

Rigorous Modelling and Experimental Results on Carbon-Dioxide Absorption into Diethanolamine Aqueous Solutions in Packed-Columns

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The present work aims to improve the acid-gases removal process using electrolytic solutions of alkanolamines especially the Diethanolamine. As a first step, a new rate-based model containing rigorous sub-models for non-ideal thermodynamics, hydrodynamics, reactions and simultaneous mass and heat transfer has been developed. The model uses Nernst-Planck equations for the liquid film and generalized Maxwell-Stefan equations for the gas film. In the second step a gas-absorption column with random packing for CO₂ capture using aqueous Diethanolamine as solvent has been constructed to generate absorption data in order to verify the model.

The homogeneous reactive separation under steady-state conditions has been simulated with a rigorous description of diffusion-reaction phenomena in film. The reactions are taken into account in the liquid phase with almost no simplification in terms of reaction mechanism. In the gas film, molecular interactions and diffusional phenomena are taken into account using the generalized Maxwell-Stefan equations. A thermodynamic model "SourWater True Species" has also been developed based on the interactions of true species in aqueous multicomponent electrolytic systems.

Experimental results of CO₂ absorption by Diethanolamine: a 2 m height gas-absorption packed-column with an inside diameter of 50 mm has been constructed. Raschig glass rings (d=5mm) have been used as packing. CO₂ is absorbed from a mixture of air and CO₂ by aqueous DEA (20%wt.) in the counter-current configuration under atmospheric pressure. The feed concentration of CO₂ is fixed at 15% which represents the typical concentration of CO₂ in flue gas. At the steady-state condition, the concentration of CO₂ in liquid and gas phases has been measured along the length of column. The temperature profile has also been obtained for the liquid phase.

The absorber had a good performance and presented no operating challenges. The model gives reasonable predictions in terms of heat and mass transfer in the presence of chemical reactions. The studied operating conditions should allow the capture of CO₂ in post-combustion of power plants.

1. Multicomponent reactive separation modeling

The design of absorbers can not be based on the equilibrium stage model, because the reactive separation processes rarely operate close to thermodynamic equilibrium since mass and heat transfer are rate-based processes governed by the gradients of chemical potential and temperature.

Here, the influence of chemical reactions on mass transfer is not neglected because the rate of mass transfer and chemical reaction are quite similar. In this work, chemical reactions have been taken into account directly in the partial mass balance equations and their impact on mass transfer is not summarized in the estimation of enhancement factor as Versteeg et al. (2007) have proposed. For multiple reversible and parallel reactions, the approximation of enhancement factor is not adequate.

1.1 Rate-based model

The rate-based model follows the principle of a non-equilibrium stage, which is characterized by the actual rates of chemical reactions and multicomponent heat and mass transfer between phases. The model uses the generalized Maxwell-Stefan equations in order to model accurately the multicomponent interactions in electrolytic mixtures. Multiple chemical reactions are written explicitly and their impact on differential mass balances is considered directly.

This work adapts the two-film theory to a non-equilibrium stage (Figure 1) and the influence of column internals and hydrodynamics is described through the calculation of film thicknesses (δ_L and δ_G). A non-equilibrium stage consists of the well-mixed phases and two diffusional film regions adjacent to the interface.

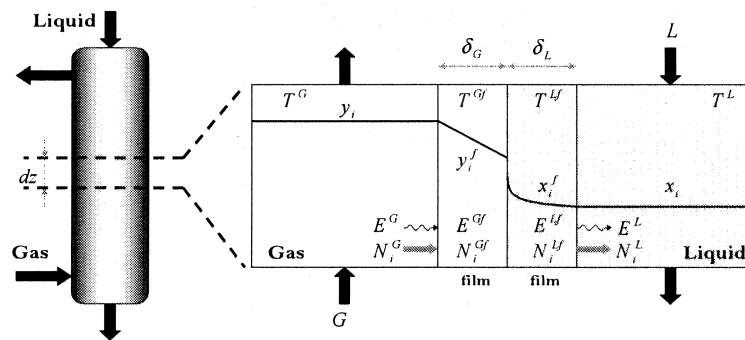


Figure 1: Non-equilibrium stage in reactive separation column (two-film model)

Bulk phases are modeled by running the component material and heat balances for a differential element of packing (Figure 1) under steady-state condition, the chemical equilibrium conditions for reactions at instantaneous equilibrium, and the summation of mole fractions. The molar and heat fluxes N_i and E are determined by modelling mass and heat transfer along the film thicknesses δ_G , δ_L (Figure 1) via film-model. Therefore, in addition to the bulk balances, the film-model is also applied in order to provide the differential molar and heat balances in films.

Molar fluxes change with reaction rates in film (Eq. 1). When there are also chemical reactions at instantaneous equilibrium in film, the chemical equilibrium conditions also have to be taken into account in film.

$$\nabla N_i - R_i = 0 \quad (i = 1, nc) \quad (1)$$

The set of equations are completed, considering the molar and heat balances for fluxes at the phase interface. In our previous paper (Ahmadi et al., 2010), the complete set of equations describing Liquid-Vapour multicomponent reactive separation has been studied in details and its numerical resolution has been discussed.

1.2 Heat and mass transfer

Heat transfer is modeled by the description of energy equations expressing the conductive and convective heat flows in film. The generalized Maxwell-Stefan equations (G.M.S.E) provide a rigorous modelling of multicomponent interactions in non-ideal phase (Taylor and Krishna, 1993):

$$\frac{x_i}{RT} \nabla \mu_i + x_i z_i \frac{F}{RT} \nabla \Phi_e = - \sum_{j=1}^{nc} \frac{(x_i N_j - x_j N_i)}{C_i D_{ij}} \quad (i = 1, nc - 1) \quad (2)$$

In electrolytic solutions with electrical potential gradients as the second driving force of diffusion, the electroneutrality condition has also to be applied. This work adapts the generalized Maxwell-Stefan equations to model the multicomponent interactions in gas, and Nernst-Planck equations for the liquid film which is the limiting case of G.M.S.E. for dilute solutions (Ahmadi et al., 2010).

1.3 Phase equilibrium

At the phase interface, the thermodynamic equilibrium is assumed (Eq. 3). K_i values are evaluated for true species (ions and molecules), taking into account fugacities in both phases and activity coefficients in liquid phase. The activity coefficients are provided by Mather's method (McGregor and Mather, 1995) which is a modified method of Pitzer. "SourWater True Species" thermodynamic model has been developed based on physical interaction of true species in electrolytic mixtures, in order to model phase equilibrium independently from instantaneous reactions at the phase interface.

$$y_i^l - K_i .x_i^l = 0 \quad (i = 1, nc) \quad (3)$$

2. Acid gases removal process

The flue gases coming from a power plant contain a variety of different polluting compounds such as sour gases and can not be emitted directly into the atmosphere. These exhaust gases have to be treated in absorption columns. Our objective is to provide a selective removal unit of acid-gases such as CO_2 , H_2S and COS , using

different amine solvents. As an example, the CO₂ capture in packed-bed unit using aqueous Diethanolamine as solvent has been investigated.

2.1 Chemical reactions of CO₂ in aqueous Alcanolamines (DEA)

The chain of reactions related to the absorption of CO₂ is the same as the scheme proposed by Rinker et al. (1996). Some reactions are reversible and kinetically controlled; and some others are reversible but at instantaneous equilibrium. The reaction between CO₂ and DEA (R₁R₂NH) follows the mechanism of zwitterion, through the formation of unstable specie known as zwitterion (R₁R₂NH⁺COO⁻).

2.2 Experimental investigation

Packed column. A gas-absorption column of 50mm inside diameter and 2m height has been constructed. The height of packing is 1 m and it contains Raschig glass rings of 5mm diameter. The height of packing is divided into 5 segments of 20 cm (Figure 2a). A special Teflon connection has been designed and placed between segments to be able to analyze liquid and gas samples along the column (Figure 2b). Gas mixture is introduced below the packing. A centrifugal pump with 0-60 L.hr⁻¹ capacity of discharge is used to send the liquid from 300 L storage tank to the top of the packing. Gas flow rates are monitored by two flow meters. All flow rates are monitored and can be regulated. Gas samples are first transported by pipelines to a chilled mirror hygrometer (DewMaster DM-C1) in order to measure the absolute humidity. Then, passing by a dry Calcium sulphate filter, they finally reach the infrared (I.R.) ADC-MGA-3000 Multi-Gas analyzer. Liquid samples are taken by accurate gas-proof and transported to the CO₂ content analysis cell. Liquid temperatures are measured at the inlet, outlet and between segments, to obtain liquid temperature profile in the column.

Sampling Teflon connection. The segments of packing are separated by the sampling Teflon connection (Figure 2b). Referring to Figure 2b, the top chamber is conceived for liquid sampling and temperature measurement in liquid. The bottom chamber is directed to the gas sampling pipelines and reaches the hygrometer and the I.R. analyzer.

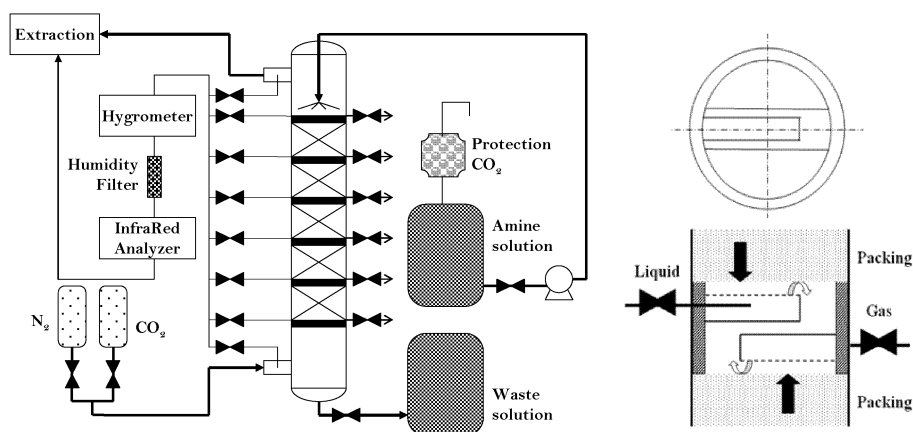


Figure 2: (a) process flow diagram, (b) Sampling connection between segments

CO₂ content analysis in liquid. Liquid samples are transported to the analysis cell to determine the total dissolved CO₂ in liquid solution. The method consists of acidifying a well measured volume of amine sample with phosphoric acid which liberates carbon dioxide from the amine solution. All ions containing carbon is now transformed to gaseous CO₂ and their mole number can be calculated monitoring the total pressure above the solution.

Operational conditions. CO₂ is absorbed from a mixture of air and CO₂ by aqueous DEA (20% wt) in the counter-current configuration under atmospheric pressure. Figure 2a illustrates the process flow diagram. The liquid solution is sent into the column without gas flow rate in order to prewet the column for 15 minutes. Then the liquid flow rate is fixed to 11,9 m³.m⁻².hr⁻¹, and gas mixture is introduced containing 0,85 Nm³.hr⁻¹ dry-air and 0,15 Nm³.hr⁻¹ of pure CO₂. Hence, a feed concentration of CO₂ at 15% is provided which represents the typical concentration of CO₂ in the flue gas. The inlet and outlet CO₂ concentration in gas, as well as liquid and gas temperatures are monitored periodically during the experiment until the steady-state condition is gained. In about 30 minutes the steady-state condition is maintained; so the concentration of CO₂ in liquid and gas phases, as well as the liquid temperature are measured along the column.

3. Results and discussions

The simulation of CO₂ capture in packed-column has been conducted with the same operating conditions as the experiment. Gas and liquid flow rates are the same as described in the above section. Inlet composition of CO₂ in gas is fixed at 14,46%vol. and liquid and gas inlet temperatures are set respectively to 18,7°C and 19,1°C.

Figure 3a shows the experimental results on CO₂ %vol. (Error = ±0,02%vol.) in gas along the column together with the simulation results. The CO₂ percentage in gas is reduced in column from 14,46%vol. to 5,49%vol. and the absorption is almost linear. Liquid temperature is increasing inside packing from top to bottom because of exothermic chemical reactions (Figure 3b).

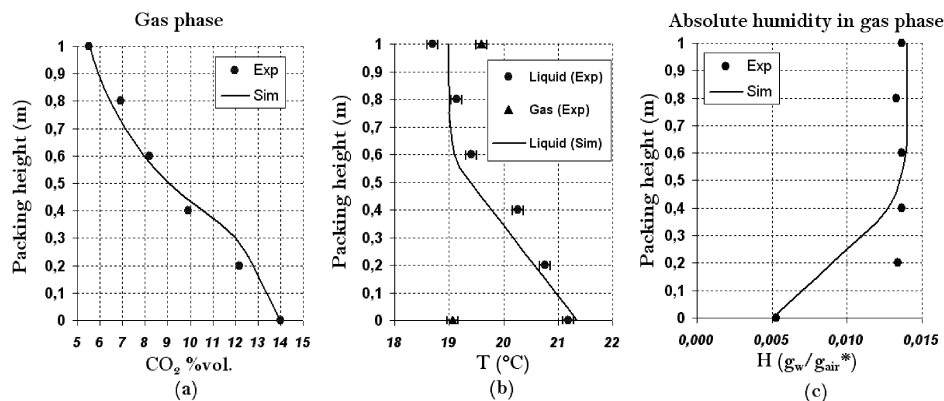


Figure 3: (a) experimental results on CO₂ (%vol.) profile in gas phase, (b) Temperature profiles in liquid and gas [points: experimental, lines: simulation]

A simultaneous counter-current transfer of CO₂ and water between phases is taking place, showing the multicomponent character of mass transfer. As we see in figure 3c, gas phase is rapidly saturated with vapor water at the bottom. The evaporation of water also cools down the liquid in the lowest segments and lowers the impact of exothermic reaction on the liquid temperature profile. The experimental values of absolute humidity (Figure 3c) have been measured with an error of $\pm 4,6 \times 10^{-8} \text{ g}_w \cdot \text{g}_{air}^{-1}$.

The absorber has a good performance and presents no operating challenges. The experimental observations are very close to the simulation results and hence they validate the model. The model can be applied for other solvents and for different packings. The next step would be to run the system with a more concentrated solution of DEA, in order to study the high transfers at the bottom of the column where concentration profiles become very important. At the bottom of the column, one 20cm segment of packing will be replaced by two 10cm segments for an adequate measurement in terms of concentration profiles.

Notations

C_i	Concentration (mol m^{-3})
D_{ij}	binary diffusion ($\text{m}^2 \text{s}^{-1}$)
E, N_i	heat and molar flux ($\text{J m}^{-2} \text{s}^{-1}$) and ($\text{mol m}^{-2} \text{s}^{-1}$)
F	Faraday constant
K_i	dimensionless gas-liquid equilibrium constant
R_i	total component reaction rate ($\text{mol m}^{-3} \text{s}^{-1}$)
T	temperature (K)
x_i, y_i	mole fraction (mol mol^{-1})
z_i	ionic charge
μ_i	chemical potential (J mol^{-1})
δ	film thickness (m)
φ	electrical potential (V)

Index and numbers: f (film), G (gas), I (interface), L (liquid), nc (components number)

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