Absorption of carbon dioxide in alkanolamines in deep eutectic solvent medium for CO₂ gas separation

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ABSTRACT

In this research, experiments have been carried out to evaluate the suitable absorbent for CO₂ gas separation. The absorption of carbon dioxide in various alkanolamines in aqueous and deep eutectic solvent medium (DES) was assessed. The amines employed in this study are monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), 2-amino-2-methyl-1-propanol (AMP) and 2-methylamino ethanol (MAE). Choline chloride and urea (ChCl:U) mixture was employed as DES medium. The molar ratio of DES was optimized to get maximum absorption of CO₂ gas. The absorption of CO₂ in alkanolamines in DES medium was found to be higher than in aqueous medium. Among the various alkanolamines in DES medium, 2-amino-2-methyl-1-propanol in DES shows higher absorption capacity for CO₂ gas. Thus alkanolamines in DES medium could be effectively used as an absorbent for CO₂ capture.

KEYWORDS: CO₂ capture, absorption, AMP, DES

INTRODUCTION

The removal of CO₂ from flue gas by absorption technique has been implemented in many industries. Generally aqueous alkanolamines are being used as absorbents. In recent years, researchers have been continuously searching for green solvents, which could serve as alternatives to conventional solvents in industrial processes. Among the most promising options are the deep eutectic solvents (DESs), which belong to a new class of ionic liquids that are made by mixing a substituted quaternary ammonium salt and a metal halide or a hydrogen bond donor. Actually, they share many unusual characteristics with room-temperature ionic liquids (RTILs) such as negligible vapor pressure, wide liquid range, high thermal and chemical stabilities, non flammability, and high solvation capacity. However, unlike the latter, DESs are easy to prepare in high purity; thus, they can be manufactured at a considerably lower cost than RTILs. Furthermore, they can be made from biodegradable components, and their toxicities are well-characterized. The objective of this paper is to experimentally investigate the absorption of CO₂ in alkanolamines in aqueous medium and alkanolamines in choline chloride-urea (DES) medium.

MATERIALS AND METHODS

Chemicals: Various alkanolamines employed in this study are monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), 2-methylamino ethanol (MAE), 2-amino-2-methyl-1-propanol (AMP) and urea. All the chemicals were purchased from the Merck Company in 96-98% purity. The chemicals were used without further purification. Research Grade CO₂ gas (99%) was purchased from Supreme Engineering Services, India.

Apparatus and procedure: A schematic diagram of the experimental setup for gas absorption measurement is shown in Fig. 1. The reactor consists of 1L capacity stainless steel cylindrical tank equipped with a stainless steel diffuser to generate fine bubbles and endure intense mixing. The tank was kept on the magnetic stirrer with hot plate for stirring. 100 mL of sample was taken from the absorption tank and desired quantity of CO₂ gas was passed from the cylinder to the tank. The experiments were carried out at 1 atmospheric pressure and at a room temperature of 28±2 °C. The samples were withdrawn from the absorption tank and analyzed to measure the carbon dioxide content by a titrimetric method. Each experimental run was conducted twice.

The CO₂ loading is obtained by the following Equation (1).

\[ \text{mole ratio}(\alpha) = \frac{\text{mole of CO}_2}{\text{mole of amine}} \]  

RESULTS AND DISCUSSION

Fig. 2 shows the effect of composition of ChCl: U mixture on the absorption of CO₂ gas. The mole ratio was optimized from 1:1 to 1:4. The CO₂ absorption capacity of DES medium initially increases with increase in ChCl: U mole ratio. But beyond 1:2 mixture, CO₂ absorption is almost similar in 1:3 and 1:4 mole ratios. Such results suggest that the 1:2 mole mixture possessed the highest capacity to dissolve CO₂. This absorption capacity (0.08) is higher than the absorption capacity of water (0.005). These results are well supported by the data provided by Li et al. and Su et al.

The absorption of CO₂ in alkanolamines in ChCl: U (1:2) medium is shown in Fig. 3a. Among the various alkanolamines the absorption of CO₂ is higher in 2-amino-2-methyl-1-propanol in DES medium. It has been reported in references that AMP has higher loading capacity (1.0 mol of CO₂/mol of amine) than other amines. This may be due to the bulkiness of the group attached to the tertiary carbon atom and higher reaction rate constant of AMP with CO₂. Following to AMP, the absorption of CO₂ is higher in MAE, which is higher than that in the most commonly used conventional amine MEA. According to the study of Mimura et.al., even though, MAE is not a hindered amine as by the definition of sterically hindered amine it is more hindered than MEA. So in such a comparison, the hindrance effect can make some differences. The absorption of CO₂ is higher in MAE when compared to DEA, which is higher than in TEA. This trend could be reasonably explained based on the rate of absorption. Even though TEA has higher CO₂ loading capacity (1.0 mol of CO₂/mol of amine) due to the very low reaction rate, the absorption of CO₂ is lower in TEA among various alkanolamines.
For the comparison purpose the absorption of CO$_2$ in aqueous alkanolamines are also measured and it is presented in Fig. 3c. The absorption of CO$_2$ in alkanolamines in DES medium was found to be higher than in aqueous alkanolamines. This might be due to the low vapour pressure and low viscosity of DES medium when compared to the aqueous medium.

![Experimental setup for gas absorption measurement](image1)

**Figure 1.** Experimental setup for gas absorption measurement

![Absorption of CO$_2$ in ChCl:U (DES) medium](image2)

**Figure 2.** Absorption of CO$_2$ in ChCl:U (DES) medium

![Absorption of CO$_2$ in alkanolamines in ChCl:U (DES) medium](image3a)

**Figure 3a.** Absorption of CO$_2$ in alkanolamines in ChCl:U (DES) medium

![Absorption of CO$_2$ in alkanolamines in aqueous medium](image3b)

**Figure 3b.** Absorption of CO$_2$ in alkanolamines in aqueous medium

The absorption of CO$_2$ in alkanolamines in ChCl: U (1:2) medium is shown in Fig. 3a. Among the various alkanolamines the absorption of CO$_2$ is higher in 2-amino-2-methyl-1-propanol in DES medium. It has been reported in references that AMP has higher loading capacity (1.0 mol of CO$_2$/ mol of amine) than other amines. This may be due to the bulkiness of the group attached to the tertiary carbon atom and higher reaction rate constant of AMP with CO$_2$. Following to AMP, the absorption of CO$_2$ is higher in MAE, which is higher than that in the most commonly used conventional amine MEA. According to the study of Mimura et.al., even though, MAE is not a hindered amine as by the definition of sterically hindered amine it is more hindered than MEA. So in such a comparison, the hindrance effect can make some differences. The absorption of CO$_2$ is higher in MEA when compared to DEA, which is higher than in TEA. This trend could be reasonably explained based on the rate of absorption. Even though TEA has higher CO$_2$ loading capacity (1.0 mol of CO$_2$/ mol of amine) due to the very low reaction rate, the absorption of CO$_2$ is lower in TEA among various alkanolamines. For the comparison purpose the absorption of CO$_2$ in aqueous alkanolamines are also measured and it is presented in Fig. 3c. The absorption of CO$_2$ in alkanolamines in DES medium was found to be higher than in aqueous alkanolamines. This might be due to the low vapour pressure and low viscosity of DES medium when compared to the aqueous medium.

**CONCLUSION**

The absorption of CO$_2$ in aqueous alkanolamines and in alkanolamines in DES medium was measured and it was found that DES medium has higher absorption capacity for CO$_2$ gas than with aqueous medium. Among the various alkanolamines in DES medium, 2-amino-2-methyl-1-propanol in DES medium showed higher absorption capacity for CO$_2$ gas. Thus the alkanolamines in DES medium could be effectively used as an absorbent for CO$_2$ gas separation.
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