



Contents lists available at ScienceDirect

## Journal of the Taiwan Institute of Chemical Engineers

journal homepage: [www.elsevier.com/locate/jtice](http://www.elsevier.com/locate/jtice)

## Carbon dioxide capture with tertiary amines. Absorption rate and reaction mechanism

Alicia García-Abuín<sup>a</sup>, Diego Gómez-Díaz<sup>a,\*</sup>, José M. Navaza<sup>a</sup>, Antonio Rumbó<sup>b</sup><sup>a</sup>Departamento de Enxeñaría Química, ETSE- Universidade de Santiago de Compostela, Santiago de Compostela, Galicia, Spain<sup>b</sup>Departamento de Química Orgánica, Facultad de Ciencias, Universidade de Santiago de Compostela, Lugo, Galicia, Spain

## ARTICLE INFO

## Article history:

Received 30 January 2017

Revised 11 May 2017

Accepted 13 July 2017

Available online xxx

## Keywords:

Carbon dioxide capture

Absorption

NMR

Bubble column

Carbamate

Bicarbonate

## ABSTRACT

Present work analyzes the overall carbon dioxide chemical absorption process using tertiary amines in aqueous solution, taking into account absorption rate experimental data and  $^{13}\text{C}$  and  $^1\text{H}$  nuclear magnetic resonance. These studies try to detect the causes because different behaviors are obtained for absorption curves at different carbon dioxide loadings. The combined use of these techniques allows to evaluate the weight of different variables (chemical kinetics, mechanism, hydrodynamics, etc) upon the absorption overall process.

© 2017 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

## 1. Introduction

The emission of large amounts of carbon dioxide to the atmosphere, as it is well known, is causing important changes in Earth's carbon cycle due mainly to human activities and it is a crucial problem in industrial processes. For this reason a worldwide aim is developing research work focused on carbon dioxide capture processes [1,2], storage strategies [3,4] and utilization [5,6] using different techniques and procedures. The optimization and development of industrial processes based on the use of new chemical solvents is one of the most important research fields that allow a higher selectivity on separation/capture operations increasing the removal capacities.

Nowadays research strategies are mainly centered on carbon dioxide separation by means of gas-liquid chemical absorption to reach the intensification of the separation by choosing a suitable solvent [7,8]. Solvents based on amino groups are still being considered the best available technique (BAT) for carbon dioxide absorption. The choice of the chemical solvent to carry out carbon dioxide separation has been centered on the use of linear, and in the last years, sterically hindered amines (SHA) [9–11] because the last type of compounds shows certain advantages over conventional non-SHA solvents which show high absorption rate but

lower carbon dioxide loadings [12–15]. In our laboratories we have proved that the use of tertiary amines at industrial scale presents the advantages associated to SHA-based solvents and overcome the negative behaviors [16]. Tertiary amines allow to reach higher amounts of carbon dioxide captured due to a suitable reaction stoichiometry [12,17] as SHA solvents though they present generally a low reaction rate in comparison with primary and secondary amines [18]. This low reaction rate could be associated to a higher liquid phase viscosity that decreases mass transfer rate [19].

On the other hand tertiary amines solvents have shown a clear decrease in the associated cost to regeneration [20] because the amount of energy to carry out this process is lower than conventional solvents and degradation is also clearly reduced. Both effects redound to a decrease in the energy penalty in solvent regeneration by stripping that is consider the highest cost in the overall carbon dioxide separation process [21].

On the basis of conclusions reached in previous studies [22] analyzing gas-liquid absorption experiments and reaction mechanism by nuclear magnetic resonance [16], it is possible to conclude that triethanolamine (TEA) aqueous solutions chemically absorbs carbon dioxide by a different reaction mechanism than the other compounds of the same family (monoethanolamine, MEA or diethanolamine, DEA), based on the presence or absence of carbamate. In this work we have proposed the study of reaction pathway of carbon dioxide chemical absorption using four different solvents based on: methyldiethanolamine, dimethylethanolamine, diethylethanolamine and triisopropanolamine.

\* Corresponding author.

E-mail address: [diego.gomez@usc.es](mailto:diego.gomez@usc.es) (D. Gómez-Díaz).

## 2. Experimental section

Gas phase was CO<sub>2</sub> (99.998% purity) supplied by Carburos Metálicos and this gas was used to feed the gas-liquid bubbling reactor. Methyldiethanolamine (MDEA, dimethylethanolamine (DMEA), diethylethanolamine (DEEA) and triisopropanolamine (TIPA) were purchased from Sigma-Aldrich with a purity of  $\geq 99\%$ ,  $99\%$ ,  $\geq 98\%$  and  $95\%$ , respectively. Aqueous solutions of these amines were prepared on mass with double distilled water.

Carbon dioxide chemical absorption studies have been carried out using a square bubble column reactor similar to other employed in previous work [16]. Carbon dioxide gas stream was put in contact with water till saturate the gas phase, and then to remove the influence of water transfer from the liquid phase to the gas one in the reactor. The inlet and outlet gas flow-rate were controlled and measured with two mass flow controllers (Alicat Scientific MC-5SLMP-D). The mass flow controllers were calibrated for the used gas flow-rate and pressure ranges by the supplier. The pressure drop was measured between the column inlet and outlet, using a Testo 512 digital manometer. The working regime was continuous in relation to the gas phase and batch regarding the absorbent liquid.

<sup>1</sup>H and <sup>13</sup>C NMR spectroscopies were applied to investigate the reaction mechanism of carbon dioxide chemical absorption in aqueous solutions of these tertiary amines. The MestReC 4.7 software developed by Mestrelab Research was used for spectra processing. Spectra were acquired on 300 MHz Varian Mercury spectrometers. Amine solution samples were taken from the middle zone of reactor system. The samples were diluted in deuterated water and they were subjected to studies using as internal reference D<sub>2</sub>O resonance (4.80 ppm) for <sup>1</sup>H NMR. Tetradeuterate methanol (CD<sub>3</sub>OD) was used as internal reference in <sup>13</sup>C NMR. The quantitative <sup>13</sup>C NMR spectra were performed using a relaxation delay of 5 times.

## 3. Results and discussion

The main aim of present work is focused on the analysis of reaction pathway during the chemical absorption of carbon dioxide in aqueous solutions of tertiary amines, and the influence of this kind of mechanism upon the gas-liquid absorption behavior. The first study carried out is shown in Fig. 1 that corresponds to carbon dioxide absorption rate ( $F_A$ ) using different solvents based on several tertiary amines under the same experimental conditions. The experimental data included in Fig. 1 shows differences in the absorption rate using different chemical solvents. The solvent with the lowest absorption rate is aqueous solutions of TIPA. On the other hand the DEEA-based solvent shows the highest absorption rate of carbon dioxide. The overall obtained sequence for carbon dioxide absorption rate is TIPA < DMEA < MDEA < DEEA. In the last few years our research team has studied the reaction mechanism between carbon dioxide and amines aqueous solutions by using nuclear magnetic resonance (NMR). The use of this kind of technique allows the study of absorption rate and mechanism along experiment time analyzing the type of species present in the liquid phase. This kind of studies has been performed in present work using aqueous solutions of tertiary amines (TEA, DMEA, DEEA, MDEA y TIPA).

The preliminary speciation study using NMR corresponding to TEA aqueous solutions has been performed in a previous work [16] reaching the conclusion that the only reaction products present during all the experiments were the equilibria of bicarbonate/carbonate and amine/protonated amine ( $\text{TEA} + \text{H}^+ \rightarrow \text{TEAH}^+$ ). The experimental data corresponding to <sup>13</sup>C NMR spectra allows to observe the previous indicated equilibrium but also a signal corresponding to bicarbonate/carbonate equilibrium. Taking into

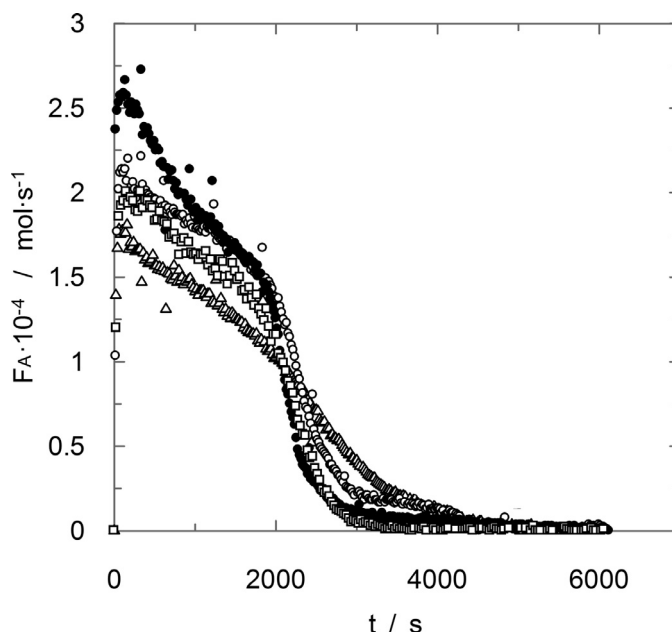


Fig. 1. Carbon dioxide absorption kinetics using different tertiary amines. (□) MDEA, (Δ) TIPA, (○) DMEA, (●) DEEA.  $Q_G = 30 \text{ L/h}$ ,  $C_B = 0.4 \text{ mol/L}$ .

account these conclusions, the <sup>13</sup>C NMR spectra contribute more information and this technique was used to be employed in this part of the work.

The first study performed in this work using the tertiary amines was dimethylaminoethanol (DMEA) (Fig. 2). At the beginning of the experiment the <sup>13</sup>C NMR shows three signals that correspond to the carbons of the pure amine. In this spectrum the signal with a chemical shift of 45.5 ppm corresponds to the methyl groups ( $\text{CH}_3$ )<sub>2</sub>N-. At 60.1 ppm appears the signal of methylene carbon at alpha position regards nitrogen -CH<sub>2</sub>N-, and the last signal corresponds to the methylene carbon of the alcohol group (-CH<sub>2</sub>OH). When the chemical absorption takes place in the liquid phase, at carbon dioxide loading of 0.16 mol CO<sub>2</sub>·mol amine<sup>-1</sup>, a new signal is observed at low field that corresponds to the equilibrium between bicarbonate ion and carbonate ion (164.9 ppm). An increasing of carbon dioxide loading with experiment time is observed and this signal moves to lower values of chemical shift reaching a value of 161.3 ppm. This fact is due to the acidification of the liquid phase due to the consumption of amine producing protonated amine by the chemical absorption of carbon dioxide. Associated to the amine-protonated amine equilibrium is observed the displacement of signals of pure amine previously commented reaching at the end of the experiment the next values: -CH<sub>2</sub>OH (59.7 ppm), -CH<sub>2</sub>N- (56.3 ppm) and ( $\text{CH}_3$ )<sub>2</sub>N- (43.7 ppm).

The same experimental procedure has been used to analyze the behavior of aqueous solutions of diethylethanolamine (DEEA). These spectra are shown in Fig. 3. The first spectrum shows the signals corresponding to pure DEEA with four peaks of each type of carbon: CH<sub>3</sub>- (11.0 ppm), CH<sub>3</sub>CH<sub>2</sub>N- (47.6 ppm), HOCH<sub>2</sub>CH<sub>2</sub>N- (54.1 ppm) and HOCH<sub>2</sub>CH<sub>2</sub>N- (50.7 ppm). In the same way, similar than DMEA aqueous solution, at early times (5 min -  $\alpha = 0.21 \text{ mol CO}_2 \cdot \text{mol amine}^{-1}$ ) the chemical reaction between DEEA and carbon dioxide causes the presence of a new signal at 166.6 ppm that corresponds to bicarbonate-carbonate ions equilibrium. This signal appears at a lower field than the first spectrum using DMEA solvent and it is due to the higher basicity of DEEA. The higher value of the chemical shift of this signal indicates a larger amount of carbonate ion in the liquid medium and this signal moves to lower values of chemical shift during the chemical absorption due to the

Download English Version:

<https://daneshyari.com/en/article/7105166>

Download Persian Version:

<https://daneshyari.com/article/7105166>

[Daneshyari.com](https://daneshyari.com)