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Influence of organic co-solvents upon carbon dioxide chemical absorption

Diego Gómez-Díaz*, Marta López, José M. Navaza, Lucas Villarquide

Departamento de Enxeñaría Química, ETSE, Universidade de Santiago de Compostela, Santiago de Compostela, E-15782, Spain

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ABSTRACT

Present research work analyzes carbon dioxide chemical absorption using different types of alkanolamines (primary, secondary and tertiary) with the presence of several organic co-solvents. These additional substances have been considered as interesting additives in previous works that can produce improvements upon the overall carbon dioxide separation process. On the basis of this hypothesis, this research analyses the influence of these solvents upon the absorption process using two parameters: absorption rate and carbon dioxide loading. Two different types of co-solvents have been tested analyzing the effect of their concentration in the liquid phase. Also the influence of these substances upon the reaction mechanism has been studied.

1. Introduction

Different mass transfer operations can be employed to separate gaseous components such as carbon dioxide. Some examples are gas-liquid absorption (physical or chemical) [1], gas-solid adsorption [2] and ceramic or polymeric membranes [3,4]. Though adsorption processes using specific solids have increased their importance in the last few years, gas-liquid absorption is still the widely used operation at industrial level. This kind of operations are commonly used in chemical industries and, in several cases, this contact is useful to produce chemical reactions between molecules from different phases. Bubbling contactors/reactors (such as columns, stirred vessels or air-lift contactors) have a wide range of uses in different types of industries (chemical, biochemical and pharmaceutical) [5], because this kind of contactors provide a suitable contact between involving phases, allowing chemical/biochemical reactions under several operation conditions. Besides, the simple construction, low operating cost and high-energy efficiency are interesting characteristics of this kind of equipments. Mass transfer rate in bubbling reactors is influenced by the physico-chemical properties of phases and equipment geometry. Also the available gas-liquid interfacial area for mass transfer can play an important role in the global absorption process [6,7]. This mass transfer operation has been the aim of different researchers in order to improve it avoiding certain negative aspects: (i) high energy requirements, (ii) solvent degradation and (iii) equipment corrosion [8,9].

The main part of these negative characteristics is involved in the solvent regeneration step that consists of a stripping column. This operation is carried out at high temperature that favors undesirable behaviors that affects upon absorption process (decreasing its efficiency) and increasing the cost of the process. Trying to avoid or decrease these negative characteristics in carbon dioxide gas-liquid absorption process, several research studies have been carried out in the last years centered on the solvent regeneration process. In one hand the configuration of stripping operation has been optimized in order to reduce the operation cost also attending to dynamic behavior [10]. On the other hand, the development of other regeneration operations has been carried out. Some examples are the use of electrodialysis [11] or ultrasounds [12] to reduce the cost of the solvent regeneration avoiding degradation. Also the use of precipitation and ion exchange operations [13,14] have shown a suitable behavior to remove reaction products and regenerate the chemical solvent.

The improvement of solvent regeneration operation can be reached by a change in the type and characteristics of the solvent. The modification of solvent generally consists of a change in the type of amine that chemically reacts with the absorbed carbon dioxide. These changes have been mainly based on the use of tertiary or sterically hindered amines [15,16]. The expected improvements by using other amines or the addition of certain substances are centered on the development of solvents with a lower heat capacity, heat of vaporization and/or binding energy [17]. Also a high cyclic capacity is desirable [18]. Some examples of

* Corresponding author.
E-mail address: diego.gomez@usc.es (D. Gómez-Díaz).

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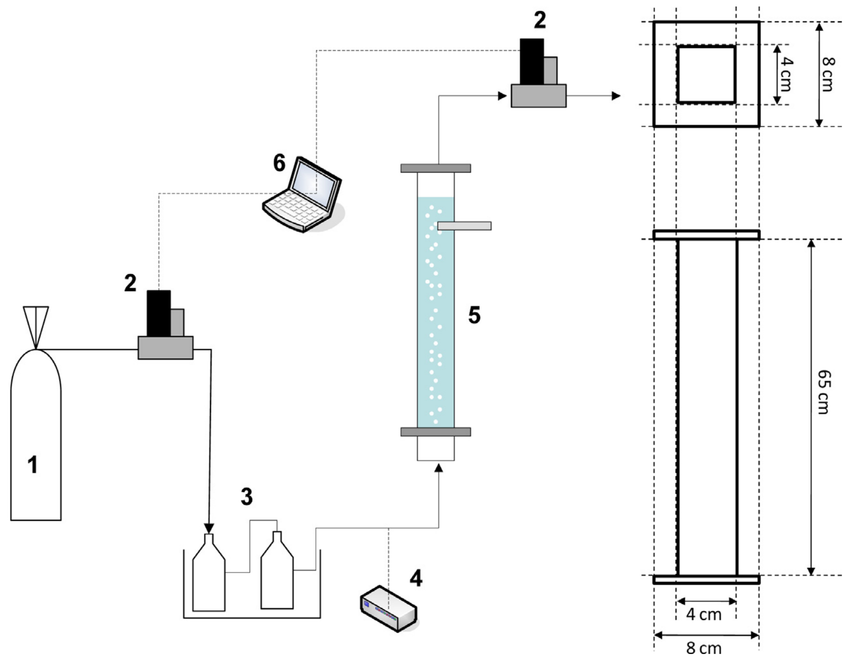

Fig. 1. Experimental set-up and bubble column geometrical characteristics. (1) CO_2 cyclinder, (2) mass flow-meters, (3) humidifier bath, (4) pressure gauge, (5) bubble column reactor, (6) experimental data recorder.

modified solvents suggested by previous studies are mainly based on the use of methanol or ethanol as organic co-solvent [19,20]. Also ethylene glycol has been employed [21].

Taking into account that the use of an organic co-solvent in commonly used chemical solvents for carbon dioxide separation (mainly based on the use of alkanolamines in aqueous solution) has been considered as an interesting option to improve the overall behavior [22] of this operation avoiding the negative characteristics, present work has been centered on a deep analysis about the influence of different amounts of some co-solvents upon absorption rate and carbon dioxide loading in several alkanolamines aqueous solutions.

Table 1
Variables analyzed in present work.

Amine type	Amine concentration (M)	Co-solvent type	Co-solvent concentration (%)	Gas flow-rate ($L{\cdot}min^{-1}$)
None	0.3	Ethanol	0	0.5
MEA			10	
DEA		Ethylene glycol	30	
TEA			50	

2. Materials and methods

2.1. Materials

The gas phase used to feed bubbling contactor was carbon dioxide supplied by Praxair with a purity of 99.99%. Aqueous solutions of three alkanolamines were used al solvents. Monoethanolamine, diethanolamine and triethanolamine were supplied by Sigma-Aldrich with purities higher than 99%. Two organic co-solvents have been employed to modify the chemical solvents. Ethanol and ethylene glycol were supplied by Panreac with purities of 99.5% and 99% respectively.

2.2. Absorption studies

Carbon dioxide absorption experiments were carried out using a square bubble column reactor (side length = 4 cm and height = 65 cm) made in perpex and using a liquid phase volume of 0.9 L. The gas phase (pure carbon dioxide) was fed to the contactor through a five-hole (diameter 0.5 mm) sparger built in Teflon®. 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 pressures ranges by the supplier. Also, Flow Vision SC software package (Alicat Scientific) was used to control the flowmeters and to record the carbon dioxide flow-rate during the experiments. 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 one. Constant gas flow-rate (0.5 $L{\cdot}min^{-1}$) and amines concentration (0.3 $mol{\cdot}L^{-1}$) were used in order to analyze the influence of co-solvents concentration upon absorption. Fig. 1 shows the experimental set-up and the characteristics of bubble contactor. The concentrations of ethanol and ethylene glycol employed in these studies are 0, 10, 30 and 50% in volume.

Table 1 shows the different variables and ranges analyzed in present work. In order to study the influence of the presence of typical organic co-solvents upon the carbon dioxide chemical absorption, two organic compounds have been employed (using different concentrations) with different types of amines (primary, secondary and tertiary).

3. Results and discussion

The first study carried out in this work consists of the analysis of absorption curves using aqueous solutions of MEA, DEA and TEA in the absence of co-solvents. These absorption curves show the different absorption behavior of each type of amine. The highest absorption rate at the beginning of experiments is observed for MEA aqueous solution. This fact is related with the high reaction rate [23,24] of this amine in comparison with the others. MEA and DEA aqueous solutions show higher absorption rate than TEA solvent because the weight of each reaction is different. Using TEA,