

Absorption Characteristics of Solvents for Carbon Dioxide Capture

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Abstract

This work focuses on absorption characteristics of solvents for CO₂ capture. The objective of the work is to develop new and more acceptable solvents or solvent mixtures whose absorption rate and loading capacity are higher than the existing ones. Absorption of CO₂ was studied at 40 °C using both alkanolamine-based and non-alkanolamine-based solvents. The absorption characteristics of solvents for CO₂ removal are mainly determined by the absorption rate and the absorption capacity of CO₂. All absorbents are compared to the commercially used MEA. The experimental results show that most absorbents tested show poorer performance than MEA, but that 30-wt% AEEA in aqueous solution might be a possible contender as it offers better absorption characteristics in the sense that both absorption rate and absorption capacity of CO₂ are higher than the most other solvents used in this work. In comparison to the performances of 30-wt% MEA, the 30-wt% AEEA gives higher absorption rate starting from loading of 0.35 and higher absorption capacity (0.82 mol CO₂/mol AEEA and 0.47 mol CO₂/mol MEA at 9.5 kPa CO₂ partial pressure).

Keywords: CO₂ capture, absorption characteristics, alkanolamines, loading

Introduction

Removal of acid gases, e.g. carbon dioxide (CO₂), is an important industrial operation. Carbon dioxide occurs in quite substantial concentrations in industrial processes such as hydrogen manufacture, ammonia production, as flue gas from combustion processes, and in natural gas purification. The reasons for the CO₂ removal are traditionally due to technical and economical concerns. Carbon dioxide present in natural gas will reduce the heating value of the gas and as an acid component it has the potential to cause corrosion in pipes and process equipment and also to cause catalyst poisoning in ammonia and LNG manufacture. Due to its corrosiveness, natural gas pipe lines usually permit from 1 to 2 percent CO₂ and sometimes as high as 5 percent (Buckingham, 1964). However, environmental concerns, such as global warming, are now brought forward as an important issue that has motivated intensive research on CO₂ capture and storage. This is due to the increasing emissions of CO₂ to the atmosphere. Tønseth *et al.* (2002) reported CO₂ emissions in 1997 for several regions in the world as shown in Figure 1.

Absorption process, a unit operation in which soluble components of a gaseous mixture dissolve in a liquid solvent, is the most commonly used gas CO₂ removal process. There are two main types of absorp-

tion processes; one based on physical solubility, and the other based on chemical reactions between solute and solvent.

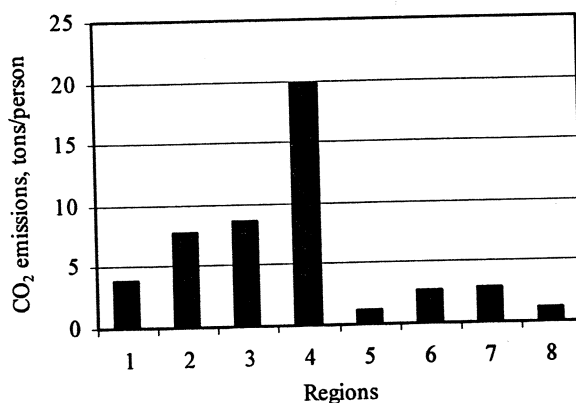


Figure 1. CO₂ emissions in 1997 for several regions in the world: 1, the world; 2, Norway; 3, EU; 4, North America; 5, Africa; 6, South America; 7, China; 8, India.

Fluor Co., one of the largest gas processing industries vendors, has introduced several patented gas purification processes, such as the Econamine, the Improved Econamine, the Econamine FG, and the Fluor Solvent processes (Fluor Co., 2003). The first three processes use diglycolamine (DGA) (Bucklin, 1982; Huval and van de Venne, 1981) and MEA as chemical solvent, while the latter uses propylene carbonate, glycerol triacetate (triacetin), butyl carbitol

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acetate, and triglycerol acetate as physical solvents (Fluor Co., 2003). Only propylene carbonate has been used commercially (Kohl and Nielsen, 1997). They also offer designs based on alkanolamines, such as methyldiethanolamine (MDEA), diethanolamine (DEA), and di-isopropanolamine (DIPA) (Fluor Co., 2003).

Although absorption with alkanolamine solvents is the most common technology for CO₂ removal today, it is a process with considerable inherent problems, particularly when used on large gas flows like exhaust resulted from fossil fuel fired power stations. The processes are bulky, leading to large investment costs, energy consumption, and the solvents in use to day are not stable and form degradation products that need to be handled. The IEA Greenhouse Gas R&D Programme has established an international work group to specifically address improvements to absorption processes for CO₂ removal, and with a focus on MEA processes.

The objective of the present experimental work is to develop new and more acceptable solvents or solvent mixtures whose absorption rate and loading capacity, a ratio between moles of CO₂ absorbed and moles of CO₂-free absorbent used, are higher than those of other amine or amine mixtures.

Materials and Methods

Materials. The CO₂ and N₂ gases used were obtained from AGA and had a minimum purity of 99.99 and 99.6% respectively. The alkanolamines were used without further purification and those selected were monoethanolamine (MEA), 2-(butylamino) ethanol (BEA), N-methyldiethanolamine (MDEA), 2-(methylamino)ethanol (MMEA), 2-(ethylamino) ethanol (EMEA), 2-(2-aminoethyl-amino)ethanol (AEEA), and reported purities were not less than 99, 98, 98.5, 99, 98, and 97%, respectively. Other absorbent chemicals tested were taurine (99%), potassium carbonate (p.a. min. 99%), piperazine (min. 99%), and the BASF® Alkazid (3.2 M). All these absorbents were selected based on their potential to chemically capture CO₂.

Apparatus and Methods. Figure 2 shows the experimental set-up. A 1-liter absorber was submerged in a thermostated water bath. Six similar absorbers were used in parallel in this work. Before starting the experiment, a 10-vol% CO₂ in N₂ with flowrate regulated by a flow-controller to 5 NL/min was circulated through a by-pass valve to calibrate the IR CO₂ gas analyzer. After calibration, the process was automatically started by closing the by-pass valve. The gas mixture passed through a saturator submerged in the water bath and containing distilled water. The saturated gas mixture was then passed to the absorber containing 750 mL of a specified solvent and solvent concentration, either a single or mixed solvent. The gas phase leaving the absorber was cooled and the water condensed to protect the gas

analyzer from water. The temperature of the bath was maintained at 40 ± 0.1 °C. The process automatically terminated when the concentration of CO₂ in the outlet reached 9.5 vol% (9.5 kPa CO₂ partial pressure).

Gas and Liquid Analyses. The gas composition was analyzed continuously by means of a Uras 3G IR CO₂ gas analyzer calibrated for the range 0-10 vol% CO₂. The gas CO₂ content, the temperatures, and gas flow rates were collected automatically using data acquisition in LabVIEW. After terminating the experiment, a liquid sample containing all bound CO₂ was analyzed by the barium chloride method.

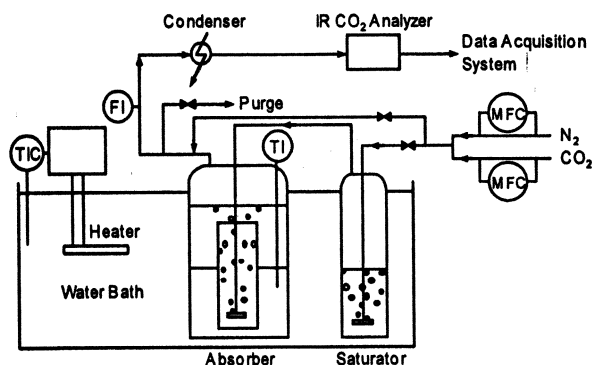


Figure 2. Screening apparatus for CO₂ capture

Results and Discussion

A chemical that is to be used as a commercial solvent will require high net capacity and reaction rate for CO₂ as well as high chemical stability, low vapor pressure, and low corrosiveness. Aqueous MEA, a primary amine, has been used extensively for removal of CO₂. It has several advantages over other commercial alkanolamines, such as high reactivity, low solvent cost, reasonable thermal stability and thermal degradation rate. It also has relatively low solubility for hydrocarbons and this reduces the hydrocarbon loss when processing natural gas and refinery gas streams. Disadvantages include high heat of reaction with CO₂ leading to high energy consumption for stripping. Also MEA forms degradation products with COS, CS₂, and oxygen-bearing gases, has a high vapor pressure, and needs corrosion inhibitors when used in 30 wt% concentration (Liu *et al.*, 1999).

Due to its wide use and advantages compared to other alkanolamines, MEA is set as a base case in this work. Absorption rates of CO₂ into an aqueous 30-wt% MEA were determined by means of the six-vessel lab-scale absorber. The experimental results are shown in Figure 3 and indicate that the absorption rates measured vary slightly between all six absorbers. These differences are mainly caused by differences in the gas distributors used. Small differences exist which affect the number and size of bubbles produced, which again affects the absorption rate. The smaller the bubble sizes the greater the interfacial area.

To enable easy comparison to the other solvents used, an arithmetic average of the absorption rates of CO_2 into the aqueous 30-wt% MEA was taken from the results of absorber 2 and absorber 3. The reason for this was that the absorption rates of CO_2 in the two absorbers were almost identical and gave relatively high values compared to the other absorbers (except for absorber 4).

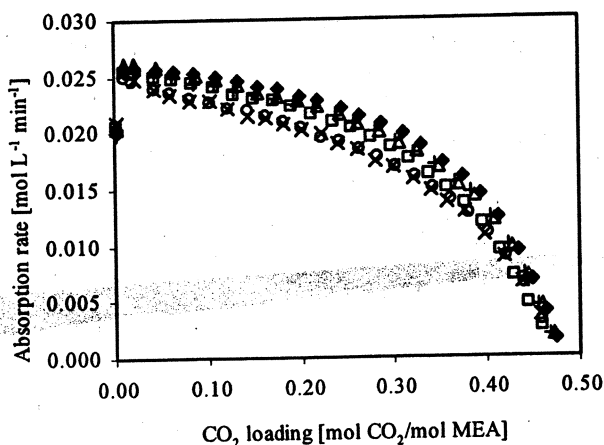


Figure 3. Absorption rate of CO_2 into aqueous 30-wt% MEA for various absorbers at 40 °C: \circ , Absorber 1; $+$, Absorber 2; Δ , Absorber 3; \blacklozenge , Absorber 4; \times , Absorber 5; \square , Absorber 6.

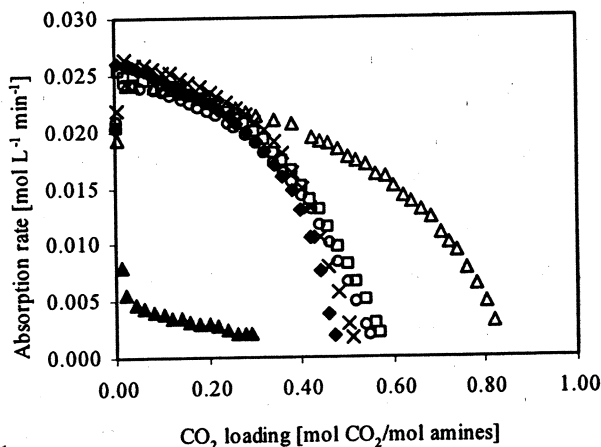


Figure 4. Absorption rate of CO_2 into aqueous 30-wt% alkanolamines at 40 °C: \blacklozenge , MEA; \circ , BEA; \blacktriangle , MDEA; \times , MMEA; \square , EMEA; Δ , AEEA.

To evaluate the absorption characteristics of the other solvents, BEA, MDEA, MMEA, EMEA, and AEEA, the same concentrations on the weight basis, as that of MEA, were used. This implies that the molar concentrations were not the same, and generally lower than that of MEA. However, the optimal operational concentrations for these absorbents are not known a priori so a comparison based on mass fraction might be as good as one based on constant molarity.

As seen from Figure 4, the absorption rate of CO_2 into aqueous 30-wt% MEA is, in the low loading

range (less than 0.2 mol CO_2 /mol amine), generally higher than into all the other alkanolamines except for MMEA. Above about 0.35 in loading, however, the absorption rates into MEA are lower than into the other alkanolamines except into aqueous 30-wt% MDEA. It is also clearly shown that the absorption rate of CO_2 into MDEA is by far the lowest compared to all alkanolamines tested over the whole loading range. As a tertiary amine, MDEA lacks the extra hydrogen atom and does not form carbamate which contributes to increase the overall rate of absorption. Hence, MDEA reacts relatively slowly with CO_2 , but it reacts rapidly with H_2S (Deshmukh and Mather, 1981; Astarita *et al.*, 1983; Savage *et al.*, 1986). That is why MDEA is frequently used for selective removal of H_2S from a gas stream containing both acid gases (Austgen *et al.*, 1991; Li and Mather, 1997).

The series of secondary amines, MMEA, EMEA, and BEA, all perform very well. MMEA has even a slightly higher absorption rate than MEA at low loading (maximum rates of 0.0263 and 0.0260 mol CO_2 /L/min respectively), and continues to outperform MEA also for higher loadings. One should keep in mind, however, that MMEA has a somewhat higher molecular weight (75 versus 61), and therefore a lower molar concentration. In addition, Suda *et al.* (1996) examined the NMR spectrum of aqueous MMEA solution containing chemically combined CO_2 , and found that MMEA has moderate carbamate stability resulting in increased absorbed amounts of CO_2 at low partial pressure. Both MMEA and BEA are foaming and MMEA is in this respect much worse than BEA. A foam inhibitor was, therefore, added at a quantity of fifty ppm into aqueous MMEA in this work, and the results shown are with foam inhibitor. Normally, a foam inhibitor will have a negative impact on the mass transfer characteristics, both by reducing interfacial area, and possibly by increasing the surface resistance. MMEA could thus have an even greater potential than shown here when used in contactors where the two phases are separated, like membrane contactors.

In addition to the evaluation of amine solvent characteristics, non-alkanolamine-based solvents were also tested such as the potassium salt of taurine (PT), potassium carbonate activated by MEA, piperazine (PZ), and the BASF® Alkazid (AZ).

Figure 5 shows the results from these tests. The absorption rate of CO_2 into the aqueous 30-wt% MEA is, in general, found to be higher than that into all solvents except for 2.5M PZ (maximum rate of 0.0280 mol CO_2 /L/min). Also 3.2M AZ performs better than MEA at higher loading.

For aqueous 20-wt% potassium carbonate (K_2CO_3), the addition of MEA as promoter increases the absorption rate of CO_2 . On these curves a saddle point occurs. At this point all the MEA has reacted and only the carbonate ions are left. Even if the amount of promoter added varies, the final loadings

(at 9.5 kPa CO₂ partial pressure) are approximately the same and about 0.45.

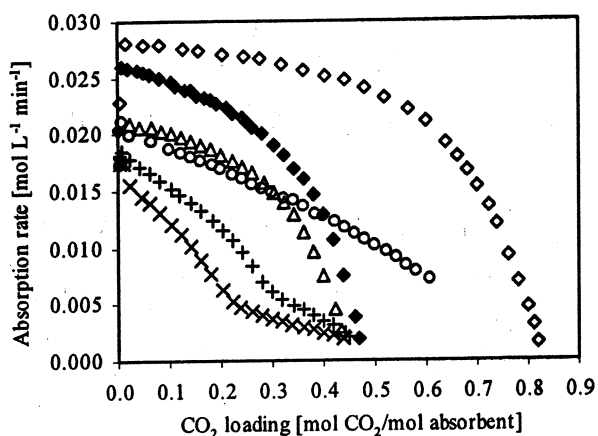


Figure 5. Absorption rate of CO₂ into non-alkanolamine-based solvents compared to 30-wt% MEA at 40 °C: Δ , 3.0 M PT; +, 20-wt% K₂CO₃ + 10-wt% MEA; x, 20-wt% K₂CO₃ + 5-wt% MEA; \diamond , 2.5 M PZ; \circ , 3.2 M AZ; \blacklozenge , 30-wt% MEA.

Absorption liquids based on amino acid salts have been developed for absorption in membrane contactors and are patented by TNO (The Netherlands). TNO has given them the trade name CORAL (CO₂ Removal Absorption Liquid). These liquids offer similar absorption characteristics as aqueous alkanolamine solutions, but have better degradation properties, no volatility, and do not wet polypropylene membranes (Kumar *et al.*, 2002). PT, one of the amino acid salts, was tested in this work at a concentration of 3.0M. The absorption rate of CO₂ into aqueous PT was found to be lower than into aqueous 30-wt% MEA.

From Figures 4 and 5, it can clearly be seen that 2.5M PZ gives the highest absorption rate among all the solvents tested, and gives the same absorption capacity of CO₂ (loading of 0.82) as aqueous 30-wt% AEEA used in this work. BASF has successfully used PZ as a promoter in MDEA systems for high-capacity CO₂ removal in ammonia plants and in natural gas processing, and patented it (Bishnoi and Rochelle, 2000). However, some environmental concerns have been raised about PZ based on its slow biodegradability. PZ is a diamine with two secondary amine groups. This explains its readiness to exceed 0.5 in loading. The low biodegradability, on the other hand, probably stems from its ring structure. AEEA is also a diamine, with one secondary and one primary amine group. It is a chain molecule and should therefore be an environmentally relatively acceptable solvent. It is also among the amines with better absorption characteristics as it has a relatively high absorption rate (maximum rate of 0.0241 mol CO₂/L/min) at low loading combined with a high absorption capacity of CO₂ (loading of 0.82 at 9.5 kPa CO₂ partial pressure).

However, according to Suda *et al.* (1997), AEEA is corrosive and this may limit its usefulness.

Conclusions

An apparatus for rapid screening of CO₂ absorption chemicals has been developed and a range of solvents was tested. In general, the main absorption characteristics of solvents for CO₂ removal are the absorption rate of and the absorption capacity for CO₂. The experimental results show that AEEA seems to be a potentially good absorbent for CO₂ according to the above criteria. It offers high absorption rate combined with high absorption capacity compared to other solvents used in this work. In addition, MMEA also needs to be considered instead of AEEA. It could have a greater potential than shown here when used in contactors where the two phases are separated, like membrane contactors. At initial loading, AEEA gives lowest absorption rate compared to those of MMEA and MEA (0.0241, 0.0263, and 0.0261 mol CO₂/L/min) but it gives highest absorption capacity compared to those of MMEA and MEA (0.82, 0.51, and 0.47 mol CO₂/mol amines respectively at 9.5 kPa CO₂ partial pressure).

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