

Kinetics in DEEA-MAPA-H₂O-CO₂ Systems for the Post-combustion CO₂ Capture by Absorption-Regeneration Using Demixing Solvents

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Abstract. This work focused on the CO₂ capture by absorption-regeneration process using amines-based solvents. To reduce significantly the thermal energy consumption for the solvent regeneration, an aqueous blend composed of a tertiary amine, N,N-Diethylethanolamine (DEEA), and a diamine, N-Methyl-1,3-propanediamine (MAPA) was studied. In specific conditions of amines concentrations and temperature, such solvent leads to a demixing phenomenon when loaded with CO₂. The objective was to develop an Aspen Plus process simulation of the CO₂ capture unit using the mix of these solvents. In addition to the chemical thermodynamics prediction developed in a previous work, reaction kinetics have been investigated. A critical literature review on the kinetics for the H₂O-DEEA-MAPA-CO₂ system was undertaken. The implementation of an external subroutine allowed to implement the kinetic models and to obtain simulations results for the different systems in good agreement with micro-pilot scale experimental measurements.

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Keywords CO₂ capture, absorption-regeneration process, kinetics, amine(s)-based solvents

Introduction

Global warming is an increasingly discussed topic at the government level. One of the main causes is the increase of CO₂ in the atmosphere. For this reason, the CO₂ emissions must be reduced to zero as Europe plans for 2050. For this purpose, carbon capture use and/or storage (CCUS) chains are studied. This work focuses on the capture part of this chain. Although there are different capture technologies, the focus was on an absorption-desorption process with an amine(s)-based solvent. The process allows to capture an important part of the CO₂ in the flue gases but in counterpart, it requires an important quantity of thermal energy to regenerate the solvent and thus concentrate the CO₂. In order to reduce this regeneration energy, studies are made on the solvent, on the adaptation of the process, on the equipment used or by combining these elements. This work focused on the first proposal. Indeed, the aqueous blend composed of a tertiary amine, N,N-Diethylethanolamine (DEEA), and a diamine, N-Methyl-1,3-propanediamine (MAPA) was studied. It has the particularity to lead to a demixing phenomenon for specific conditions of temperature, amines concentrations and CO₂ loading. A review of the kinetics reactions with CO₂ absorption into DEEA, MAPA and their mixture has been done in a first step. This review allowed to implement the kinetics in the simulations developed in a previous modeling work of micro-pilot tests. Thus, the experimental results could be compared to the simulated ones for the different systems.

Simulation of micro-pilot experiments

In a previous work¹, simulation on Aspen Plus V10 (Fig. 1) representing micro-pilot unit was carried out to compare experimental results acquired for various amines as well as the DEEA+MAPA mixture and the amines alone on this micro-pilot. The micro-pilot apparatus is composed of an absorption column and a desorption column of 1m each that work at atmospheric pressure. The outlet of the absorber containing the CO₂ rich stream is sent to the last stage of the stripper after passing through the internal exchanger allowing to heat the rich solution thanks to the thermal energy provided by the CO₂ poor stream coming out of the bottom of the stripper and feeding the top of the absorber. These two streams have respectively a preheater and a cooler after the internal exchanger in order to return at a temperature around of 40°C for the absorber and 90°C for the stripper. The flue gas to be treated feeds the absorber's bottom with a molar concentration of CO₂ of about 20% which is close to the cement plants case. During the micro-pilot tests, data were collected allowing to calculate: the absorption rate (A) thanks to the concentration in CO₂ at the inlet and outlet gas stream, the regeneration energy (E_{reg}) by dividing the reboiler duty supplied to the reboiler by the CO₂ mass flow leaving the stripper, and the CO₂ loading as the number of moles of CO₂ divided by the number of moles of amine(s)

present in the solution. In parallel, a consequent work on the thermodynamic aspect of these systems was done to develop the eNRTL² model allowing to calculate the activity coefficients and the Redlich Kwong equation of state used for the vapor phase. After having validated the thermodynamic model thanks to experimental equilibrium data, the experimental points from micro-pilot were compared to the simulation's values. The basic kinetic aspects were already addressed in this previous work, but the present work allowed to improve the implementation of kinetic models. Indeed, due to the specificities of each reaction mechanism, it was necessary to implement a Fortran subroutine linked to Aspen Plus in order to properly integrate these reaction kinetic expressions.

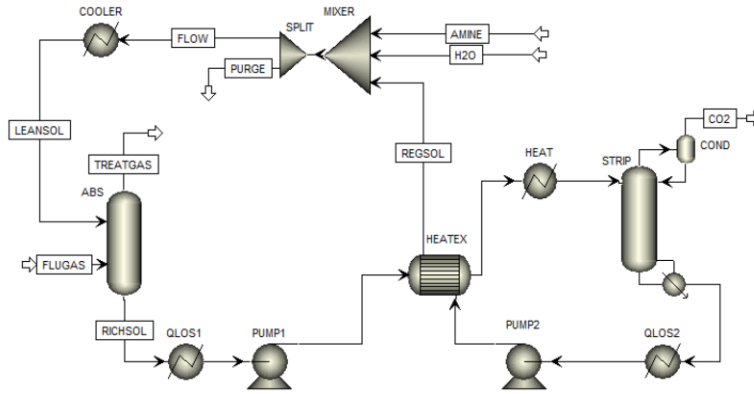
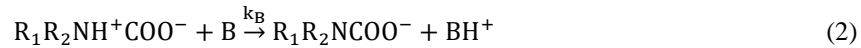
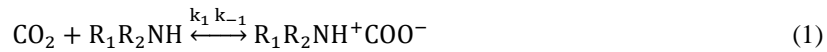


Fig. 1 Micro-pilot modelling on Aspen Plus

Review of reaction kinetics

Amines are of several types depending on the number of radicals bounds. Thus, primary, secondary and tertiary amines have respectively 2, 1 and 0 number of labile hydrogen atoms.

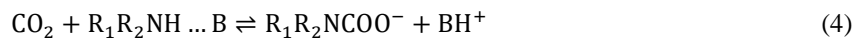
In the literature, two reaction mechanisms are proposed for primary and secondary amines. The Zwitterion mechanism proposed by Danckwerts³ is carried out in 2 steps. The first reaction is between an amine and carbon dioxide to produce the zwitterionic form. Then it reacts with a base B such as water or amine to form a carbamate and a protonated base.



The zwitterion formation reaction (1) is the kinetically limiting step. Versteeg et al.⁴ presented a steady-state principle to the intermediate zwitterion. The reverse reaction in equation (1) is smaller than deprotonation of the zwitterion represented by $k_B c_B$. The reaction rate is a second order reaction which is influenced by the concentrations of amine and CO_2 .

$$r_{\text{CO}_2} = k_1 c_{\text{CO}_2} c_{\text{R}_1\text{R}_2\text{NH}} \quad (3)$$

The termolecular mechanism is introduced by Crooks and Donnellan⁵ to express carbamate formation kinetics. The amine reacts with a base and CO_2 in one step. The initial product is a loosely bound encounter complex.



If amine is the base, the stoichiometry of the overall reaction is 2 moles of amines for 1 mole of CO_2 . The proposed reaction rate depends on the different bases present in the solution and is given by:

$$r_{\text{CO}_2} = \left(\sum_B k_B c_B \right) c_{\text{CO}_2} c_{\text{R}_1\text{R}_2\text{NH}} \quad (5)$$

For tertiary amine in aqueous solution, the mechanism is the protonation of the amine. The amine reacts with CO_2 and H_2O to form a bicarbonate ion and a protonated amine. Since no hydrogen atoms are bonded to the nitrogen, a carbamate cannot be formed^{6,7}.

The stoichiometry of the overall reaction is 1 mole of amine for 1 mole of CO₂. This implies that tertiary amines can be more loaded with CO₂ than primary or secondary amines. The reaction kinetics are of the second order. It is given by the equation (6).

$$r_{\text{CO}_2} = k_{\text{CO}_2} C_{\text{R}_1\text{R}_2\text{NH}} \quad (6)$$

A review of the kinetic data was made for DEEA, MAPA and their blend to highlight the experimental data and kinetic modelling available in the literature: mechanism, operating range (concentrations, temperature...) and kinetic models deduced. The aim of this review was to determine the kinetic models to be selected for an adequate system modeling. The Table 1 lists the various articles that were subsequently analyzed with the systems studied as well as the mechanism describing the reactions of CO₂ with primary and secondary amines.

Table 1.

Summary of the system studied in the different articles.

Article	Systems studied	CO ₂ -Amine mechanism
Majeed 2013 ⁸	MAPA models and experimental data DEEA-MAPA experimental data	Termolecular
Monteiro et al. 2014 ⁹	MAPA models and experimental data	Termolecular
Monteiro et al. 2015a ¹⁰	DEEA experimental data and review	/
Monteiro et al. 2015b ¹¹	DEEA-MAPA model and experimental data	Termolecular
Garcia et al. 2017 ¹²	DEEA-MAPA experimental data	Zwitterion
Kierzkowska-Pawlak and Kruszczyk 2017 ¹³	DEEA model and experimental data	Termolecular
	DEEA-MAPA experimental data	
Joseph et al. 2018 ¹⁴	DEEA-MAPA experimental data	Zwitterion
Jiang et al. 2018 ¹⁵	DEEA experimental data and review	/

In the kinetic study of CO₂ absorption, a pseudo-first order observed constant is calculated based on the type of instrumentation used in the experiment. This constant multiplied to the CO₂ concentration gives the CO₂ absorption rate in the solvent.

DEEA-H₂O-CO₂ system analysis

This section completes the review of the kinetic data for the DEEA-H₂O-CO₂ system carried out by Monteiro et al.¹⁰ in 2015a. Experimental points (Fig. 2) from the different sources presents some divergence between the different modelling of k_{DEEA}. In these studies, the concentration varying below 3M. Only Monteiro et al.¹⁰ conducted an experiment for a concentration above 3M at a single temperature.

The kinetic study of the DEEA-H₂O-CO₂ is done by considering:

- the carbonation of water: $\text{H}_2\text{O} + \text{CO}_2 \xrightarrow{k_{\text{H}_2\text{O}}} \text{H}_2\text{CO}_3$
- the formation of bicarbonate: $\text{OH}^- + \text{CO}_2 \xrightarrow{k_{\text{OH}^-}} \text{HCO}_3^-$
- the protonation of the amine and its deprotonation: $\text{DEEA} + \text{H}_2\text{O} + \text{CO}_2 \xrightleftharpoons[k_{-\text{DEEA}}]{k_{\text{DEEA}}} \text{DEEAH}^+ + \text{HCO}_3^-$

The carbonation and deprotonation are neglected by the authors because they are slow reactions and the quantity of OH⁻ is negligible compared to the tertiary amine which implies that the formation of bicarbonate is negligible. The authors are divided regarding the order for the protonation of DEEA. The reaction rate can be declined between a second order or a third order. Most of the authors consider that the second order reaction is a second order like it is demonstrated for other tertiary amines¹². The reaction rate of CO₂ absorption is therefore defined by the equation 7.

$$r_{\text{CO}_2} = k_{\text{DEEA}} C_{\text{DEEA}} C_{\text{CO}_2} \quad (7)$$

Among the different modelling results presented in the literature, they can be divided into three groups. First, the highest values represent three overlapping models from Li et al.¹⁷, Xu et al.¹⁸ and Jiang et al.¹⁵. Then three models, Littel et al.¹⁶ and both of Kierzkowska-Pawlak^{13,19}, corresponding to an average value in relation to the two extremities. Finally, the modelling of Sotelo et al. adapted by Monteiro¹⁰ presents the model with the lowest kinetic constant results.

A model of each group was tested in the simulation to highlight which kinetics can represent the best the experimental results. For the extremities, Sotelo et al. adapted by Monteiro¹⁰ and Jiang et al.¹⁵ are taken to represent respectively the lower and the higher value of k_{DEEA} and the average range is represented by the model of Kierzkowska-Pawlak and Kruszczyk¹³.

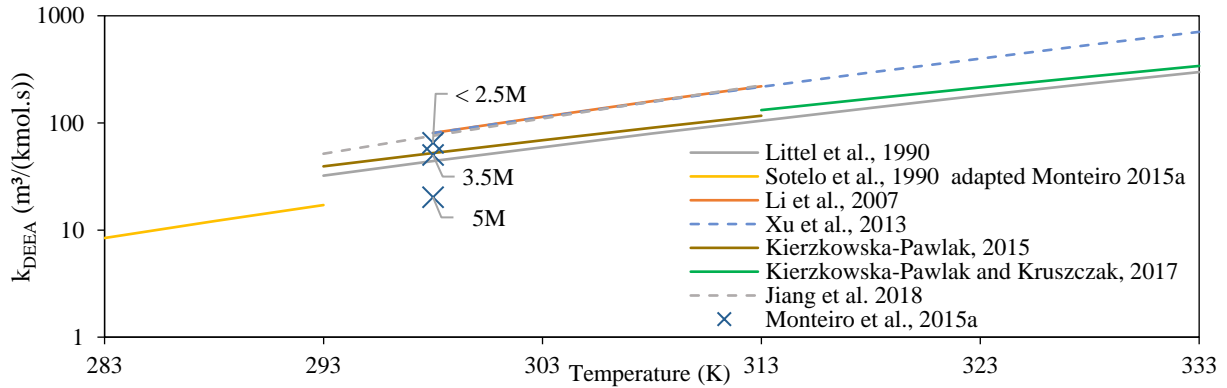


Fig. 2 Experimental data (point) and modelling (line) k_{DEEA} for DEEA solutions (Tag is for Monteiro et al.¹⁰ results that have variation of k_{DEEA} with the concentration)

MAPA-H₂O-CO₂ system analysis

For the kinetic study of MAPA-H₂O-CO₂ system, the reactions considered for the absorption of CO₂ in the solvent are the carbonation of water and the formation of carbamate. The contributions from the carbonation of water and the formation of bicarbonate with the hydroxide ion and CO₂ are not considered since they are relatively weak due to slow reaction rate and weak concentration in OH⁻. Thus, only the formation of carbamate is considered. The bases can be H₂O, MAPA or OH⁻. However, the hydroxide ion being weakly present, its contribution is negligible in the kinetic expression of the absorption rate.



$$r_{\text{CO}_2} = (k'_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}} + k'_{\text{MAPA}}c_{\text{MAPA}})c_{\text{MAPA}}c_{\text{CO}_2} = k_{\text{obs}}c_{\text{CO}_2} \quad (9)$$

Majeed⁸ and Monteiro et al.⁹ have established models based on their experimental points. Their experimental measurements thus made it possible to calculate k_{obs} for the system. An important observation is that they presented the same reaction mechanisms (i.e. termolecular) and have a similar justification for the final k_{obs} expression. This makes it possible to compare the models proposed by each author to model the k_{obs} . The experimental results are in the same range that is between 10^5 s^{-1} and 10^6 s^{-1} . However, concerning the models, Monteiro⁹'s model fits better with the experimental points. One of the reasons is the use of a kinetic model integrating the MAPA concentration and not just an Arrhenius model as proposed by Majeed⁸. It is therefore Monteiro⁹'s model that has been used in our simulations.

DEEA-MAPA-H₂O-CO₂ system analysis

In the kinetic studies for the DEEA-MAPA-H₂O-CO₂ system, the reactions considered are the same as for the simple amine systems. Thus, we find the carbonation of water, the formation of bicarbonate with hydroxide ion and CO₂, the protonation of DEEA and the formation of MAPA carbamate. In this case, the contributions of water carbonation and DEEA protonation are small due to the low reaction rate and the fact that bicarbonate formation is also negligible due to the small amount of hydroxide ion. Thus, only the formation of MAPA carbamate is considered in the rate of CO₂ uptake when it reacts with the bases H₂O, DEEA or MAPA.

$$r_{\text{CO}_2} = (k'_{\text{H}_2\text{O}}c_{\text{H}_2\text{O}} + k'_{\text{MAPA}}c_{\text{MAPA}} + k'_{\text{DEEA}}c_{\text{DEEA}})c_{\text{MAPA}}c_{\text{CO}_2} \quad (10)$$

Several researchers studied the DEEA-MAPA-H₂O-CO₂ system. However, only Monteiro et al.¹¹ proposes a model for determining the second order kinetic constant for the reaction between MAPA and DEEA forming the MAPA carbamate.

A concentration range of 1 to 5M was studied by Majeed⁸ and Monteiro et al.¹¹ which allows a comparison of their k_{obs} results for the different concentrations. Garcia et al.¹² studied the kinetics during the loading of the amine solvent for a concentration of 3M DEEA and 2M MAPA. The range of kinetic constant is around the 10^5 - 10^6 s⁻¹ for the different blends. The kinetic constant obtained by Garcia are lower than those of Monteiro. The author justified this by a different use of the partial pressure in CO₂. Kierzkowska-Pawlak and Kruszcak¹³ and Joseph¹⁴ studied a single temperature system for MAPA concentration below 0.5M. It is therefore not possible to compare its results with another work.

According to Monteiro et al.¹¹, as only the formation of MAPA carbamates governs the kinetics, k_{obs} is determined as:

$$k_{obs} = (k'_{H_2O}c_{H_2O} + k'_{MAPA}c_{MAPA} + k'_{DEEA}c_{DEEA})c_{MAPA} \quad (11)$$

The contributions related to the H₂O and MAPA come from a previous work performed by Monteiro et al.⁹ to calculate the k_{obs} . However, this model overestimates the experimental data. When the contributions $k'_{H_2O}c_{H_2O}$ and $k'_{MAPA}c_{MAPA}$ are calculated, data for these contributions presented in Monteiro et al.⁹ do not match. Nevertheless, by multiplying these two contributions by the activity coefficient (as already used previously by Monteiro et al.²⁰) calculated with the thermodynamic model of Mouhoubi et al.¹, a modelling fitting to the experimental results is obtained.

Simulation results

The experiments have shown very fast kinetics for MAPA contrary to DEEA. One of the reasons is the difference of reaction mechanisms between these two amines. The mixture of these two amines allows to obtain kinetics similar to MAPA except for DEEA 5M - MAPA 2M which is larger by a factor of 10 compared to the other blends. Moreover, it is one of the solutions that when it contains a certain load in CO₂ demixes in a range of temperature. The results of the micro-pilot tests are presented in a parity plot (Fig. 2) to compare with the simulated values. During the micro-pilot tests, data were collected allowing to calculate the absorption rate, the regeneration as well as the CO₂ loading. For the different systems, reactions are considered at equilibrium except the limiting reactions for CO₂ absorption. The different models for DEEA are tested in the simulation and the one of Jiang et al.¹⁵ fits best with the experimental results. Concerning the MAPA system, the carbamate formation is calculated at equilibrium thanks to the Gibbs free energy in the first step. The model of Monteiro et al.⁹ is used to implement kinetics. The results are conclusive for the 1M MAPA but not for the 2M solution. An investigation is necessary to find out what is the reason for the deviance at this concentration. For the amines mixtures, the system giving the best results is the one in which the DEEA model of Jiang et al.¹⁵ was implemented. Globally, the simulated results are in the range of $\pm 15\%$ for the different calculated parameters which is quite good considering the deviation observed with some models.

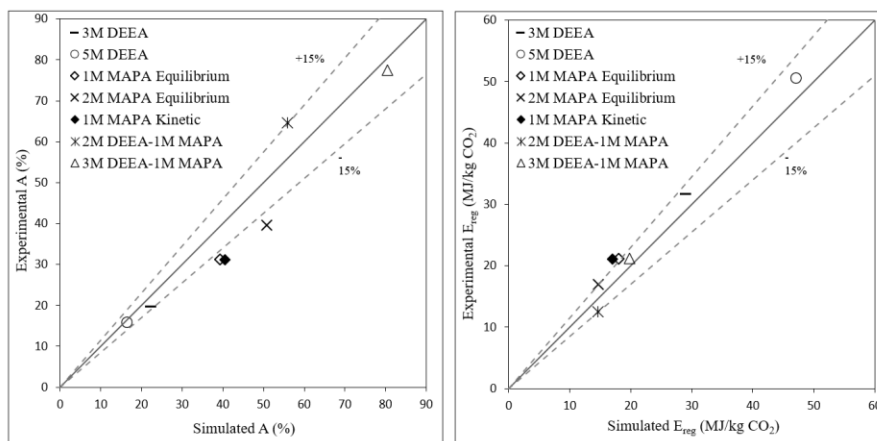


Fig. 2 Parity plot for absorption rate (%) and regeneration energy (MJ/kg CO₂) between experimental and simulation results

Conclusion

This work brought together available kinetic data presented in the literature for MAPA-DEEA-H₂O-CO₂ systems. Unfortunately, only a few articles concerned MAPA (alone or mixed with DEEA)-H₂O-CO₂ kinetics. Nevertheless, the available kinetic data were used to simulate absorption-regeneration tests performed with a micro-pilot unit. Thanks to these tests and the simulations developed by Mouhoubi et al.¹, the absorption-desorption performances related to the different chemical systems could be simulated and compared to the experimental results within an error range of

±15%. These simulations allowed to point out some lacks in available data. More specifically, it was highlighted that a study of the kinetics for a larger concentration range and with a higher temperature range should be envisaged to confirm or not the models and the different experimental results. In conclusion, this work shows that there is still research to be done in the field of chemical absorption, whether at the experimental or simulation level.

Acknowledgements

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