



Characterization of MIPA and DIPA aqueous solutions in relation to absorption, speciation and degradation



A.B. López^b, M.D. La Rubia^{b,*}, J.M. Navaza^a, R. Pacheco^b, D. Gómez-Díaz^a

^a PF&PT Research Team, Department of Chemical Engineering, ETSE, University of Santiago de Compostela, Santiago de Compostela, Galicia, Spain

^b Bioprocesos Research Team, Department of Chemical, Environmental and Materials Engineering, EPS, University of Jaén, Jaén, Andalucía, Spain

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ABSTRACT

The carbon dioxide absorption process by 1-amino-2-propanol (MIPA) and bis(2-hydroxypropyl)amine (DIPA) aqueous solutions in bubble column reactor have been studied considering the influence of liquid phase physical properties and the amine group substitution on the overall process. The main objective of this work was to establish the carbon dioxide capture reaction mechanism for these systems, and then to obtain the predominant stoichiometry to calculate the mass transfer coefficient. NMR technique was used to determine the species present in the liquid phase during the absorption process and to confirm the reaction mechanism. The degradation of these amines was also evaluated.

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1. Introduction

The development of more efficient processes for carbon dioxide capture has been the aim of an important number of research projects and studies in the last years. These studies have been focused on different premises, mainly on the use and development of new solvents [1–3] or the mixture of commonly used substances for carbon dioxide separation such as amines [4,5]. There is no consensus about the possibility of substituting the best available technique, which is the use of monoethanolamine as solvent, by blends of other amines.

On the one hand, in comparison with the use of single amines, these systems have been proven to be efficient by several studies where an enhancement in the absorption rate, as well as, an increase in carbon loading, were observed [6]. On the other hand some research teams observed an increase in carbon dioxide loading probably caused by a more favorable reaction mechanism in relation with the stoichiometry but no enhancement of absorption rate was detected [7].

In any case, the use of amine blends is not the most suitable alternative for carbon dioxide capture and only certain blends have shown positive results [8,9]. While some systems show an

increase in carbon dioxide loading despite of an improvement in mass transfer rate is not observed, others system are not better than single amine solutions [10]. Furthermore, even though the absorption process is enhanced; the regeneration process has worse behavior than the best available technique. In general the effect of amine blend upon absorption kinetics is not well-established nowadays [8].

The regeneration step is a necessary process accomplished with the absorption process. In chemical absorption the regeneration process involves the use of high temperatures which is necessary in order to produce the reversible reaction. The liquid phase for capturing carbon dioxide needs a suitable thermal stability to avoid its degradation which could be caused by oxidative or thermal processes [11]. A high degradation rate implies the use of higher amine solutions make-up flow-rates, increasing the operation costs and environmental impact.

The aim of this work is to study the use of new amines for carbon dioxide capture by chemical absorption, by means of the analysis of mass transfer rate, reaction mechanism, stoichiometry and degradation kinetics. These substances allow analyzing the influence of the substitution degree in the nitrogen atom. Also, studies performed in this work allow evaluating the suitability of these solvents for carbon dioxide capture at an industrial level. At the same time degradation studies of these amines aqueous solutions have been also included, in order to analyze the overall process.

* Corresponding author. Tel.: +34 953212920.

E-mail address: mdrubia@ujaen.es (M.D. La Rubia).

2. Experimental

2.1. Materials

Commercial grade CO₂ of 99.998% purity, supplied by Carbueros Metálicos, was used as gas phase in present work to be fed to bubble column contactor. 1-amino-2-propanol (MIPA) and bis(2-hydroxypropyl)amine (DIPA) were supplied by Merck ($\geq 98\%$ purity) and Sigma-Aldrich ($\geq 98\%$ purity), respectively. Aqueous solutions of these amines were prepared by mass with double distilled water.

2.2. Absorption studies

These experiments were performed in an experimental set-up used in previous studies [12] which is shown in Fig. 1. The gas–liquid contactor was a square bubble column absorber with an internal side length of 4 cm and a height of 65 cm. The reactor was made in polymethylmethacrylate and the liquid phase volume was 0.9 L. The carbon dioxide stream was humidified and then fed to the gas–liquid contactor from the bottom of the bubble reactor using a five-hole sparger. The inlet and outlet gas flow-rate were measured and controlled with mass flow controller (Alicat Scientific MC-5SLMP-D), calibrated for carbon dioxide streams by the supplier. The gas flow-rates employed were within the interval 18 to 40 L h⁻¹. The amine concentrations in the liquid phase used in absorption experiments were 2.5, 5, 7.5 and 10 mass%. All the experiments were performed at room temperature (medium temperature = 23 °C).

2.3. NMR studies

¹H and ¹³C NMR spectroscopies were applied to investigate qualitatively the MIPA and DIPA aqueous solutions loaded with carbon dioxide in the capture process by chemical absorption. The MestReC 4.7 software developed by MestreLab Research was used for spectra processing. Spectra were acquired on 300 MHz Varian Mercury spectroscope. The samples of amine solution were taken from the middle zone of the bubble column reactor.

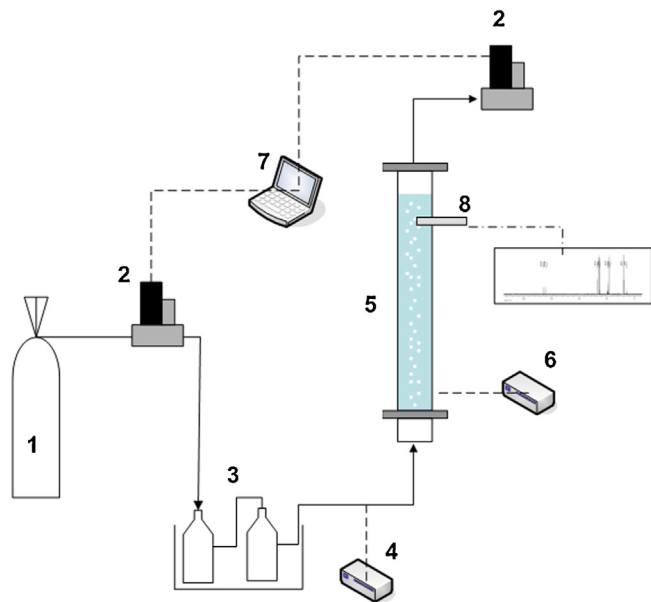


Fig. 1. Experimental set-up employed in absorption experiments. (1) Carbon dioxide cylinder; (2) mass flowmeter/controller; (3) humidifier and thermostatic bath; (4) pressure gauge; (5) square bubble column reactor; (6) thermometer; (7) flow data recorder; (8) sample port for NMR studies.

Tetradecuterated methanol (CD₃OD) (TMS) was used as internal reference for the processing of ¹³C NMR spectra.

2.4. Degradation studies

Amine degradation studies were performed to check if these compounds are suitable for carbon dioxide separation in industrial processes. For this reason amine aqueous solutions have been maintained at boiling temperature in glass vessels connected to a condenser to avoid solvent evaporation. A magnetic stirrer with heating (Selecta Agimatic-N) was used to maintain the amine aqueous solutions in the same experimental conditions along time. Samples were taken from the vessel through a septum to analyze the influence of time upon amine concentration.

A HPLC unit (Varian 920-LC) equipped with a refractive index detector (RID) and a Varian IonoSpher C column was used to quantify each component. The liquid sample was fed by an automatic liquid sampler to decrease the uncertainty. Reagent grade potassium dihydrogen phosphate was used to prepare 0.05 kmol m⁻³ HPLC mobile phase solution. Also, 85% (w/w) phosphoric acid was used to adjust the pH of the mobile phase to 2.6. Mobile phases were degassed before their use in the HPLC analysis. The column was controlled isothermally at 303 K. The isocratic mode of 100% mobile phase at the flow rate of 1 ml min⁻¹ was used throughout to perform the analysis. The refractive index detector was used to detect MIPA and DIPA peaks. The optical unit was set at 303 K and operated in the positive mode.

Calibration curves of MIPA and DIPA were used to determine amines concentration in all degraded samples using concentrations ranging from 0 to 20% weight percentage. Each calibration point was repeated three times to ensure reproducibility. Amine peak areas in all samples were obtained using the same HPLC technique and calibration curves.

3. Results and discussion

The experimental studies about carbon dioxide absorption in MIPA and DIPA aqueous solutions were based on the quantification of carbon dioxide absorbed along time until reach the equilibrium (solubility). Fig. 2 shows an example of experimental data corresponding to absorbed molar flow-rate in DIPA aqueous solutions using different amine concentrations. This figure shows that absorption rate decreases monotonically from the beginning of the experiment until reaches the saturation. The experimental

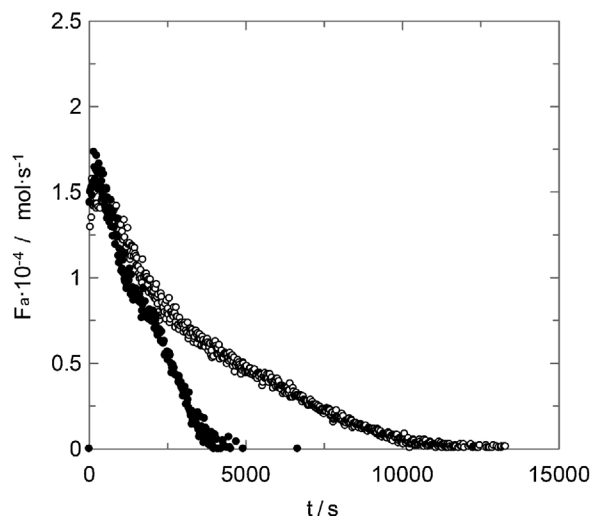


Fig. 2. Effect of amine concentration upon absorption rate for DIPA aqueous solutions. (○) C_{DIPA} = 10%. (●) C_{DIPA} = 5%. Q_g = 18 L h⁻¹.

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