

## MODELING AND EXPERIMENTAL STUDY OF CARBON DIOXIDE ABSORPTION INTO AQUEOUS AMINE BASED SOLVENTS

Lionel Dubois and Diane Thomas

Chemical Engineering Department, Faculty of Engineering, University of Mons, Rue de l'Epargne, 56, 7000 Mons, Belgium, Email: Diane.Thomas@umons.ac.be

### Abstract

This work focused on the CO<sub>2</sub> capture by absorption into amines based absorbents. Aqueous mixtures containing different types of amines (MEA, MDEA, AMP, PZ and PZEA) are experimentally compared in a special gas-liquid contactor (a cables-bundle contactor) with respect to the CO<sub>2</sub> removal performances at 25°C and atmospheric pressure. This absorption process was also simulated with the use of published data on physico-chemical properties (densities, viscosities, diffusivities, Henry coefficients) of the CO<sub>2</sub>-amines systems. The different experiments clearly highlighted the positive effect of activators such as PZ and PZEA on the absorption performances measured with MEA, MDEA and AMP solutions. Regarding the simulation results, they matched quite satisfactorily the experimental values concerning individual amines solutions, but improvements should be envisaged in order to simulate successfully the CO<sub>2</sub> absorption into amines mixtures.

**Keywords:** CO<sub>2</sub> capture, amine based solvents, absorption with chemical reaction, simulation

### 1. Introduction

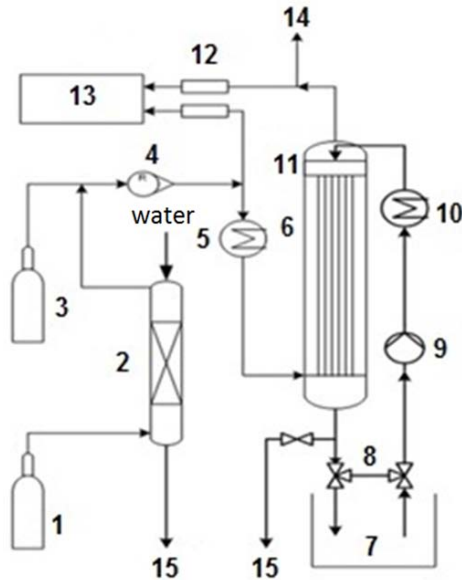
Environmental solutions are necessary to reduce the CO<sub>2</sub> emissions mainly responsible of anthropogenic greenhouse effect. This study focused on one of the solutions, namely the post-combustion CO<sub>2</sub> capture, and especially in the present work, on the absorption into amines based absorbents. This classical CO<sub>2</sub> capture process is applied in a system of two coupled columns for absorption of CO<sub>2</sub> by the lean CO<sub>2</sub>-amine solution and regeneration of the rich one. Different types of amine based solvents, presenting some advantages and drawbacks, can be used (alone or blended) to absorb CO<sub>2</sub>:

- the primary (and secondary) alkanolamines, such as monoethanolamine (MEA), are characterized by fast kinetics<sup>1</sup> but higher energy requirements for regeneration ;
- the tertiary and sterically hindered amines (SHA), such as N-methyldiethanolamine (MDEA) and 1-amino-2-propanol (AMP) respectively, have slower absorption kinetics<sup>2,3</sup> than the previous ones but higher absorption capacities with low solvent regeneration costs.
- the absorption activators, such as piperazine (PZ) and (piperazinyl-1)-2-ethylamine (PZEA), cyclical polyamines, lead to faster absorption kinetics when added to other amines<sup>4,5</sup>.

Reaction mechanisms of carbon dioxide with these amines solutions were already largely discussed in the literature<sup>6,7</sup>, the activation phenomenon remaining sometimes quite unclear and very specific to each chemical system. This work aimed actually at comparing the CO<sub>2</sub> absorption performances into aqueous amine solutions (MEA, MDEA, AMP, PZ and PZEA) and their blends. Some mixtures were previously investigated in the literature by achieving absorption test runs in wetted wall columns, as for example in the works of Samantha et al. 2009<sup>8</sup> (AMP+PZ) or Paul et al. 2009<sup>5</sup> (MDEA+PZEA). In the present study, new blends composed of MEA+PZEA and AMP+PZEA, never experimented in previous studies, are considered. As detailed later in this paper, our experiments were carried out using an unique installation and identical operating conditions: a comparison of absorption performances was sufficient to get information about the efficiency of each solution in comparison with the results presented in the literature, obtained with largely varying types of installations and operating conditions. The experimental results were moreover compared with simulated ones obtained with a modelling method for the absorption process accompanied by chemical reaction(s). Physico-chemical and kinetic properties could therefore be checked. Globally, the experimental device and procedure here described will be used for further studies in order to test innovating mixtures and to deduce their physico-chemical and kinetic characteristics.

## 2. Experimental set up and procedure

The experimental equipment, which includes a scrubber, a liquid and gas supply, and a gas sampling part, illustrated in Fig. 2, is completely detailed in our previous works<sup>9,10</sup>. The amine based absorbent is fed to the top distributing chamber thanks to a peristaltic pump and distributed on all the vertical yarns contacting continuously and counter-currently the gas.



**Table 1.** Operating conditions of our absorption tests

Pressure (P)	1 atm
Temperature (T)	298.15 K
Liquid flow rate (L)	0.191 l/min ( $u_L = 0.0025$ m/s)
Gas flow rate (G)	0.81 m <sup>3</sup> /h ( $u_G = 0.17$ m/s)
CO <sub>2</sub> contents ( $y_{CO_2,in}$ )	4 - 18 %
$C_{AMP}$	15 - 30 wt.%
$C_{MEA}$	10 - 30 wt.%
$C_{PZ}$	5 - 10 wt.%
$C_{PZEA}$	5 - 10 wt.%
$C_{MDEA}$	30 wt.%

} Different mixtures

**Figure 1.** Experimental apparatus including the gas-liquid contactor: 1. carrier gas (N<sub>2</sub>) cylinder, 2. humidification column, 3. solute (CO<sub>2</sub>) cylinder, 4. flow indicator/control, 5. heat exchanger, 6. cables-bundle contactor, 7. solution tank, 8. switch for solution recycling, 9. liquid pump, 10. heat exchanger, 11. liquid distributor, 12. membrane dryers, 13. gas analysis, 14. hood, 15. sewer.

The gas phase is composed of nitrogen humidified in a saturator (packed column fed with water), in which CO<sub>2</sub> is added to obtain the desired concentration (4 - 18 vol. %). The total gas flow rate is metered by a rotameter. Sampling of gas simultaneously at the input and the output of the column is performed continuously through membrane dryers followed by an IR analyser giving respectively the molar fractions  $y_{CO_2,in}$  and  $y_{CO_2,out}$  allowing to calculate the absorption efficiency  $A$  of CO<sub>2</sub>:

$$A = (y_{CO_2,in} - y_{CO_2,out}) / y_{CO_2,in} \quad (1)$$

All the experiments were carried out at atmospheric pressure and at a temperature equal to 298.15 K. The operating conditions applied in this work were kept constant and are summarized in Table 1.

## 3. Modeling of the absorption process

### 3.1 Definition and theory used for the modeling

The modelling method of the absorption performances, similar to the one we previously developed<sup>10</sup>, is based on the two-film theory for CO<sub>2</sub> absorption accompanied by an irreversible chemical reaction between the solute, CO<sub>2</sub>, and the liquid reactant, amine. This classical modeling method was successfully experimented by other authors (e.g. Gabrielsen et al. 2006<sup>11</sup>) and leads to results with a sufficient precision. The details of the estimation of the mass transfer characteristics of the packing and of the different absorption parameters needed for the modelling can be found in our previous works<sup>9,10</sup>. Based on Hatta number  $Ha$  [-] criteria<sup>12</sup>, the chemical reaction regime can be slow, moderately fast or fast depending on the liquid phase concentration and the CO<sub>2</sub> loading of the amine. In our case, due to kinetic characteristics of the reaction of the amines studied and CO<sub>2</sub>,  $Ha$  is defined as:

$$Ha = \sqrt{k_2 \cdot D_{CO_2/Amine} \cdot C_{Amine}} / k_L \quad (2)$$

where  $k_2$  [m<sup>3</sup>/kmol.s] is the kinetic constant of the CO<sub>2</sub> reaction with the amine,  $D_{CO_2/Amine}$  [m<sup>2</sup>/s] is the diffusion coefficient for CO<sub>2</sub> in the amine solution,  $c_{Amine}$  [kmol/m<sup>3</sup>] is the molar concentration of amine and  $k_L$  [m/s] is the liquid-phase mass transfer coefficient. Considering that the CO<sub>2</sub> concentration in the liquid film is virtually nul ( $c_{CO_2} = 0$ ) due to the reaction which proceeds and consumes the solute, the absorption flux  $R_{CO_2}$  [kmol/m<sup>2</sup>.s] can be written, as:

$$R_{CO_2} = k_G \cdot (p_{CO_2} - p_{CO_2,i}) = E \cdot k_L \cdot c_{CO_2,i} \quad (3)$$

where  $k_G$  [kmol/m<sup>2</sup>.s.Pa] is the gas-phase mass transfer coefficient,  $p_{CO_2}$  [Pa] is the partial pressure of CO<sub>2</sub>, and  $E$  [-] the enhancement factor. For the conditions of a high reactivity of CO<sub>2</sub> with the amine, which is the case with the amines studied, and an amine concentration in the liquid bulk being much greater than the CO<sub>2</sub> interfacial concentration, leading to large Hatta numbers ( $3 < Ha < E/2$  with  $E_i$  being the value of  $E$  for the instantaneous reaction), the kinetics of the reaction becomes pseudo-first order and fast, and the enhancement factor  $E$  is almost equal to  $Ha$ <sup>12</sup>. Eq. (4) was then used to compute the liquid side absorption flux  $R_{CO_2}$ :

$$R_{CO_2} = \frac{\sqrt{k_2 \cdot D_{CO_2/Amine}}}{H_{CO_2/Amine}} \cdot \sqrt{c_{Amine} \cdot p_{CO_2,i}} = GPA \cdot \sqrt{c_{Amine} \cdot p_{CO_2,i}} \quad (4)$$

In relations 3 and 4,  $p_{CO_2,i}$  [Pa] and  $c_{CO_2,i}$  [kmol/m<sup>3</sup>] are respectively the interfacial values of the CO<sub>2</sub> partial pressure and concentration assuming a Henry's equilibrium relation (Eq. (5)) at the gas-liquid interface with the Henry's coefficient  $H_{CO_2/Amine}$  [Pa.m<sup>3</sup>/kmol]:

$$p_{CO_2,i} = H_{CO_2/Amine} \cdot c_{CO_2,i} \quad (5)$$

The factor multiplying  $\sqrt{c_{Amine} \cdot p_{CO_2,i}}$  is defined as the Global Parameter of Absorption (GPA). This parameter could be preferred to conventional enhancement factors or Hatta numbers in order to design scrubbing towers because it is a lumped parameter taking account of the coupling between the chemical kinetics and the solubility and diffusivity of CO<sub>2</sub> in the liquid phase. Moreover, the GPA does not contain  $k_L$  and is therefore theoretically independent of the hydrodynamic conditions occurring in the column<sup>13</sup>.

### 3.2 Computation of performances for continuous absorption test runs

For all test runs the simulation of the column was made by means of a finite difference method considering small height (dh=0.01 m) incremental volumes, the molar fraction of CO<sub>2</sub> ( $y_{CO_2}$ ), the amine concentration ( $c_{Amine}$ ) and the absorption flux ( $R_{CO_2}$ ) being centered in these elements. Classical steady-state mass balances were used to compute the CO<sub>2</sub> partial pressure (molar fraction) and the amine concentration in the liquid along the column taking account of the fluid flow rates ( $L$  and  $G$ , values given in Table 1):

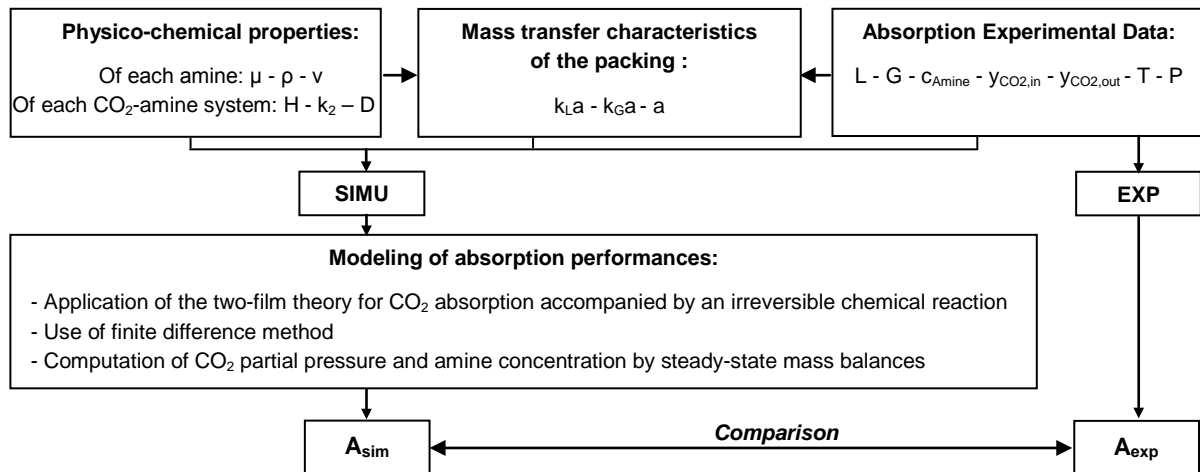


Figure 2. Methodology principles

**Table 2.** Physico-chemical properties of each CO<sub>2</sub>-amine system at 25°C  
Note: [x] = the reference number x

	AMP	MDEA	MEA	PZ	PZEA *
CO <sub>2</sub> liquid diffusivity: $D_{CO_2/Amine}$	Stokes-Einstein relation [15]: $D_{CO_2/Amine}(T) = D_{CO_2/water}(T) \cdot \mu_{water}(T)^{0.8} / \mu_{Amine}(T)^{0.8}$ **				
Dynamic viscosity: $\mu_{amine}$	[16]	[15]	[15]	[4]	[19]
Density: $\rho_{amine}$	[16]	[18]	[18]	[4]	[19]
Kinematic viscosity: $\nu_{amine}$	$\nu_{amine} = \mu_{amine} / \rho_{amine}$				
Henry's law constant: $H_{CO_2/Amine}$	[17]	[15]	[15]	[4]	[19]
Kinetic constant: $k_2$ (m <sup>3</sup> /kmol.s)	1048 [2] ( $k_{2,AMP,1}$ ) 560 [20] ( $k_{2,AMP,2}$ )	12.24 [3] ( $k_{2,MDEA}$ )	8088 [21] ( $k_{2,MEA}$ )	76000 [22] ( $k_{2,PZ}$ )	24582 [5] ( $k_{2,PZEA}$ )

\* The data from Paul et al. 2009<sup>19</sup> about PZEA were available in a narrow concentration range (0-1.5 kmol/m<sup>3</sup>) and have been extrapolated from 30°C, 40°C and 50°C to 25°C.

\*\* The diffusion coefficient of CO<sub>2</sub> in water ( $D_{CO_2/water} = 1.92 \cdot 10^{-9}$  m<sup>2</sup>/s), and the dynamic viscosity of water ( $\mu_{water} = 8.96 \cdot 10^{-4}$  Pa.s) at 25°C are based on the data from Versteeg et al. 1988<sup>15</sup>.

$$c_{Amine,O} = c_{Amine,I} - n \cdot R_{CO_2} \cdot a \cdot S \cdot dh / L \quad (6)$$

$$y_{CO_2,I} = y_{CO_2,O} + R_{CO_2} \cdot a \cdot S \cdot dh \cdot R \cdot T / (P \cdot G) \quad (7)$$

where I and O refer respectively to the inlet and the outlet of the incremental volume,  $a$  [1/m] is the specific interfacial area,  $S$  [m<sup>2</sup>] is the section of the contactor and  $n$  corresponds to the stoichiometry of the global reaction CO<sub>2</sub>/Amine and is equal to 1 for MDEA, AMP and PZEA, and is equal to 2 for MEA and PZ. Starting from the top of the contactor ( $y_{CO_2,out}$  and  $c_{Amine,in}$  are given) the program provides finally the CO<sub>2</sub> inlet molar fraction ( $y_{CO_2,in}$ ), which was compared to the experimental value or in terms of absorption efficiencies (A). It is also possible with our program to deduce  $k_2$  values for new amine solvents investigated. The modeling applied for CO<sub>2</sub> absorption into blended amines solutions is substantially similar to the one described here above for the pure amine solutions, requiring nevertheless some adaptations relative to:

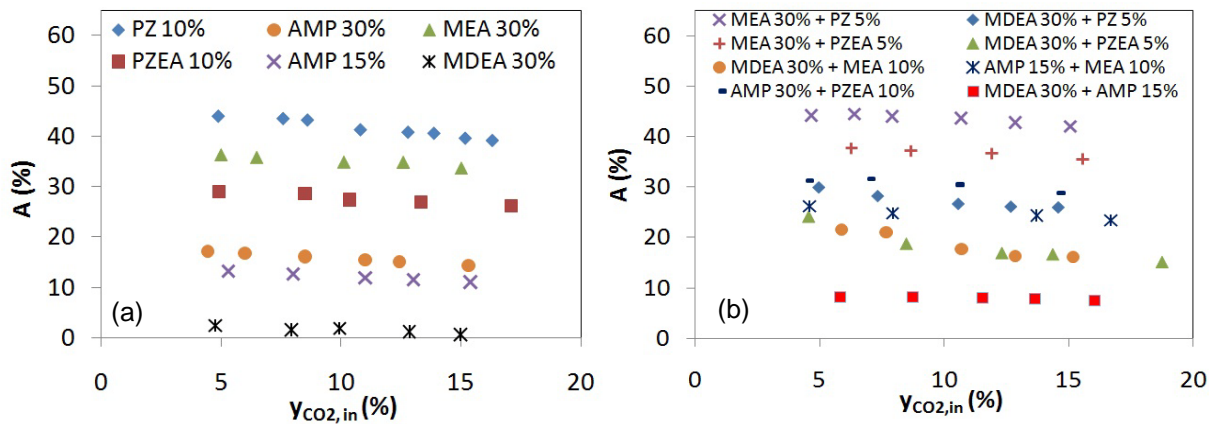
- the physical and chemical properties of blended amines solutions, obtained by applying mixing rules detailed in our last work<sup>10</sup>;
- the kinetic term, obtained by summing the contributions (kinetic constants multiplied by corresponding concentrations) of each amine as proposed in the literature<sup>10,14</sup>.

A schematic representation of the methodology applied in our work is given in Fig. 2, and Table 2 gives the literature references of the physico-chemical properties:  $H_{CO_2/Amine}$  and  $D_{CO_2/Amine}$ , whose values are quite similar in the whole range of  $c_{Amine}$  and adequately selected kinetic data which have very different orders of magnitude for each CO<sub>2</sub>-amines systems.

## 4. Results and discussion

### 4.1 Experimental results of the CO<sub>2</sub> absorption into aqueous amine solutions

A slightly decreasing absorption efficiency can be generally observed as the CO<sub>2</sub> molar concentration in the gas phase is increased as illustrated on Fig.3 (a) and (b). This is due to an increased amine consumption which slightly decelerates the absorption process. Fig. 3 (a) illustrates that the highest CO<sub>2</sub> absorption rates are reached with a 10 wt. % piperazine solution, with a factor 20 higher than the lowest CO<sub>2</sub> absorption rates measured with a 30 wt. % MDEA solution. Regarding the absorption efficiencies with PZEA and AMP solutions, these are intermediate between the performances measured with MEA and MDEA 30 wt. % solutions. It can also be noted that an increasing amine concentration leads obviously to better absorption efficiencies (as highlighted on Fig. 3 (a) with the comparison of AMP concentrations of 15 and 30 wt. %) due to a faster liquid phase reaction and greater Hatta numbers (eq. (2)). For CO<sub>2</sub> absorption into aqueous blended amines solutions, as it can be seen in Fig. 3 (b), by adding an activator such as PZ or PZEA (5-10 wt. %) in MDEA, AMP or MEA aqueous solutions (30%), CO<sub>2</sub> absorption rates can be substantially increased.

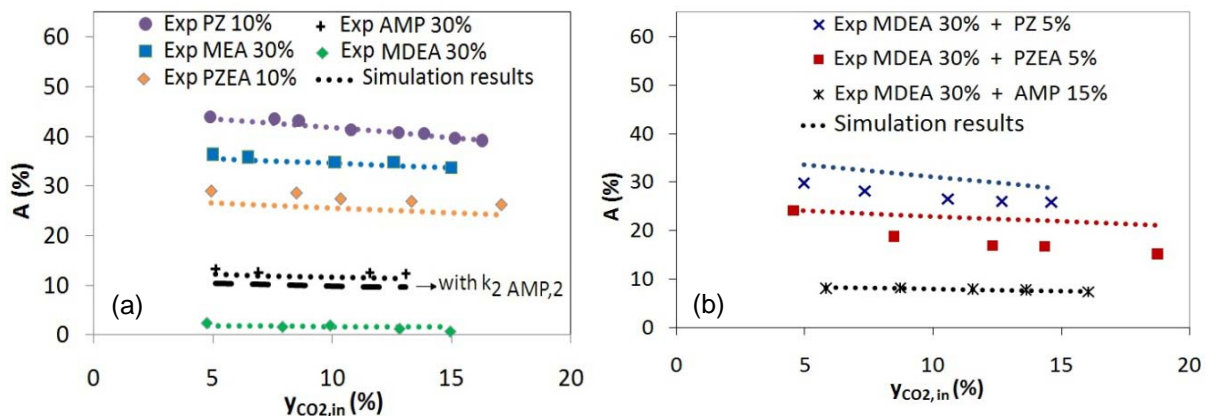


**Figure 3.** Experimental CO<sub>2</sub> absorption rates variation with  $y_{CO_2,in}$  and comparison for the different individual amines (a) and blended amines solutions (b)

The activation effect seems to be higher with PZ than with PZEA: as illustrated by the comparison of MDEA activation by PZ 5 wt. % and by PZEA 5 wt. %. This beneficial activation phenomenon was also observed by adding a primary alkanolamine (MEA) to a SHA (AMP). In the case of blended solutions of AMP and MDEA, the CO<sub>2</sub> absorption performances are better than in the case of a simple MDEA solution, but no real activation seemed to take part to the absorption-reaction process. From a general point of view, it has to be concluded that a gradual increase in the CO<sub>2</sub> absorption performances can be reached by mixing different types of amines: tertiary (MDEA) or sterically hindered amines (AMP) mixed with an activator (PZ, PZEA) or a primary alkanolamine (MEA).

#### 4.2 Comparison of experimental results with simulated ones

As detailed in the third point, the simulation can provide absorption efficiencies which can be compared to the experimental ones by using adequate data and method. In the case of individual aqueous amines systems, the simulation results (see Fig. 4(a)) are concordant with experimental ones. Nevertheless, the obvious dependence of the choice of the kinetic constant has to be noted: a lower kinetic constant leads to reduced simulated absorption rates, as depicted on Fig. 4 (a) for the case of AMP 30 wt. %. Beside the dependence on the choice of the kinetic constant, a less satisfactory agreement can be observed between simulations and experimental results for the aqueous blended amines solutions (see Fig. 4 (b)) than with individual amines solutions, certainly due to quite inadequate mixing rules used in the simulation<sup>4</sup> (requiring further measurements of the physico-chemical properties) but also due to the activation phenomenon which takes place. Actually, in the case of the solution composed of MDEA 30 wt. % and AMP 15 wt. %, for which no real activation phenomenon was observed (see Fig. 3 (b)), the experimental results are in good concordance with the simulated ones.



**Figure 4.** Comparison of the experimental and simulated CO<sub>2</sub> absorption rates obtained with different individual amines (a) and blended amines solutions (b) using  $k_{2,MEA}$ ,  $k_{2,MDEA}$ ,  $k_{2,PZ}$ ,  $k_{2,PZEA}$  and  $k_{2,AMP,1}$  (see Tab. 2)

Globally, it can be therefore assumed that improvements have to be envisaged to model the CO<sub>2</sub> absorption into amines mixtures by taking account of the several reactions taking place in series or in parallel during the absorption, as explained in Versteeg et al. 1990<sup>23</sup> and applied in Mandal et al. 2001<sup>24</sup> in the case of the activation of MDEA and AMP by MEA.

## 5. Conclusions and perspectives

The present study concerned the carbon dioxide capture, focusing more specifically on the absorption both into simple and mixed-amine based absorbents. The absorption test runs were achieved at 25°C in a laboratory cables-bundle scrubber. The purpose of this study was to compare CO<sub>2</sub> absorption performances for different types of amines solutions (MEA, MDEA, AMP, PZ and PZEA), simple and blended, confirming some effects and illustrating some new ones. Our continuous absorption experiments clearly highlighted the very positive effect of an activator on the absorption performances and particularly with PZ. As original results of our work, a gradual increase in the CO<sub>2</sub> absorption efficiencies can be reached by mixing different types of amines: tertiary (MDEA) or sterically hindered amine (AMP) with an activator (PZ, PZEA) or a primary amine (MEA). The simulation results, by application of the two-film theory for CO<sub>2</sub> absorption accompanied by an irreversible chemical reaction in the amines solution, were found to match quite satisfactorily the experimental values relative to individual amine solutions, validating the kinetic and physico-chemical properties used. Nevertheless, improvements are required to simulate successfully the CO<sub>2</sub> absorption into amines mixtures, adequately taking the activation effect into account, and requiring therefore a thorough comprehension of the complex reaction mechanisms involved during absorption. As short-term perspectives, absorption and regeneration tests in a laboratory micro-pilot coupling two columns, will be considered for the best amines mixtures preliminarily screened, in order to take account of the regeneration performances of the solvents. The methodology developed here could be suitable to achieve similar runs at several higher temperatures (for example at 313 K as in the industrial process) or to characterize others solutions of amines, involving in particular, more complex mechanisms.

## Acknowledgements

L. Dubois is grateful to the Chemical Engineering Department of the Faculty of Engineering (University of Mons) for this research achieved during his thesis.

## References

1. G.F. Versteeg *et al.*, *Chem. Eng. Comm.*, 1996, 144, 113.
2. M. Sharma, *Trans. Faraday Soc.*, 1965, 61, 681.
3. P.M.M. Blauwhoff *et al.*, *Chem. Eng. Sci.*, 1983, 38 (9), 1411.
4. P.W.J. Derks, PhD Thesis, Twente University of Technology, 2006.
5. S. Paul *et al.*, *Chem. Eng. Sci.*, 2009, 64, 1618.
6. P.D. Vaidya and E.Y. Kenig, *Chem. Eng. Technol.*, 2007, 30 (11), 1467.
7. P.M.M. Blauwhoff *et al.*, *Chem. Eng. Sci.*, 1984, 39 (2), 207.
8. A. Samanta and S.S. Bandyopadhyay, *Chem. Eng. Sci.*, 2009, 64, 1185.
9. S. Colle *et al.*, *Chem. Eng. Process.*, 2004, 43 (11), 1397.
10. L. Dubois and D. Thomas, *Chem. Eng. Technol.*, 2009, 32 (5), 710.
11. J. Gabrielsen *et al.*, *A.I.Ch.E. J.*, 2006, 52 (10), 3443.
12. C. Roizard *et al.*, *Tech. Ing., Traité Génie des procédés*, 1997, Ref. J 1 079.
13. D. Thomas *et al.*, *Chem. Eng. Process.*, 2003, 42 (6), 487.
14. G-W. Xu *et al.*, *Ind. Eng. Chem. Res.*, 1992, 31 (3), 921.
15. G.F. Versteeg and W.P.M. Van Swaaij, *J. Chem. Eng. Data*, 1988, 33 (1), 29.
16. A. Henni *et al.*, *J. Chem. Eng. Data*, 2003, 48 (3), 551.
17. A.K. Saha and S.S. Bandyopadhyay, *J. Chem. Eng. Data*, 1993, 38, 78.
18. R.H. Weiland *et al.*, *J. Chem. Eng. Data*, 1998, 43 (3), 378.
19. S. Paul *et al.*, *Chem. Eng. Sci.*, 2008, 64, 313.
20. A.K. Saha *et al.*, *Chem. Eng. Sci.*, 1995, 50, 3587.
21. J.K.A. Clarke, *I. and EC Fundamentals*, 1964, 3 (3), 239.
22. P.W.J. Derks *et al.*, *Chem. Eng. Sci.*, 2006, 61 (20), 6837.
23. G.F. Versteeg *et al.*, *Chem. Eng. Sci.*, 1990, 45 (1), 183.
24. B. P. Mandal *et al.*, *Chem. Eng. Sci.*, 2001, 56, 6217.