Chemical Absorption of Carbon Dioxide into Ethanolamine Solutions of Polar Solvent

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INTRODUCTION

Aqueous solutions of alkanolamine have been widely employed for removal of acid gases (Wall, 1975). Many studies have been done on the mechanisms and kinetics of the reaction between carbon dioxide and various amines (Blauwhoff et al., 1983). The reaction media, however, are restricted to aqueous solutions. In an earlier work (Sada et al., 1985), the absorption rates of carbon dioxide into nonaqueous (alcoholic) solutions of mono- and diethanolamine were measured in a stirred tank with a plane gas-liquid interface, and the rate data under the fast reaction regime were analyzed to investigate the orders of reaction and the reaction rate constants. The order of reaction with respect to carbon dioxide concentration was found to be 1, while the order of reaction with respect to ethanolamine concentration ranged from 1 to 2, depending on the species of nonaqueous solvent. The latter reaction orders in nonaqueous solvents could be interpreted in terms of a new reaction mechanism comprising formation of a zwitterion followed by the removal of proton by a base (i.e., ethanolamine), proposed by Danckwerts (1979). The logarithms of the reaction rate parameters appearing in the reaction scheme were found to be approximately linear to the solubility parameter of the solvent.

In the present note, an analytical approximate solution of the enhancement factor for gas absorption with reaction via the zwitterion (Danckwerts) is presented on the basis of film theory model by using the van Krevelen approximation. The approximate enhancement factor was compared with the numerical solution. The agreement between approximate and numerical solutions is quite satisfactory from the standpoint of practical use. The maximum error was estimated to be about 10%. Furthermore, the enhancement factors for absorption of carbon dioxide into aqueous and alcoholic (methanol) solutions of diethanolamine were determined specifically at low amine concentrations, where the fast reaction regime condition is not met. The experimental values of the enhancement factor were compared with numerical (or approximate) solutions. The maximum deviation was found to be about 10%. It was therefore confirmed that the values of rate parameters derived from the absorption rate data under the fast reaction regime (Sada et al., 1985) were valid for the reaction via the zwitterion (Danckwerts, 1979). It was further supported that the reaction of carbon dioxide with ethanolamine in polar solvents obeys the new reaction scheme proposed by Danckwerts.

THEORETICAL CONSIDERATION

According to Danckwerts carbon dioxide reacts with mono- and diethanolamine in polar solvents via a zwitterion. As regards diethanolamine, the reaction takes place in two steps:

$$CO_2 + R_2NH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R_2NH^+CO_2^- \tag{i}$$

$$R_2NH^+CO_2^- + R_2NH \xrightarrow{k_3} R_2NH_2^+ + R_2NCO_2^- \tag{ii}$$

where the radical R designates $HO \cdot CH_2 \cdot CH_2 \cdot$. When a pseudosteady-state condition can be assumed for the zwitterion ($R_2NH^+CO_2^-$), a homogeneous rate of reaction is written as

$$r = -\frac{dC_A}{dt} = \frac{C_A C_B}{\dfrac{1}{k_1} + \dfrac{k_2}{k_1 k_3 C_B}}. \tag{1}$$

When the gaseous reactant A is absorbed into the liquid medium containing liquid-phase reactant B, as takes place in reactions i and ii, the film theory material balance equations of components A and B can be written as

$$D_A \frac{d^2C_A}{dz^2} = \frac{k_1 C_A C_B}{1 + \dfrac{k_2}{k_3 C_B}} \tag{2}$$

and

$$D_B \frac{d^2C_B}{dz^2} = \frac{\nu k_1 C_A C_B}{1 + \dfrac{k_2}{k_3 C_B}}, \tag{3}$$

respectively. The boundary conditions to be imposed are

$$\text{at } z = 0, \quad C_A = C_{Ai}, \ dC_A/dz = 0 \tag{4}$$

$$\text{at } z = z_L, \quad C_A = 0, \ C_B = C_{BO}. \tag{5}$$

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The basic mass balance equations, Eqs. 2 and 3, can be put into the following dimensionless form:

$$\frac{d^2Y_A}{dx^2} = \frac{M\,Y_AY_B^2}{1 + \alpha Y_B} \tag{6}$$

$$\frac{d^2Y_B}{dx^2} = \frac{1}{r_Bq_B}\frac{M\,Y_AY_B^2}{1 + \alpha Y_B} \tag{7}$$

with the boundary conditions

$$\text{at } x = 0,\quad Y_A = 1,\ dY_B/dx = 0 \tag{8}$$

$$\text{at } x = 1,\quad Y_A = 0,\ Y_B = 1. \tag{9}$$

Approximate Solution

An approximate solution for the gas absorption rate or enhancement factor was obtained by using the van Krevelen approximation that the concentration of reactant B in the liquid film is considered to be constant and equal to its interfacial concentration. That is, Eq. 6 reduces to

$$\frac{d^2Y_A}{dx^2} = \frac{M\,Y_{Bi}^2Y_A}{1 + \alpha Y_{Bi}} \tag{10}$$

and hence the enhancement factor can be derived in the same manner as the case of the first-order reaction:

$$\phi = \frac{\sqrt{M'}}{\tanh\sqrt{M'}} \tag{11}$$

where

$$\sqrt{M'} = \sqrt{\frac{M\,Y_{Bi}^2}{1 + \alpha Y_{Bi}}} \tag{12}$$

Y_{Bi} in the above equation is given as

$$Y_{Bi} = \frac{\phi_\infty - \phi}{\phi_\infty - 1}. \tag{13}$$

Numerical Solution

The solution of the basic mass balance equations, Eqs. 6 and 7, poses a nonlinear boundary value problem. So the simultaneous differential equations 6 and 7 with the boundary conditions of Eqs. 8 and 9 were numerically solved by using the quasi-linearization technique proposed by Lee (1968). The implicit finite-difference equations were simplified by linearizing the reaction term. A set of simultaneous linear equations was solved by the method of tridiagonal equations. The numerical results were expressed by the enhancement factor defined as

$$\phi = -\left(\frac{dY_A}{dx}\right)_{x=0}. \tag{14}$$

Comparison of Approximate and Numerical Solutions

To check the validity of the approximate solution of the enhancement factor, it was compared with the numerical value. The results were calculated for wide range of $\sqrt{M}$ at r_Bq_B = 10 and 100. Figure 1a shows the comparison of the approximate values of the enhancement factor with numerical values. The maximum error was as small as 2%. Even when r_Bq_B increases to 1,000, the deviation is estimated within 10% (Figure 1b). Therefore, the accuracy of this approximation is found to be quite satisfactory from the standpoint of practical application.

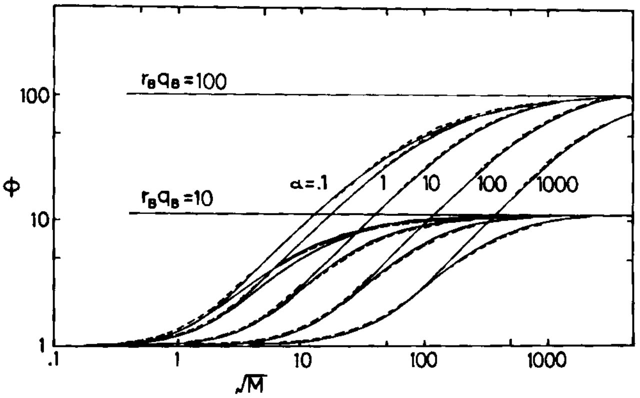

Figure 1a. Comparison of approximate solutions with numerical solutions for enhancement factor when r_Bq_B = 10 and 100.

EXPERIMENTAL RESULTS AND DISCUSSION

The absorptions of carbon dioxide into aqueous and methanol solutions of diethanolamine were performed using a stirred tank with a plane gas-liquid interface at 303 K, and the enhancement factors for both systems were determined specifically at lower concentrations of diethanolamine. The experimental apparatus and procedures were described in detail in an earlier paper (Sada et al., 1985). In the earlier work the values of reaction rate parameters in Eq. 1 were determined by analyzing the absorption rate data under the fast reaction regime, which was met here above 0.5 mol/dm³ diethanolamine [k_1 = 1,100 dm³/mol·s and k_1k_3/k_2 = 1,320 dm⁶/mol²·s in aqueous solutions, and k_1 = 340 dm³/mol·s and k_1k_3/k_2 = 340 dm⁶/mol²·s in methanol solutions]. In the present work, the values of enhancement factor for low concentrations of diethanolamine (0.1–0.5 mol/dm³; values of α correspond to 0.12–0.6 in aqueous solutions and 0.1–0.5 in methanol solutions) will be compared with the theoretical values calculated via the above procedure.

The observed absorption rates were converted to the enhancement factors according to

$$\phi = \frac{N_A}{C_{Ai}k_L^o}. \tag{15}$$

Here, k_L^o refers to the physical liquid-side mass transfer coefficient for absorption of carbon dioxide into diethanolamine solutions, and is assumed to be equal to that for absorption

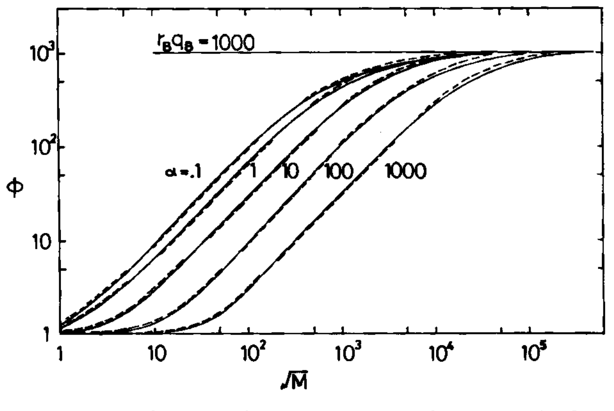

Figure 1b. Comparison of approximate solutions with numerical solutions for enhancement factor when r_Bq_B = 1,000.

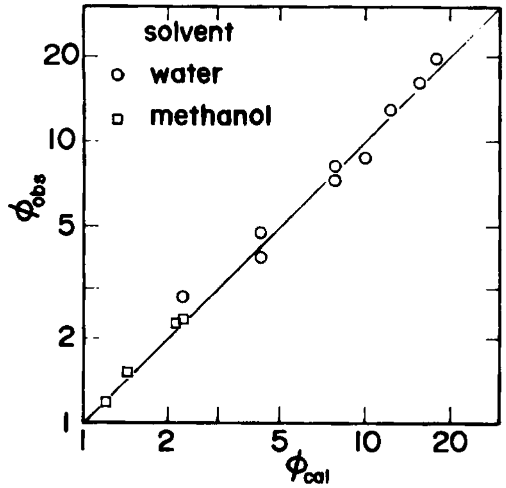

Figure 2. Comparison of calculated enhancement factors with observed values for absorptions of carbon dioxide into aqueous and methanol solutions of diethanolamine.

into water (3.22×10^{-3} cm/s at 303 K) or into methanol (1.93×10^{-2} cm/s at 303 K), because the amine concentration covered is rather low. Also, the solubilities of carbon dioxide in aqueous and methanol solutions of diethanolamine were assumed to be equal to those in water (i.e., $H_A = 3.41$ MPa·dm³/mol at 303 K) and in methanol ($H_A = 0.715$ MPa·dm³/mol at 303 K), respectively, because according to our previous work (Sada et al., 1976), the solubilities of nitrous oxide in aqueous solutions of diethanolamine below 0.5 mol/dm³ are decreased only by 1% relative to that in water. The diffusivities of carbon dioxide in aqueous and methanol solutions of diethanolamine were also assumed to be equal to those in water and methanol, respectively. The value of diffusivity of amine in water or methanol at infinite dilution was estimated by the method of Wilke (1949). The comparison of observed and calculated enhancement factors is shown in Figure 2. The values of the enhancement factor in the range of $\phi_\infty/\phi < 4$ in aqueous solutions and $\phi < 3$ in methanol solutions where the fast reaction regime does not hold at all, were compared with the theoretical values. The observed enhancement factors agreed within an error of 10% with the theoretical values.

CONCLUSION

The reaction between carbon dioxide and ethanolamine in polar solvents has been confirmed to be presented by a new scheme via a zwitterion proposed by Danckwerts (1979). The analytical approximate expression of the enhancement factor for this scheme of reaction was derived on the basis of film theory model and the values of approximate solution were compared with the numerical values. The deviation was estimated to be less than 2% in the range of $r_Bq_B < 100$. Even when r_Bq_B was increased to 1,000, the maximum deviation was less than 10%.

The enhancement factors for absorption of carbon dioxide into aqueous and methanol solutions of 0.1–0.5 molar diethanolamine were measured and compared with the theoretical values. The observed values, which were determined under $\phi_\infty/\phi < 4$ in aqueous solutions and $\phi < 3$ in methanol solutions, where the fast reaction regime was not met, agreed within an error of 10% with the theoretical values calculated with estimates of reaction parameters derived from the absorption rate data under the fast reaction regime (Sada et al., 1985). The reaction of carbon dioxide with ethanolamine in polar solvents was confirmed again to be expressed by the above stated reaction scheme.

NOTATION

C = concentration in liquid phase, mol/dm³ or mol/cm³
D = diffusion coefficient in liquid phase, cm²/s
H = Henry's law constant, Pa·dm³/mol
k_L^o = physical liquid-side mass transfer coefficient of solute gas, cm/s
$\sqrt{M}$ = reaction-diffusion modulus defined by $\sqrt{k_1k_3C_{BO}^2D_A/k_2}/k_L^o$
$\sqrt{M}'$ = modified reaction-diffusion modulus defined by Eq. 12
N_A = absorption rate of carbon dioxide, mol/s · cm²
k_1, k_2, k_3 = reaction rate constants defined in Eqs. i, ii, and 1
q_B = C_{BO}/C_{Ai}
r = reaction rate, mol/s · cm³
r_B = diffusivity ratio = D_B/D_A
x = dimensionless distance from gas-liquid interface = z/z_L
z = distance into liquid phase from gas-liquid interface, cm
z_L = thickness of liquid film in film theory concept, cm
α = k_3C_{BO}/k_2
ν = stoichiometric coefficient appearing in the reaction $A + \nu B \rightarrow$ Products
ϕ = enhancement factor
ϕ_∞ = enhancement factor for an instantaneous reaction defined by $1 + (D_B/D_A)(C_{BO}/\nu C_{Ai})$

Subscripts

A = solute gas component (carbon dioxide)
B = liquid-phase reactant (ethanolamine)
i = gas-liquid interface
O = bulk liquid phase

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Manuscript received Aug. 8, 1984, and revision received Jan. 3, 1985.