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Optimal Ratio of Methyldiethanolamine and Monoethanolamine Based on Regenerative Energy and Absorption Capacity Analysis

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Chemical absorption using alkanolamine is the most used technique for carbon dioxide capture and storage (CCS). The energy required for regenerating the alkanolamine aqueous solution accounts for 70 - 80 % of the whole process. In this work, a new method was proposed to optimize the optimum ratio of mixed amines to reduce the regeneration heat. This method was developed base on slope analysing. The regeneration heat was characterized by absorption heat, sensible heat, and vaporization heat, which were calculated with the improved expression bases on expression reported by Nwaoha. The absorption heat, sensible heat, and vaporization heat of mixed amine with the wide range mass ratios of MDEA:MEA = 0:1, 0.2:0.8, 0.4:0.6, 0.6:0.4, 0.8:0.2, 1:0 were calculated. The results show that sensible heat is the main contribution of regeneration heat. Increasing the ratio of MDEA can reduce the sensible heat. The optimal mixed amine mass ratio is MDEA:MEA = 0.4:0.6, which has 34.51 % regeneration heat reduction compare with 30 wt.% MEA. The optimal ratio of mixed amine solution can reduce the regenerative heat to the greatest extent to reduce carbon emissions.

1. Introduction

Currently, carbon dioxide capture and storage (CCS) is a viable way to reduce carbon emissions (Lameh et al., 2020). Alkanolamines such as Monoethanolamine (MEA), Methyldiethanolamine (MDEA), Diethanolamine (DEA), Triethanolamine (TEA) is commonly used solvents used to absorb CO_2 in the chemical absorption method (Chen et al., 2018). The biggest disadvantage of the chemical absorption method is the high energy consumption of amine solution regeneration. The regeneration energy of the MEA solvent is high up to 70 – 80 % from the capturing plant cost (Bravo et al., 2021). Mixed amine solutions are often used to reduce the heat of regeneration (Murshid et al. 2020). MEA solution has a higher absorption rate, but the absorption heat is up to 85 kJ·mol^{-1} CO_2. The absorption heat of MDEA is 58.8 kJ·mol^{-1} CO_2 which is much lower than MEA, but absorption rate is also much lower than MEA (Abd et al., 2020). Amine blends can combine the different advantages of the two amines to achieve the overall performance improvement effect. How to optimize the ratio of mixed amine solution is a difficult problem, which has never been reported in previous literature.
The purpose of this paper is to develop an optimization method to optimize the optimal proportion of mixed amine under a wide range of mixed amine concentration ratios. Regeneration heat and absorption capacity are two main factors of this method. The regeneration heat is calculated by summing absorption heat, sensible heat, and vaporization heat. This method can accurately determine the optimal ratio of amine solution.

2. Theory and method

2.1 Regeneration heat

The regeneration heat has a crucial impact on the total cost of CO_2 capturing plants, and therefore it is considered as the main criterion in the economic evaluation of CO_2 capturing. The regeneration heat (Abd et

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al., 2020) consists of three elements: absorption heat, sensible heat, and vaporization heat; it can be formulated by Eq(1).

$$Q_{reg} = Q_{abs} + Q_{sen} + Q_{vap} \tag{1}$$

where Q_{reg} is regeneration heat (kJ/mol CO_2); Q_{abs} is absorption heat, which means the energy required to break the CO_2 carrying species (carbamate, bicarbonate, and carbonate) formed during the amine–CO_2 reactions (kJ/mol CO_2); Q_{sen} is sensible heat, which is the energy required to increase the temperature of the rich amine solution to a regeneration temperature (kJ/mol CO_2); Q_{vap} is vaporization heat, the heat of water vaporization which is the energy required to produce the water vapor for regeneration process (kJ/mol CO_2).

2.2 Absorption heat

The absorption of CO_2 by the amine solution is an exothermic reaction. The absorbed heat is the heat released by the amine protons and carbon dioxide to form carbamate, bicarbonate, and carbonate. The energy is required to break the carbamate, bicarbonate, and carbonate in the regeneration column. These two kinds of heat are numerically equal, shown in Eq(2).

$$\left|Q_{abs}\right| = \left|Q_{\mathrm{dis}}\right| \tag{2}$$

where Q_{dis} is dissolution heat (Abd et al., 2020). The absorption heat can be calculated by Eqs(3) and (4).

$$Q_{abs} = \Delta H_0 \left[\Delta C p_{a\,\mathrm{min}\,e} \Delta T\right]^n \tag{3}$$

$$\ln(Q_{abs}) = n \ln\left(\left[\Delta C p_{a\,\mathrm{min}\,e} \Delta T\right]\right) + \ln\left(\Delta H_0\right) \tag{4}$$

where ΔH_0 is absorption heat of standard condition (kJ/mol CO_2), Cp_{amine} is the specific heat capacity of an amine solution (kJ/mol), T is the temperature of amine solution (°C). $ln([\Delta C p_{a\,min\,e} \Delta T])$ and $ln(Q_{abs})$ (Kim and Svendsen, 2007) can be obtained from experimental data in the literature (El Hadri et al., 2017), then $ln(\Delta H_0)$ and n can be obtained by regression.

2.3 Sensible heat

Sensible heat is the energy required to increase the temperature of the rich amine solution to a regeneration temperature, which can be calculated by Eq(5).

$$Q_{sen} = \frac{\omega_{total} C p_{mol} \Delta T}{\left(\alpha_{co_2-rich} - \alpha_{co_2-lean}\right) \omega_{a\,\mathrm{min}\,e}} \tag{5}$$

where ω_{total} is the total concentration of species (amine and CO_2) in the saturated amine solution (mol/L), α_{co_2} is the CO_2 loading of both the saturated amine solution and lean amine solution (mol CO_2/mol amine).

2.4 Vaporization heat

In the process of regenerating amine solution, a part of water will turn into vapor. The amount of energy required to vaporized steam in the stripper depends on the amount of water vaporized and the latent heat of the water. The vaporization heat can be calculated by Eqs(6) - (8) (Nwaoha et al., 2017a).

$$Q_{vap} = \Delta H_{vap-H_2O} \frac{P_{H_2O}}{P_{CO_2}} \tag{6}$$

$$P_{H_2O} = P^{sat} x_{H_2O-lean} \tag{7}$$

$$P_{CO_2} = 101.3 - P^{sat} x_{H_2O-lean} \tag{8}$$

where ΔH_{vap-H_2O} is the latent heat of water at regeneration temperature (kJ/mol), P_{H_2O} and P_{CO_2} are the partial pressures of water and CO_2 (kPa), P^{sat} is the saturation pressure of water at desorption temperature (kPa), $x_{H_2O-lean}$ is the mole fraction of water in the lean amine solution.

2.5 Absorption capacity

Aspen Hysys is used to determine the absorption capacity of the mixed amine solution, and the flow chart is shown in Figure 1a. The flow rate and concentration of the amine solution are fixed, gradually increase the flow of carbon dioxide. Since the absorption of CO_2 by the amine solution is an exothermic process, the temperature of the mixture solution increases gradually. The temperature reaches its maximum when the amine solution reaches saturation. The process of temperature change is shown in Figure 1b. When the temperature reaches its maximum, the absorption capacity can be calculated from the flow of CO_2. As shown in Eq(9):

$$C_{CO_2} = \frac{q_{CO_2}}{q_{amine}\omega_{amine}} \tag{9}$$

where C_{CO_2} is absorption capacity (mol CO_2/mol amine), q_{CO_2} is the flow of CO_2 (mol/min), q_{amine} is the flow of amine (L/min), ω_{amine} is the concentration of amine solution (mol/L).

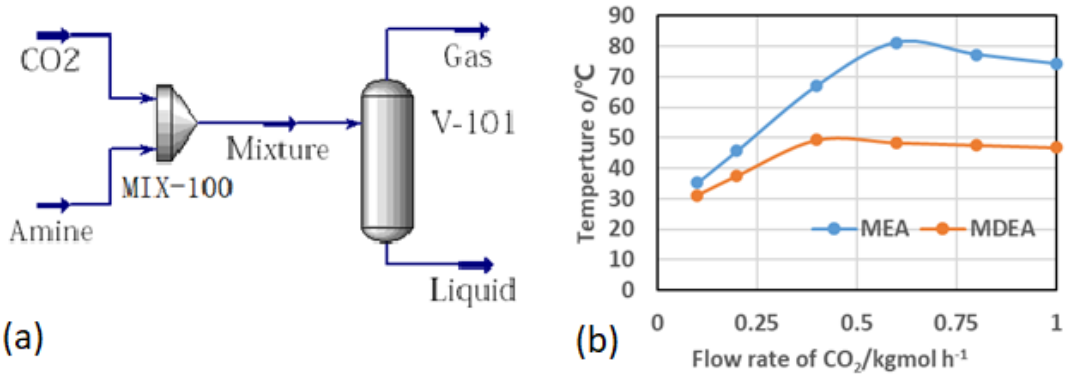

Figure 1: (a) Flow chart of Aspen Hysys, (b) Temperature change under different flow rates of CO_2.

3. Results and discussion

3.1 Absorption heat

Three different amines (MEA, MDEA, and TEA) were used to regression the parameters of $\ln(\Delta H_0)$ and n in Eq(4). The amines were used with the concentration of 30 wt.% (Svensson et al., 2013). The regression results are shown in Figure 2a. The regression accuracy is good, R squared is 0.975. According to the regression result, Eq(4) could be modified to Eq(10).

$$Q_{abs} = \exp\left(0.2035\ln\left(\left[\Delta Cp_{amine}\Delta T\right]\right) + 4.5345\right) \tag{10}$$

According to Eq(10), the absorbed heat of MEA, MDEA, and DEA was calculated. The absolute relative deviation (ARD) from the experimental value is shown in Table 1. ARD of three amines was less than 3.45 %. The heat absorbed is a function of ΔCp_{amine} and ΔT. When the absorption heat of the mixed amine system was calculated, Cp_{amine} and T of different ratios of mixed amine solution were obtained by Aspen Hysys (Version 11.0, Package: Acid Gas - chemical solvent). The absorption heat of the mixed amine system calculated with Eq(10) at different mixing ratios is shown in Figure 2b. Adding MDEA in MEA can effectively reduce the heat absorption of MEA; this is because the heat absorption of MDEA (58.8 kJ/mol CO_2) is smaller than MEA (85 kJ/mol CO_2).

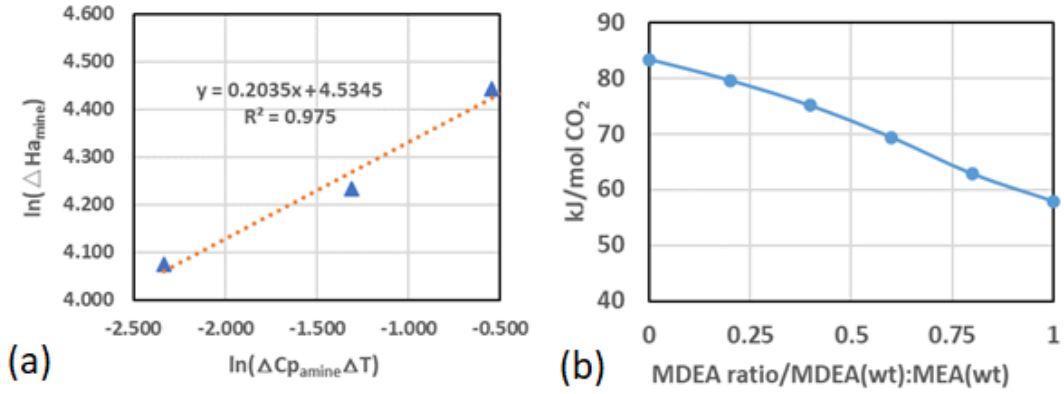

Figure 2: (a) Absorption heat regression, (b) Absorption heat of mixed amine vs ratio of mixed amine

Table 1 Estimated heat of absorption of MEA, MDEA, DEA using Eq(10) compared to literature data

30wt.%	Literature (kJ/mol CO_2)	(Nwaoha et al.， 2017)	ARD[c]	This work	ARD
MEA	85[a]	84.3	0.82	83.37	1.92
MDEA	58.8[b]	57.9	1.53	57.96	1.43
DEA	69[a]	72.6	5.22	71.38	3.45

Note: a: the data come from El Hadri et al. (2017)

Note: b: the data come from Kim et al. (2014)

Note: c: $$ARD = 100\frac{abs(x_{calcuation} - x_{experiment})}{x_{experiment}} \quad (11)$$

3.2 Sensible heat, Vaporization heat, and Absorption capacity

Sensible heat is the energy needed to raise the temperature of the CO_2 saturated amine solution to the desorption temperature, which was calculated using Eq(5). The sensible heat of mixed amine with different MDEA ratios was displayed in Figure 3a. The sensible heat can be significantly reduced by adding MDEA. The reason is that the addition of MDEA in a blended solvent provides R_3N and HCO_3^-, which split and thus decrease the free energy gaps, resulting in tremendously lower sensible heat. The important role of R_3N and HCO_3^- were described in detail in the work of Shi et al. (2014).

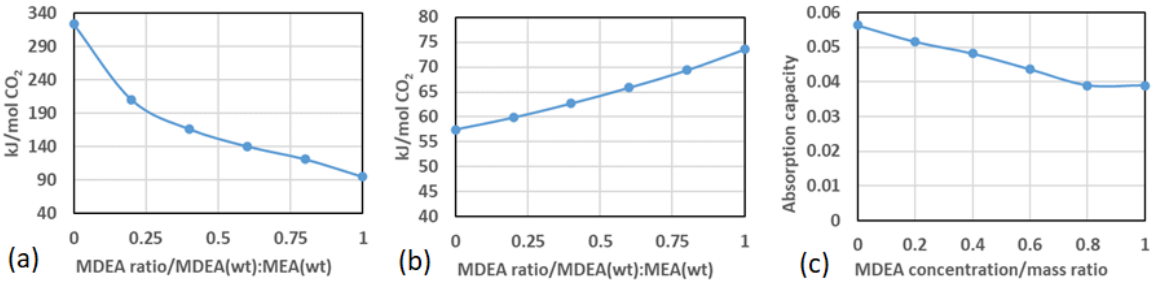

Figure 3: Heat duty and absorption capacity of mixed amine with different MDEA ratios, (a) Sensible heat, (b) Vaporization heat, (c) Absorption capacity

The vaporization heat of mixed amine calculated by Eqs(6) - (8) was given in Figure 3b, which shows that the vaporization heat is slightly increasing with the concentration of MDEA. Chakma (1997) stated that the heat of vaporization of aqueous amine solutions depends on its water concentration. In this work, the concentration of water is constant (70 wt.%). The author believes that the main reason is the difference in the boiling point of MDEA and MEA. The boiling point of MEA (170.9 °C) is much lower than that of MDEA (246 °C). This will result in a lower mole fraction of water in the gas phase.

The absorption capacity of mixed amine at different mixing ratios is calculated by Eq(9) shown in Figure 3c. With the increasing MDEA ratio, the absorption capacity of mixed amine decreases. The reaction rate of MEA and CO_2 is much faster than MDEA. The addition of MDEA can reduce the absorption rate of the mixed amine. Therefore, the absorption capacity of mixed amine decreases with the addition of MDEA.

3.3 The optimal ratio of mixed amines

The regeneration heat of mixed amine calculated based on the addition of the absorption heat, sensible heat, and vaporization heat was displayed in Figure 4a. The main contribution of regeneration heat was sensible heat. The regeneration heat declines with the increase of the ratio of MDEA. The same pattern can be observed in absorption capacity in Figure 3c. The addition of MDEA reduces the regeneration heat and amine absorption capacity at the same time. If the minimum regeneration heat is used as the evaluation index, pure MDEA is the optimal result, If the maximum absorption capacity is used as the evaluation index, pure MEA is the best result. But our goal is to achieve maximum absorption capacity with minimum regeneration heat, and it is necessary to determine the appropriate mixture ratio of amine solution. To better compare regenerative heat and absorption capacity, Eq(11) is used to normalize the data, and the result was showed in Figure 4b.

$$data_{normalization} = \frac{data_i - data_{\min}}{data_{\max} - ata_{\min}} \tag{11}$$

where data is absorption capacity or regeneration heat.

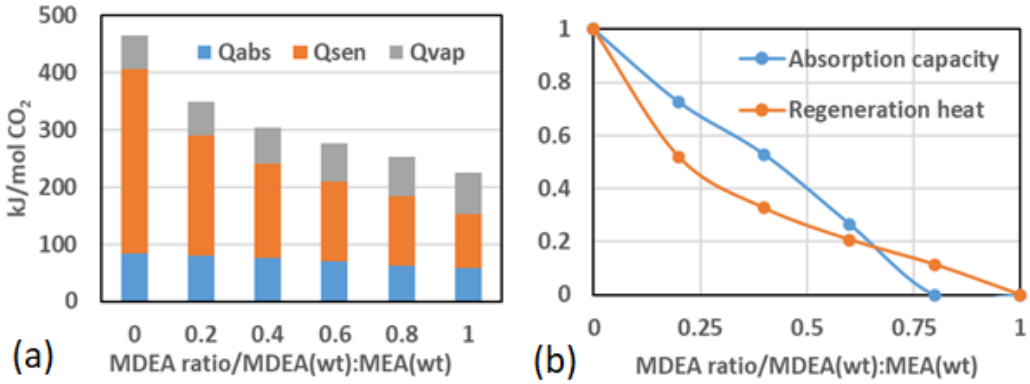

Figure 4: *(a) Regeneration heat of mixed amine, (b) Normalization of regeneration heat and absorption capacity.*

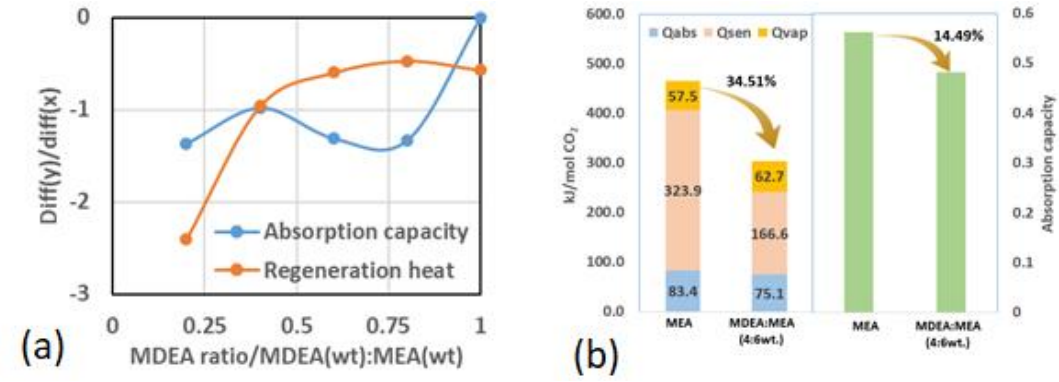

Figure 5: (a)Slopes of mixed amine, (b)Comparison of regeneration heat and absorption capacity

As can be seen from Figure 4b, with the increase of the MDEA ratio, the decrease rates of regeneration heat and amine absorption capacity are different. The slope is the best way to show how fast the curve is changing; slopes of these two curves were calculated, as shown in Figure 5a. As can be seen from Figure 5a, when the MDEA ratio is between 0 and 0.4, the slope of regeneration heat is smaller than that of absorption capacity, which means that in this interval, the decreasing speed of regeneration heat is faster than that of absorption capacity. If the MDEA ratio continues to increase, the decreasing rate of absorption capacity will be greater than that of regenerative heat, that is not what the authors want. Therefore, when the ratio of MDEA is 0.4, we can obtain maximum absorption capacity with minimum heat regeneration. Figure 5b shows the comparison results of absorption capacity and regeneration heat between 30 wt.% MEA solution and mixed amine solution with an MDEA ratio of 0.4 (MDEA:MEA = 0.4:0.6). Under this condition, the regeneration heat decreased by 34.51 % and the absorption capacity by 14.49 %. The decrease rate of regeneration heat is 2.4 times that of absorption capacity.

4. Conclusions

The calculation expression of absorbed heat base on specific enthalpy was improved, the ARD of the improved expression of the three amines (MEA MDEA DEA) was 1.92 %, 1.43 %, and 3.45 %.
A novel method for accurately determining the absorption capacity of CO_2 using the Aspen Hysys was developed, and this method can accurately assess the absorption capacity of amine.
Regeneration heat containing absorption heat, sensible heat, and vaporization heat of mixed amine with a large range mass ratio of MDEA were analyzed, it was found out that the main contribution of regeneration heat was sensible heat.
A new method for determining the optimal MDEA ratio base on slope analyzing was developed. The mass ratio of mixed amine was 4:6 (MDEA:MEA), which can reduce the regeneration heat by 34.51 % compared with 30 wt.% MEA.

Nomenclature

Q_{reg} – Regeneration heat, kJ/mol CO_2
Q_{abs} – Absorption heat, kJ/mol CO_2
Q_{sen} – Sensible heat, kJ/mol CO_2
Q_{vap} – Vaporization heat, kJ/mol CO_2
ΔH_0 – Standard absorption heat, kJ/mol CO_2
Cp_{amine} – Specific heat capacity, kJ/mol °C
T – Temperature, °C
C_{co2} – Absorption capacity, mol CO_2/mol amine
q_{co2} – Flow of CO_2, mol/min
q_{amine} – Flow of amine, L/min
ω_i – Concentration, mol/L
α_{co2} – CO_2 loading, mol CO_2/mol amine
ΔH_{vap} – latent heat, kJ/mol
P_i – Partial pressures, kPa
P^{sat} – Saturation pressure, kPa
x_i – Mole fraction of component i.

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