorname{erf}\left(\sqrt{\frac{\beta}{D_B}}\right)} + \frac{\frac{C^o}{nA^*}\sqrt{\frac{D_C}{D_A}}\exp\left(\frac{\beta}{D_A} - \frac{\beta}{D_B}\right)}{1-\operatorname{erf}\left(\sqrt{\frac{\beta}{D_C}}\right)} \tag{8}$$

where n is the stoichiometric coefficient for the reaction, $A + nC \rightarrow$ Products; D_A, D_B, and D_C are the liquid-phase diffusion coefficients of species A, B, and C, respectively (cm^2/s); and C^o is the initial bulk concentration of species C (mol/cm^3). The derivation of Eq. 8 closely parallels the derivation by Sherwood and Pigford (1952) for gas absorption into a liquid where it undergoes a single irreversible instantaneous reaction, but we include one additional differential equation for species C. For convenience, Eq. 8 can be rewritten in the following form

$$y = \frac{\operatorname{erf}(x)\exp[(1-b^2)x^2]}{1-\operatorname{erf}(bx)} + \frac{R\operatorname{erf}(x)\exp[(1-c^2)x^2]}{1-\operatorname{erf}(cx)} \tag{9}$$

where

$$R = \frac{\dfrac{C^o}{nA^*}\sqrt{\dfrac{D_C}{D_A}}}{\dfrac{B^o}{mA^*}\sqrt{\dfrac{D_B}{D_A}}} \qquad c = \sqrt{\frac{D_A}{D_C}}$$

$$x = \sqrt{\frac{\beta}{D_A}} \qquad y = \sqrt{\frac{D_A}{D_B}}\,\frac{mA^*}{B^o} \qquad b = \sqrt{\frac{D_A}{D_B}}$$

The expression for E_i for this case is still given by Eq. 5. The same set of series manipulations described earlier can be performed on Eqs. 5 and 9 (using Mathematica) to obtain an asymptotic series solution for E_i in terms of y for small y. The third and fourth coefficients in this series solution are much more complicated than in Eq. 6 (because there are two additional parameters c and R) and will not be shown here. The first two terms are, however, given by

$$E_i = \frac{1}{y}\left[(1+R) + \frac{b+cR}{1+R}y + O(y^2)\right] \tag{10}$$

which can be written as

$$E_i = \frac{B^o + C^o}{B^o\sqrt{\dfrac{D_B}{D_A}} + C^o\sqrt{\dfrac{D_C}{D_A}}} + \frac{B^o}{mA^*}\sqrt{\frac{D_B}{D_A}} + \frac{C^o}{nA^*}\sqrt{\frac{D_C}{D_A}} \tag{11}$$

The formula given by Eq. 11 is analogous to the solution of Danckwerts (Eq. 3) for one gas reacting with one liquid-phase reactant. Enhancement factors calculated from the four-term series solution of Eqs. 5 and 9 (not shown) for this case differ significantly from the exact numerical solution as y approaches unity. In addition, direct application of the Padé acceleration technique to the four term series gives a very complicated and intractible expression for E_i. However, upon careful examination, it is found that the four-term series for this case (1 gas/2 liquids) can be conveniently expressed as the sum of three series, that is

$$E_i = \frac{1}{z(R+1)}[P_b + RP_c + P_{bc}] \tag{12}$$

where P_b is the same as the series in the brackets of Eq. 6 with y replaced by z; P_c is the same as the series in the brackets of Eq. 6 with b replaced by c and with y replaced by z; the dimensionless variable $z = y/(R+1)$; and P_{bc} is given by the following expression

$$P_{bc} = \frac{R}{R+1}(c^2 - b^2)z^2 + A_3z^3 + O(z^4) \tag{13}$$

where A_3 is a complicated coefficient which will not be shown here. The terms P_b and P_c are interpreted as representing the power series portion of the solutions for the enhancement factor for each liquid-phase reactant (B and C) independent of each other. The term P_{bc} can be interpreted as representing the coupling between species B and C. Since P_b and P_c have the same form as the series in the brackets of Eq. 6, they can be expressed by the (2,1) Padé expression in the brackets of Eq. 7 with y replaced by z, thus eliminating the divergent behavior of each series. The series for P_{bc} given by Eq. 13 has only two terms because the original series was truncated after the $O(z^3)$ term. A comparison of the exact numerical solution of Eqs. 5 and 9 with predictions from Eq. 12, including and excluding P_{bc}, revealed that including P_{bc} only slightly improved the accuracy of Eq. 12 for very small y but caused the predictions of Eq. 12 to diverge significantly from the exact solution as y becomes larger. This behavior is not unusual for series solutions. Thus, to improve the accuracy over a larger range, the P_{bc} term in Eq. 12 is neglected and the recommended asymptotic solution for the case of two liquid-phase reactants is

$$E_i = \frac{1}{z(R+1)}[P_b + RP_c] \tag{14}$$

where

$$P_b = \frac{1 + \dfrac{8b}{3}z + \left(\dfrac{5b^2}{3} - \dfrac{\pi}{4}(b^2-1)\right)z^2}{1 + \dfrac{5b}{3}z} \tag{15}$$

$$P_c = \frac{1 + \dfrac{8c}{3}z + \left(\dfrac{5c^2}{3} - \dfrac{\pi}{4}(c^2-1)\right)z^2}{1 + \dfrac{5c}{3}z} \tag{16}$$

Comparison with Exact Numerical Solutions for E_i

The exact numerical solution for Eqs. 4 and 5 and Eqs. 5 and 9 were obtained using the Delta-Square method (Hanna and Sandall, 1995). In the case of one gas reacting with one liquid-phase reactant for the parameter space $0.5 < b < 2$ and $0 < y < 2$, Eq. 7 predicts E_i with a maximum deviation of 5% from the exact numerical solution. The solution due to Danckwerts (Eq. 3) predicts E_i with a maximum deviation of about 30% for the same parameter space. The maximum deviation between Eq. 7 and the exact solution is about 10% for $2 < y < 5$ and $0.5 < b < 2$. It should be mentioned that both Eqs. 3 and 7 agree exactly with the numerical solution (for all $y > 0$) for the special case of $b = 1$. The worst agreement between Eq. 7 and the exact numerical solution for $0.5 < b < 2$ corresponds to the case where $b = 2$. The predictions of Eqs. 3 and 7 along with the exact numerical results are plotted in Figure 1 for the case of $b = 2$.

In the case of one gas absorbing and reacting with two different liquid-phase reactants, Eq. 14 and the exact numeri-

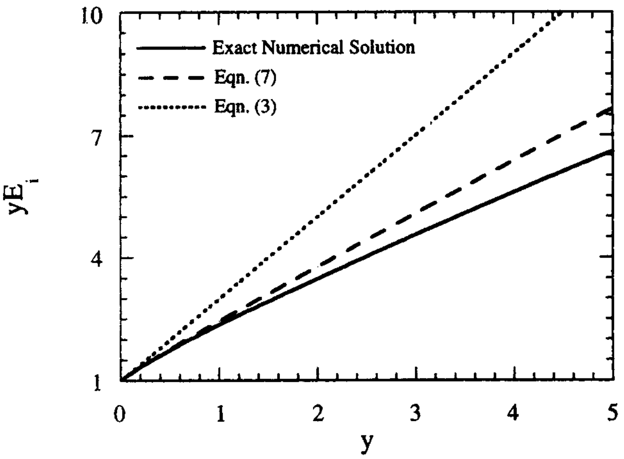

Figure 1. Comparison of predicted enhancement factors for a gas reacting with one liquid-phase reactant for $b = 2$.

cal solution of Eqs. 5 and 9 were compared for the conditions: $0.5 < b < 2$, $0.5 < c < 2$, $0.5 < R < 2$ and $0 < y < 2$. The maximum deviation of the predictions of Eq. 14 from the exact solution is about 4% for this range of parameters. Equation 10 predicts E_i with a maximum deviation of about 18% for the parameter space given above. For the case of $b = 1$ and $c = 1$, Eqs. 10 and 14 are in exact agreement with the numerical solution for all $y > 0$. The worst case for this parameter space is for $R = 0.5$, $b = 2$ and $c = 0.5$. The predictions of Eqs. 10 and 14 along with the results of the exact numerical solution are plotted in Figure 2 for this worst case.

Experimental Apparatus and Procedure

A laminar-jet absorber was used to measure the rate of absorption of H_2S into aqueous solutions of MDEA and mixtures of MDEA and DEA. The apparatus and its operation is described in detail by Al-Ghawas et al. (1989). Pure H_2S saturated with water at the temperature of the liquid jet was introduced into the absorption chamber and the rate of absorption was measured volumetrically using a soap-film meter. All experiments were carried out at ambient pressure and at a temperature of 25°C. In addition, the absorption experiments were carried out for gas-liquid contact times ranging from 0.005 to 0.01 s.

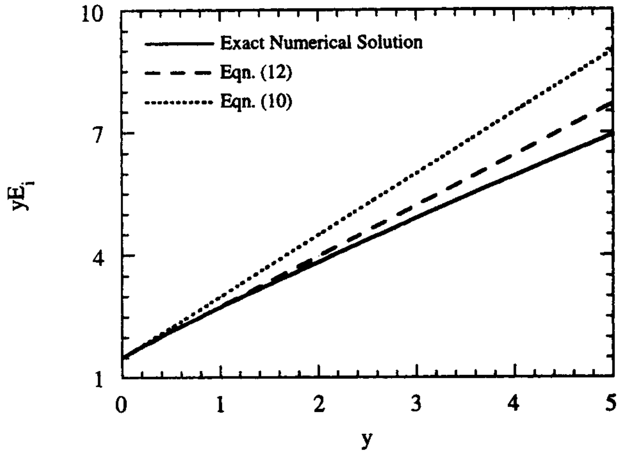

Figure 2. Comparison of predicted enhancement factors for a gas reaction with two liquid-phase reactants for $R = 0.5$, $b = 2$, and $c = 0.5$.

Initial experiments with H_2S absorption into aqueous MDEA resulted in absorption rates that were as great as ten times higher than expected from Eqs. 3 or 7. It is thought that these high absorption rates were due to interfacial turbulence resulting from variations in surface tension (Maragoni effects). We found that these unpredictably large absorption rates could be eliminated by adding 0.1 wt. % of the surfactant Petrowet R, manufactured by the DuPont Company. In earlier experiments performed in our laboratory, we have shown that this low concentration of surfactant has no effect on the physical absorption rate of CO_2 into water (Benitez-Garcia et al., 1990), indicating that this addition of surfactant does not affect the ideal jet hydrodynamics.

Physicochemical Properties

In order to compare model predictions with the experimental H_2S absorption data, it is necessary to know the physical solubility of H_2S in the amine solutions and the liquid-phase diffusion coefficients of H_2S, MDEA, and DEA. The diffusion coefficients for MDEA and DEA were obtained from Snijder et al. (1993). The diffusion coefficient of H_2S cannot be measured directly in the amine solutions since H_2S reacts chemically with the amines. To estimate the liquid-phase diffusivity of H_2S in the aqueous amine solutions, we measured the diffusion coefficient of H_2S in water over the temperature range of 20 to 95°C using a wetted-sphere absorber (Tamimi et al., 1994). These data were fitted to a modified Stokes-Einstein equation as

$$\frac{D_{H_2S}}{T} = 2.24\times 10^{-9}\eta^{-0.725} \qquad (17)$$

where η is the dynamic viscosity, g/cm·s, and T is absolute temperature, K. To estimate the diffusion coefficient of H_2S in the amine solutions, we assume that Eq. 17 is valid in these solutions with the effect of the amine on D_{H_2S} given by the change in solution viscosity. The viscosities of the aqueous amine solutions have been measured in previous work in our laboratory (Rinker et al., 1994).

The physical solubility of H_2S also cannot be measured directly in the amine solutions because of chemical reactions. In this work, we measured the physical solubility of H_2S in aqueous DEA and MDEA solutions which were completely protonated (that is, with all amine present as $MDEAH^+$ or $MDEAH^+$) with a slight excess of HCl so that the amines could not react with H_2S. The apparatus and procedure used to measure the physical solubilities are described in detail by Rinker and Sandall (1996).

Since the reactions of H_2S with aqueous DEA and MDEA are considered to be instantaneous, all of the amine at the gas-liquid interface is assumed to be completely protonated (that is, as $DEAH^+$ and $MDEAH^+$). As a result, it is desirable to measure physical solubilities of H_2S in completely protonated amine solutions. However, when the amines are protonated with HCl, the anion present in solution is Cl^- while the main anion present in the amine solution which reacted with H_2S is HS^-. The method due to van Krevelen and Hoftijzer (1948) as reported by Danckwerts (1970) for correlating physical solubilities of gases in electrolyte solutions should allow us to correct for the presence of Cl^- instead of HS^-. But according to this method, the quantity $\log_{10}(H_A/H_A^o)$ should be a linear function of the ionic strength of the solution. (H_A is Henry's constant for species A, atm L/gmol. H_A^o is Henry's constant of species A in pure water, atm L/gmol.) The physical solubility data measured in this work for H_2S is protonated DEA and MDEA do not show a linear relationship to the ionic strength, but instead show a maximum at intermediate ionic strength. As a result, we were not able to correct for the presence of Cl^- (instead of HS^-) in the protonated amine solutions. Instead, we assumed that the effect of the Cl^- anion in place of HS^- was small and used the measured physical solubility data directly for the prediction of absorption rates for H_2S absorption into aqueous MDEA.

Comparison of Predicted and Experimental Enhancement Factors

For the purposes of comparison of the experimental data with the model predictions, it is more informative to express the data in terms of the rate of absorption instead of the mass-transfer enhancement factor. The rate of gas absorption is related to the enhancement factor by

$$\overline{R}_A = k_\ell^o A^* E_i \tag{18}$$

where $\overline{R}_A$ is the average rate of absorption of species A per unit area, mol/cm^2·s. The experimental rates of H_2S absorption into aqueous 10 and 50 wt. % MDEA solutions are shown in Figure 3 where they are compared to the rates of absorption predicted by Eqs. 7 and 18. It is seen that the predictions of Eq. 7 are in good agreement with the experimental data with an absolute mean deviation of 4.6%. Figure 4 shows the H_2S absorption data for the mixed amine solutions compared to the predictions of Eqs. 14 and 18. The absolute mean deviation of the predictions from the data is 2.4%. The absorption data in Figure 4 are for 50 wt. % total amine with DEA to MDEA mole ratios of 1/20, 1/4, 1/2, and 2/3.

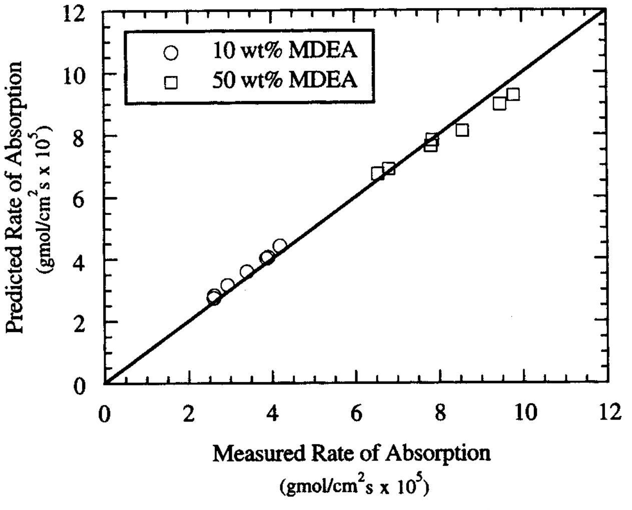

Figure 3. Comparison of enhancement factors predicted by Eq. 7 with experimental enhancement factors for H_2S absorption into aqueous MDEA.

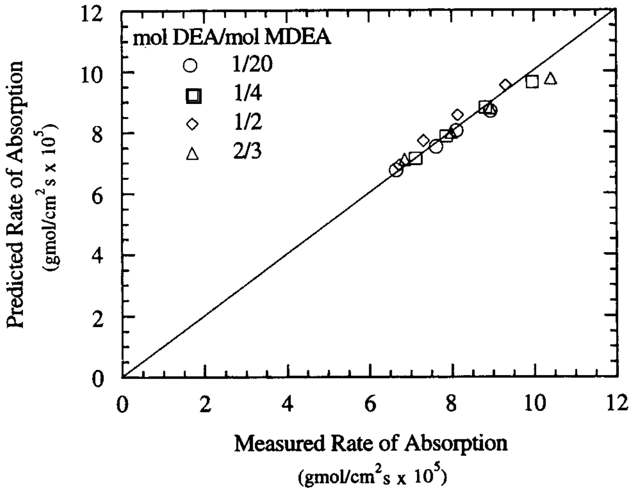

Figure 4. Comparison of enhancement factors predicted by Eq. 12 with experimental enhancement factors for H_2S absorption into aqueous mixtures of DEA and MDEA.

Total amine concentration is 50 wt. %.

Conclusion

Asymptotic solutions for the cases of a gas component absorbing into a liquid where it undergoes irreversible instantaneous chemical reaction(s) with one or two liquid-phase reactants were developed in this work. For the case of one liquid-phase reactant, the asymptotic solution developed in this work shows greater range and accuracy than the two term asymptotic solution reported by Danckwerts (1970). The significantly improved range and accuracy of these solutions is attributed to the "acceleration" of the four-term asymptotic power series solutions by the Padé acceleration technique. Experimentally obtained enhancement factors for the example cases of H_2S absorption into aqueous MDEA and H_2S absorption into mixtures of DEA and MDEA were predicted using the accelerated asymptotic solutions with mean deviations of 4.6% and 2.4%, respectively. These asymptotic solutions are useful for predicting gas absorption rates into solutions where fast chemical reactions take place and can also be used to indirectly determine unknown physicochemical properties such as liquid-phase diffusion coefficients or physical gas solubilities from gas absorption data and known physicochemical property data.

It should be pointed out that even though the approximate solution presented here agrees very well with the exact solution of the model equations, in practice, there could be considerable uncertainty in the physicochemical properties needed to implement the model.

Acknowledgment

This work was funded by the Gas Research Institute and the Gas Processors Association.

Literature Cited

Al-Ghawas, H. A., D. P. Hagewiesche, G. Ruiz-Ibanez, and O. C. Sandall, "Physicochemical Properties Important for Carbon Dioxide Absorption in Aqueous Methyldiethanolamine," *J. Chem. Eng. Data*, **34**, 385 (1989).

Benitez-Garcia, J., G. Ruiz-Ibanez, A. Bidarian, and O. C. Sandall, "Kinetics of the Reaction Between Carbon Dioxide and Triethylamine in Aqueous Solutions," *Chem. Eng. Sci.*, **45**, 3407 (1990).

Brian, P. L. T., J. F. Hurley, and E. H. Hasseltine, "Penetration Theory for Gas Absorption Accompanied by a Second Order Chemical Reaction," *AIChE J.*, **1**, 226 (1961).

Danckwerts, P. V., *Gas-Liquid Reactions*, McGraw-Hill, New York (1970).

Hanna, O. T., and O. C. Sandall, *Computational Methods in Chemical Engineering*, Prentice Hall, Englewood Cliffs, NJ (1995).

Matheron, E. R., and O. C. Sandall, "Gas Absorption Accompanied by a Second-Order Chemical Reaction Modeled According to the Danckwerts Surface Renewal Theory," *AIChE J.*, **24**, 552 (1978).

Pearson, J. R. A., "Diffusion of One Substance into a Semi-Infinite Medium Containing Another with Second-Order Reaction," *Appl. Sci. Res. Sec. A*, **11**, 321 (1963).

Rinker, E. B., and O. C. Sandall, "Solubility of Nitrous Oxide in Aqueous Solutions of Methyldiethanolamine, Diethanolamine, and Mixtures of Methyldiethanolamine and Diethanolamine," *Chem. Eng. Comm.*, **144**, 85 (1996).

Rinker, E. B., D. W. Oelschlager, A. T. Colussi, K. R. Henry, and O. C. Sandall, "Viscosity, Density, and Surface Tension of Binary Mixtures of Water and N-methyldiethanolamine and Water and Diethanolamine and Tertiary Mixtures of these Amine with Water over the Temperature Range 20–100°C," *J. Chem. Eng. Data*, **39**, 392 (1994).

Sherwood, T. K., and R. L. Pigford, *Absorption and Extraction*, McGraw-Hill, New York (1952).

Snijder, E. D., M. T. M. te Riele, G. F. Versteeg, and W. P. M. van Swaaij, "Diffusion Coefficients of Several Aqueous Alkanolamine Solutions," *J. Chem. Eng. Data*, **38**, 475 (1993).

Tamimi, A., E. B. Rinker, and O. C. Sandall, "Diffusion Coefficients for Hydrogen Sulfide, Carbon Dioxide, and Nitrous Oxide in Water over the Temperature Range 293–368 K," *J. Chem. Eng. Data*, **39**, 330 (1994).

Wolfram, S., *Mathematica: A System for Doing Mathematics by Computer*, 2nd ed., Addison-Wesley, Redwood City, CA (1991).

Manuscript received Apr. 29,1996, and revision received July 22, 1996.