CO₂ Absorption in Aqueous Monoethanolamine/Methyldiethanolamine/Diethylenetriamine and Their Blends Solutions

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This paper compares the loading and extent of CO₂ uptake by various amines and their mixtures. A quantity of CO₂ was introduced into a 292 mL stainless steel batch reactor containing 10 mL amine solutions at a constant temperature, then the reactor was sealed, pressurized with a CO₂ containing gas and the system pressure was recorded. The CO₂ absorption into the amines was recorded as a pressure decrease and used to calculate the amount and loading of CO₂ in the amines. In particular, diethylenetriamine was found to be effective in enhancing the performance of other amines. Diethylenetriamine was added into aqueous monoethanolamine and methyldiethanolamine solutions and its effects were investigated. The results indicated that CO₂ removal extent and absorption amount increased with aqueous amine solution concentration, while CO₂ loading decrease with aqueous amine solution concentration. diethylenetriamine has a good absorption characteristic and adding a small quantity of diethylenetriamine was found to promote the absorption characteristics of monoethanolamine or methyldiethanolamine aqueous solutions.

Key Words: CO₂ absorption, Blended amine, Loading, Removal extent.

INTRODUCTION

It is essential to control the emission of greenhouse gas CO₂ to alleviate the damage to environment brought about by this gas. A number of techniques have been developed for removing CO₂ from the power plants flue gases. One of the proposed techniques for the removal of CO₂ is chemical absorption by various absorbents such as hot aqueous alkali, amines, ammonia water and ionic liquids. In industrial CO₂ absorption processes, monoethanolamine and methyldiethanolamine have been and still are the chosen adsorbents¹, meanwhile, a different class of chemical absorbents, enamine such as diethylenetriamine, triethylenetetramine have been proposed as new CO₂ absorbents because of their advantages in absorption capacity and absorption rate. The use of blends of alkanolamines, a solution of two or more amines in varying concentration, has been shown to produce absorbents with excellent absorption characteristics². A series of studies have been undertaken to assess the properties of monoethanolamine, methyldiethanolamine and diethylenetriamine in CO₂ absorption. Park *et al.*^{3,4} studied the kinetics of the reactions between CO₂ with monoethanolamine and methyldiethanolamine. Lee *et al.*⁵⁻⁷ studied the equilibrium solubility of CO₂ in aqueous monoethanolamine, methyldiethanolamine and mixtures of

monoethanolamine with methyldiethanolamine solutions. Hartono *et al.*^{8,9} investigated the speciation in diethylenetriamine-CO₂-H₂O using NMR and measured the kinetics of CO₂ absorption in unloaded aqueous solution with the diethylenetriamine using a string of discs contactors.

The main purpose of this work is to characterize the absorption of CO₂ into aqueous monoethanolamine, methyldiethanolamine and diethylenetriamine solutions based on experimental data for different concentrations of absorbents and temperatures. The removal extent, absorption amount and CO₂ loading for monoethanolamine, methyldiethanolamine, diethylenetriamine and the addition of diethylenetriamine into aqueous monoethanolamine/methyldiethanolamine solutions were measured. Diethylenetriamine solution was added to enhance the absorption characteristics of aqueous monoethanolamine and methyldiethanolamine solution and its effects were investigated. The performances were evaluated under various operating conditions in order to investigate the absorption characteristics of the absorbents.

EXPERIMENTAL

The experiments were conducted using a 292 mL stainless steel batch reactor. Heat supplied to the reactor was controlled by a constant temperature water bath (G25792 Polyscience

U.S.A). The temperature and pressure in the reactor was monitored by SR4 + ACR System. Amine solutions of the desired compositions were prepared from mixtures of Milli-Q deionized water and the appropriate quantities of amine(s). The monoethanolamine, methyldiethanolamine and diethylenetriamine were analytical purchased from Sigma-Aldrich Canada, Ltd. with stated purities of 99 ± 0.1 %.

For a typical run, 10 mL of aqueous amine solution of the desired composition was placed in the reactor. The reactor was then sealed and heated to the desired operating temperature. Once the temperature had stabilized, carbon dioxide was induced into the reactor from a pressurized cylinder until the desired total system pressure was reached, then the inlet valve to the reactor was closed and the system pressure was recorded.

Following the contact of CO₂ with the amine solution, the total system pressure dropped gradually and equilibrium was deemed to have been attained when the system pressure did not change for times of at least 1 h. At equilibrium, the reactor was then shut down and cleaned for another set of runs.

The absorption amount can be calculated by

$$\Delta P \times V = \Delta n \times RT$$

and then the removal extent and loading can be obtained by formulas as below:

$$\text{Removal extent} = \frac{\text{CO}_2 \text{ absorption amount (mol)}}{\text{CO}_2 \text{ initial amount (mol)}}$$

$$\text{Loading} = \frac{\text{CO}_2 \text{ absorption amount (mol)}}{\text{Amine amount (mol)}}$$

In addition to the main experiments that were performed under the aforementioned conditions, other experiments were conducted with water + monoethanolamine, water + diethylenetriamine, water + methyldiethanolamine, water + methyldiethanolamine + diethylenetriamine and water + monoethanolamine + diethylenetriamine. And by 5 repeats experiments at the same condition, the results indicate that the experimental error is much smaller than that variation caused by different temperature, pressure or concentration of amine.

RESULTS AND DISCUSSION

CO₂ removal extent: Fig. 1 shows a notable decrease in removal extent with temperature in the studied range from 25 to 65 °C using 1 mol/L methyldiethanolamine solution. However, the removal extent for 1 mol/L monoethanolamine and diethylenetriamine solution increased with temperature increased from 25 to 45 °C and then decreased slowly with temperature increased from 45 to 65 °C.

It is known that equilibrium absorption capacity decreases with increasing temperature according to exothermic absorption nature and an increase in reaction rate with increasing temperature according to the Arrhenius equation¹⁰. Thus, a decrease in removal extent for aqueous methyldiethanolamine solution with temperature ranged from 25 to 65 °C seemed to be more affected by a decrease in equilibrium capacity than by an increase in reaction rate and the removal extent for aqueous monoethanolamine and diethylenetriamine solutions with

Fig. 1. Dependence of removal extent on temperature for different amine solutions (MEA = monoethanolamine, MDEA = methyldiethanolamine, DETA = diethylenetriamine)

temperature ranged from 25 to 45 °C seemed to be more affected by an increase in reaction rate than by a decrease in equilibrium capacity, but more affected by a decrease in equilibrium capacity than by an increase in reaction rate at higher temperatures beyond 45 °C.

To compare with various absorbent concentrations at 25 °C, the CO₂ removal extent of aqueous monoethanolamine, methyldiethanolamine and diethylenetriamine solutions are shown in Fig. 2. It was observed that with an increase of absorbent concentrations from 1 to 2 mol/L, the CO₂ removal extent of aqueous monoethanolamine, methyldiethanolamine and diethylenetriamine solutions increased from 32, 25.6 and 32 % to 44, 30.6 and 59.6 %, respectively and with the concentration increased from 2 to 3 mol/L, the CO₂ removal extent of aqueous monoethanolamine solution increased to 47.8 %, while the CO₂ removal extent of aqueous methyldiethanolamine solution increased to 37 %. Therefore, 2 mol/L is optimum concentration for CO₂ removal.

Fig. 2. Effect of absorbent concentrations on CO₂ removal extent using aqueous monoethanolamine (MEA), methyldiethanolamine (MDEA) and diethylenetriamine (DETA) solutions

Fig. 3 shows that in 1 h, the CO₂ removal extent using the 20 wt % mixed amine solutions containing monoethanolamine or methyldiethanolamine with diethylenetriamine were higher than those using the single 20 wt % amine solutions containing monoethanolamine or methyldiethanolamine solution. The reason for the mixed solution containing methyldiethanolamine and diethylenetriamine not comparable to the mixed solutions containing monoethanolamine with diethylenetriamine was due to the low reaction rate of methyldiethanolamine with CO₂.

Fig. 3. Removal extent *versus* time (MEA = monoethanolamine, MDEA = methyldiethanolamine, DETA = diethylenetriamine)

CO₂ absorption amount: It can be seen from Fig. 4 that the CO₂ absorption amount did not change significantly when temperature was increased from 25 to 65 °C. This observation indicated that the reaction of alkanolamines with CO₂ was not affected by temperatures. And the CO₂ absorption amount decreased slightly with an increase in temperature from 45 to 65 °C, this may be for the reason that CO₂ absorption is exothermic in nature and thus an increase in temperature should decrease the extent of chemical absorption in accordance with Le Chatelier's principle¹¹.

Fig. 4. Dependence of absorption amount on temperature for different amine solutions (MEA = monoethanolamine, MDEA = methyldiethanolamine, DETA = diethylenetriamine)

CO₂ absorption into various aqueous solutions of different concentration at T = 25 °C is illustrated in Fig. 5. It can be seen that the absorption amount of CO₂ in aqueous monoethanolamine, methyldiethanolamine and diethylenetriamine solutions increased rapidly with the concentration of amine solutions increased from 1 to 2 mol/L, then increased slightly with the concentration increased from 2 to 3 mol/L. This indicates that concentration of amine solutions affects CO₂ absorption strongly in the range of 1-2 mol/L. And with a further increased concentration up to 3 mol/L, the viscosity of the liquid may increased at the same time, which may results in slowing down the mass transfer in liquid and thus bring a low CO₂ absorption amount.

It can be seen that in the four single and blended amine aqueous solutions of 20 wt %, monoethanolamine + diethylenetriamine aqueous solution had a rapid absorption rate and larger absorption amount of CO₂ than the aqueous solutions of single monoethanolamine and methyldiethanolamine

Fig. 5. Effect of absorbent concentrations on CO₂ absorption amount using aqueous monoethanolamine (MEA), methyldiethanolamine (MDEA) and diethylenetriamine (DETA) solutions

+ diethylenetriamine blended solutions. The absorption amount of CO₂ in 20wt % single methyldiethanolamine solution was low, but with the addition of diethylenetriamine, the absorption of CO₂ was remarkably promoted and nearly achieved the same as that of 20 wt % single monoethanolamine solution at 1 h.

Fig. 6. Absorption amount *versus* time (MEA = monoethanolamine, MDEA = methyldiethanolamine, DETA = diethylenetriamine)

CO₂ absorption loading: Fig. 7 shows the effect of temperature on the CO₂ loading values for 1 mol/L various amine solutions. The CO₂ loading decreased slowly with temperature for monoethanolamine and methyldiethanolamine solutions. However, temperature had a significant effect on the CO₂ loading for the solutions containing diethylenetriamine, implying that 45 °C might be optimal temperature choice for CO₂ absorption in diethylenetriamine.

The CO₂ loading of aqueous monoethanolamine, methyldiethanolamine and diethylenetriamine solutions decreased from 0.46, 0.85 and 1.10 to 0.35, 0.72 and 0.95 respectively as the concentration of the amine solutions was increased from 1 to 2 mol/L and beyond 2 mol/L, the CO₂ loading of aqueous monoethanolamine solution decreased slightly. monoethanolamine provided the lowest CO₂ loading, while diethylenetriamine provided the highest CO₂ loading.

Fig. 7. Dependence of loading on temperature for different amine solutions (MEA = monoethanolamine, MDEA = methyldiethanolamine, DETA = diethylenetriamine)

In 1 h, at 25 °C, the mixed alkanolamine solution containing 4 wt % diethylenetriamine and 16 wt % methyldiethanolamine/monoethanolamine had higher CO₂ loadings of 0.66 and 0.49, respectively, than that value of 20 % single methyldiethanolamine and monoethanolamine solutions by 0.05 and 0.12, respectively (Fig. 8 and 9). The results implied that adding diethylenetriamine into monoethanolamine solution has a significant effect on improving monoethanolamine absorption characteristics, which is in accordance with the conclusion that the absorption rate and capacity of CO₂ can be remarkably enhanced by the system of diethylenetriamine and methyldiethanolamine proposed by Xiang fei¹².

Fig. 8. Effect of absorbent concentrations on CO₂ loading using aqueous monoethanolamine (MEA), methyldiethanolamine (MDEA) and diethylenetriamine (DETA) solutions

Fig. 9. Loading versus time (MEA = monoethanolamine, MDEA = methyldiethanolamine, DETA = diethylenetriamine)

Conclusion

The chemical absorption of CO₂ with various single and mixed amine solutions at different temperature and concentration was studied. The CO₂ removal extent was found to increase with increasing temperature in the range of 25 to 45 °C. It was also found to be dependent on concentration of amine solutions. With an increased concentration of amine solutions, the absorption amount increased while the CO₂ loading decreased. The effect of temperatures ranging from 25 to 65 °C on absorption amount and CO₂ loading was small. The optimal condition suggested for CO₂ absorption with single amine solution was 45 °C and 2 mol/L. From the measured CO₂ removal extent, absorption amount and CO₂ loading, the 20 wt% amine aqueous solutions containing 4 wt % diethylenetriamine and 16 wt % monoethanolamine or methyldiethanolamine were found to be very effective absorbents to capture CO₂. The absorption characteristics of monoethanolamine or methyldiethanolamine single aqueous solutions can be promoted by adding a small quantity of diethylenetriamine. And to apply the blended amine solution for industrial use, the investigation of degradation and corrosion of these absorbents should be studied in the further step.

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