

## ABSORPTION RATES OF CO<sub>2</sub> INTO SOLUTIONS OF MEA/2-PROPANOL

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### Abstract

Effective interfacial mass transfer area is a parameter of great importance in evaluating and determining the efficiency of separation column internals. A viable chemical method identified for determining this parameter is the reactive absorption of CO<sub>2</sub> into solutions of primary amines. The experiments were conducted on a wetted wall experimental set-up, which was verified with data obtained from a previous study. The absolute and specific absorption rates of CO<sub>2</sub> into solutions of MEA/2-propanol as functions of surface area and column height at various CO<sub>2</sub> and MEA concentrations and system pressures were determined. The specific absorption rate expression proposed by the previous study<sup>4</sup> is insufficient in predicting the absorption rates at higher CO<sub>2</sub> gas concentrations and it is recommended that a non-linear rate expression derived from fundamental kinetics should be developed.

**Key Words:** Reactive absorption, mono-ethanolamine (MEA), specific absorption rate, effective interfacial mass transfer area, wetted wall.

### 1. Introduction

In distillation and other thermal separation techniques, the separation efficiency of a gas-liquid contactor is strongly dependant on the effective interfacial mass transfer area achieved on the column internals. A need therefore exists to develop methods for determining effective interfacial mass transfer area to assist in the design of more efficient column internals. One such method is the reactive absorption of CO<sub>2</sub> with primary amines. In this study the absorption rates of CO<sub>2</sub> into solutions of MEA with 2-propanol as solvent were investigated. The reason for investigating this system is to link the data to a parallel study which is aimed at determining the reaction kinetics of CO<sub>2</sub> and MEA in 2-propanol<sup>2</sup>. The integration of the absorption and reaction kinetic data should provide sufficient information to aid in the design of a method to determine effective interfacial mass transfer area of column internals. The aim of this study is to determine the specific absorption rates of high CO<sub>2</sub> gas concentrations into solutions of MEA/2-propanol to see how the data correlates with the parallel reaction kinetic study. Specifically, this study aims to determine if the absorption rates show the same non-linear trends noticed in the kinetic study. The development of the method to determine effective interfacial mass transfer area should be based on absorption data at low CO<sub>2</sub> concentrations<sup>1</sup> to eliminate liquid side mass transfer limitations. The low concentration study will therefore only be addressed in a follow-up study.

### 2. Theory

The effective interfacial mass transfer area for various types of separation column internals is currently being estimated by means of empirical correlations applicable only to the type of packing material it was derived for. A fundamentally determined absorption rate expression would provide the foundation for deriving expressions of more general use in determining the effective interfacial mass transfer area on various types of packing material. The derivation of such a fundamental expression would start off with a mass balance performed on a short length of packing material. The absolute absorption rate,  $n_{CO_2}$ , is measured from the amount of CO<sub>2</sub> absorbed for a certain gas – liquid contact time on a known absorption surface area. Since the absorption area is known, the specific absorption rate may be calculated from:

$$N_{CO_2} = \frac{n_{CO_2}}{a_{\text{Wetted Wall}}} \quad (1)$$

The specific absorption rate may be expressed in the form of a reaction rate expression as a function of species concentration. The absolute absorption rate through the height of the packing material may be expressed as the height integral of the specific absorption rate. Separating the variables, integrating across the height of the packing material and rearranging the result yields the following expression for determining the effective interfacial mass transfer area:

$$a_e = \frac{n_{\text{CO}_2}}{A_s \int_{z=0}^{z=h} N_{\text{CO}_2} dz} \quad (2)$$

Equation 2 shows that the specific absorption rate has to be determined as a function of column height.

### 3. Experimental

In order to be able to determine the effective interfacial mass transfer area, the absorption rate per unit area of the absorbing gas must be determined and modelled as a rate expression function. This is achieved by performing absorption experimental runs on a gas-liquid contactor of known surface area. The experiments were conducted on a wetted wall set-up, as illustrated in Figure 1.

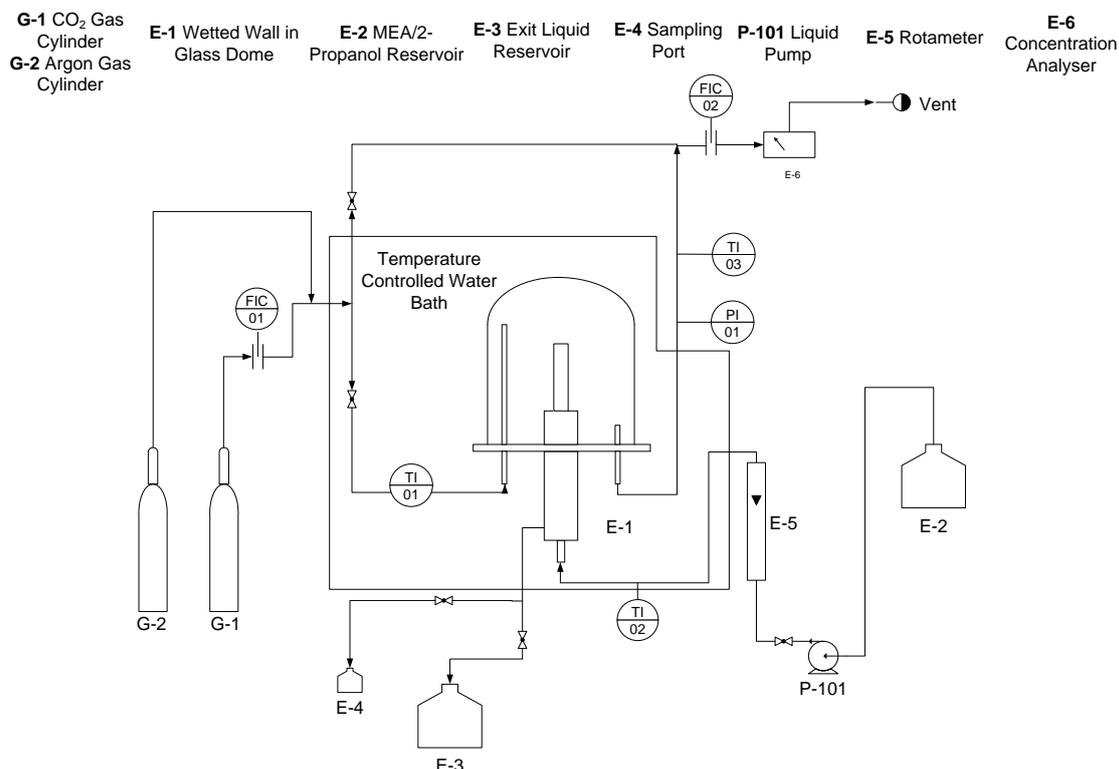


Figure 1. P&ID of the Wetted Wall Experimental Set-up

The CO<sub>2</sub> and argon gas cylinders supply gas at their specified flow rate to the dome of the wetted wall set-up. The CO<sub>2</sub> flow rate entering the dome is set at various inlet flow rates by the inlet mass flow controller (MFC) (FIC 01) whilst the argon flow was varied to achieve the desired inlet CO<sub>2</sub> mass% at the same total gas outlet flow rate before each experimental run. This total outlet flow rate before absorption was calculated to ensure that the dome pressure is near 1 atm and is consistent for each experimental run. From the change in the exit gas flow meter (FIC 02) reading during absorption, together with the assumption of argon being negligibly soluble in the liquid mixture the quantity of CO<sub>2</sub> absorbed can be determined. The mass flow controllers were calibrated for pure CO<sub>2</sub> and argon as well as a mixture of these two gases. The MEA/2-propanol mixture is pumped from its reservoir to the wetted wall where it is distributed evenly over the circumference of the cylindrical wetted wall, allowing

the gas to absorb into a known surface area. The loaded liquid exits the bottom of the wetted wall set-up and is collected in a reservoir. A sample is drawn and analysed for MEA concentration via standard acid titration with diluted HCl using Congo Red as indicator. To ensure that isothermal conditions prevail, the whole set-up is submerged in a temperature controlled water bath with the gas and liquid lines passing through a pre-heater before entering the set-up.

Validation of the set-up was done by performing experiments at similar conditions to a previous study<sup>3</sup>. This study then proceeded to determine the absolute and specific absorption rates at CO<sub>2</sub> mass percentages of 100%, 78%, 55% and 30% into solutions with MEA concentrations of 0.25, 0.3 and 1 mol/L at temperatures of 25°C and 30°C. The wetted wall was designed to facilitate absorption studies at various column heights. The studies were conducted at column heights of 60, 90 and 105 mm.

#### 4. Results and Discussion

The effects of different MEA concentrations at 30°C and various CO<sub>2</sub> concentrations were evaluated and are illustrated in Figure 2. From Figure 2 it is seen that the specific rate of absorption increases with an increase in both CO<sub>2</sub> mass percentage and MEA concentration. The increase in absorption rate due to an increase in CO<sub>2</sub> concentration may be attributed to the greater driving force for gas absorption at higher CO<sub>2</sub> concentrations in the gas side boundary layer. The increase in absorption rate at higher MEA concentrations may be attributed to the increase in the reaction rate within the liquid which is in accordance with the reaction kinetics of the reaction of CO<sub>2</sub> with MEA<sup>2</sup>.

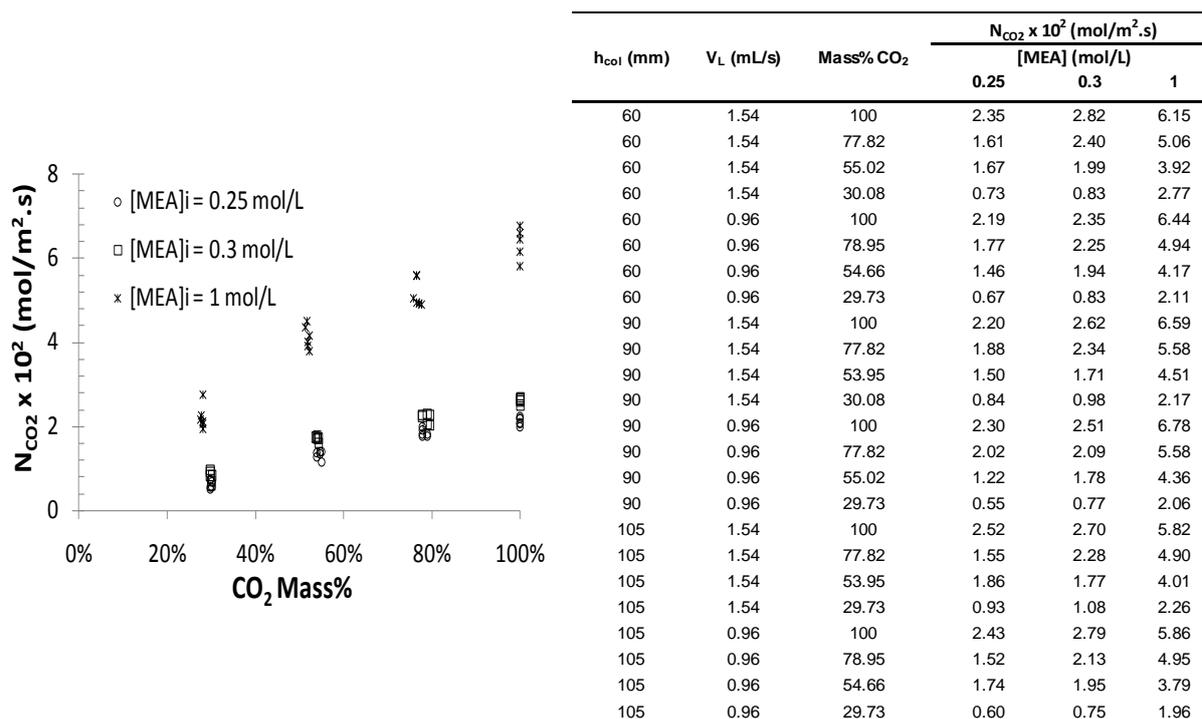


Figure 2. MEA concentration effect on the specific absorption rate at P = 104.3 kPa

The effect of MEA concentration on the reaction rate was investigated in a parallel study and the results are illustrated in Figure 3. CO<sub>2</sub> and MEA were dissolved in their respective 2-propanol reservoirs and the mixtures pumped to a small CSTR. The reaction was stopped at the exit stream of the CSTR by scavenging the unreacted MEA with an excess amount of benzoyl chloride to form an amide precipitate which was analysed with high performance/pressure liquid chromatography (HPLC). The unreacted CO<sub>2</sub> was evaporate off and was collected in a series of CaOH traps to form CaCO<sub>3</sub> precipitate. This was repeated for different reagent flow rates to vary the residence time within the reactor and allowing the construction of a concentration-residence time profile for both CO<sub>2</sub> and MEA. From the concentration profiles it was possible to calculate conversion and reaction rate (Figure 3)

profiles as well. Figure 2 indicates a non-linear increase in the difference in specific absorption rate with an increase in the MEA concentration. This is an expected result and is reflected in Figure 3, which shows that the reaction rate in the liquid phase increases with an increase in reagent initial concentration<sup>3</sup>. The effect of temperature on the specific absorption rate is illustrated in Figure 4.

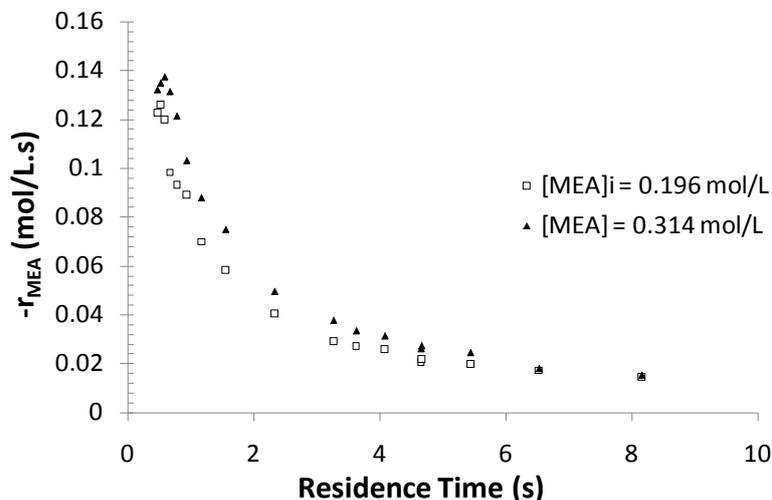


Figure 3. Effect of MEA concentration on MEA reaction rate at 30°C<sup>3</sup>

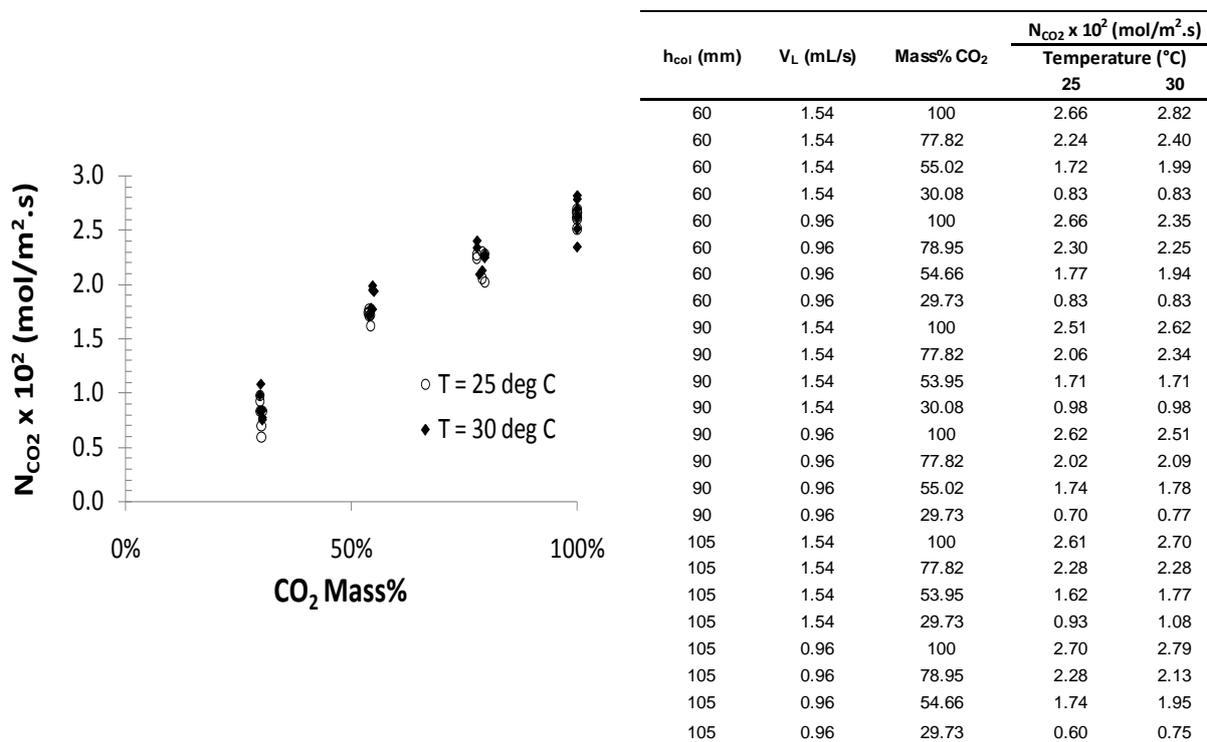
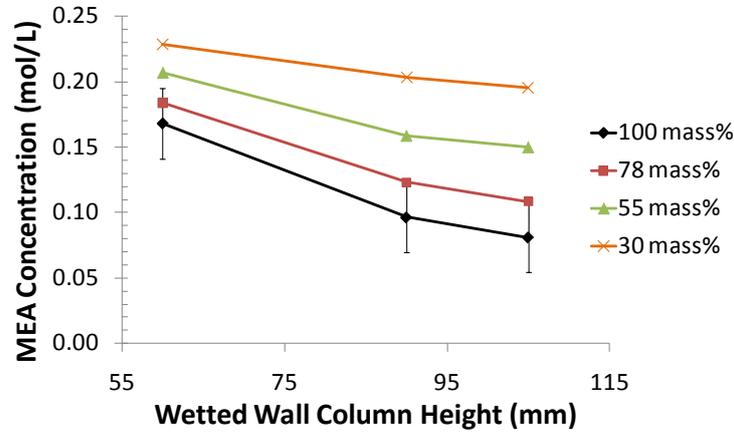


Figure 4. Temperature effect on the specific absorption rate at P = 104.3 kPa

From Figure 4 it can be seen that at constant pressure a change in temperature has no significant effect on the specific rate of absorption. There is however the dual effect of solubility and the rate of reaction to consider when the effect of temperature is evaluated: An increase in temperature leads to a decrease in CO<sub>2</sub> solubility which decreases the specific absorption rate. On the other hand, an

increase in temperature results in an increase in the liquid phase reaction rate<sup>2</sup> as well as the diffusivity of CO<sub>2</sub> in the liquid, which in turn results in an increase in the specific rate of absorption. The true temperature effect may become clear when a wider temperature range is considered, which will form part of future investigations. The effect of column height on the measured MEA concentration is illustrated in Figure 5.



**Figure 5.** MEA measured concentration as a function of column height at P = 104.3 kPa

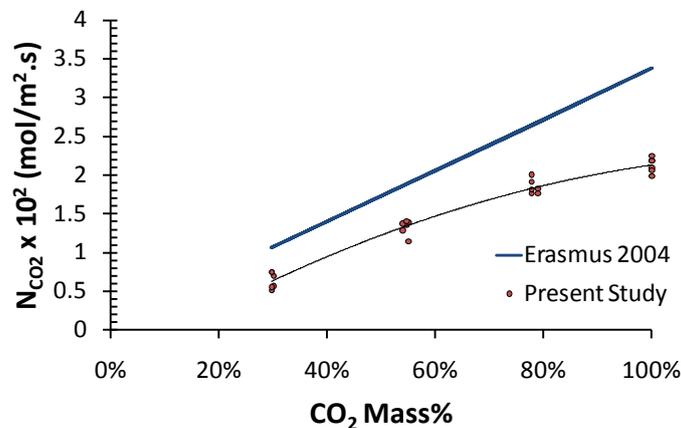
From Figure 5 the expected decrease in MEA concentration with an increase in column height can be seen. The type of non-linear decline in the MEA concentrations is not obvious from Figure 5 but it may be concluded that a linear concentration profile, which is often assumed for solving equation 2, is also not observed. A more accurate method of MEA analysis will be investigated in future. Erasmus<sup>4</sup> proposed a correlation for the specific absorption rate that takes the contribution of the CO<sub>2</sub> to the system pressure into account. The correlation is valid at low CO<sub>2</sub> partial pressures and is expressed as follows:

$$N_{\text{CO}_2} = k \cdot p_{\text{CO}_2}^{0.9} \cdot C_{\text{MEA}}^{0.93} \quad (3)$$

With  $k$  being temperature dependent according to the following expression:

$$k = -3.818 \times 10^{-6} \cdot T + 2.985 \times 10^{-3} \quad (4)$$

A comparison of equation 3 and the specific absorption data at 25 °C and initial MEA concentration of 0.25 mol/L is illustrated in Figure 6.



**Figure 6.** Evaluation of Equation 4 at 25 °C and initial MEA concentration of 0.25 mol/L 104.3 kPa

From Figure 6 it can be seen that equation 3 over-predicts the experimentally determined specific absorption rates at higher CO<sub>2</sub> mass% considerably. This may be attributed to the difference in CO<sub>2</sub> solubility for the different solvents used. The same trend is noticed throughout with an increase in the over prediction as the MEA concentration increases. The increase in overprediction is an indication that equation 3 is limited to the concentration ranges used by Erasmus. It is further noticeable from Figure 6 that equation 3 does not follow the non-linear trend in the data. This may be because equation 3 was derived at low CO<sub>2</sub> mass% where the absorption rate is near linear. This study is not an evaluation of equation 3, but an investigation on how it predicts absorption rates at higher CO<sub>2</sub> mass%. However, from Figure 6 it may be concluded that an alternative expression should be derived to model these absorption rates.

## 5. Conclusions and Recommendations

A fully functional wetted wall set-up was designed, constructed and implemented. Experimental measurements on the reactive absorption of CO<sub>2</sub> into a MEA/2-propanol solution at high CO<sub>2</sub> concentrations were investigated to observe the effect of higher CO<sub>2</sub> concentrations on its specific absorption. It was found that an increase in MEA concentration resulted in an increase in the absorption rate. Additionally, it was found that the effect of temperature is linked to the solubility of CO<sub>2</sub> in the solution. An increase in temperature results in an increase in the absorption rate of CO<sub>2</sub> due to an increase in its liquid side diffusivity, but since an increase in temperature results in a decrease in the solubility the net result is that it seems that temperature has no significant effect. It was further found that the absorption rate of CO<sub>2</sub> increases non-linearly with an increase in column height. The elementary absorption rate expression of equation 3 was found to be insufficient at predicting absorption rates at higher CO<sub>2</sub> gas side concentrations. This, along with the fact that non-linear concentration profiles as a function of column height exist, results in a recommendation that a non-elementary specific absorption rate expression should be explored for determining effective interfacial mass transfer area of separation column internals.

## Nomenclature

$A_s$	Cross sectional area of column (m <sup>2</sup> )
$a_e$	Effective mass transfer area (m <sup>2</sup> /m <sup>3</sup> )
$C$	Concentration (mol/L)
$k_i$	Rate Constant (Reaction order dependent)
$N_i$	Specific absorption rate (mol/s.m <sup>2</sup> )
$n_i$	Absolute absorption rate (mol/s)
$p_i$	Partial pressure (Pa)
$z$	Directional unit vector (height)

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## References

1. J.C. Charpentier, *Mass Transfer Rates in Gas-Liquid Absorbers*, Advances in Chemical Engineering, Vol. 11 Academic Press, New York (1981).
2. L.J Du Preez, C.E. Schwarz; J.H. Knoetze, *Evaluating reaction rate expressions for CO<sub>2</sub> and MEA in 2-Propanol*, Presentation at the 8<sup>th</sup> World Congress of Chemical Engineering, Montreal, Canada, 23-27 August 2009.
3. L.J. Du Preez, *The Reactive Absorption of CO<sub>2</sub> into Solutions of MEA/2-Propanol*, M.Sc dissertation in Chemical Engineering, University of Stellenbosch, South Africa (2010).
4. A.B. Erasmus, *Mass Transfer in Structured Packing*, Ph.D dissertation in Chemical Engineering, University of Stellenbosch, South Africa (2004).
5. G.E.H. Joosten and P.V. Danckwerts, *Chem. Eng. Sci.*, 28, (1972) 453.
6. J. Tokunaga, *J. Chem. and Eng. Data*, 20, (1975) 41.