

APPLICATIONS OF NEW ABSORPTION KINETICS AND VAPOR/LIQUID EQUILIBRIUM MODELS TO SIMULATION OF A PILOT PLANT FOR CARBON DIOXIDE ABSORPTION INTO HIGH CO₂-LOADED, CONCENTRATED MONOETHANOLAMINE SOLUTIONS

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Introduction

Kinetics, modeling and simulation studies were conducted for the absorption of carbon dioxide (CO₂) into highly concentrated and loaded monoethanolamine solutions (MEA) in the temperature range 293 to 333K. A new comprehensive mathematical absorption-rate/kinetics model was developed which takes into account the coupling between chemical equilibrium, mass transfer and chemical kinetics of all possible chemical reactions. The mathematical model is capable of predicting gas absorption rates and enhancement factors from the system hydrodynamics and the physico-chemical properties, and can also predict the kinetics of the reaction from experimental absorption data. These results allowed us to develop a new termolecular-kinetics model for CO₂ reaction with MEA solutions, which proved to be better than previously published kinetic models. As a practical application, the new termolecular kinetics model and the vapor/liquid equilibrium model were integrated with a process-simulation program for CO₂ absorption into an aqueous MEA solution in a packed column. Accurate behavior of CO₂ absorption into this solution in terms of the temperature and concentration profiles was obtained. The results further showed that by using the new kinetics model, the deviation between the predicted and the actual bed-height of the packed column is less than 1.0%.

Theory

A rigorous computer simulation-program for predicting the behavior of CO₂-MEA absorption in packed columns was written based on three main components. The first is the material and energy balance model developed by Pandya [1]. The second is the vapor-liquid equilibrium (VLE) model and the termolecular-kinetics model both of which were developed in this work. The third is comprised of the physical properties published in the literature. This computer simulation program was eventually utilized mainly to test the applicability of using the termolecular-kinetics model to predict the behavior of CO₂ into MEA solution on a pilot plant scale.

Vapor-Liquid Equilibrium Model. Liquid bulk concentrations of all chemical species are required for the simulation process and the kinetic analysis. A vapor-liquid equilibrium (VLE) model to estimate the CO₂ partial pressure and the liquid bulk concentrations of all the chemical species present in the solution was developed. The input data of the model include the initial concentration of the MEA solution, the initial CO₂ loading of the MEA solution, the equilibrium constants of the reactions, and the solubility of CO₂ into MEA solution.

Kinetics Model. A comprehensive absorption rate/kinetics model was developed for interpreting the laminar jet absorption data of CO₂ into MEA solutions from which the kinetics data were extracted. The model takes into account the coupling between chemical equilibrium, mass transfer, and chemical kinetics of all possible chemical reactions. These resulted in a system of unsteady-state partial differential equations referred to as the mathematical model. This mathematical model is capable of predicting gas absorption rates and enhancement factors from the system hydrodynamics and the physico-chemical properties, as well as predicting the kinetics of the reaction from experimental absorption data. A rigorous numerical method to solve the system of unsteady-state partial differential equations was developed. The model was validated by comparing its predictions with the experimental data of CO₂ absorption into water and MEA solutions, as well as N₂O absorption into MEA solutions as reported elsewhere [2]. In brief, the diffusion equation in Equation 1 is the one most frequently used to represent the absorption of gas into liquid jets. Equation 1 governs the variation in time and space of the concentration of the reactants and the products in the liquid phase (one equation for each component or material balance).

$$D_j \frac{\partial^2 C_j}{\partial x^2} = \frac{\partial C_j}{\partial t} + r_i \quad (1)$$

where D denotes diffusivity, C denotes the concentration of the chemical species, t denotes the time, r denotes reaction rate, and x denotes the distance normal to the jet surface (independent spatial variable measured from the gas liquid interface into the liquid bulk), noting that a laminar jet absorber was used to collect the kinetics data.

Process Simulation Model. In the gas absorption industry, CO₂ removal from gaseous mixtures with alkanolamine solutions is classified as "adiabatic gas absorption with chemical reaction." The first design technique of the gas absorption with chemical reaction in adiabatic packed towers was introduced by Pandya [1]. This design technique accounts for the major heat effects (absorption, reaction, solvent evaporation, and condensation), chemical reaction in the liquid phase, and mass-transfer resistance and heat-transfer resistance in both phases. The main model equations resulting from the mass and energy balance of this model were implemented in this work to obtain the concentration and temperature profiles.

Model Parameters. The calculations in the Absorption-rate/Kinetics model and the process-simulation model presented in this work require knowledge of the physico-chemical properties of the fluids involved in the absorption process. These include density, viscosity, solubility, diffusivity, surface tension, and reaction rate constants. Our new kinetics model and the published physico-chemical properties from literature were utilized in this study.

Experimental Work

In industrial practice, high loading (carbonation ratio) and highly concentrated solutions are frequently encountered [3], and it is therefore important to consider what happens when CO₂ is absorbed in these solutions. The main experimental contribution in this work consists of data on absorption rates of CO₂ in highly loaded and highly concentrated MEA solutions on both pilot plant scale (packed columns) and laboratory scale (laminar jet absorber). These comprehensive data and its analysis assisted in the understanding of the behavior of this absorption process.

A laminar jet apparatus was used to generate kinetics data for the absorption of CO₂ into high CO₂-loaded and concentrated solutions of MEA. The experimental kinetic data for the present study were obtained by absorption of CO₂ into aqueous MEA solutions. The total MEA concentrations were in the range from 3.0 to 9.0 mol/L and the total CO₂-loading in solution ranged from ~0.1 to 0.49 mol CO₂/mol MEA. All the kinetic experiments were conducted at atmospheric pressure and at temperatures in the range from 293 to 333K.

A pilot plant was used to collect comprehensive data on the absorption of CO₂ into highly loaded and concentrated MEA solutions over a wide range of operating conditions. Absorption of CO₂ from simulated flue gas into MEA was performed in a pilot plant consisting of three identical absorption columns and a regenerator. Each absorption column was made of acrylic plastic tubing (2.4 m high, 10.1 cm inside diameter, and 0.64 cm wall thickness). The first and second columns were packed with random packing: Pall Rings-16 mm and IMTP#15, respectively, while the third column was packed with A4-structured packing. The regenerator column was made of QVF glass pipe (1.52 m high and 10.1 cm inside diameter) and packed with 16 mm Pall Rings. Insulating the absorber columns with insulation tubing (AP Armaflex insulation tubing, 104 mm ID and 13 mm wall) minimized heat losses, so that the process was essentially adiabatic.

The absorption process was conducted in a counter-current mode at preset operating conditions. These conditions were: (1) Total MEA concentrations from 3.0 to 9.0 kmol/m³; (2) CO₂ loading in the liquid feed from 0.078 to 0.353 mol CO₂/mol MEA; (3) superficial liquid flow rate from 6.6 to 24.0 m³/m² h; (4) superficial gas flow rate from 28.1 to 65.5 kmol/m² h; (5) feed CO₂ concentration in air from 5.0 to 20.3%; and (6) types of packing materials used, Pall Rings-16 mm, IMTP#15 and A4-structured packing. When steady state operation was attained, the gas concentration and the temperature profiles along the column were measured and

recorded. As well, the outlet liquid composition was analyzed for its CO₂ loading.

Results and Discussion

The reliability of the laminar jet absorber was tested as a function of temperature by experimentally determining the temperature effect on the diffusivity of CO₂ in water within the temperature range from 288 to 333 K, the typical temperature range found in gas absorbers. Figure 1 shows this experimental diffusivity as well as the predicted diffusivity from the model developed by Versteeg and van Swaaij [4]. The results showed that excellent agreement between the measured and predicted diffusivity was obtained. The average absolute deviation of the measured diffusivity from the predicted diffusivity was 1.7%. This indicates that the behavior of the laminar jet is excellent within this temperature range, the same temperature range for the kinetic data of this work.

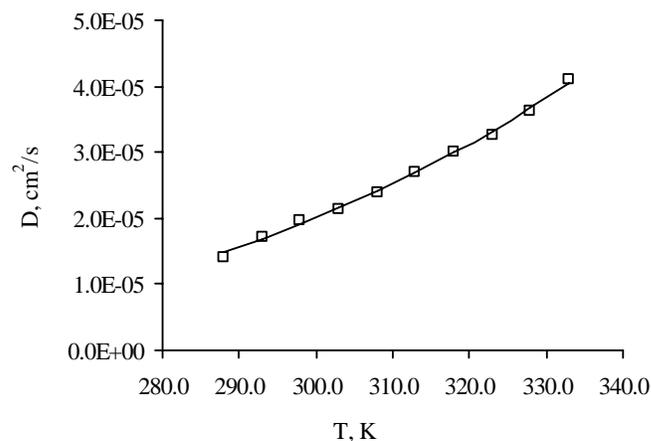


Figure 1. Diffusivity of CO₂ in water as a function of temperature obtained in Laminar Jet Apparatus. Points are our experimental data and line is predicted by Versteeg/van Swaaij Model [4].

All experimental absorption rate data obtained in the laminar jet absorber were interpreted by our numerically solved absorption-rate/kinetics model. For each absorption rate data obtained, the calculated enhancement factor was fitted to the experimentally observed enhancement factor with the apparent reaction-rate constant (k_{app}) as an adjustable parameter. The experimental results of these k_{app} constants are presented in Figure 2. A definite temperature dependence of the overall reaction rate can be observed for the five temperatures studied (293, 303, 313, 323, and 333K).

Numerical calculation of the kinetics of the reaction is usually achieved by assuming a reaction mechanism and interpreting experimental-absorption rate data with the aid of a numerically solved absorption-rate model. The forward reaction rate for termolecular mechanism of Crooks and Donnellan [5], as presented in Equation 2, was assumed in this work.

$$r_{CO_2-MEA} = -(k_{RNH_2}[RNH_2] + k_{H_2O}[H_2O])[RNH_2][CO_2] \quad (2)$$

where

$$k_{app} = k_{RNH_2}[RNH_2]^2 + k_{H_2O}[H_2O][RNH_2] \quad (3)$$

In order to calculate the reaction rate constants of Equation 2, all the experimental k_{app} constants in Figure 2 obtained from the absorption-rate/kinetics model were fitted to the termolecular mechanism expression in Equation 3.

A linear regression analysis for these data gave the kinetics expressions of Equations 4 and 5 based on the termolecular reaction rate equation as represented in Equation 2.

$$k_{RNH_2} = 4.61 \times 10^9 \exp\left(\frac{-4412}{T}\right) \quad (4)$$

$$k_{H_2O} = 4.55 \times 10^6 \exp\left(\frac{-3287}{T}\right) \quad (5)$$

This new kinetics model was proven to give accurate representation for CO₂-MEA systems for solutions of low and high concentrations as well as for high CO₂ loaded solutions as documented elsewhere [6]. In this work, the new termolecular kinetics model has been integrated with the process-simulation program in order to verify its applicability and as a demonstration of its practical utilization. The simulation results of this integration are discussed below.

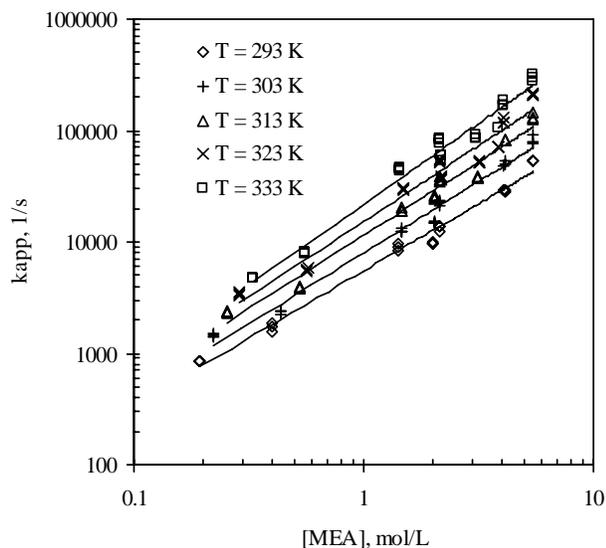


Figure 2. Experimental results of the apparent reaction-rate constants for CO₂ reaction with MEA solutions

First, the validity of using our new termolecular-kinetics model (Equations 2, 4, and 5) for the simulation of CO₂ absorption into MEA solutions in packed column was

confirmed by comparing the predictions of the column concentration profiles with the experimental data. Figure 3 shows the comparison between the experimental results and the model predictions. There is very good agreement between the actual and predicted (solid line in Figure 3) CO₂ concentration profile, thereby confirming the validity of using the new termolecular-kinetics model as well as the computer simulation program. In addition, the behavior of the column is also well predicted even with the integration of other published kinetics models with the process simulation program. These include the model of Hikita et al. [7] (the most frequently referenced model), the model of Versteeg et al. [8] (which compiled many kinetics data in literature), and the model of Horng and Li [9] (the most recently published model). The kinetics models of Hikita et al. [7] and Versteeg et al. [8] gave identical and good predictions for the concentration profile along the column as can be seen in Figure 3, dotted line.

The kinetics model of Horng and Li [9] gave poor predictions for the concentration profile at the top part of the column (dashed line in Figure 3). The output of the simulation program using the four kinetics models is also presented in terms of predicting the height of the absorption column. It has been found that very good predictions for the height of the packed column were obtained by using the kinetics model of this work (0.8% deviation), the kinetics model of Hikita et al. (1.3% deviation), and the kinetics model of Versteeg et al. (1.7% deviation). The height of the packed column was overestimated by more than 12% when the kinetics model of Horng and Li was used. This proves that the termolecular-kinetics model developed in this work is better than the previous published kinetics models for predicting the behavior of CO₂ absorption into MEA solutions in packed columns.

Second, with the aid of the termolecular kinetics model, the CO₂ concentration profiles along the packed column at various operating conditions were predicted and compared with measured CO₂ concentration profiles. These are shown in Figure 4. The CO₂ concentration in the feed was varied from 10 to 20%. During the absorption process, the CO₂ loading varied from about 0.18 to 0.47 mol/mol and the temperature in the liquid phase changed from 24 to 44 °C along the column. The predicted results of the CO₂ concentration profiles have been found to be in good agreement with the experimental data.

Third, the validity of the developed termolecular-kinetics model was reconfirmed by comparing the predictions with the published experimental data of Tontiwachwuthikul et al. [10]. The absorber used by these workers is located at the University of British Columbia (UBC), Vancouver, Canada, and consisted of six sections each of 1.2 m height and 0.1 m in diameter. The packed height of each section was about 1.1 m of 12.7-mm ceramic Berl Saddles. The total height of this absorption column was 7.2 m, which is equal to three times the height of the column used in this study (2.4 m).

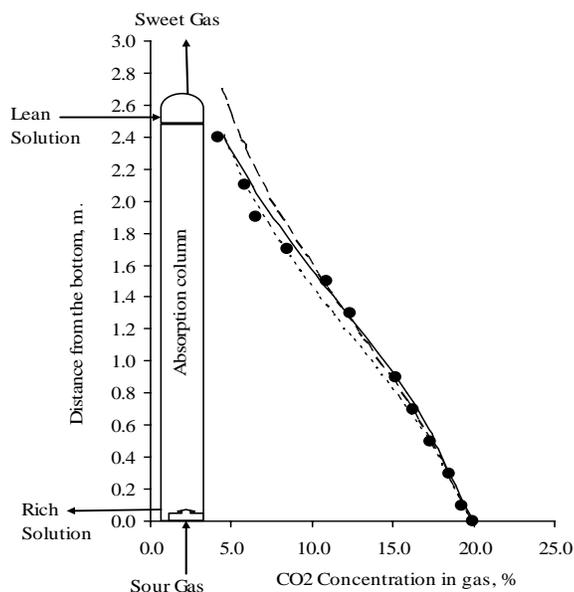


Figure 3. Measured and predicted CO₂ concentration profiles along the packed column using various kinetics models. Points are measured, solid line is predicted by using our new termolecular-kinetics model, dotted line is predicted by using Versteeg and Hikita kinetics models, and dashed line is predicted by using Hornig kinetics model.

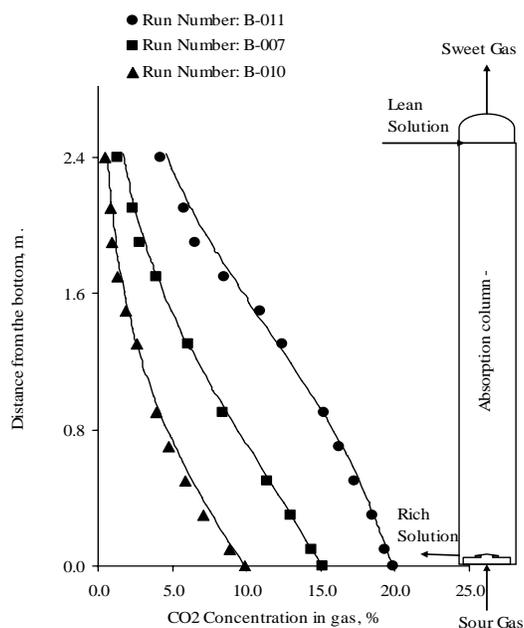


Figure 4. Measured and predicted CO₂ concentration profiles along the packed column at various operating conditions. Points are measured and lines are predicted using the termolecular-kinetics model of this work.

A comparison between the experimental results and the model predictions under the reported operating conditions showed a very good agreement between the actual and predicted CO₂ concentration profiles in the gas and liquid phases, as well as with the liquid temperature profile shown in Figure 5. Therefore, the integration of the termolecular-kinetics model with the process-simulation model will enable the accurate prediction of the concentration profiles and the temperature profiles along the absorption columns.

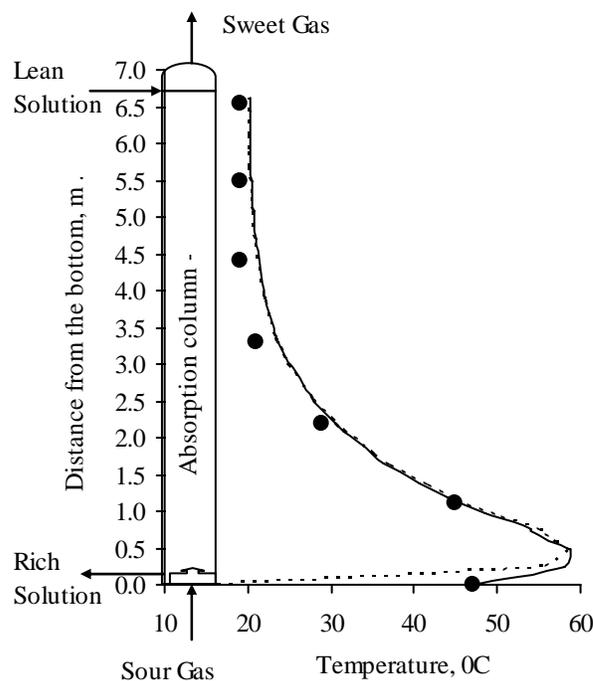


Figure 5. Measured and predicted temperature profiles along the packed column. Points are measured and lines are predicted using the termolecular-kinetics model of this work.

Conclusion

A new termolecular-kinetics model for the reaction of CO₂ with MEA solutions has been reported for the reaction of CO₂ with highly concentrated and loaded MEA solutions. When this new termolecular-kinetics model and the recently published physico-chemical properties correlations were integrated with the process-simulation model, accurate predictions for the concentration and temperature profiles along the packed columns were obtained for different types of packing materials.

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