

Development of a New Experimental Tool to Identify CO₂ Absorption Parameters in Aqueous Amine Solutions

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ABSTRACT

This work deals with the development of an original experimental method to identify the kinetic parameters of the carbon dioxide (CO₂) absorption in aqueous amine solutions. This absorption is studied in a Hele-Shaw cell and small refractive index variations of the liquid phase, correlated to the concentration variations, are observed in the vicinity of the gas-liquid interface, using a digital holographic Mach-Zehnder interferometer. First, experiments are performed with aqueous solutions of monoethanolamine (MEA), which is used as a reference case. The deduced parameters are in agreement with the values found in the literature. Secondly, the same procedure is applied to study the CO₂ absorption in an amine mixture provided by Cansolv.

Keywords: CO₂ capture, amine, gas-liquid absorption, reaction, interferometry

1 INTRODUCTION

The gas-liquid carbon dioxide (CO₂) absorption by aqueous solutions of amine mixture is one of the up-to-date CO₂ capture technology. This work deals with the development of an original experimental method to identify the kinetic parameters of the CO₂ absorption in aqueous amine solutions. It is realized in collaboration with Cansolv Technologies Inc., which is a design office specialized in CO₂ capture technologies by amine solutions.

The solvents developed by Cansolv consist in various mixtures of several amines. A lot of amine mixtures have to be tested in order to identify the best one, which combines a fast reaction rate with the CO₂, a high absorption capacity, a high stability and a low energetic regeneration cost. Therefore, an accurate estimation of the kinetic gas-liquid CO₂ absorption parameter is required to select the best amine mixture and to design the gas-liquid reactors.

The procedure presented in this paper is used in the case of the CO₂ absorption in monoethanolamine (MEA) aqueous solution. MEA is used as a reference case to validate the developed procedure.

2 MATERIALS AND METHOD

The MEA is noted RNH₂, where R corresponds to OH-CH₂-CH₂-. When CO₂ is absorbed by an aqueous solution of MEA, several chemical reactions take place in the liquid phase [1,2,3]. The set of chemical reactions can be simplified by these two following chemical reactions [1,4]:



During the gas-liquid CO₂ absorption, the chemical reactions induce small refractive index variations of the liquid phase take place in the vicinity of the gas-liquid interface. These refractive index variations are correlated with the concentration variations.

2.1 Experimental setup

The absorption of a pure CO₂ gaseous phase in an aqueous MEA solution is realized in a Hele-Shaw cell and the refractive index variations are visualized using a Mach-Zehnder interferometer.

Experiments are realized at room temperature. An aqueous solution of MEA fills the bottom part of a 500 μm gap between two glass plates (5 X 10 cm) and forms a horizontal free surface. A CO₂ gas flow with a pressure of 1 bar is forced to flow along this interface.

The Hele-Shaw cell is set in the Mach-Zehnder interferometer as shown in Figure 1. The He-Ne laser beam is expanded and cleaned using a spatial filter, towards a first beamsplitter, which splits it into a reference beam and an object beam. The reference beam passes through the ambient air while the object beam passes through the test cell. Finally, the two beams are recombined by a second beamsplitter and imaged on a CCD camera.

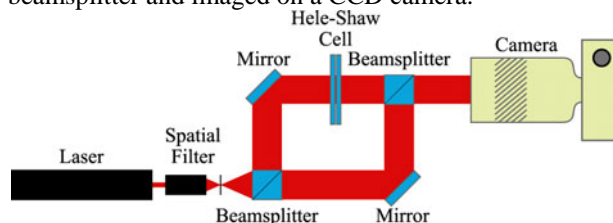


Figure 1: Schematic view of the Mach-Zehnder interferometer.

As the optical paths of the two beams are different, there is a phase difference between the two beams. Therefore, an image presenting interference fringes (called interferogram) is observed. The second mirror is set in order to get a linear phase difference in the horizontal direction. In this case, vertical interference fringes are observed in the interferogram.

Each interferogram has 1024 X 1024 pixels. The calibration of the image size is performed using a Ronchi Ruling by the procedure described by Dehaeck [5]. It is estimated that the observation window size is 4mm X 4mm.

The refractive index variations depend on the transfer time and the distance from the interface. Therefore, the optical path the object beam passing through the liquid is modified by the local time evolution of the refractive index. At the scale of the interferogram, the refractive index variations during the absorption lead to a time and space evolution of the fringe positions, which are called fringe bendings.

An image processing program, developed by Dehaeck et al. [6], is used to compute the refractive index variations from fringe bending in the interferograms. Refractive index variation fields are then obtained at different times. By averaging each field below the interface in the horizontal direction, the experimental refractive index variation profiles can be obtained (refractive index variations versus the distance from the interface).

Each experiment is performed during 10 s and 30 interferograms per second are recorded. After 10 s of CO₂ transfer, chemo-hydrodynamic instabilities appear and the results cannot be compared to the diffusion-reaction model.

2.2 Calibration

In order to correlate the dissolved CO₂ amount with the refractive index variations, calibration curves are determined. Several solutions with various MEA concentrations and various dissolved CO₂ concentrations are prepared. The refractive index of each solution is then measured using an Abbe refractometer.

The refractive index variation is related to the variations of RNH₂ and RNHCOO⁻ concentrations. It is expressed by the following relation [4]:

$$\Delta n = \frac{\partial n}{\partial [\text{RNH}_2]} \Delta [\text{RNH}_2] + \frac{\partial n}{\partial [\text{RNHCOO}^-]} \Delta [\text{RNHCOO}^-] \quad (3)$$

The experimental measures of the refractive index are plotted versus the RNH₂ concentration and versus the transferred CO₂ in Figures 2 and 3, respectively.

The partial derivatives in Eq. (3) are estimated by a linear regression of the experimental measurements, as presented in Figures 2 and 3. The following values are identified: $\frac{\partial n}{\partial [\text{RNH}_2]} = 0.006$ and $\frac{\partial n}{\partial [\text{RNHCOO}^-]} = 0.0134$.

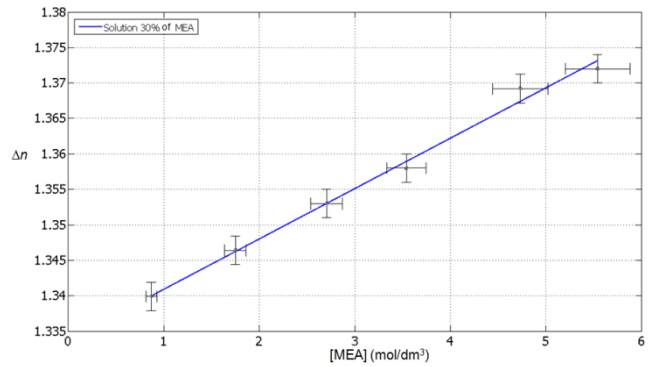


Figure 2: Measured refractive index versus the MEA concentration

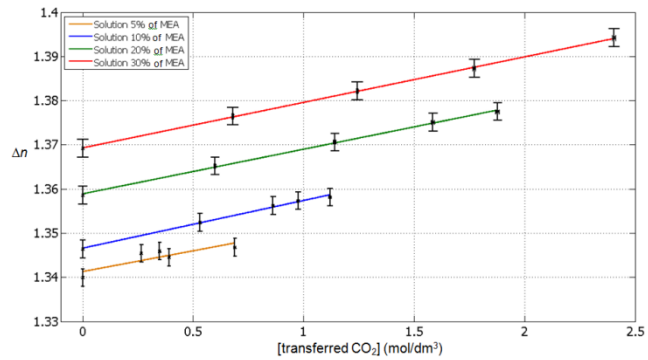


Figure 3: Measured refractive index versus the transferred CO₂ for several initial MEA concentrations.

2.3 Reaction-diffusion model and simulation

During the CO₂ absorption, it is observed that the fringes bend but remain parallel. It means that the liquid refractive index variations are homogeneous in the horizontal direction. A front of refractive index variations penetrates following the vertical direction. It can be assumed that the concentration gradients are significant only in the direction perpendicular to the gas-liquid interface. Therefore, the evolution of the observed boundary layer can be modeled by a one-dimensional (1-D) transient equation system.

Let x be the vertical axis, perpendicular to the interface and pointing towards the liquid phase. x corresponds to the depth in the liquid from the interface. Let t be the time.

As the liquid phase is stationary, the diffusion is the only mass transfer mechanism. This diffusion process is coupled with chemical reactions in the liquid phase, induced by the CO₂ absorption. Let r_1 and r_2 be the reaction rate of the reaction (1) and (2), respectively. They are calculated by:

$$r_1 = k_1 [\text{CO}_2] [\text{RNH}_2] \quad (4)$$

$$r_2 = k_2 [\text{RNHCOO}^-] - k_{-2} [\text{RNH}_2] [\text{HCO}_3^-] \quad (5)$$

where k denotes the kinetic constants.

The 1-D transport-reaction equations are obtained from mass balances of each reacting species in the liquid phase on a 1-D infinitesimal element of liquid. They writes:

$$\frac{\partial[\text{CO}_2]}{\partial t} = D_{\text{CO}_2} \frac{\partial^2[\text{CO}_2]}{\partial x^2} - r_1 \quad (6)$$

$$\frac{\partial[\text{RNH}_2]}{\partial t} = D_{\text{RNH}_2} \frac{\partial^2[\text{RNH}_2]}{\partial x^2} - 2r_1 + r_2 \quad (7)$$

$$\frac{\partial[\text{RNH}_3^+]}{\partial t} = D_{\text{RNH}_3^+} \frac{\partial^2[\text{RNH}_3^+]}{\partial x^2} + r_1 \quad (8)$$

$$\frac{\partial[\text{RNHCOO}^-]}{\partial t} = D_{\text{RNHCOO}^-} \frac{\partial^2[\text{RNHCOO}^-]}{\partial x^2} + r_1 - r_2 \quad (9)$$

$$\frac{\partial[\text{HCO}_3^-]}{\partial t} = D_{\text{HCO}_3^-} \frac{\partial^2[\text{HCO}_3^-]}{\partial x^2} + r_2 \quad (10)$$

where D_A corresponds to the diffusion coefficient of the species A.

At the initial state ($t=0$), the concentrations are assumed to be homogeneous and at equilibrium.

At the interface position ($x=0$), the CO_2 concentration is assumed to be at equilibrium with the gaseous phase:

$$[\text{CO}_2](x = 0, t) = h_{\text{CO}_2} p_{\text{CO}_2} \quad (11)$$

where p_{CO_2} is the CO_2 pressure in the gaseous phase and h_{CO_2} is the Henry coefficient. As the other species do not pass through the interface, their flux is assumed to be zero.

Far from the interface (for $x \rightarrow \infty$), the concentration of all the species is assumed to be homogeneous, therefore their flux is zero.

The values of all the parameters can be estimated using correlations found in the literature [2,7,8,9,10,11].

The Partial Differential Equation (PDE) system is solved numerically by a finite element method, using the COMSOL Multiphysics software. This resolution allows getting the concentration profiles (concentration versus the distance x from the interface) at all time for each species.

These concentration profiles can be converted into refractive index variations profiles using Eq. (3) and the parameters identified in the section 2.2 .

2.4 Parameter estimation procedure

The proposed device and procedure are used to estimate some physico-chemical parameters of the model from the experimentally observed refractive index variation profiles, in order to validate the procedure. Before realizing the parametric estimation, a sensitivity analysis of the simulated refractive index variation profiles is performed in order to determine the most sensitive parameters. The most sensitive parameters are D_{RNH_2} , k_1 and h_{CO_2} .

These parameters are estimated using a non-linear quadratic fitting method [12]. This method estimates the values of the parameters which minimize the differences between the simulated refractive index variation profiles and the experimental ones.

Let $\Delta n_{\text{exp}}(t_j, x_i)$ be the experimental refractive index variation at the time t_j and at the distance x_i from the interface. For a set of parameters P, let $\Delta n_{\text{sim}}(t_j, x_i, P)$ be the simulated refractive index variation computed at this time t_j at this position x_i . The cost function C_F is defined as the sum of the squares of the differences between the experimental and the simulated density variation for each x_i and t_j . It is expressed as follows:

$$C_F = \sum_j \sum_i (\Delta n_{\text{exp}}(t_j, x_i) - \Delta n_{\text{sim}}(t_j, x_i, P))^2 \quad (12)$$

The set of parameters which minimize the values of the cost function are the fitted parameters. This minimization is achieved using the *fminsearch* routine in a COMSOL script of COMSOL Multiphysics. Starting from initial guesses of the parameters, the script computes the concentration profiles, converts them into density variation profiles and compute the cost function. The *fminsearch* routine changes iteratively the values of the parameters in order to decrease the value of the cost function, until it minimizes the cost function.

3 RESULTS AND DISCUSSION

The developed procedure is applied for an aqueous solution containing 30% in mass of MEA and 6% of initially dissolved CO_2 . The results of the parametric estimation of D_{RNH_2} , k_1 and h_{CO_2} are presented in Table 1. Moreover, the fitted values of these parameters are compared to the values calculated with the correlation of the literature. It is observed the fitted values are close from the correlation value.

When the refractive index variation profiles are computed with the fitted parameters values and are compared to the experimental refractive index variation profiles, a good agreement is observed for all cases. An example of such a comparison, with fitted parameters, is presented in Figure 4.

These results show the ability of the procedure presented in this paper to estimate physico-chemical parameters of the mass transfer.

Parameters	Fitted value	Correlation value
D_{RNH_2} [m ² /s]	$5.63 \cdot 10^{-10}$	$8.56 \cdot 10^{-10}$ [2]
k_1 [m ³ /mol s]	8.33	5.91 [1]
h_{CO_2} [mol/m ³ Pa]	$5.865 \cdot 10^{-4}$	$5.874 \cdot 10^{-4}$ [7]

Table 1: Fitted values of the parameters evaluated by the parametric estimation and comparison with the values estimated with the correlation of the literature.

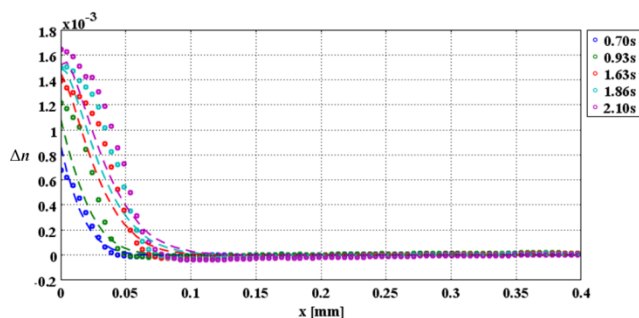


Figure 4 : Comparison of the experimental (dashed lines) and the simulated (points) refractive index variation profiles with the fitted values of the parameters.

4 CONCLUSION

This paper presents a new experimental procedure to estimate experimentally physico-chemical parameters of gas-liquid CO₂ absorption coupled with chemical reactions in aqueous amine solutions. This procedure is applied with MEA solutions as a reference case.

This absorption is realized in a Hele-Shaw cell and induces refractive index variations in the liquid phase below the interface. These refractive index variations are correlated with the concentration variations in the liquid caused by the CO₂ absorption.

By comparing the experimental refractive index variation profiles with simulated ones, thanks to a reaction-diffusion model and calibration, the most sensitive physico-chemical parameters can be estimated using a non-linear quadratic fitting method.

The simulated refractive index variation profiles, using the fitted parameter values, agree quite well with the experimental ones. Moreover, the fitted parameter values are in agreement with the values estimated using literature correlation.

As the developed procedure seems to be operational for the CO₂ absorption in MEA aqueous solutions with a weak load in CO₂, this procedure will be applied to study the gas-liquid CO₂ absorption parameters in solvents provided by Cansolv.

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