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## Influence of sulphuric acid on absorption kinetic of carbon dioxide in monoethanolamine

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### Abstract

The absorption of carbon dioxide into monoethanolamine (MEA) solution has been studied. A specific setup allowing controlling gas-liquid interface has been studied. It is based on a stirred reactor. This study presents the determination of physicochemical and kinetic parameters. Determination has been done for MEA solution with and without sulphuric acid. This acid will illustrate the accumulation of SO<sub>x</sub> present in the fumes of a typical industrial process.

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*Keywords:* Gas-liquid transfer; CO<sub>2</sub> capture kinetics

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### 1. Introduction

Carbon dioxide emission from human activities forms a major point of attraction for scientists in the world because it is considered as predominantly responsible for the global warming [1]. The soaring demand for energy caused by demographic changes and economic development through the world is the main source of CO<sub>2</sub> emission. A number of technologies have been tested to reduce or capture carbon dioxide emissions (Chemical absorption, physical absorption, cryogenic separation, membrane separation and biology fixation). Chemical solvent absorption is the most mature of them considering its reliability and competitiveness [2,3].

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## Nomenclature

[j]	Molar concentration of specie j ( $\text{mol.m}^{-3}$ )
A	Interfacial area ( $\text{m}^2$ )
D	Diffusivity ( $\text{m}^2.\text{s}^{-1}$ )
E	Enhancement factor
$E_i$	Instantaneous enhancement factor
Ha	Hatta number
$H_e$	Henry's constant ( $\text{Pa.m}^3.\text{mol}^{-1}$ )
k	Kinetic constant ( $\text{m}^3.\text{mol.s}^{-1}$ )
$k_G$	Mass transfer coefficient in the gas side ( $\text{mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ )
$k_L$	Mass transfer coefficient in the liquid side ( $\text{m.s}^{-1}$ )
$p_i$	Partial pressure of species i (Pa)
R	Ideal gas constant ( $8.3144 \text{ J.mol}^{-1}.\text{K}^{-1}$ )
T	Temperature (K or $^{\circ}\text{C}$ )
$V_L$	Liquid volume ( $\text{m}^3$ )
$V_g$	Gas volume ( $\text{m}^3$ )

## Subscripts

b	bulk
g	gas
i	Interface
l	liquid
w	Water

## Greek Symbols

$\phi$	Rate of absorption by volume's unity of reactor ( $\text{mol.m}^{-3}.\text{s}^{-1}$ )
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## Molecule

$\text{CO}_2$	Carbon dioxide
MEA	Monoethanolamine
$\text{N}_2\text{O}$	Nitrous oxide

Moreover, post combustion sources are characterized by high gas volume and low CO<sub>2</sub> concentration flue gas, and these characteristics are further espoused by the absorption/desorption process with chemical reaction.

The general absorption/desorption process flow diagram is shown on figure 1. The gas flue to be treated gets in the bottom of the absorption column. Then it progresses in contact with the solvent from the bottom to the top of the column. As upflow of gas whilst liquid trickles downward over the packing, the carbon dioxide transfers from the gas phase to the liquid phase and it reacts with the species present in the solvent. The treated gas flue goes out at the top of the column. For energy saving, the loading solvent passes through a heat exchanger before entering in the desorption column. At this point, the solvent is regenerated by heating and the carbon dioxide liberated is collected from the top of the desorption column.

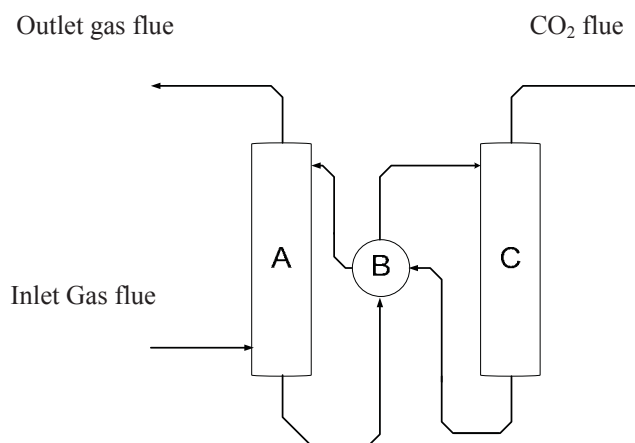


Fig. 1. Process flow diagram of an amine absorption process

(A: Absorption column; B: Heat exchanger; C: Desorption column)

This process has been extensively studied in order to optimize operating conditions, energy cost or estimating solvent degradation. In this work, we focused on transfer phenomena in the absorption column. We particularly study the influence of liquid composition along the column on absorption kinetic of carbon dioxide. Few factors drive the rate of absorption of CO<sub>2</sub> (mass transfer of the acid gas in the solvent and kinetic reaction) [4]. Many works have also been done around process modelling but most of time by considering homogeneous kinetic parameters on the absorption process. However, the absorption column is a place where composition of the liquid and gas phase are strongly modified.

Several kinds of solvents can be used to react with CO<sub>2</sub>. The first is monoethanolamine (MEA) [4–6] but other amines (DEA, AMP, etc.) [5], KOH or NaOH [6,7], ammonia [8,9] and mixed solvents [10,11] can be used. In this paper, we deal with the system MEA/CO<sub>2</sub>/H<sub>2</sub>O.

## 2. Experimental

### 2.1. Experimental Setup

Studying the absorption kinetics directly on a packed column can be driven but access to the exchange surface can be obtained by some empiric correlations. Then it is more powerful to achieve a specific setup allowing fixing the area by which mass transfer occurred.

In the literature, several measurement devices are reported for absorption kinetic's determination (Laminar liquid jet absorber [12,13], Wetted wall column [8,14], wetted sphere [15] and stirred reactor [16]). All of them permit to determine the constant kinetic by fixing exchange surface between gas and liquid phases. For the first three devices, both inlet and outlet of gas and liquid have to be measured. The residence time is short and allows considering homogeneous composition in each phases.

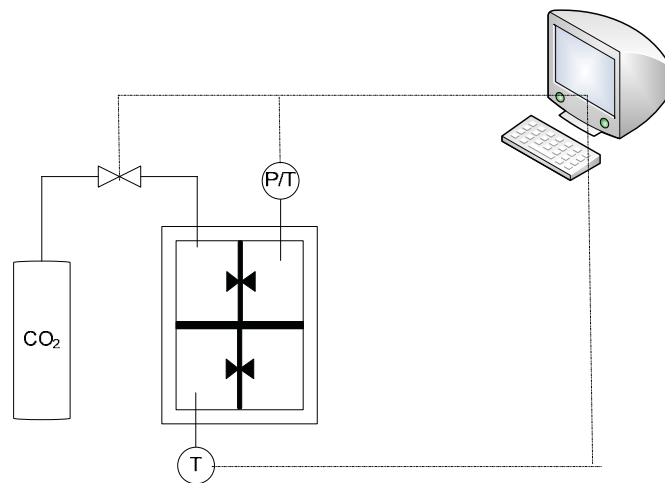


Fig. 2. Stirred reactor scheme (Lewis cell type)

Our setup is based on a stirred reactor (Fig. 2). (Volume: 1L and inner diameter: 80mm). The low part of the reactor is fulfilled with the liquid and the upper part contains the gas. It is composed of a cylindrical glass vessel. The system is equipped with a double jacket which permits to be in isothermal condition. Two turbines, one in the gas phase and another in the liquid phase, mix separately and independently the reactor. The reactor is equipped with temperature and pressure sensors. A gas reservoir with pressure sensor permits to control the injected amount. A pneumatic valve controls the inlet gas. This valve permits to do micro-injections of gas (10 kPa).

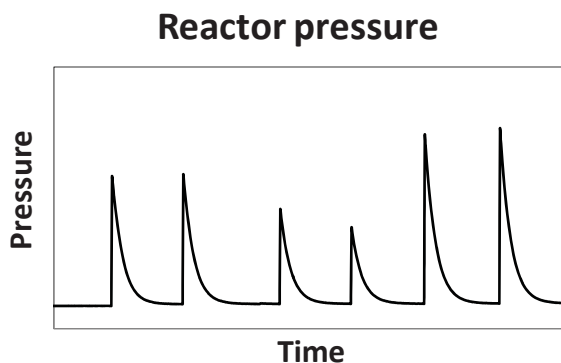


Fig. 3. Data from the reactor

The solvent is sucked up from the bottom into the reactor by the vacuum pump and the air is also removed. The experience is started after the stabilization of the pressure and the temperature in the reactor. Carbon dioxide is injected into the reactor automatically when the pressure and temperature are stabilized.

In these experimental conditions, we can consider that the small amount of absorbed carbon dioxide does not modify the chemical composition of the liquid. Liquid can also be considering homogeneous and with constant physical properties during a single injection. FigureFig. 3 shows a typical behaviour of the reactor pressure during the experimental procedure with several injections. The experiences are stopped when the solutions are saturated by the gas.

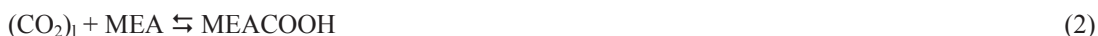
## 2.2. Chemicals

All solvents are prepared with deionised water, MEA from Fisher chemical (>99% purity) and sulphuric acid from Fischer chemical (>95%). The dioxide carbon was purchased from Air Liquid (>99.9% vol. purity).

## 3. CO<sub>2</sub> absorption in MEA solution

### 3.1. Chemical mechanism

The reactions 1-3 describe the CO<sub>2</sub> absorption into MEA solution. The reaction 1 corresponds to the mass transfer. The reaction 2-3 is the chemical reactions.



### 3.2. Mass transfer equation

The global flux of CO<sub>2</sub> transferred between the gas and the liquid can be defined considering the driving force caused by the difference of concentration between the bulk (b) of the liquid and the interface (i).

$$\varphi = Ek_L A ([CO_2]_l^i - [CO_2]_l^b) \quad \text{or} \quad (4)$$

The Henry's law is used to determine the concentration of CO<sub>2</sub> at the interface from the pressure in the gas phase. The kinetics constant would then be estimated by monitoring the pressure inside the reactor.

$$\varphi = Ek_L A \left( \frac{p_i}{He} - [CO_2]_l^b \right) \quad (5)$$

Using ideal gas law, the partial pressure of dioxide carbon can be expressed in concentration.

$$[CO_2]_l^i = \frac{p_i}{He} = \frac{[CO_2]_g RT}{He} \quad (6)$$

With sufficient agitation in the reactor, the absorption is driven by kinetic of reaction. After a single injection, the composition of the solution remains unchanged thanks to the micro-injection of the gas. Then we can consider a pseudo 1st order for this reaction. In this case, the Hatta number can be use in condition if this number is superior to 3 and inferior to E<sub>i</sub>/2 (E<sub>i</sub>: instantaneous enhancement factor).

$$Ha = \frac{\sqrt{k[MEA]D_{CO_2}}}{k_L} \quad (7)$$

Then the global flux in case of the chemical absorption in pseudo 1st order is defined by:

$$\varphi = A \sqrt{k_1[MEA]D_{CO_2}} \left( \frac{[CO_2]_g RT}{He} - [CO_2]_l^b \right) \quad (8)$$

Following Kucka's method [16], the equation (9) has been used to represent the absorption of CO<sub>2</sub> into a basic solvent. This equation assumed that the absorption of CO<sub>2</sub> is in pseudo 1st order.

$$\frac{d[CO_2]_g}{dt} = - \frac{A \sqrt{k_1[MEA]D_{CO_2}}}{V_g} \left( \frac{[CO_2]_g RT}{He} - [CO_2]_l^b \right) \quad (9)$$

The CO<sub>2</sub> diffusivity and Henry 'constant of CO<sub>2</sub> in the solution are determined by analogy with nitrous oxide (N<sub>2</sub>O) .[17,18]

$$D_{CO_2/s} = D_{N_2O/s} \left( \frac{D_{CO_2}}{D_{N_2O}} \right)_w \quad He_{CO_2/s} = He_{N_2O/s} \left( \frac{He_{CO_2}}{He_{N_2O}} \right)_w \quad (10)$$

#### 4. Results and discussion

Firstly, the experiences are done in MEA solution 30%wt. at difference temperature. That permits to observe the influence of the temperature and the solution loading on the absorption profile. The figure Fig. 4 shows the absorption profile of CO<sub>2</sub> in MEA 30%wt. solution at different loading. With increasing the loading, the slope of the curve is lower. The slope of the curve depends on the concentration of MEA like it is written in the equation 9.

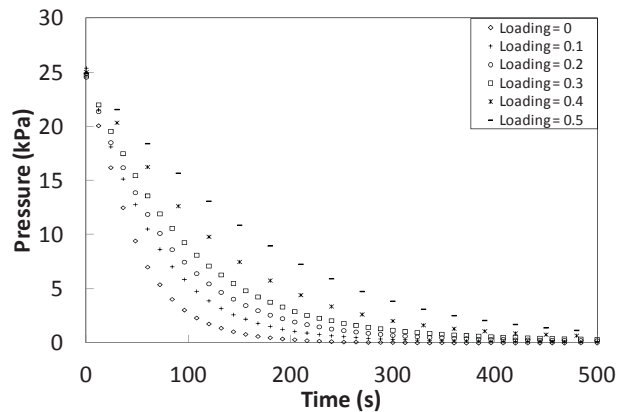


Fig. 4. Absorption of CO<sub>2</sub> in 30% MEA solution in stirred reactor (loading= mole of CO<sub>2</sub>/mole of base)

By fitting experimental point with the model, we can determine the kinetic constant which is the only unknown parameter in our equations.

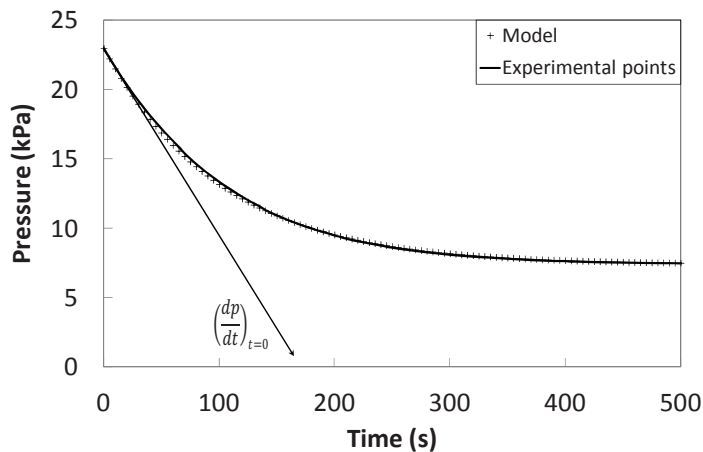


Fig. 5. Absorption profile between experimental data and the model



The figure 5 shows that we obtained a good agreement between experimental and modelling pressure.

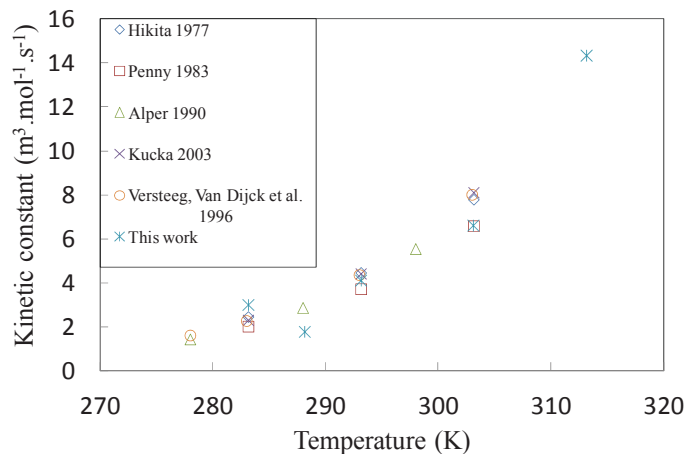


Fig. 6. Kinetic constant between MEA and dioxide carbon in the literature [16,19–21]

All estimated constant are in the figure 6 and compared with the literature. The estimated kinetic constant is coherent with the literature. The hypotheses (homogenous in the liquid, pseudo first order) in the model are correct. To be more convenient, in results presentation, we will estimate the kinetic at the beginning of the absorption. To achieve this, we will plot the derivative of the pressure at  $t=0$  for each absorption profile. Figure 7 and 8 are built considering the gradient at the origin.

The figure 7 presents the results from experiences realized with MEA 30%wt. solutions at the different temperatures. For a low mole  $\text{CO}_2$  injected, the gradient is high when the temperature increases. For the same concentration of MEA, the absorption profile depends on the kinetic constant (eq. 9) which depends itself on the temperature following the Arrhenius's law. With an increase of the temperature, the kinetic constant increases too. So that's why the gradient at the origin of the curve increases with the temperature. Moreover, whatever the temperature, the absorption's rate decreases with saturation of the liquid by carbon dioxide.

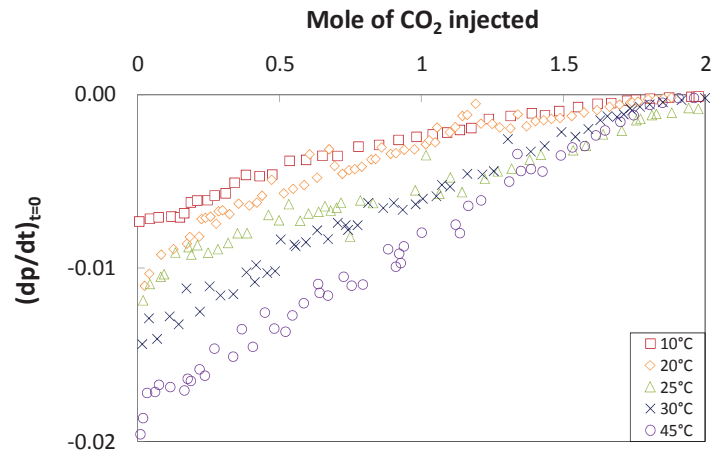


Fig. 7. Gradient at the origin of pressure for MEA 30% at different temperature

Below, are presented the results from experiences realized in presence of sulphuric acid at 25°C. The sulphuric acid is the product from the reaction between water and  $\text{SO}_x$  which is present in the industrial fumes.

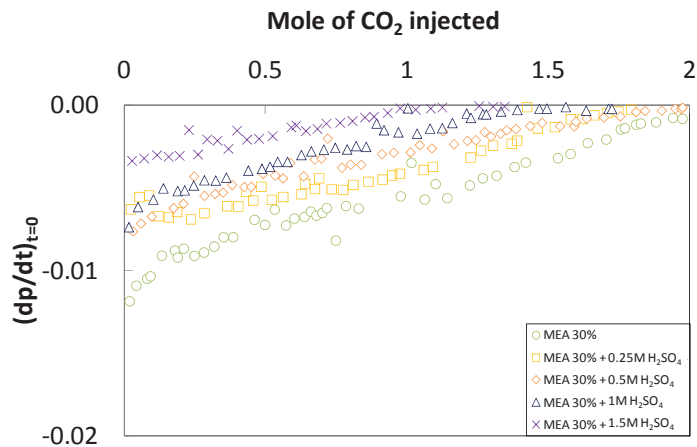


Fig. 8. Gradient at the origin of pressure for MEA 30% with different concentrations of acid sulphuric at 25°C

The figure 8 shows clearly that sulphuric acid adding to the MEA solution has a strong influence on initial kinetic behaviour. First, increasing sulphuric acid concentration leads to a decrease of the kinetic.

Second, presence of sulphuric acid leads to a quicker saturation of the solution by carbon dioxide. (Example: 1.5M H<sub>2</sub>SO<sub>4</sub>, saturation occurs with 1 mol of CO<sub>2</sub>). From a chemical point of view, sulphuric acid causes a neutralization of MEA. Each molecule blocks 2 molecules of MEA as explain in equation 11.



## 5. Conclusion

The absorption of CO<sub>2</sub> is done with several solutions of MEA with and without sulphuric acid. Using the comparison of the gradient at the origin for each absorption profile, we observed the influence of temperature, loading solution and the concentration of sulphuric acid on the gradient at the origin for each absorption profile.

Following Kucka's method, the kinetic constant is determined the absorption of CO<sub>2</sub> into 30%wt. solution of MEA. For this method, an analogy between N<sub>2</sub>O and CO<sub>2</sub> is used to determine CO<sub>2</sub> diffusivity and Henry's constant for the liquid phase. Those parameters are determined for N<sub>2</sub>O in several alkanolamine solutions without CO<sub>2</sub>. In the literature, the ionic strength influences these parameters with negative effect. [22–24] Going further, the ionic strength and other pollutants will be study to determine their influences on the physicochemical parameters.

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