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Regeneration Energy Analysis of Aqueous Tri–Solvent Blends Containing 2–Amino–2–Methyl–1–Propanol (AMP), Methyldiethanolamine (MDEA) and Diethylenetriamine (DETA) for Carbon dioxide (CO_2) Capture

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Abstract

This study investigated the contribution of absorption heat, sensible heat and heat of vaporization towards the regeneration energy (Q_{reg}, kJ/g-CO_2) of AMP–MDEA–DETA tri–solvent blends. The experiment was conducted at atmospheric pressure and 363 K. Their CO_2 absorption prior to their regeneration was conducted at 313 K, 101.3 kPa and 15.1 v/v% CO_2. The regeneration energy was estimated using two different methods (experimental and correlation) and the results showed similar trend. Results showed that the AMP–MDEA–DETA blends have lower regeneration energy than MEA and this was due to a much lower sensible heat of the blends. It was also discovered that higher absorption heats does not necessarily indicate higher regeneration energy, rather the effects of both sensible heat and/or heat of vaporization can greatly affect the regeneration energy.

Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: Carbon dioxide (CO_2) Capture; Regeneration Energy; Absorption Heat; Sensible Heat; Heat of Vaporization; 2-amino-2-methyl-1-propanol (AMP); Methyldiethanolamine (MDEA); Diethylenetriamine (DETA), Monoethanolamine (MEA)

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1. Introduction

Carbon dioxide (CO_2) capture from fossil fuel processing and utilization by chemical absorption using amine solvents is the most matured technology. The most popular and standard amine solvent is monoethanolamine (MEA), but it is associated with high cost of solvent regeneration. It was reported in previous pilot plant study that this can be as high as 70 % of plant operating cost [1]. Therefore, it is very important to investigate novel amine blends that will offer a much lower energy of solvent regeneration. To investigate this, it is integral to understand the various parameters that contribute to the regeneration energy (Q_{reg}, kJ/g–CO_2) as shown in Equation 1.

$$Q_{\mathrm{reg}} = (Q_{\mathrm{des}}) + (Q_{\mathrm{sen}}) + (Q_{\mathrm{vap}}) \quad (1)$$

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

This study is aimed at identifying the effect and contribution of each heat towards regeneration energy.

2. Experiment

2.1. Chemical and materials

AMP (≥ 97 %) was purchased from Fluka Analytical, USA. MDEA (≥ 99 %), DETA (99 %) and MEA (≥ 98 %) were all obtained from Sigma–Aldrich (Missouri, USA). All the solvents were used without any additional purification. Hydrochloric acid, HCl (1 kmol/m^3) used for titration was purchased from Fisher Chemical (New Jersey, USA). The actual amine concentration and their CO_2 loading were confirmed at the endpoint of methyl orange. Premixed gas (15 v/v% CO_2 balanced with N_2) was acquired from Praxair Inc. (Ontario, Canada). ProMax® 4.0 licensed by Bryan Research & Engineering, USA was used to estimate the density and specific heat capacity of the amine solutions.

2.2. Experimental run

Prior to the regeneration experiment, all the aqueous amine solutions (single and tri–solvent blends) were subjected to CO_2 absorption (15.1 v/v% CO_2, 101.3 kPa and 313 K) using similar experimental set–up reported by Tontiwachwuthikul et al. [2]. The regeneration set–up is displayed in Fig. 1 [3]. The regeneration was conducted at 101.3 kPa and 363 K. The experimental procedure for both the CO_2 absorption and regeneration is explained in our previous publication [3].

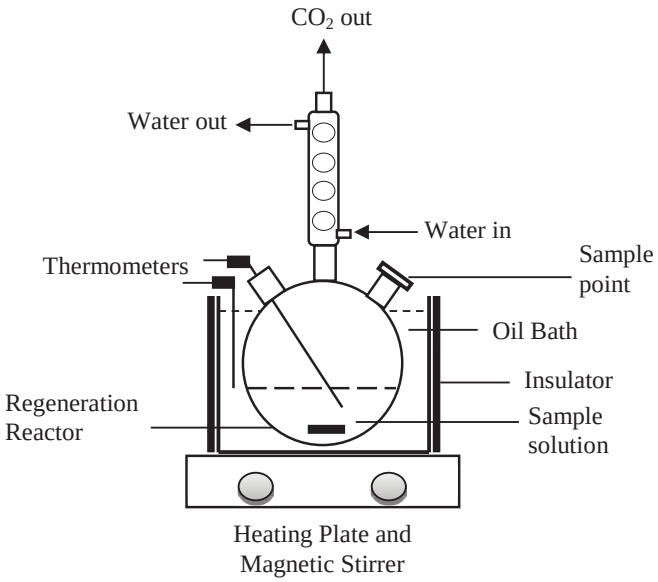

Fig. 1. Regeneration process experimental apparatus.

3. Results and discussion

3.1. Regeneration energy (Experimental method)

The regeneration heat duty (regeneration energy, Q_{reg}, kJ/g–CO_2) of the studied aqueous amine solutions were determined by dividing the heat input (Q_{input}) which was experimentally obtained by the amount of desorbed CO_2 as a function of time as shown in Equation 2 [4]. The heat input was calculated using heat transfer correlation for conduction.

$$Q_{\mathrm{reg}} = \frac{Q_{input}}{(\alpha CO_{2\_rich} - \alpha CO_{2\_lean})C_{amine}} \quad (2)$$

Where Q_{input} is the heat transfer rate to the sample (kJ/hr), C_{amine} is the amine concentration (kmol/m^3), αCO_2_rich is the equilibrium CO_2 loading (mol CO_2/mol amine) while αCO_2_lean is the lean amine after the regeneration (mol CO_2/mol amine).

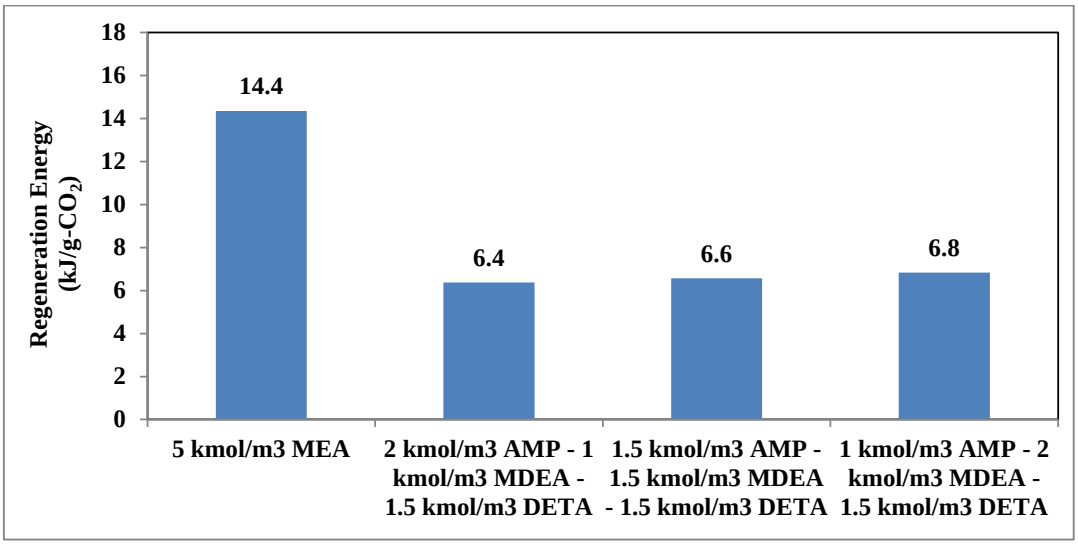

Fig. 2. Regeneration energies of MEA and all the AMP–MDEA–DETA blends using the correlation of Equation 2.

The regeneration energy of the AMP–MDEA–DETA blends as displayed in Fig. 2 indicates 46.4 – 51 % decrease compared to 5 kmol/m^3 MEA. It is believed that the presence of more bicarbonates (HCO_3^-) in the tri–solvent blends when compared to MEA. According to Shi et al. bicarbonates play a double role of deprotonating protonated amines and also releasing CO_2 as shown in Equations 3–4 [4]. These reactions will be more in the tri–solvent blends compared to MEA, hence the much lower regeneration energy [3].

$$AmineH^+ + HCO_3^- \leftrightarrow Amine + H_2CO_3 \quad (3)$$

$$H_2CO_3 \leftrightarrow CO_2 + H_2O \quad (4)$$

3.2. Regeneration energy (Correlation method)

The second method of determining regeneration energy of the amine solutions is depicted in Equations 5–7 for absorption heat, sensible heat and heat of vaporization [5–7].

3.2.1 Absorption heat

$$\Delta H_{abs} = \sum_{i=1}^{m} \frac{C_i}{C_T} \Delta H_{abs\_i} \quad (5)$$

Where ΔH_{abs} is the absorption heat of the blended amine solution (kJ/g–CO_2), C_i is the concentration of the ith amine in the blended amine solution (kmol/m^3), C_T is the total concentration of the amine solution (kmol/m^3), while

ΔH_{abs_i} is the absorption heat of the i^{th} amine in the blended amine solution (kJ/g–CO_2).

Table 1 Absorption heat of the AMP–MDEA–DETA tri–solvent blends using Equation 5

Amine solutions	ΔH_{abs} (kJ/g-CO_2)	References
MEA	1.93	[8]
AMP	1.84	[9]
MDEA	1.33	[10]
DETA	2.03	[11]
2 kmol/m^3 AMP – 1 kmol/m^3 MDEA – 1.5 kmol/m^3 DETA	1.77	Equation 5
1.5 kmol/m^3 AMP – 1.5 kmol/m^3 MDEA – 1.5 kmol/m^3 DETA	1.72	Equation 5
1 kmol/m^3 AMP – 2 kmol/m^3 MDEA – 1.5 kmol/m^3 DETA	1.67	Equation 5

Results displayed in Table 1 show that the absorption heat of the AMP–MDEA–DETA blends has slightly lower absorption heat than MEA. Considering the blends, it is noticed that the absorption heat decreased as AMP/MDEA ratio decreased. This can be due to the presence of more MDEA which increased the MDEA–CO_2 reaction pathway.

3.2.2 Sensible heat

Sensible heat is the second energy that makes up the regeneration energy. It is defined as the energy required to raise the temperature of the CO_2 saturated amine solution to the regeneration temperature.
The correlation in Equation 6 [12] was used to predict the sensible energy requirements of MEA and AMP – MDEA – DETA blends.

$$Q_{\text{sen}} = \frac{\rho C_p \Delta T}{(\alpha CO_{2_{rich}} - \alpha CO_{2_{lean}})\, C_{amine}] M_{CO2}} \quad (6)$$

Where Q_{sen} is the sensible heat (kJ/g–CO_2), Cp is the specific heat capacity of the amine solution (kJ/kg.K), ρ is the density of the amine solutions, M_{CO2} is the molecular weight of CO_2 (44 g/mol) while ΔT is the temperature difference between absorption and regeneration (50 K).

Table 3 Density and specific heat capacity of 5 kmol/m^3 MEA and AMP–MDEA–DETA tri–solvent blends at 363 K using ProMax® 4.0 simulator while cyclic capacity has been previously reported by Nwaoha et al. [3].

Amine solutions	Cyclic Capacity (mol CO_2/L amine soln.)	ρ (kg/L)	Cp (kJ/kg/K)
5 kmol/m^3 MEA	0.6	0.9729	3.85
2 kmol/m^3 AMP – 1 kmol/m^3 MDEA – 1.5 kmol/m^3 DETA	1.35	1.0	3.55
1.5 kmol/m^3 AMP – 1.5 kmol/m^3 MDEA – 1.5 kmol/m^3 DETA	1.31	0.9997	3.59
1 kmol/m^3 AMP – 2 kmol/m^3 MDEA – 1.5 kmol/m^3 DETA	1.26	0.9986	3.64

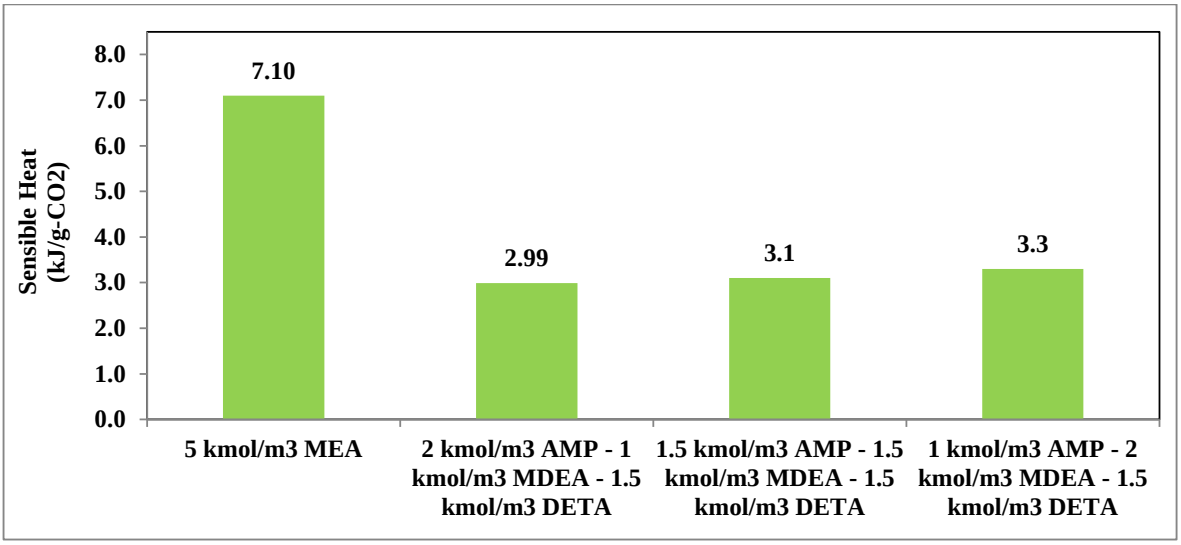

Fig. 3. Sensible heat of the amine solutions using Equation 6.

Fig. 3 displays the sensible heat of single solvent MEA and the AMP–MDEA–DETA tri–solvent blends. It can be noticed that all the blends have lower sensible heat (53.5 – 57.9 % lower) than MEA. It was also discovered that as the AMP/MDEA mole ration decreased, the sensible heat increased. This can be attributed to increase in AMP concentration which led to an increased HCO_3^- concentration [3].

3.2.3 Heat of vaporization

Heat of vaporization is third heat that adds up to the regeneration energy (Equation 1). Chakma stated that water concentration in the amine solution determines that heat of vaporization required [13]. This is the reason why 50

wt.% TEA (triethanolamine) has less vaporization heat than 30 wt.% MEA [13]. Therefore, Equation 7 [7,14] was used to determine the heat of vaporization of the amine solutions in this study.

$$Q_{\text{vap}} = \Delta H_{vap,H2O} \frac{P_{H2O}}{P_{CO_2}} \frac{1}{M_{CO_2}} \quad (7)$$

Where $\Delta H_{vap,H2O}$ is the enthalpy of water vaporization at 363 K (41 kJ/mol or 0.932 kJ/g), P_{CO2} and P_{H2O} is the partial pressures of CO_2 and water at 363 K (kPa). The partial pressure of water was determined by multiplying the water mole fraction in the amine solution by the vapour pressure of water at 363 K. The vapour pressure of water at 363 K was calculated using Antoine equation. The partial pressure of CO_2 was estimated by subtracting the water partial pressure from the atmospheric pressure.

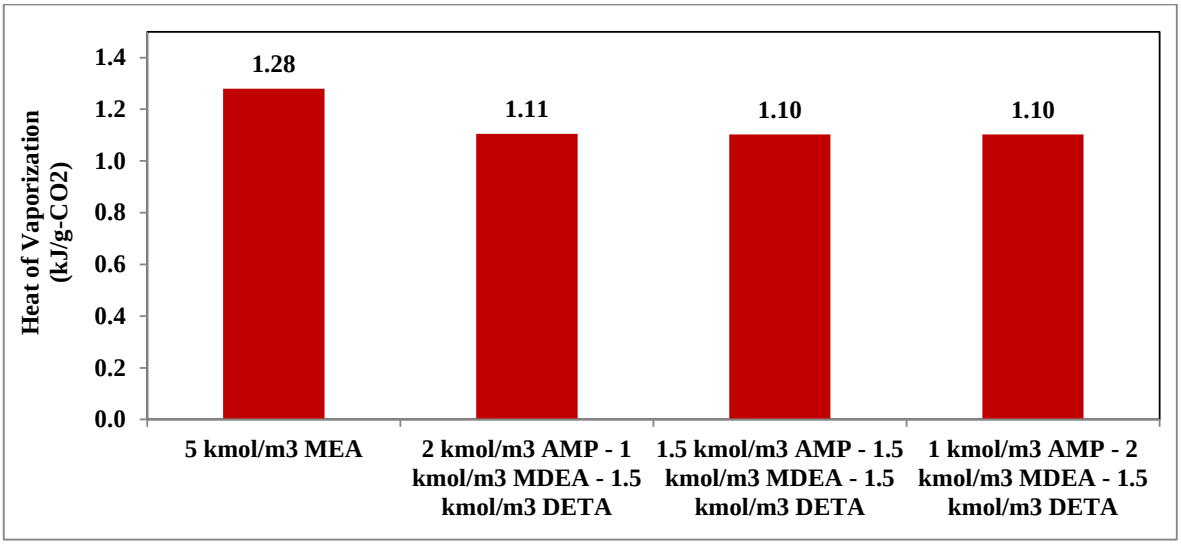

Fig. 4. Heat of vaporization of all amine solutions,

Fig. 4 reveals that the heat of vaporization of single solvent MEA was slightly higher than the tri–solvent blends. This is because the concentration of water in MEA is slightly higher than those of the blends. Comparing the blends amongst themselves, it can be said that there was no difference in their heat of vaporization.

4. Conclusion

Results from this study have shown that it is important to consider the contribution of absorption heat, sensible heat and heat of vaporization towards regeneration energies of amine solutions. This will provide a clear insight which of

the heats to optimize in order to reduce the regeneration energy. It was also discovered in this study that the sensible heat of the tri–solvent blends contributed immensely towards their low regeneration energy. The absorption heat of AMP–MDEA–DETA blends were only slightly lower than that of 5 kmol/m^3 MEA. It was also found out that higher absorption heat does not necessarily mean high regeneration energy when comparing amine solutions. This was evident in the AMP–MDEA–DETA tri–solvent blends

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