Asian Journal of Chemistry; Vol. 25, No. 1 (2013), 563-566

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13620

CO_2 Absorption in Aqueous Monoethanolamine/Methyldiethanolamine/ Diethylenetriamine and Their Blends Solutions

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(*Received*: 18 February 2012; *Accepted*: 7 August 2012) AJC-11926

This paper compares the loading and extent of CO_2 uptake by various amines and their mixtures. A quantity of CO_2 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 CO_2 containing gas and the system pressure was recorded. The CO_2 absorption into the amines was recorded as a pressure decrease and used to calculate the amount and loading of CO_2 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 CO_2 removal extent and absorption amount increased with aqueous amine solution concentration, while CO_2 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: CO_2 absorption, Blended amine, Loading, Removal extent.

INTRODUCTION

It is essential to control the emission of greenhouse gas CO_2 to alleviate the damage to environment brought about by this gas. A number of techniques have been developed for removing CO_2 from the power plants flue gases. One of the proposed techniques for the removal of CO_2 is chemical absorption by various absorbents such as hot aqueous alkali, amines, ammonia water and ionic liquids. In industrial CO_2 absorption processes, monoethanolamine and methyldiethanolamine have been and still are the chosen adsorbents[1], meanwhile, a different class of chemical absorbents, enamine such as diethylenetriamine, triethylenetetramine have been proposed as new CO_2 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 characteristics[2]. A seris of studies have been undertaken to assess the properties of monoethanolamine, methyldiethanolamine and diethylenetriamine in CO_2 absorption. Park *et al.*[3,4] studied the kinetics of the reactions between CO_2 with monoethanolamine and methyldiethanolamine. Lee *et al.*[5-7] studied the equilibrium solubility of CO_2 in aqueous monoethanolamine, methyldiethanolamine and mixtures of monoethanolamine with methyldiethanolamine solutions. Hartono *et al.*[8,9] investigated the speciation in diethylenetriamine-CO_2-H_2O using NMR and measured the kinetics of CO_2 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 CO_2 into aqueous monoethanolamine, methyldiethanolamine and diethylenetriamine solutions based on experimental data for different concentrations of absorbents and temperatures. The removal extent, absorption amount and CO_2 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 CO_2 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:

$$\text{Removal extent} = \frac{CO_2 \text{ absorption amount (mol)}}{CO_2 \text{ initial amount (mol)}}$$

$$\text{Loading} = \frac{CO_2 \text{ absorption amount (mol)}}{\text{Amine amount (mol)}}$$

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

CO_2 removal extent: Fig. 1 shows a notable decrease in removal extent with temperature in the studied range from 25 to 65 ºC 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 ºC and then decreased slowly with temperature increased from 45 to 65 ºC.

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 equation[10]. Thus, a decrease in removal extent for aqueous methyldiethanolamine solution with temperature ranged from 25 to 65 ºC 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

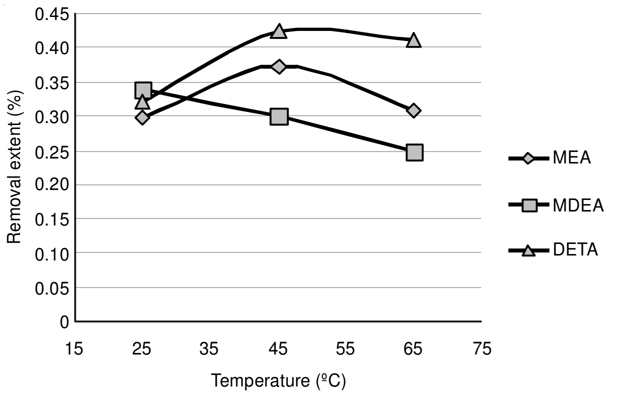

Fig. 1. Dependence of removal extent on temperature for different amine solutions (MEA = monoethanolamine, MDEA = methyldiethanolamine, DETA = diethylenetriamine)

temperature ranged from 25 to 45 ºC 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 ºC.

To compare with various absorbent concentrations at 25 ºC, the CO_2 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 CO_2 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 CO_2 removal extent of aqueous monoethanolamine solution increased to 47.8 %, while the CO_2 removal extent of aqueous methyldiethanolamine solution increased to 37 %. Therefore, 2 mol/L is optimum concentration for CO_2 removal.

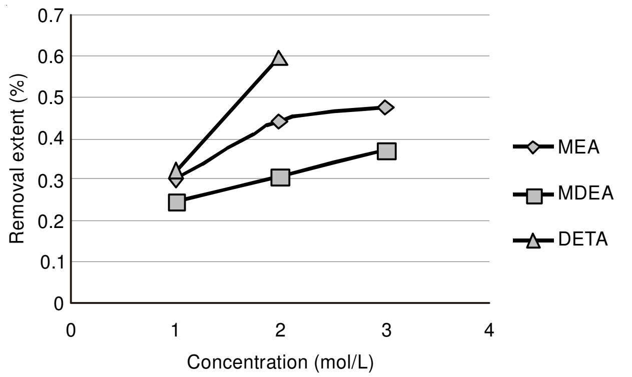

Fig. 2. Effect of absorbent concentrations on CO_2 removal extent using aqueous monoethanolamine (MEA), methyldiethanolamine (MDEA) and diethylenetriamine (DETA) solutions

Fig. 3 shows that in 1 h, the CO_2 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 CO_2.

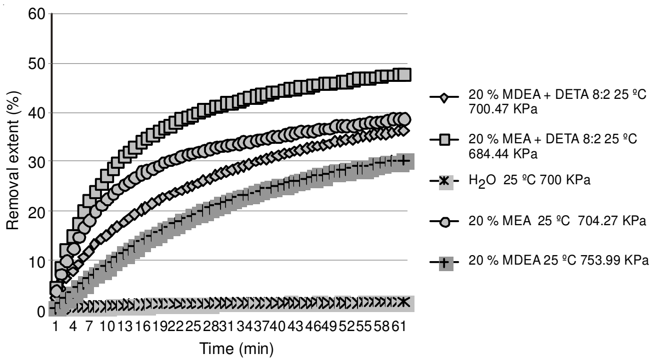

Fig. 3. Removal extent *versus* time (MEA = monoethanolamine, MDEA = methyldiethanolamine, DETA = diethylenetriamine)

CO_2 absorption amount: It can be seen from Fig. 4 that the CO_2 absorption amount did not change significantly when temperature was increased from 25 to 65 ºC. This observation indicated that the reaction of alkanolamines with CO_2 was not affected by temperatures. And the CO_2 absorption amount decreased slightly with an increase in temperature from 45 to 65 ºC, this may be for the reason that CO_2 absorption is exothermic in nature and thus an increase in temperature should decrease the extent of chemical absorption in accordance with Le Chatelier's principle[11].

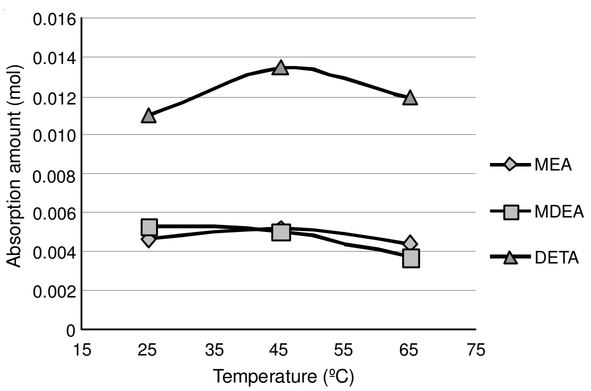

Fig. 4. Dependence of absorption amount on temperature for different amine solutions (MEA = monoethanolamine, MDEA = methyldiethanolamine, DETA = diethylenetriamine)

CO_2 absorption into various aqueous solutions of different concentration at T = 25 ºC is illustrated in Fig. 5. It can be seen that the absorption amount of CO_2 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 CO_2 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 CO_2 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 CO_2 than the aqueous solutions of single monoethanolamine and methyldiethanolamine

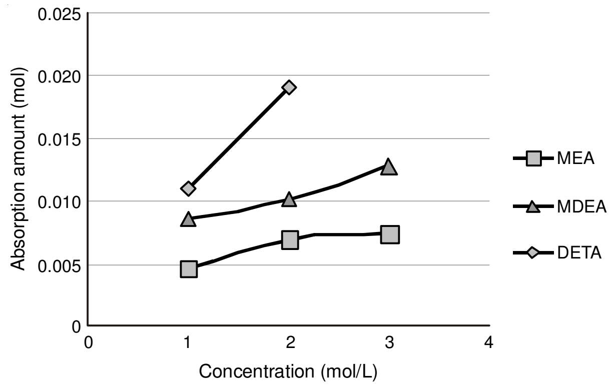

Fig. 5. Effect of absorbent concentrations on CO_2 absorption amount using aqueous monoethanolamine (MEA), methyldiethanolamine (MDEA) and diethylenetriamine (DETA) solutions

+ diethylenetriamine blended solutions. The absorption amount of CO_2 in 20wt % single methyldiethanolamine solution was low, but with the addition of diethylenetriamine, the absorption of CO_2 was remarkably promoted and nearly achieved the same as that of 20 wt % single monoethanolamine solution at 1 h.

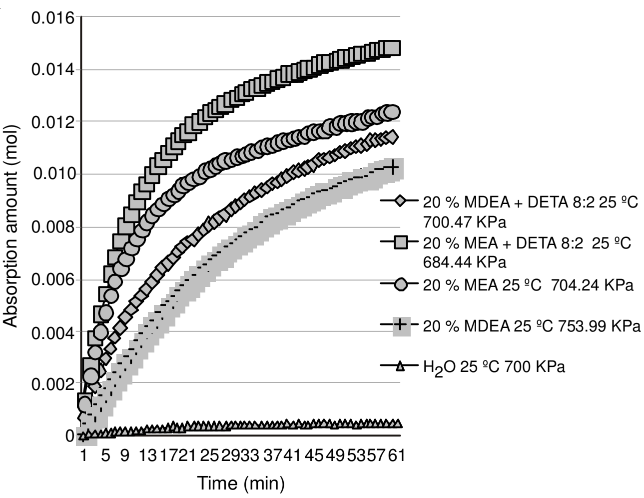

Fig. 6. Absorption amount *versus* time (MEA = monoethanolamine, MDEA = methyldiethanolamine, DETA = diethylenetriamine)

CO_2 absorption loading: Fig. 7 shows the effect of temperature on the CO_2 loading values for 1 mol/L various amine solutions. The CO_2 loading decreased slowly with temperature for monoethanolamine and methyldiethanolamine solutions. However, temperature had a significant effect on the CO_2 loading for the solutions containing diethylenetriamine, implying that 45 ºC might be optimal temperature choice for CO_2 absorption in diethylenetriamine.

The CO_2 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 CO_2 loading of aqueous monoethanolamine solution decreased slightly. monoethanolamine provided the lowest CO_2 loading, while diethylenetriamine provided the highest CO_2 loading.

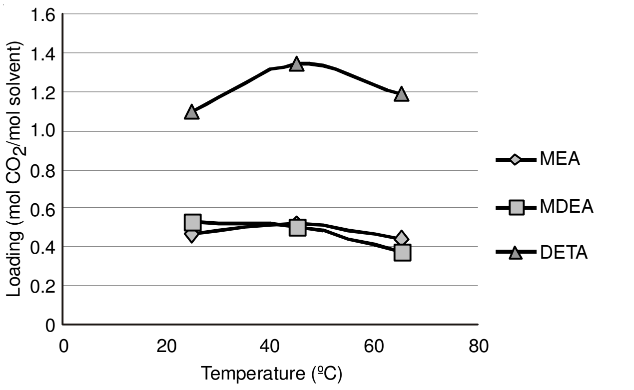

Fig. 7. Dependence of loading on temperature for different amine solutions (MEA = monoethanolamine, MDEA = methyldiethanolamine, DETA = diethylenetriamine)

In 1 h, at 25 ºC, the mixed alkanolamine solution containing 4 wt % diethylenetriamine and 16 wt % methyldiethanolamine/monoethanolamine had higher CO_2 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 CO_2 can be remarkably enhanced by the system of diethylenetriamine and methyldiethanolamine proposed by Xiang fei[12].

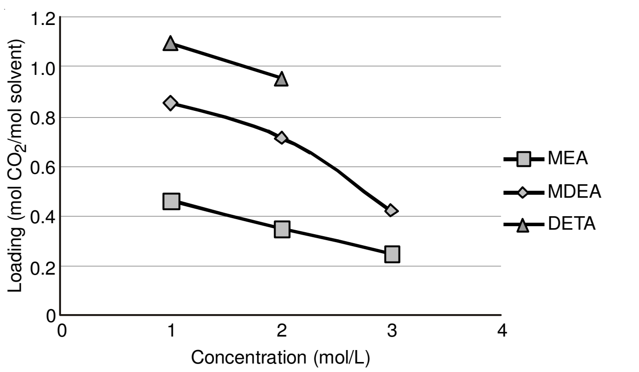

Fig. 8. Effect of absorbent concentrations on CO_2 loading using aqueous monoethanolamine (MEA), methyldiethanolamine (MDEA) and diethylenetriamine (DETA) solutions

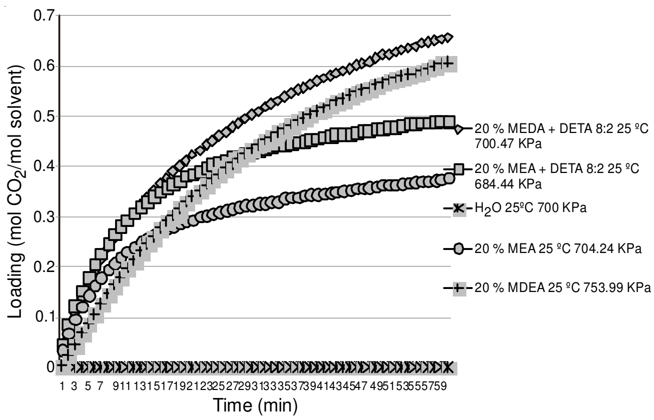

Fig. 9. Loading *versus* time (MEA = monoethanolamine, MDEA = methyldiethanolamine, DETA = diethylenetriamine)

Conclusion

The chemical absorption of CO_2 with various single and mixed amine solutions at different temperature and concentration was studied. The CO_2 removal extent was found to increase with increasing temperature in the range of 25 to 45 ºC. 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 CO_2 loading decreased. The effect of temperatures ranging from 25 to 65 ºC on absorption amount and CO_2 loading was small. The optimal condition suggested for CO_2 absorption with single amine solution was 45 ºC and 2 mol/L. From the measured CO_2 removal extent, absorption amount and CO_2 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 CO_2. 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.

ACKNOWLEDGEMENTS

The authors are grateful to the University of Toronto and the University of Chongqing for financial and other supports. This research was supported by The Fundamental Research Funds for Central Universities of China (Project No. CDJZR-10130022).

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