



## Carbon dioxide absorption using a phase transitional alkanolamine–alcohol mixture



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### ABSTRACT

Some alkanolamine–alcohol mixtures separate into a CO<sub>2</sub> rich phase and a CO<sub>2</sub> lean phase after the absorption of CO<sub>2</sub>, which makes possible a new approach to CO<sub>2</sub> capture. In this study, CO<sub>2</sub> absorbent solutions with various concentrations of monoethanolamine (MEA) and diethanolamine (DEA) were prepared by mixing them with alcohol. The CO<sub>2</sub> absorption capacities of the alkanolamine–alcohol mixtures were investigated by using a semi-batch reactor at 313 K. The species distributions of the absorbents were identified in order to determine the CO<sub>2</sub> absorption mechanism of these solutions. Although the CO<sub>2</sub> absorption capacities of the phase transitional absorbents are lower than that of aqueous solutions, we conclude from our experimental results that the phase transitional solutions have the economic advantages, and in particular lower regeneration energies, because only the CO<sub>2</sub>-rich phase needs to be transported to the stripper.

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### 1. Introduction

Concerns about climate change due to greenhouse gases are increasing. One part of the response has been to use aqueous solutions to remove carbon dioxide (CO<sub>2</sub>) from gaseous mixtures that are produced industrially. Recently, CO<sub>2</sub> removal from flue gases emitted by coal-fired power plants has been studied extensively. CO<sub>2</sub> capture by absorption and stripping with aqueous amines is a well-understood and widely used technology. In the absorption/stripping process, the cost of the regeneration of the absorbent accounts for 70–80% of the overall operation costs [1,2]. Therefore, it is important to develop absorbents with reduced regeneration energies.

Amino acid salt solutions have been proposed as absorbents with low regeneration energies. Several researchers have studied the solubility and kinetics of CO<sub>2</sub> in aqueous solutions of potassium salts of amino acids. Hook [3] conducted CO<sub>2</sub> absorption and desorption experiments in such solutions. Kumar et al. [4] investigated the kinetics of the reaction between CO<sub>2</sub> and aqueous potassium salts of taurine and glycine. Aqueous potassium salts of glycine undergo no precipitation even at very high CO<sub>2</sub> loadings. However, precipitation does occur in some aqueous amino acid–salt solutions when CO<sub>2</sub> is absorbed at

increased CO<sub>2</sub> loadings, which can result in operational problems such as equipment fouling and plugging or decrease liquid phase gas transfer [5]. The drawbacks of carbonate salt precipitation work against the use of these absorbents as direct replacements for monoethanolamine (MEA) in conventional processes. On the other hand, amino acid salt solutions have lower regeneration energies [6,7]. The precipitates are neutral amino acids and/or their carbonate salts [8]. Fernandez and Goetheer [6] and Brouwer et al. [8] have pointed out that a DECAB process based on precipitating amino acids could make use of the same kind of spray towers as used in flue gas desulphurization. They showed that the costs of the DECAB process per ton of captured CO<sub>2</sub> could be half those of the MEA process.

IFP Energies nouvelles have studied several absorbents known as DMX solvents. Raynal et al. [9] investigated the solvent DMX-1, which exhibits a liquid–liquid phase separation. The DMX<sup>TM</sup> process is based on the particular properties of solvents that form two immiscible liquid phases under specific CO<sub>2</sub> loadings or temperature conditions. In the DMX<sup>TM</sup> process, the CO<sub>2</sub>-loaded solvent is delivered to a decanter. The decanter is positioned after the heat exchanger and before the regenerator in order to preheat and separate the CO<sub>2</sub>-loaded absorbent into two phases. Raynal et al. [10] and Aleixo et al. [11] have shown that the DMX process has a lower regeneration energy (2.3 GJ/t CO<sub>2</sub>) than processes using 30 wt% MEA (3.7 GJ/t CO<sub>2</sub>).

Zhang et al. [12,13] studied an aqueous lipophilic amine solvent, activated dimethylcyclohexylamine (a-DMCA), and developed a

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new technology using hydrophobic solvents to extract the CO<sub>2</sub>-loaded amine from the aqueous phase into the organic phase. The heterogeneous solvents (initial solutions) were converted to homogeneous solutions or emulsions (CO<sub>2</sub>-loaded solutions) at 30–40 °C by varying the solvent temperature and performing agitation. Extractive regeneration of the CO<sub>2</sub> loaded solution was carried out by the addition of an inert solvent that is insoluble in water, with simultaneous CO<sub>2</sub> release. Extractive regeneration using inert hydrophobic solvents can reduce the desorption temperature to 40–50 °C and intensify absorbent recovery, releasing more than 90% of CO<sub>2</sub> through multiple-stage extraction.

The use of chemical phase transitional absorbents is receiving attention as an alternative to that of conventional aqueous solutions. A few researchers have studied the chemical phase transitional absorption of CO<sub>2</sub> by non-aqueous amine solutions. Hu [14–18] proposed a new absorption process that uses an alkanolamine–alcohol mixture. Hu [15] presented a comparison of the absorption properties of an alkanolamine–alcohol mixture and a 30 wt% aqueous MEA solution. These results show that the regeneration energy requirements of the phase transitional absorption process are approximately 15% of those of the MEA-based process. Furthermore, the capital cost requirements are less than 80% of those of the conventional process.

In this study, Hu's approach to phase transitional absorption for absorption/regeneration was adopted. Hu has investigated the rates of absorption of CO<sub>2</sub> of alkanolamine–alcohol mixtures. However, there have been no studies of the solubility of CO<sub>2</sub> in alkanolamine–alcohol mixtures or of their absorption mechanism. In this study, the solubility of CO<sub>2</sub> in MEA/alcohol and DEA/alcohol was measured by using an absorption apparatus. Further, the CO<sub>2</sub> absorption mechanism was investigated through an analysis of the species distribution with NMR spectroscopy. MEA and diethanolamine (DEA) are the most widely used amines for the capture of CO<sub>2</sub>. The low molecular weight of MEA, which results in its high solution capacity at moderate concentrations, and its high alkalinity are notable advantages. The low vapor pressure of DEA makes it suitable for low-pressure operation as vaporization losses are negligible. 1-Heptanol, 1-octanol, and isooctanol are inert solvents for CO<sub>2</sub>, and have advantages such as high boiling point and low vapor pressures compared to water. The alkanolamine–alcohol mixtures are separated into a CO<sub>2</sub>-rich phase and a CO<sub>2</sub>-lean phase after the absorption of CO<sub>2</sub>. Only the CO<sub>2</sub>-rich phase is transported to the stripper, so the regeneration cost is reduced.

## 2. Experiment

### 2.1. Materials

CO<sub>2</sub> (30 mol%) and N<sub>2</sub> (99.999 mol%) gases were obtained from Special Gas Co., Korea. The absorbents were prepared by mixing each organic solvent with 10 wt%, 20 wt%, 30 wt%, or 40 wt% MEA or DEA. The following materials were used as received: MEA

(Samchun Chemicals, 99%), DEA (Samchun Chemicals, 99%), 1-heptanol (Junsei, 99%), 1-octanol (Junsei, 98%), and isooctanol (Sigma Aldrich, 99.6%). High concentrations of amines necessitate the use of additives such as corrosion inhibitors. Therefore, 20 wt% MEA/isooctanol and DEA/isooctanol were selected and their species distributions were identified with nuclear magnetic resonance (NMR) analysis.

### 2.2. Experimental setup and procedure

Fig. 1 shows CO<sub>2</sub> absorption/regeneration by an alkanolamine–alcohol mixture [15]. The process is similar to a conventional MEA process, except that a settler is added to produce the separation of the two phases. Phase transitional absorption systems use absorbents that have two- or multiple-phases after the absorption of CO<sub>2</sub>. The separated phases are a CO<sub>2</sub>-rich phase and a CO<sub>2</sub>-lean phase. The CO<sub>2</sub>-rich phase is transported to the regenerator. The regenerated phase is then recombined with the CO<sub>2</sub>-lean phase. Therefore, this process can reduce the operating costs of regeneration.

The CO<sub>2</sub> absorption capacities were measured in a six-station reactor based on a threaded glass vessel (STEM Omni Reacto Station Series 6250 from Thermo Scientific). The CO<sub>2</sub> absorption capacity is CO<sub>2</sub> loading calculated as the amount of absorbed CO<sub>2</sub> in the absorbent (mol CO<sub>2</sub>/mol solute). The number of moles of absorbed CO<sub>2</sub> can be calculated through the integration of the data area obtained from a gas chromatograph (GC). The experimental setup is schematically illustrated in Fig. 2. A volume of 250 mL absorbent was used in the experiment. The reactor containing the absorbent was heated to 313 K. The temperature was maintained with a heating system during these experiments. In order to avoid vapor loss, cooling water was circulated from the cooler to the top of the vessel. The reactor was saturated with N<sub>2</sub> gas for 2 h to remove any residual gas before injecting CO<sub>2</sub>. The CO<sub>2</sub> gas was fed into the reactor through the bubbler. N<sub>2</sub> and CO<sub>2</sub> gases were fed into the reactor by using a mass flow controller (MFC) at 200 mL/min. In each experiment, the stirring speed in the reactor was set at 500 rpm in order to maximize the surface area. The temperature of the absorbent in the reactor was measured with a K-type thermocouple, and the pressure of the gas was measured with a PSH model pressure sensor (range: –1–10 kg<sub>f</sub>/cm<sup>2</sup>) from Sensys Ltd., Korea. After passing over the absorbent, the gas was transported to a 7890A GC from Agilent for analysis. A 80/100 Porapack-Q column and a TCD detector were installed in the GC device. Helium (He) was used as the carrier gas, and the temperatures of the detector and the oven were set at 250 K and 120 K, respectively.

The phases of the CO<sub>2</sub> loaded alkanolamine–alcohol mixture were separated by using a separatory funnel. Each phase was investigated with NMR spectroscopy to determine the species distribution. <sup>1</sup>H NMR and <sup>13</sup>C NMR measurements were conducted at 293 K. Methanol-d<sub>4</sub> (CD<sub>3</sub>OD) was added to the NMR tube containing the sample and employed in the analysis.

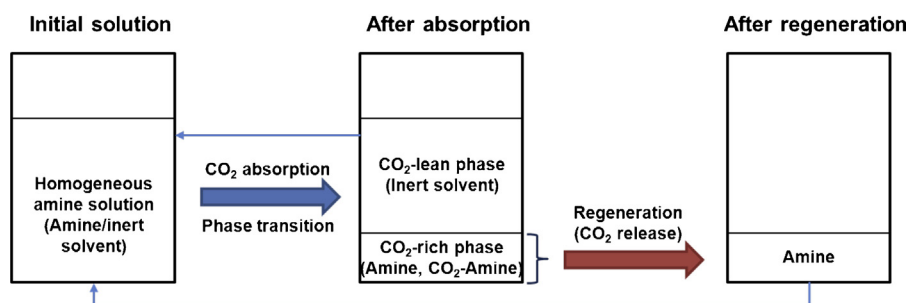


Fig. 1. CO<sub>2</sub> absorption/regeneration using a chemical phase transitional absorbent.

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