Modeling of CO_2 Absorber Using an AMP Solution

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An explicit model for carbon dioxide (CO_2) solubility in an aqueous solution of 2-amino-2-methyl-1-propanol (AMP) has been proposed and an expression for the heat of absorption of CO_2 has been developed as a function of loading and temperature. A rate-based steady-state model for CO_2 absorption into an AMP solution has been proposed, using both the proposed expression for the CO_2 solubility and the expression for the heat of absorption along with an expression for the enhancement factor and physicochemical data from the literature. The proposed model has successfully been applied to absorption of CO_2 into an AMP solution in a packed tower and validated against pilot-plant data from the literature. © 2006 American Institute of Chemical Engineers
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Introduction

Using aqueous solutions of alkanolamines for carbon dioxide (CO_2) capture from process streams is an established concept that has achieved wide industrial practice but usually for applications on a much smaller scale than power plant flue gas cleaning. The process has been used commercially since the early 1930s[1] and is based on a reaction of a weak base (alkanolamine) with a weak acid (CO_2) to produce a water-soluble salt. This reaction is reversible and the equilibrium is temperature dependent. The ability of a chemical solvent to remove carbon dioxide depends on its equilibrium solubility as well as mass transfer and chemical kinetics. The greatest problems concerning the use of alkanolamines as absorbents for CO_2 from power plant flue gases are the amount of energy needed to regenerate the CO_2-rich solvent and the size of the CO_2 capture plant. Conventional alkanolamines can be classified into three chemical categories: primary, secondary, and tertiary amines. Among these three categories the primary amines, such as monoethanolamine (MEA), are considered the most suitable for flue gas cleaning because of the low partial pressure of CO_2 in the flue gas. MEA is considered an attractive solvent at low partial pressures of CO_2 in the flue gas because it reacts at a rapid rate and the cost of the raw materials is low compared to that of secondary and tertiary amines. However, the costs of absorption processes using MEA are high because of the high energy consumption in regenerating and operation problems such as corrosion, solvent loss, and solvent degradation.[2] Furthermore, MEA can be loaded up to only 0.5 mol of CO_2/mol of MEA as a result of the stable carbamates formed. Tertiary alkanolamines, such as methyldiethanolamine (MDEA), can reach loadings of 1 mole of CO_2/mole alkanolamine and the energy consumption for regeneration is lower, although the low rates of CO_2 absorption make them infeasible for flue gas cleaning. Sartori and Savage[3] presented a group of amines, called sterically hindered amines, that have low carbamate stability, making loadings up to 1 feasible and the reaction rates are much higher compared to that of MDEA. Sterically hindered amines can be an attractive option for flue gas cleaning. Reliable process models are necessary, however, to develop efficient processes for separation of CO_2 from flue gases.

In the literature several publications concerning modeling of adiabatic rate–based CO_2 absorption in packed columns exist, but very little has been done with a sterically hindered amine as solvent. Following is a brief summary of the main different

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approaches used for rate-based modeling of CO_2 absorption in alkanolamine solutions. The first work concerning modeling of adiabatic rate–based CO_2 absorption was done by Pandya.[4] He set up differential mass and enthalpy balances and used ideal gas and ideal solution to describe the gas and liquid phases and an explicit expression for the enhancement factor, resulting in a boundary value problem that was solved by using a shooting method. Pandya[4] showed one calculation example with aqueous MEA as solvent, although no validation against experimental data was presented. Tontiwachwuthikul et al.[5] used principally the same model for systems with aqueous NaOH and MEA as solvents and compared to experimental pilot-plant data carried out in their work. The enhancement factor was calculated by an explicit model presented by Welleck et al.[6] Their calculations show good agreement with experimental data for NaOH–CO_2 and MEA–CO_2 systems. Furthermore, they presented experimental data for CO_2 absorption with aqueous 2-amino-2-methyl-1-propanol (AMP) solutions, a sterically hindered alkanolamine, but no modeling of the AMP–CO_2 system was proposed. Pacheco and Rochelle[7] used RATEFRAC, the rate-based distillation module of Aspen Plus™ combined with electrolyte–NRTL to account for the nonidealities in the liquid phase and using Maxwell–Stefan and enhancement factor theory for absorption of CO_2 and H_2S into aqueous solutions of MDEA.

In the most elaborate modeling effort presented so far Kucka et al.[8] set up a rigorous rate-based model for sour gas absorption and applied it to CO_2 absorption in aqueous MEA. The model involves solving a system of partial differential and algebraic equations discretizing in both axial and film directions. They used Aspen Custom Modeler™ to solve the systems of equations. The use of enhancement factors was not implemented in their work. To verify the model, published pilot-plant data[5] were simulated with good accuracy for the partial pressure of CO_2, but the temperature of the liquid phase was not captured with the same accuracy. In their work the electrolyte–NRTL model was used to account for the nonidealities in the liquid phase, whereas in the gas phase the Soave–Redlich–Kwong (SRK) equation of state was used. The only published results for CO_2 absorption in a packed column using aqueous AMP was done by Alatiqi et al.[9] A rate-based approach was used to model absorption of CO_2 in MEA, DEA, and AMP solutions. The results of the AMP modeling were not validated with experimental data, but compared only to absorption of CO_2 in MEA and DEA solutions; only the MEA results were verified using experimental data. Furthermore, values of the physicochemical properties used in the model and their sources are very unclear, such as the heat of absorption is claimed to be obtained from Weiland et al.,[10] although this reference has data for MEA solutions only. In addition to the models presented in the literature several different commercial software packages, custom made for modeling acid gas capture with alkanolamines, are available.

In the present work a mathematical model for the absorption of CO_2 in an aqueous solution of AMP in a packed column is proposed. Furthermore, an explicit model for estimating CO_2 solubility in aqueous solutions of AMP is proposed and the heat of absorption of CO_2 is derived from the solubility model. The proposed model is validated with pilot-plant data.

Model Development

When designing absorption with chemical reaction there are several factors to account for. One of the most important considerations is the temperature variation within the column arising from the heat of absorption of the acid gas and the heat of evaporation of solvent. The temperature influences not only the equilibrium line, but also the rate of the chemical reactions involved and the physical properties of the liquid and the gas. For all absorption columns with dumped or structured packings the fluid dynamics of counter-current, two-phase flow have to be considered to describe mass transfer, pressure drop, load limits, and liquid holdup. The occurrence of chemical reaction in absorption systems has two different distinct effects on the overall behavior of the system. First, when a component is absorbed in the liquid it reacts and is therefore consumed. This implies that the driving force for additional absorption remains higher than it would be if no chemical reaction was involved. The second effect is that the mass-transfer coefficient may be significantly increased when chemical reactions take place. Reactive absorption of CO_2 in an aqueous solution of AMP can be described by a five-component system: (1) an insoluble carrier gas, (2) one reactive acid gas, (3) one volatile component of solution, (4) a nonvolatile reactive solvent, and (5) nonvolatile products. Gas dissolved in the liquid phase reacts reversibly with nonvolatile reactive component and forms nonvolatile products. The absorption reaction occurs only in the liquid phase.

Chemistry

AMP is a sterically hindered primary alkanolamine. A *sterically hindered amine* is defined structurally as a primary amine in which the amino group is attached to a tertiary carbon atom, or a secondary amine in which the amino group is attached to a secondary or tertiary amino group.[3] Sterically hindered alkanolamines are not expected to form stable carbamate, which is the case for primary and secondary alkanolamines. The chemical equilibrium reactions taking place in the liquid phase when CO_2 is absorbed in an aqueous solution of AMP can be written with the following equations, where AMP is written as RNH_2:

$$2H_2O \rightleftarrows H_3O^+ + OH^- \tag{1}$$

$$CO_2 + 2H_2O \rightleftarrows H_3O^+ + HCO_3^- \tag{2}$$

$$HCO_3^- + H_2O \rightleftarrows H_3O^+ + CO_3^{2-} \tag{3}$$

$$RNH_3^+ + H_2O \rightleftarrows H_3O^+ + RNH_2 \tag{4}$$

$$RNHCOO^- + H_2O \rightleftarrows RNH_2 + HCO_3^- \tag{5}$$

The carbamate stability is low and the loading is in the region where the physical absorption of CO_2 is not significant Thus, the reaction of CO_2 with aqueous AMP can be approximated by a single chemical equilibrium reaction:

$$AMPH^+ + HCO_3^- \rightleftarrows AMP + CO_2(aq.) + H_2O \tag{6}$$

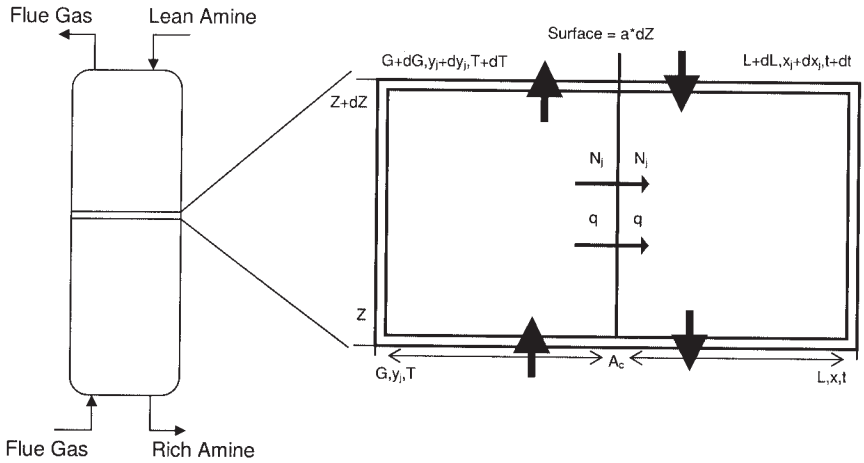

Figure 1. Differential element of a packed column.

Equation 6 is assumed to be valid in the loading range between 0.01 and 1.0 and neglects the presence of both hydroxide (OH^-) and carbonate ions (CO_3^{2-}) because the concentrations of these ions are very small.

Packed column model

Due to the nature of the process a rate based model is chosen and since it is a packed column differential mass and energy balances are set up. The model in this work is based on the model developed by Pandya[4] where the process is described by the two-film theory and use of Assumptions 1–7:

(1) The reaction is fast enough to take place in the liquid film and the bulk of the liquid is in equilibrium.

(2) The liquid-side heat-transfer resistance is small compared to the gas phase, and thus the interface temperature is the same as the bulk temperature.

(3) The liquid-side mass-transfer resistance for the volatile solvent is negligible.

(4) The interfacial surface area is the same for both heat and mass transfer.

(5) Axial dispersion is not accounted for.

(6) The absorption tower is considered to be adiabatic.

(7) Both the liquid phase and the gas phase are formally treated as ideal mixtures.

The last assumption concerning liquid phase ideality may seem unrealistic, given that the system described contains weak electrolytes. Several different thermodynamic models that account for the chemical equilibrium reactions as well as liquid phase nonidealities exist. These models can be used for calculating CO_2 partial pressure and liquid speciation over a large loading area. Common features shared by the models that take nonidealities into account include complexity and a large number of adjustable parameters that have to be fitted to experimental solubility data. The models require solving a set of nonlinear equations, thus making all of the models computationally time-consuming. Furthermore, it seems uncertain that the quality of experimental data for the solubility of CO_2 in aqueous alkanolamines is good enough to justify the use of elaborate models with many adjustable parameters.[11] Thus a simple model based on liquid-phase ideality and one chemical equilibrium reaction with the nonidealities accounted for in the combined Henry's Law and equilibrium constant is found adequate for the conditions encountered in flue gas cleaning.

As may be seen in Eq. 6 there are only two products in the equilibrated solution resulting from the reaction between CO_2 and aqueous AMP. The changes in concentration of reactants and products can be related to the rate of absorption of CO_2 by stoichiometry through

$$\frac{N_{CO_2}aA_C}{1} = \frac{L}{1}\frac{dx_B}{dz} = \frac{L}{1}\frac{dx_{H_2O}}{dz} = \frac{L}{-1}\frac{dX_{CO_2}}{dz} = \frac{L}{-1}\frac{dx_{AMPH^+}}{dz} \tag{7}$$

where the mole fraction of chemically bound CO_2 in the bulk of the liquid phase is equal to the mole fraction of bicarbonate ions in the bulk of the liquid phase ($X_{CO_2} = x_{HCO_3^-}$). The total material and energy balance equations and the component material balances for each phase are set up using a differential segment of the packed absorber as shown in Figure 1. Then by including the stoichiometric relations for the chemical reaction the following system of eight differential equations can be set up:

$$\frac{dG}{dz} = -(N_{CO_2} + N_{H_2O})aA_C \tag{8}$$

$$\frac{dy_{CO_2}}{dz} = \frac{N_{CO_2}aA_C(y_{CO_2} - 1) + N_{H_2O}y_{CO_2}aA_C}{G} \tag{9}$$

$$\frac{dy_{H_2O}}{dz} = \frac{N_{H_2O}aA_C(y_{H_2O} - 1) + N_{CO_2}y_{H_2O}aA_C}{G} \tag{10}$$

$$\frac{dL}{dz} = -N_{H_2O}aA_C \tag{11}$$

$$\frac{dX_{CO_2}}{dz} = \frac{(N_{H_2O}X_{CO_2} - N_{CO_2})aA_C}{L} \tag{12}$$

$$\frac{dx_{H_2O}}{dz} = \frac{[N_{H_2O}(x_{H_2O} - 1) + N_{CO_2}]aA_C}{L} \quad (13)$$

$$\frac{dT_G}{dz} = -\frac{qaA_C}{Gc_{p,G}} \quad (14)$$

$$\frac{dT_L}{dz} = \frac{(N_{CO_2}c_{p,CO_2} + N_{H_2O}c_{p,H_2O})aA_C(T_L - T_G)}{Lc_{p,L}} - \frac{qaA_C}{Lc_{p,L}} + \frac{(N_{CO_2}\Delta H_{CO_2} + N_{H_2O}\Delta H_{H_2O})}{Lc_{p,L}} \quad (15)$$

Heat and mass transfer

The heat-transfer coefficient in the gas phase was calculated by the Chilton–Colburn analogy and the heat flux between the gas and the liquid phase is given by:

$$q = h(T_G - T_L) \quad (16)$$

The flux of the volatile components over the phase boundary can be expressed by:

$$N_i = K_{Gi}(p_i - p_i^*) \quad (17)$$

where p_i^* is the partial pressure of component i that would have been in equilibrium with the liquid phase and p_i is the partial pressure of component i in the gas bulk. Mass-transfer coefficients and the specific gas–liquid interfacial area are calculated using correlations from Billet and Schultes.[12] Assuming no liquid-side resistance for the mass transfer of water the overall mass transfer coefficient for water is:

$$K_{G,H_2O} = k_{G,H_2O}$$

Using the two-film model for the gas- and liquid-side mass-transfer coefficients K_{G,CO_2} is expressed as:

$$\frac{1}{K_{G,CO_2}} = \frac{1}{k_{G,CO_2}} + \frac{H_{CO_2}}{Ek_{L,CO_2}} \quad (18)$$

The increased absorption rate resulting from the chemical reaction can be calculated using the expression for the enhancement factor proposed by van Krevelen and Hoftijzer[13]:

$$E = \frac{\sqrt{M\dfrac{E_\infty - E}{E_\infty - 1}}}{\tanh\left(\sqrt{M\dfrac{E_\infty - E}{E_\infty - 1}}\right)} \quad (19)$$

To calculate E two dimensionless groups are needed:

(1) The enhancement factor for instantaneous reaction, assuming that the formation of unstable carbamates is the rate-determining reaction:

$$E_\infty = \left(1 + \frac{D_{AMP,L}c^0_{AMP}}{2D_{CO_2,L}c^{inf}_{CO_2}}\right) \quad (20)$$

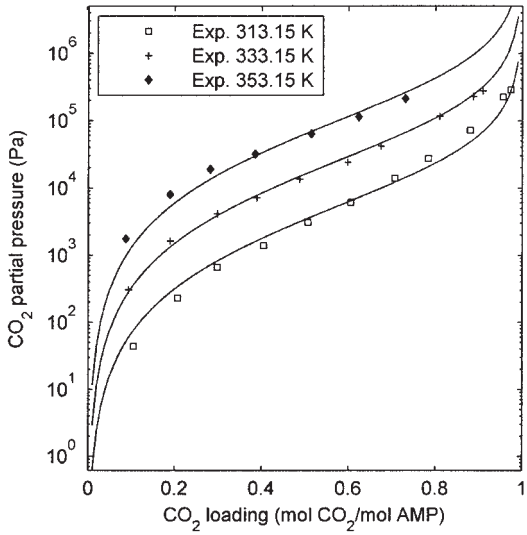

Figure 2. Comparison of model correlation results (solid lines) with experimental data[14] for CO_2 equilibrium partial pressures over an aqueous 30 wt % AMP solution.

A Henry's Law relationship is used to find the concentration of dissolved, but unreacted CO_2 at the liquid interface ($c^{inf}_{CO_2}$). (2) The dimensionless number M given by the following equation:

$$M = \frac{k_2 D_{CO_2,L} c^0_{AMP}}{k^2_{L,CO_2}} \quad (21)$$

In the system conditions modeled in this work the value of E is between 4 and 7.

Vapor–liquid equilibrium thermodynamics

Adapting the vapor–liquid equilibrium (VLE) model for aqueous solutions of alkanolamines, presented in Gabrielsen et al.,[11] to AMP gives the following expression for the equilibrium partial pressure of CO_2 over the solution:

$$p^*_{CO_2} = K_{CO_2} X_{CO_2} \frac{\theta}{(1 - \theta)} \quad (22)$$

A combined Henry's Law and chemical equilibrium (K_{CO_2}) constant is given by Eq. 23 and has three adjustable parameters:

$$\ln K_{CO_2} = 37.30 - \frac{8161}{T} + 23826\frac{\theta}{T^2} \quad (23)$$

VLE data from Park et al.[14] and Roberts and Mather[15] were used when fitting the parameters for K_{CO_2} for aqueous AMP solutions, and 51 experimental points were included in the parameter regression. These experimental data were chosen because they cover a concentration and temperature range and they are quite consistent even though they come from different sources. Figure 2 shows a comparison between the model

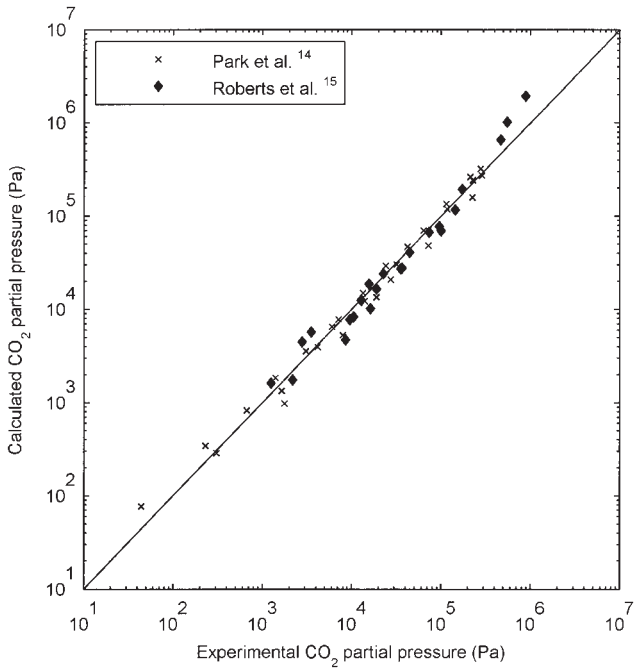

Figure 3. Comparison of model correlation with all experimental data[14,15] for the partial pressure of CO_2 used in the parameter regression for aqueous AMP solutions.

correlation and the experimental data[14] for CO_2 partial pressures over a 30 wt % aqueous solution of AMP. It can be seen that the correlation gives satisfactory results over the loading range and temperatures considered.

Figure 3 shows a comparison of model correlation with all experimental data for the partial pressure of CO_2 used in the parameter regression. Figure 4 shows a comparison between CO_2 partial pressures calculated using the proposed model and experimental data from Teng and Mather[16] and Tontiwachwuthikul et al.,[17] not included in the parameter regression, for CO_2 partial pressures over an 18 wt % aqueous solution of AMP. The experimental data for 313.15 K are from Teng and Mather[16] and Tontiwachwuthikul et al.,[17] 343.15 K is from Teng and Mather,[16] and for 333.15 and 353.15 K the data are from Tontiwachwuthikul et al.[17] It can be seen that the model reproduces the data fairly well, although there is an inconsistency between the two different data sets that is clearly seen at the lowest temperature. Moreover, four data points from Teng and Mather[16] at low loading are completely misrepresented, likely explained by erroneous measurements. Figure 4 may serve as an illustration of the problems in finding reliable and consistent experimental VLE data for CO_2–AMP–H_2O.

By using the Gibbs–Helmholtz equation as shown in Gabrielsen et al.,[11] the heat of absorption of CO_2 in the AMP solution (ΔH_{CO_2}) can be found, resulting in the following expression:

$$\Delta H_{CO_2} = R\left(-8161 + 47652\,\frac{\theta}{T}\right) \tag{24}$$

No experimental calorimetric data for CO_2 in aqueous AMP solutions were found in the literature to verify ΔH_{CO_2}.

The equilibrium partial pressure of water ($p^*_{H_2O}$) over the solution is expressed by an Antoine equation.[18] The heat of condensation of water (ΔH_{H_2O}) is derived from the Antoine equation using the Gibbs–Helmholtz equation.

Reaction kinetics

Despite the fact that the chemical kinetics of CO_2 absorption in AMP solutions has been the subject of numerous studies, there is no universal agreement on the relevant chemical kinetic expressions.[19,20] A second-order reaction rate constant for the reaction between CO_2 and AMP is found in Saha et al.[19]:

$$k_2 = 1.943 \times 10^7 \exp(-5176.49/T) \tag{25}$$

Saha et al.[19] show that the most likely reaction scheme for CO_2 absorption in aqueous AMP is the formation of carbamate, through a zwitterion mechanism acting as a transition intermediate, followed by carbamate reversion to bicarbonate. Thus, for an equilibrated solution, Eq. 6 is the overall chemical equilibrium for the stable species in the solution. The expression for the second-order reaction rate constant (Eq. 25) is valid in the temperature range 21–45°C and the AMP concentration range 0.5–2.0 kmol/m^3. Camacho et al.[21] recently presented an expression for the second-order reaction rate constant where possible temperature profiles in the reaction zone were taken into account. This expression gives values for k_2 that are approximately two orders of magnitude lower than that of Eq. 25. In this work Eq. 25 is used because it gives the best results and is in closer agreement with other studies of k_2.

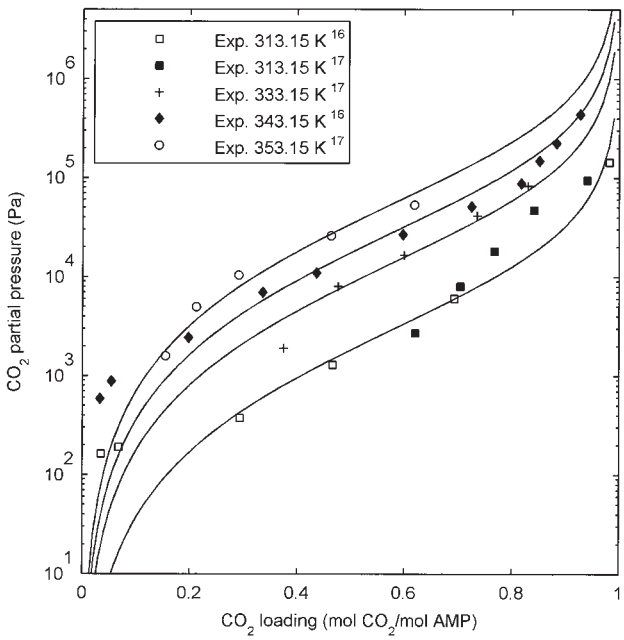

Figure 4. Comparison of model results (solid lines) with experimental data[16,17] not included in parameter regression for CO_2 equilibrium partial pressures over an aqueous 18 wt % AMP solution.

Table 1. Physical and Chemical Properties Used in the Absorber Model

Property	Source	Comment
Liquid density	Xu et al.[22]	Linear mixing
Specific heat of gas components	Reid et al.[23]	
Specific heat of liquid solution	Chiu et al.[24] and Cheng et al.[25]	Linear mixing
Diffusivity of CO_2 in the liquid solution	Ko et al.[26]	Based on the N_2O analogy
Viscosity of the gas	Reid et al.[23]	Method of Wilke
Thermal conductivity of the gas	Reid et al.[23]	Eucken for pure compounds, Mason and Saxena for mixture
Diffusivity of CO_2 and water in the gas phase	Reid et al.[23]	Fuller equation
Surface tension of the liquid solution	Vazquez et al.[27]	
Viscosity of the liquid solution	Henni et al.[28] and Cheng et al.[25]	The data from Henni et al.[28] was used for correlating pure AMP viscosity and then Grunberg and Nissan with zero interaction parameter was used.
Henry's Law constant of CO_2 in the liquid solution	Saha et al.[29] and Browning et al.[30]	Based on the N_2O analogy and using an expression to account for the salting out effect with increased CO_2 loading.
Diffusivity of AMP in the liquid solution	Chang et al.[31]	

Physical properties

The physical properties used in the model with literature sources are given in Table 1.

The salting-out effect on free CO_2 resulting from the increased ionic strength is accounted for in the expression for the Henry's Law constant of CO_2 in the liquid solution using the van Krevelen correlation. The coefficients for the different ions in the solution were taken from Browning and Weiland.[30] The van Krevelen coefficient for protonated AMP was not available in this reference so the value for protonated MEA was used.

Model implementation

The model was programmed in MATLAB® version 7.0 (The MathWorks, Natick, MA) and the system of ordinary differential equations was solved by using a built-in routine called *bvp4c*, which implements a collocation method for the solution of boundary value problems. The boundary values needed are given by the conditions of the gas and liquid entering the column.

Results and Discussion

Validation of the proposed model is done by comparison of simulation results with experimental data. The experimental data are taken from Tontiwachwuthikul et al.,[5] where results for eight runs of CO_2 absorption into an aqueous AMP solution in a packed column are reported. The absorption is at atmospheric pressure in a column with 0.1 m inner diameter filled with 12.7 mm ceramic Berl saddles, and the total packing height is 6.55 m. The concentration of CO_2 in the gas at inlet conditions is between 15 and 19 vol % and the AMP concentration is 2.0 kmol/m^3. The experimental data include concentration and temperature profiles along the column. The proposed model should be able to describe both composition and temperature profiles along the column to be a useful tool.

Figures 5–7 show comparisons between experimental data from runs T26, T25, and T28 of the proposed model. These three runs were chosen because they cover a large area of the liquid CO_2 loading presented in the available data. Run T26 covers the largest loading range of the reported data and run T28 is the run that has the highest liquid loading. In Figure 5 the maximum experimental CO_2 loading in the liquid phase is about 0.41. The proposed model gives good results and the

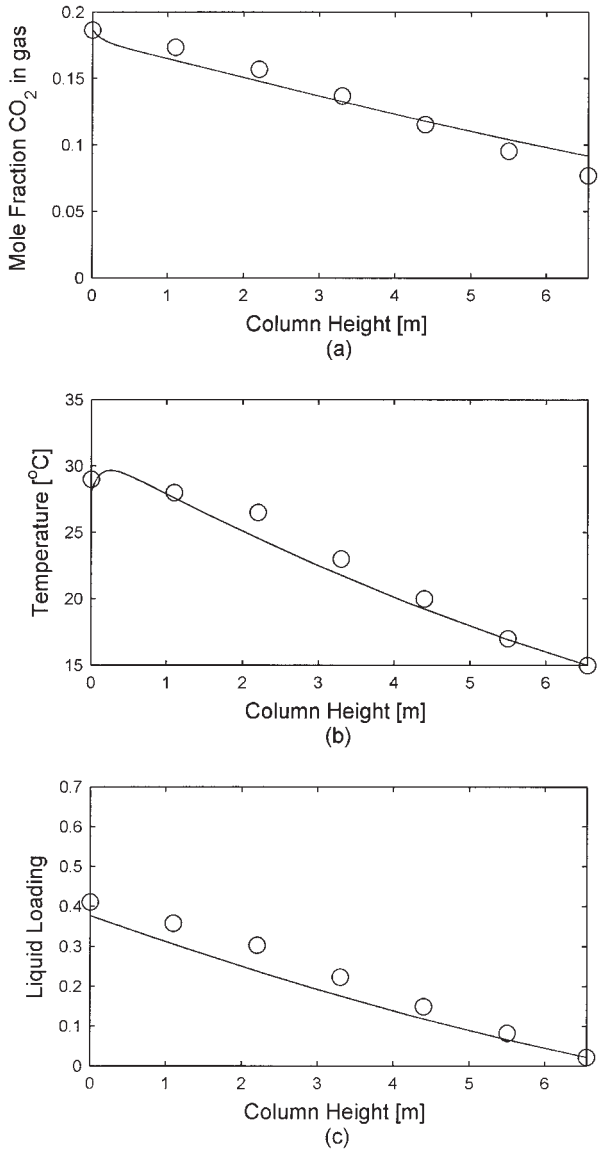

Figure 5. Modeled (lines) results and experimental data (circles) for the AMP–CO_2 system (run T26).

(a) Concentration profiles, (b) liquid temperature profiles, (c) liquid loading.

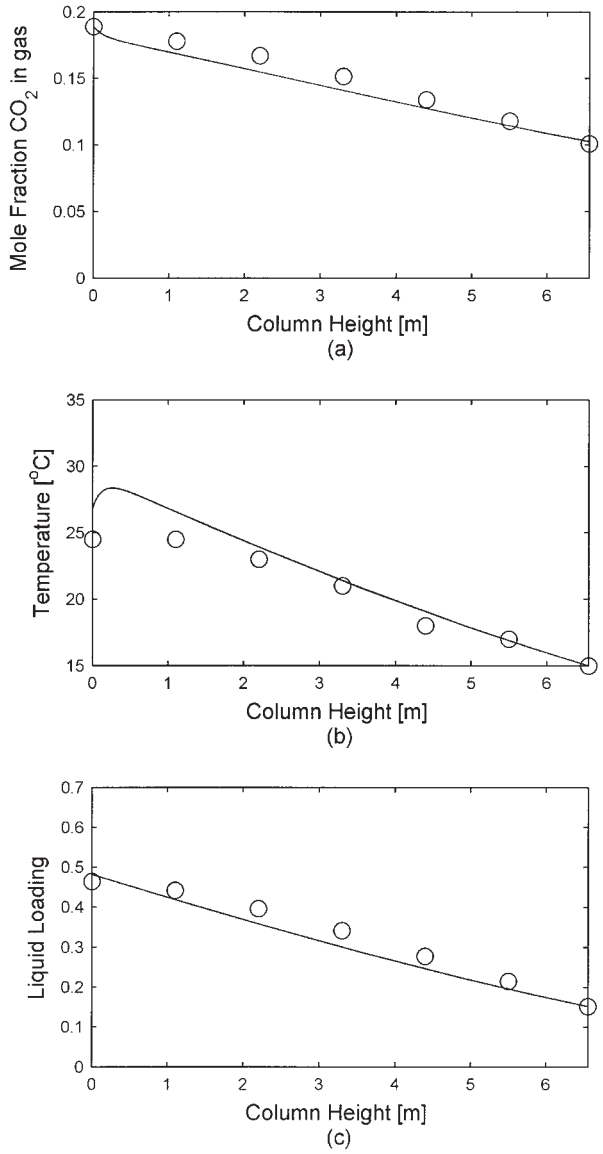

Figure 6. Modeled (lines) results and experimental data (circles) for the AMP–CO_2 system (run T25).

(a) Concentration profiles, (b) liquid temperature profiles, (c) liquid loading.

largest discrepancy is the mole fraction of CO_2 in the gas leaving the column. The predicted CO_2 mole fraction is slightly too low. In Figure 6 the maximum experimental CO_2 loading in the liquid phase is about 0.46. The results using the proposed model are very good for the CO_2 concentration in both the gas and the liquid phases, although the liquid temperature is slightly overpredicted at the bottom of the column. Furthermore, one can see that the mole fraction of CO_2 in the gas leaving the column is more accurately predicted than the rich liquid loading. This discrepancy arises from material balance issues in the experimental data. The absolute value of the error in the experimental mass balance in this specific run is 7.53%. In Figure 7 the maximum experimental CO_2 loading in the liquid phase is about 0.58. The proposed model gives good results; the largest discrepancy is in the liquid temperature. A tendency that can be seen when looking at all three runs presented is that at increasing loading the liquid temperature is overpredicted. This discrepancy is most likely explained by a too high value of the heat of absorption of CO_2. Therefore it would be of interest to find experimental data for the heat of absorption of CO_2 in aqueous AMP solutions and at different CO_2 loadings to compare with the expression developed and used in this work. Unfortunately no such data were found in the literature.

Sensitivity analysis

A sensitivity analysis of the mass-transfer based model was carried out. The parameters selected for the analysis were $p^*_{CO_2}$ and the physicochemical properties influencing M, E_∞ and the mass transfer correlation. Sensitivity of the model with respect

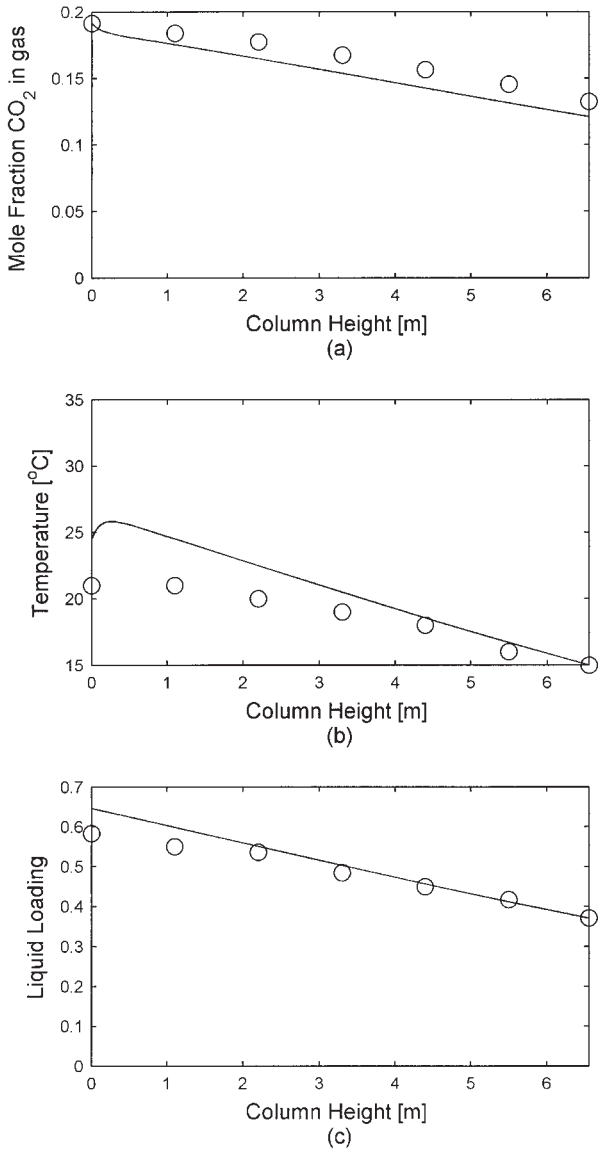

Figure 7. Modeled (lines) results and experimental data (circles) for the AMP–CO_2 system (run T28).

(a) Concentration profiles, (b) liquid temperature profiles, (c) liquid loading.

Table 2. Parameter Sensitivity Tabulating Percentage Deviation in Both Loading Rich Solution and Mole Fraction CO_2 in the Clean Gas When the Input Parameter Is Increased by 10%

Input Parameter	Percentage Deviation	
	Rich Loading	$y_{CO_2}^{OUT}$
Calculated equilibrium partial pressure of CO_2	−0.04	0.10
Diffusivity of CO_2 in the liquid solution	2.04	−4.39
Diffusivity of AMP in the liquid solution	0.15	−0.20
Surface tension of the liquid solution	−3.28	4.39
Viscosity of the liquid solution	0.87	−1.07
Henry's Law Constant for CO_2 in the liquid solution	−4.15	5.46
Reaction rate constant	2.10	−2.73

to the input parameters was checked by increasing a chosen parameter by 10% and then calculating the change in the two important variables: rich liquid loading and mole fraction CO_2 in the clean gas. The results are shown in Table 2. Run T25 was chosen as a base case because it represents a wide loading range similar to what one might encounter in flue gas cleaning. At the conditions encountered in this work it is clear that the model is most sensitive to liquid surface tension, H_{CO_2} and $D_{CO_2,L}$. The surface tension is crucial when calculating the effective mass transfer area. H_{CO_2} is used when calculating E_∞, but more important it is used in the expression for the overall mass-transfer coefficient. $D_{CO_2,L}$ is used when calculating E and the liquid-side mass-transfer coefficient. Furthermore, it is evident that sensitivity toward the physicochemical properties is used only to calculate mass-transfer coefficients and E_∞ is not very high. This could be expected, given that the absorption is in the fast-reaction regime. The absorption is liquid-side controlled for all the runs simulated in this work; the gas-side mass-transfer coefficient never exceeds 2% of the overall mass-transfer coefficient in any of the simulations carried out. In this work the column is never run under pinch conditions and, as expected, $p^*_{CO_2}$ has only a slight influence. However, for a larger tower operating at higher temperature, which would be the case in flue gas cleaning, it is likely that $p^*_{CO_2}$ would be of higher significance. Experimental and modeling studies of CO_2 absorption at higher temperatures in a column with structured packing using aqueous solutions of AMP will be addressed in a subsequent work.

Conclusion

An explicit model for CO_2 solubility and an expression for the heat of absorption of CO_2 as a function of temperature and liquid CO_2 loading in aqueous solution of AMP have been proposed. A rate-based model for CO_2 absorption into an AMP solution has been proposed, using both the proposed expression for the CO_2 solubility and the expression for the heat of absorption along with an expression for the enhancement factor and physicochemical data from the literature. The proposed model has successfully been applied to absorption of CO_2 into an AMP solution in a packed tower and validated with pilot-plant data from the literature. A parameter sensitivity test including physicochemical properties has been carried out and the model is most sensitive to the surface tension of the liquid solution, the Henry's Law constant for CO_2, and the diffusivity of CO_2 in the liquid solution for an absorber under the conditions considered in this work.

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Notation

a = specific wetted area for mass transfer, m^2/m^3
A_C = cross-sectional area of the column, m^2
c^0_{AMP} = concentration of AMP in the bulk liquid, mol/m^3
$c^{inf}_{CO_2}$ = concentration of molecular CO_2 at the liquid interphase, mol/m^3
$c_{p,i}$ = molar heat capacity of component i in the gas phase, J mol^{-1} K^{-1}
$c_{p,L}$ = molar heat capacity of the liquid, J mol^{-1} K^{-1}
$D_{i,L}$ = diffusivity of component i in the liquid, m^2/s
E = enhancement factor
E_∞ = enhancement factor for instantaneous reaction
G = molar gas flow, mol/s
h = heat transfer coefficient in gas, J s^{-1} K^{-1} m^{-2}
H_{CO_2} = Henry's Law constant for CO_2, Pa m^3 mol^{-1}
ΔH_{H_2O} = heat of condensation of H_2O, J/mol
ΔH_{CO_2} = heat of absorption of CO_2, J/mol CO_2
$k_{G,i}$ = gas-side mass-transfer coefficient of component i, mol m^{-2} s^{-1} Pa^{-1}
$k_{L,i}$ = liquid-side mass-transfer coefficient of component i, m/s
k_2 = rate constant, m3 mol^{-1} s^{-1}
$K_{G,i}$ = overall mass-transfer coefficient of component i, mol m^{-2} s^{-1} Pa^{-1}
K_{CO_2} = combined Henry's Law and chemical equilibrium constant for CO_2 partial pressure, Pa
L = molar liquid flow, mol/s
M = dimensionless number used in the enhancement factor
N_i = molar flux of component i, mol m^{-2} s^{-1}
p_i = partial pressure of component i in the bulk gas phase, Pa
p^*_i = partial pressure of component i gas phase if it were in equilibrium with the liquid phase, Pa
q = heat flux, J m^{-2} s^{-1}
T_G = gas-phase temperature, K
T_L = liquid-phase temperature, K
x_i = liquid-phase mole fraction of component i, mol/mol
X_{CO_2} = liquid-phase mole fraction of CO_2 in both reacted and unreacted forms, mol/mol
y_i = gas-phase mole fraction of component i, mol/mol
z = height of packing, m

Greek letter

θ = loading, mole CO_2/mole initial amine

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