Effect of Chemical Structure of New Tertiary Amines Used for the Post Combustion Capture Process on Carbon dioxide (CO$_2$) Kinetic Absorption and Regeneration, and Heats of Regeneration

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Abstract
This work focused on the reaction kinetic absorption and regeneration rate of the new tertiary amines; 4-(dimethylamino)-2-butanol (DMAB), 4-(dipropylamino)-2-butanol (DPAB), 4-(dibutylamino)-2-butanol (DBAB), 4-((2-hydroxyethyl)(methyl)amino)-2-butanol (HEMAB) and 4-((2-hydroxyethyl)(ethyl)amino)-2-butanol (HEEAB). The results showed that three amines (i.e. DMAB, HEMAB and HEEAB) had the fast CO$_2$ absorption rate (0.082, 0.111 and 0.142 mol CO$_2$/min) and CO$_2$ regeneration rate (0.512, 0.452 and 0.295 mol CO$_2$/min) while maintaining low heat input of CO$_2$ regeneration (39.73, 60.48 and 72.44 kJ/mol CO$_2$) compared to MDEA and DEAB. Based on these results, DMAB, HEMAB, and HEEAB can be considered to be promising amine components for blending for a post combustion CO$_2$ capture process.

1. Introduction
Our newly developed tertiary amines, 4-(dimethylamino)-2-butanol (DMAB), 4-((2-hydroxyethyl)(methyl)amino)-2-butanol (HEMAB) and 4-((2-hydroxyethyl)(ethyl)amino)-2-butanol (HEEAB) have shown quite an improvement from methyldiethanolamine (MDEA) solvent in terms of increased CO$_2$ absorption capacities and cyclic capacities. However, it is essential to evaluate the reaction kinetics of CO$_2$ absorption and regeneration in order to evaluate the potential of amine for use to capture CO$_2$ and for designing of a CO$_2$ capture plant. This work investigates the kinetics of the reactive absorption and regeneration of CO$_2$, and heat input for regeneration of the newly synthesized tertiary amines (i.e. DMAB, HEMAB and HEEAB) as compared with DEAB and MDEA.

2. Experimental Section
The chemical structures of the new tertiary amines in this study are shown in Fig. 1 compare DEAB and MDEA.
The experimental set-up for measurement of the absorption and regeneration kinetics is shown in Fig. 2.

For an absorption run, 100 mL of a desired amine solution (2 mol/L) was transferred into the flask and placed in the hot oil bath. After the amine temperature had reached 313 K, 15 kPa CO$_2$ feed regulated at 200 mL/min ($\pm 2$ accuracy) was introduced into the amine solution through the gas dispersion tube. Reaction time at zero was marked when the first bubble emerged into the solution from the disperser tip. First sample was taken by pipetting 1 mL of amine after 15 min had passed. The next samples were taken at 15, 30, and 45 min intervals, respectively during the first, second and third hour and onwards. CO$_2$ loading was determined using the chittick apparatus. CO$_2$ loading and time were plotted and used to determine the absorption kinetic rate based on its slope. The loaded amine after the test was used later for the regeneration rate measurement.

For regeneration run, the same set-up shown in Fig. 2 used for the absorption rate measurement was used. However, the gas dispersion tube was removed and replaced by a lid. In this test, 90 mL of the rich amine obtained earlier from the absorption test was transferred into the flask. The loaded amine was heated to the test temperature set at 363 K. Once the temperature had reached and become stabilized. Sample was taken by carefully pipetting 1 mL of the amine to quickly determine its CO$_2$ loading. Sampling was continued every 8 min to determine the amine’s loading. The calculation was similar to the absorption rate measurement.

3. Results

The rate of CO$_2$ absorption at 313 K was largely affected by the amine structure showing an increase in the order of 0.063, 0.082, 0.088, 0.111 and 0.142 mol CO$_2$/min for MDEA, DMAB, DEAB, HEMAB and HEEAB, respectively. By comparing the CO$_2$ absorption rate within the group of di-alkyl substituted amines, DEAB showed a slightly higher absorption rate than that of DMAB.
This was probably the influence of a better electron-donor group of DEAB which also dominated over its own steric effect.

In case of the group of hydroxy-alkyl-alkyl substituted amines, HEMAB and HEEAB both showed an excellent enhancement of the absorption with the rates one to two folds higher than that of DMAB, DEAB, and MDEA. In addition to electron donating ability within this group of amines, having an extra -OH group could have been a factor in boosting up the absorption rate of HEMAB and HEEAB. Presence of more -OH groups likely increased the ability for water to solvate the amine molecule which was essential in CO₂ absorption reactions shown in Eq. (1) to (4).

\[
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad (1)
\]

\[
\text{H}_2\text{O} + \text{R}_3\text{N} \overset{\text{fast}}{\rightleftharpoons} \text{R}_3\text{NH}^+ + \text{OH}^- \quad (2)
\]

\[
\text{H}^+ + \text{R}_3\text{N} \overset{\text{fast}}{\rightleftharpoons} \text{R}_3\text{NH}^+ \quad (3)
\]

\[
\text{CO}_2 + \text{OH}^- \overset{\text{slow, K}_{\text{OH}^-}}{\rightleftharpoons} \text{HCO}_3^- \quad (4)
\]

The CO₂-amine regeneration rate increased in the order of 0.220, 0.243, 0.295, 0.452 and 0.512 mol CO₂/min for MDEA, DEAB, HEEAB, HEMAB and DMAB, respectively. This trend of the rate data has shown quite an improvement of all new amines from the heavily used conventional MDEA in terms of easy to regenerate property. Specifically, the CO₂ regeneration ability of DMAB and HEMAB have also improved quite significantly from their starting DEAB.

In terms of heat input for regeneration, DMAB also stands out as seen from only 39.73 kJ/mol heat input required in the CO₂ regeneration test, compared to 72.44, 60.48, 56.59, and 54.37 kJ/mol CO₂ for HEEAB, HEMAB, MDEA, and DEAB respectively. Methyl group in DMAB could be a reason of the amine having such a low heat input due to its least contribution to the amine electron density, thus a weaker bond with the CO₂ to be broken.

4. **Summary**

Hydroxy-alkyl-alkyl substituted amines, HEMAB and HEEAB showed an excellent enhancement of the CO₂ absorption rates which were the highest, due to a presence of more -OH. DMAB was found to have the fastest rate of regeneration while requiring the lowest heat input for regeneration between all amines.