

## Kinetics Study and Simulation of CO<sub>2</sub> Absorption into Mixed Aqueous Solutions of Methyl-diethanolamine and Diethanolamine

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This study investigated kinetics of CO<sub>2</sub> absorption into mixed MDEA and DEA solutions in a Lewis cell reactor. The experiments were conducted over the temperature range of 293–313 K, MDEA/DEA wt% ratio of 20/20 and 30/20. Results show that absorption kinetics of blended MDEA/DEA 30/20 is faster than absorption kinetics of blended MDEA/DEA 20/20. The Absorption/Regeneration system was simulated using the software Aspen plus™ for a pulverized coal fired power plant (CF) in a post-combustion process. Model analysis established that blended MDEA/DEA 30/20 solvent gives the lowest energy consumption than those of MDEA and DEA.

### 1. Introduction

Carbon dioxide capture & storage (CCS) is an option to reduce greenhouse gas emissions, in particular from thermal power plants. The appropriate method to capture CO<sub>2</sub> from a Pulverized Coal (PC) power plant is post-combustion. This technique involves treating exhaust gases on the output side of the PC. With reference to the capture in post-combustion, chemical solvents remain the best solution to absorb CO<sub>2</sub> due to the low levels of CO<sub>2</sub> partial pressures in exhaust gases (Kanniche et al., 2010). Monoethanolamine (MEA) is the most used solvent because it allows a high recovery rate even with a low partial pressure of CO<sub>2</sub> (Martin et al., 2012). However, MEA presents an easy degradation and high energy requirements for its regeneration. Kinetic is an important characteristic for designing the absorption columns. Nevertheless, it must be considered the energy requirement for solvent regeneration. Current research targets to identify chemical solvents that have high absorption capacity and are less energy consuming for regeneration (Gonzalez-Garza et al., 2009.). For instance, blended amines have been proven to outperform conventional single amine solutions (Liao and Li, 2002). A rapid kinetic reaction, like that of the reaction between CO<sub>2</sub> and diethanolamine (DEA), will be able to reduce solvent flow but often this will be compensated by an increase in the heat duty necessary to recover the CO<sub>2</sub> from solvent. Slow kinetic reactions, like that of the reaction between CO<sub>2</sub> and methyl-diethanolamine (MDEA), despite of higher solvent flow, the energy required to reverse amine-acid gas reaction and stripping carbon dioxide will be lower. Besides, MDEA has higher loading capacities than primary and secondary amines like MEA and DEA. Thus, aqueous (MDEA+DEA) is considered an attractive blend of amines solvent for absorption of CO<sub>2</sub>. Glasscock and Rochelle (1991) investigated the absorption/desorption of aqueous MDEA/MEA and MDEA/DEA solutions with a gas-stirred cell reactor. They concluded that CO<sub>2</sub> mass transfer rate for the mixture of MEA/MDEA and DEA/MDEA can be represented by a combined mass transfer/equilibrium model based on the zwitterions mechanism. Rinker et al. (2000) measured the rate of absorption of CO<sub>2</sub> into an aqueous

solution of MDEA and DEA in a laminar jet absorber and a stirred cell absorber. They developed a model for the absorption of CO<sub>2</sub> into aqueous blends of DEA/MDEA based on penetration theory. Afterwards, Mandal and Bandypahayay (2006) examined simultaneous absorption of CO<sub>2</sub> and H<sub>2</sub>S into aqueous blends of MDEA and DEA. More recently Lin et al. (2009) study the kinetics of the absorption of CO<sub>2</sub> into MDEA/DEA using a wetted wall column apparatus. As well, they measured solubilities and diffusivities of N<sub>2</sub>O in the studied amine systems. They determined the overall pseudo first-order reaction rate constants from the measured kinetic data based on the pseudo first-order for the CO<sub>2</sub> absorption. They found that the addition of small amounts of DEA to MDEA results in a significant enhancement of CO<sub>2</sub> absorption rates. In the present paper, additional data on the kinetics of the reaction between CO<sub>2</sub> and blended aqueous MDEA-DEA solutions are reported. The obtained results were used to simulate CO<sub>2</sub> capture in a Pulverized Coal (PC) power plant. This work identifies the most favorable blended composition (MDEA/DEA) to reduce energy cost.

## 2. Materials and methods

### 2.1 Experimental apparatus

Experiments were carried out in a closed reactor of the Lewis cell type (Figure 1). Lewis cell can be used for acid gases absorption or desorption experiments (Cadours et al., 1997). This system enables to easily follow the evolution of pressure, while maintaining temperature constant and creating an optimum contact between the gaseous and liquid phases. The upper bracket includes a pressure sensor that monitors the change in pressure over time in the gaseous phase. The lower flange includes a probe that measures the temperature of the liquid phase at any moment. The agitation of the gas phase is accomplished by a propeller driven by a magnet bar located inside the cell and set in motion by a magnetic stirrer located outside the cell. The magnetic stirring of the liquid phase is provided by a Rushton turbine. The cell's volume is  $(0.3695 \pm 0.0005) 10^{-3} \text{ m}^3$ . The interfacial surface area is  $(15.34 \pm 0.05) 10^{-4} \text{ m}^2$ . The data of interest is collected and analyzed using dedicated software (Benchlink Data Logger). The main acquired readings are pressure and temperature, both in the Lewis cell and in the carbon dioxide reservoir.

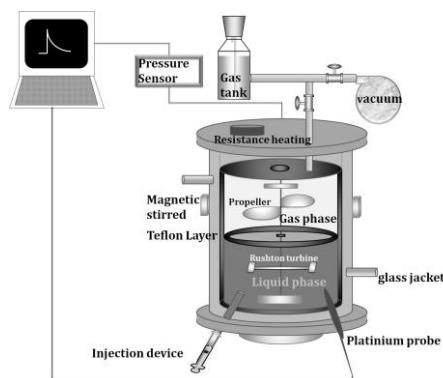


Figure 1: Scheme of experimental device

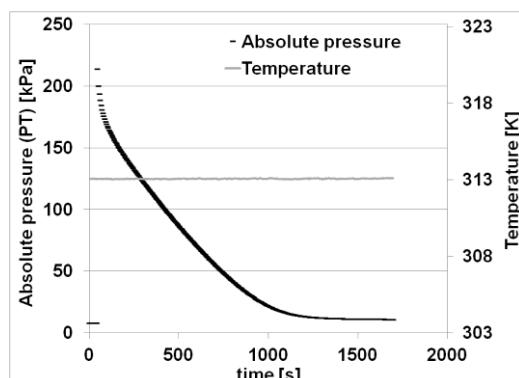


Figure 2: CO<sub>2</sub> absorption in an aqueous solution of MDEA 20 wt% and DEA 20 wt%, T = 313.15 K

### 2.2 Procedure and Mass transfer model

The aqueous solutions are prepared under vacuum. The uncertainties on the solvent composition are lower than  $\pm 0.01\%$ . The vacuum is made in the Lewis cell. Then the solvent is introduced in it. Once the temperature and the pressure are stabilized in the cell, the data acquisition starts (Figure 2). First the vapor pressure of the solution is recorded. Then the gaseous stream containing CO<sub>2</sub> is introduced resulting in an increase in the total pressure. Then a pressure drop can be observed because of the

$\text{CO}_2$  absorption by the aqueous solution. Finally, the system reaches equilibrium. The reproducibility of the experiment is within  $\pm 10\%$ . The mass balance is described by the following equation:

$$\varphi_{\text{CO}_2} \cdot a = -\frac{d(n_{\text{CO}_2})}{dt} = -\frac{V_G}{R \cdot T} \cdot \frac{d(P_{\text{CO}_2})}{dt} \quad (1)$$

$a$  = interfacial area ( $\text{m}^2$ ),  $T$  = temperature (K),  $R$  = gas constant,  $V_G$  =  $\text{CO}_2$  volume ( $\text{m}^3$ ),  $n_{\text{CO}_2}$  =  $\text{CO}_2$  moles absorbed in liquid phase. The chemical absorption rate  $\varphi_{\text{CO}_2}$  is determined by:

$$\varphi_{\text{CO}_2} = \frac{E \cdot k_L}{H_{\text{CO}_2}} \cdot (P_{\text{CO}_2,\text{int}} - P_{\text{CO}_2,b}) \quad (2)$$

$P_{\text{CO}_2,b}$  = pressure of  $\text{CO}_2$  in the liquid bulk,  $H_{\text{CO}_2}$  = Henry's law constant

$$P_{\text{CO}_2,b} = H_{\text{CO}_2} \cdot C_{\text{CO}_2,b} \quad (3)$$

The  $\text{CO}_2$  partial pressure at the gas-liquid interface ( $P_{\text{CO}_2,\text{int}}$ ) is calculated from the absolute pressure ( $P_T$ ) in the cell and the vapor pressure of the solvent ( $P_{\text{solv}}$ ). The gas side mass transfer resistance is neglected.

$$P_{\text{CO}_2} = P_T - P_{\text{solv}} \quad (4)$$

The enhancement factor  $E$  is determined using Eq(4) in which the  $\beta$  correspond to the slope of the linear representation of the experimental data:

$$\beta = a \cdot k_L \cdot E \cdot \frac{R \cdot T}{V_G \cdot H_{\text{CO}_2}} \quad (5)$$

### 2.3 Liquid side mass transfer

The mass-transfer coefficient,  $k_L$ , was calculated using a dimensionless correlation Eq (6) established by Amararene and Bouallou (2004). The liquid side mass transfer coefficient was determined by physical absorption of  $\text{N}_2\text{O}$  in aqueous solutions of MDEA. It implies three dimensionless numbers: the Reynolds number ( $Re$ ) (Eq(7)), the Schmidt number ( $Sc$ ) (Eq(8)) and the Sherwood number ( $Sh$ ) (Eq(9)). This correlation is valid for a Reynolds number ranging from 215 to 5,666, a Schmidt number varying from 46 until 21,710 and a Sherwood number included in the range 378 – 985.  $\mu$  = dynamic viscosity ( $\text{Pa s}$ )  $d_{\text{cell}}$  = inner diameter of the Lewis cell (m)  $D$  = diffusivity ( $\text{m}^2 \text{s}^{-1}$ )  $d_{\text{rush}}$  = diameter of the Rushton turbine (m)  $\rho$  = solvent density ( $\text{kg m}^{-3}$ ).

$$Sh = 0.352 Re^{0.618} Sc^{0.434} \quad (6)$$

$$Re = \frac{\rho N_L d_{\text{rush}}^2}{\mu} \quad (7) \quad Sc = \frac{\mu}{\rho D} \quad (8) \quad Sh = \frac{k_L d_{\text{cell}}}{D} \quad (9)$$

The chemical reaction between  $\text{CO}_2$  and aqueous amines solutions are expressed by the followings global reaction equation:



The global reaction rate between CO<sub>2</sub> and blended MDEA/DEA can be expressed as:

$$r_{\text{CO}_2-\text{MDEA/DEA}} = k_{\text{MDEA/DEA}} [\text{CO}_2] [\text{MDEA/DEA}]_{30/20} \quad (12)$$

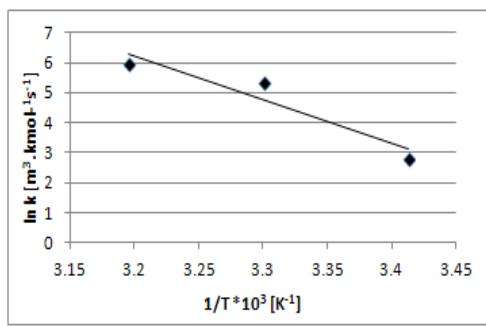
### 3. Results and Analysis

#### 3.1 Kinetics

CO<sub>2</sub> absorption experiments were carried out between 293 and 313 K for 2 different compositions. The MDEA concentration was either 20 or 30 wt% and the DEA concentration 20 wt%. The estimation of the Arrhenius law coefficients for the reaction constants was carried out considering experimental data at temperatures from 293 to 313 K. Experimental conditions for these data are presented in Table 1.

Table 1: Parameters of CO<sub>2</sub> Absorption by MDEA/DEA Solutions

T (K)	MDEA/DEA wt%	V <sub>G</sub> (cm <sup>3</sup> )	D 10 <sup>-10</sup> (m <sup>2</sup> s <sup>-1</sup> )	H <sub>CO<sub>2</sub></sub> (Pa.m <sup>3</sup> mol <sup>-1</sup> )	P <sub>T-P<sub>solv</sub></sub> (Pa)	k <sub>L</sub> 10 <sup>-6</sup> (m s <sup>-1</sup> )	E	E <sup>∞</sup>
293		214	2.46	3400.36	178237	3.59	26.0	220
303	20/20	210	5.02	4191.90	160710	7.27	38.2	400
313		217	5.99	5081.81	158766	8.53	71.2	7000
293		213	2.39	3590.41	249968	3.49	35.2	235
303	30/20	215	4.81	4415.86	236239	6.98	88.7	11400
313		216	5.38	5281.51	205543	7.65	115.9	19700



For all experiments the condition for the overall pseudo first-order reaction rate constants is satisfied. The Hatta numbers are all greater than 3 ( $E = \text{Hatta}$ ). Moreover, the enhancement factors for instantaneous reaction ( $E^\infty$ ) are an order higher than the values of  $E$ . The plot of  $\ln(k)$  is a function of  $1/T$  (Figure 3) and the slope coefficient of the regression line is equal to the rate  $k$  of the chemical reaction. CO<sub>2</sub> absorption by blended amines conforms to Arrhenius law in the range of experimental temperature as follows:

Figure 3: Arrhenius plot for k MDEA/DEA (30/20 wt%)

$$k_{\text{CO}_2-\text{MDEA30/DEA20}} = 1.0 \times 10^8 \exp\left(-\frac{3444}{T}\right) \quad (\text{m}^3 \text{kmol}^{-1} \text{s}^{-1}) \quad (13)$$

$$k_{\text{CO}_2-\text{MDEA20/DEA20}} = 1.5 \times 10^8 \exp\left(-\frac{3756}{T}\right) \quad (\text{m}^3 \text{kmol}^{-1} \text{s}^{-1}) \quad (14)$$

The absorption rates coefficient increases with temperature and decreases with the increasing of conversion (mol<sub>CO<sub>2</sub></sub>/mol<sub>amine</sub>) as in the case of Zhang et al., (2002). In this work DEA concentration is

constant, the absorption rate coefficient increase with the increasing of weight ratio of MDEA to DEA. The kinetics constant of blended MDEA/DEA is lower than the constant determined by Lin et al. (2009) who use higher temperatures for the experiments and the kinetics at 293 is not much faster due to viscosity of solution. Based on the results, we can infer that kinetics absorption of blended MDEA/DEA 30/20 is faster than kinetics absorption of blended MDEA/DEA 20/20.

### 3.2 Simulation

The absorption of CO<sub>2</sub> by blended MDEA-DEA and regeneration of the solution or CO<sub>2</sub> release was simulated with the software Aspen Plus TM V7.2. The flue gas studied coming from a Coal-Fired power plant (CF) is shown in Table 2. Figure 4 shows flowsheet of CO<sub>2</sub> capture by blended amines. The flue gas is compressed to 0.12 MPa and cooled to 313 K before to the entry column. CO<sub>2</sub> is washed by a countercurrent with the solvent. The rich solvent leaving the absorber is pumped to 0.2 MPa and sent to a heat exchanger where it is preheated by the regenerated solvent recovered at the bottom of the stripper. After regeneration, lean solvent is recycled to the absorber. The condenser at the top of the stripping column withdraws the bulk of water present in this stream by cooling. The CO<sub>2</sub> stream is compressed to 6.5 MPa in a compressor. Then it is dehydrated by a triethylene glycol process.

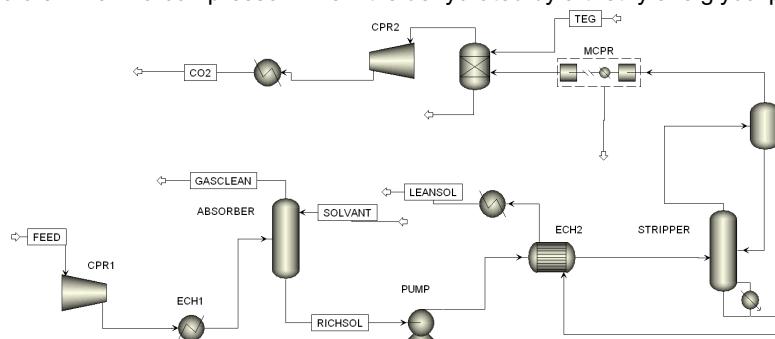


Figure 4: Flowsheet of CO<sub>2</sub> capture by blended amines

Table 2: Flue gases characteristics (CF)

Composition/% mol	Operating conditions		
H <sub>2</sub> O	5.55		
CO <sub>2</sub>	11.71	Flow/kmol.s <sup>-1</sup>	646
O <sub>2</sub>	6.69	Pressure/MPa	0.0913
N <sub>2</sub>	76.05	Temperature/K	369

The thermodynamic model used in this simulation, NRTL electrolyte, is dedicated to an aqueous solution and it is suited for electrolytic aqueous solutions. The kinetic reactions and the equilibrium were employed in the absorber. A sensitivity study was carried out on the number of the theoretical stages of the absorber and the stripper. This is done in order to minimize the solvent flow in the absorber and to minimize the heat duty in the reboiler. By setting a 90 % CO<sub>2</sub> recovery, the evolution of the solvent flow was analysed according to the number of stages. The energy consumption, which represents the heat duty per ton of recovered CO<sub>2</sub>, is given in Table 3 for all the solvents studied. The process using blended MDEA/DEA 30/20 seems to be the best solution. The energy consumption and solvent flow of MDEA/DEA 30/20 are lower than those of MDEA and DEA alone and blended MDEA20 %/DEA20 %. The rich CO<sub>2</sub> loading of DEA solvent is the highest compared to other solvents. For the process using MDEA30 %/DEA20 %, the best solution corresponds to a lean CO<sub>2</sub> loading of 0.08 mol CO<sub>2</sub> / mol MDEA-DEA. The energy consumption reaches 2.78 GJ/t CO<sub>2</sub>.

Table 3: Performance of solvents regarding energy consumption of the reboiler ( $\text{CO}_2$  recovery = 90 %)

Solvent	MDEA 50%	DEA 30%	MDEA20%/DEA20%	MDEA30%/DEA20%
Lean $\text{CO}_2$ loading $\text{mol}_{\text{solvent}}/\text{mol}_{\text{CO}_2}$	0.05	0.18	0.08	0.08
Solvent flow $\text{kmol.s}^{-1}$	119.89	135.55	127.51	113.79
Solvent flow $\text{kg.s}^{-1}$	3,818.63	3,338.79	3,504.31	3,650.12
Absorber trays	5	6	5	5
Stripper trays	8	10	8	8
Rich $\text{CO}_2$ loading $\text{mol}_{\text{solvent}}/\text{mol}_{\text{CO}_2}$	0.20	0.40	0.24	0.24
Energy consumption $\text{GJ.ton}_{\text{CO}_2}^{-1}$	3.39	3.46	3.27	<b>2.78</b>

#### 4. Conclusions

The aim of this study was to find the most favourable blend composition to capture  $\text{CO}_2$ .  $\text{CO}_2$  absorption rates into MDEA-DEA aqueous solutions are measured in a temperature ranged from 293 to 313 K. The kinetics of blended amines has been determined. Since DEA is very reactive with  $\text{CO}_2$ , it was proposed to use this amine as an activator for an aqueous MDEA solution. The addition of DEA leads to a significant enhancement of the absorption rates in comparison to an aqueous MDEA solution. Results show that kinetics absorption of blended MDEA/DEA 30/20 is faster than kinetics absorption of blended MDEA/DEA 20/20. Comparative flowsheet simulations for  $\text{CO}_2$  capture of flue gas for a coal-fired power plant show that blended amines lead to reduced solvent flow. Blended MDEA/DEA 30/20 solvent gives the lowest energy consumption of those of MDEA and DEA.

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