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Heat of Absorption of CO₂ in Aqueous Solutions of DEEA, MAPA and their Mixture

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Abstract

A reaction calorimeter was used to measure the differential heat of absorption of CO₂ in phase change solvents as a function of temperature, CO₂ loading and solvent composition. The measurements were taken for aqueous solutions of 2-(diethylamino)ethanol (DEEA), 3-(methylamino)propylamine (MAPA) and their mixture. The tested compositions were 5M DEEA, 2M MAPA and their mixture, 5M DEEA + 2M MAPA which gives two liquid phases on reacting with CO₂. Experimental measurements were also carried out for 30% MEA used as a base case. The measurements were taken isothermally at three different temperatures 40, 80 and 120°C at a CO₂ feed pressure of 600 kPa. In single aqueous amine solutions, heat of absorption increases with increase in temperature and depends on the type of amine used. DEEA, a tertiary amine, has lower heat of absorption compared to MAPA being a diamine with primary and secondary amine functional groups. For amine mixtures, heat of absorption is a function of CO₂ loading and temperature. The heat of absorption against CO₂ loading depends on the composition of the amines in the mixture. All the measured data in this work were compared with 30% MEA at absorption (40°C) and desorption (120°C) conditions.

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1. Introduction

Carbon dioxide absorption using amines is the most common operation for CO₂ capture from power plant flue gases. The amine-based absorption processes selectively absorb CO₂ and release a high-purity

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CO₂ off-gas stream upon heating in a stripper column which is suitable for storage without any further treatment. However, these processes are known for their high energy requirements for solvent regeneration [1, 2]. The challenge is to develop solvent systems with improved energy efficiency while retaining the favorable properties of high CO₂ loading capacity, fast reaction rate, low solvent degradation and being environmental friendly. In order to have better energy efficiency, the absorbents should have reasonable heat of absorption with high equilibrium temperature sensitivity thereby reducing the need for stripping steam [3].

Based on the number of hydrogen atoms attached to the nitrogen atom, amines are divided into three types; primary (two H atoms), secondary (one H atom) and tertiary (no H atom). Both primary and secondary amines are very reactive towards CO₂ as they form carbamates and they have high heats of reaction and fast reaction rate [4]. Consequently, the energy needed for reversing the reaction during regeneration will be high. Tertiary amines, on the other hand, form bicarbonates through base catalysis of CO₂ hydration [5]. Due to the lack of hydrogen on the amine group, these amines do not form carbamate with CO₂ and have low heat of reaction which results in low energy requirements for the reversion of the CO₂ reaction. These amines generally have high CO₂ loading capacity and low reaction rates for CO₂ absorption compared to primary and secondary amines [4]. None of the amine types has ideal properties for CO₂ absorption, so mixed amine systems have become very popular in order to exploit the favorable properties of these different types of amines e.g. aqueous blends of monoethanolamine (MEA), a primary alkanolamine, and methyl diethanolamine (MDEA), a tertiary alkanolamine, have shown potential to reduce the energy requirement in the solvent regeneration stage [6]. A new set of solvents, which may be called phase change solvents, have recently emerged which have a potential to reduce the energy requirements for solvent regeneration e.g. the DMXTM process developed by IFP EN [7]. In this process, the single phase solvents absorb CO₂ and split into two liquid phases. The amine rich phase with very low CO₂ loading recycles back to the absorber without regeneration and only the water rich phase with very high CO₂ loading goes to the stripper for thermal regeneration. Therefore, the energy consumption for solvent regeneration can be lowered due to reduced liquid flow rate in the stripper and changes to the CO₂ equilibrium.

In this work we are investigating a solvent system consisting of two different amines, 2-(diethylamino)ethanol (DEEA) and 3-(methylamino)propylamine (MAPA). DEEA is a tertiary alkanolamine and MAPA has two amine functional groups, a primary and a secondary. On one hand we can exploit the favorable properties of different types of amines by blending DEEA and MAPA and on the other hand these amine blends have an additional benefit of making a liquid-liquid split when reacted with CO₂. Previous studies have shown that the single phase aqueous blend of DEEA-MAPA turns into two liquid phases upon CO₂ absorption with an upper phase lean in CO₂ and a lower phase rich in CO₂, see Fig. 1 [8]. If only the lower phase is regenerated, energy requirements for solvent regeneration can be reduced due to low liquid circulation rate in the stripping section. Also, there is a potential of reduction both in capital and operational costs due to decrease in size of the desorption column.

Heat of reaction is an important parameter for designing unit operations for acid gas removal. It is directly related to the energy requirement for stripping CO₂ through the regeneration of the solvent in the capture process. The magnitude of the heat of absorption is a significant factor in determining the thermal effects observed in gas treating processes through both its direct influence on the heat required for reaction reversion and also its indirect influence on the temperature sensitivity of the equilibrium curves [9]. In this work, enthalpy of absorption of CO₂ in aqueous solutions of DEEA, MAPA and their mixture were measured as a function of CO₂ loading, temperature and amine composition. The selected composition on amines in the mixture gave two liquid phases when reacted with CO₂. The measurements were carried out in a commercially available reaction calorimeter over industrially important temperature range of 40-120°C.

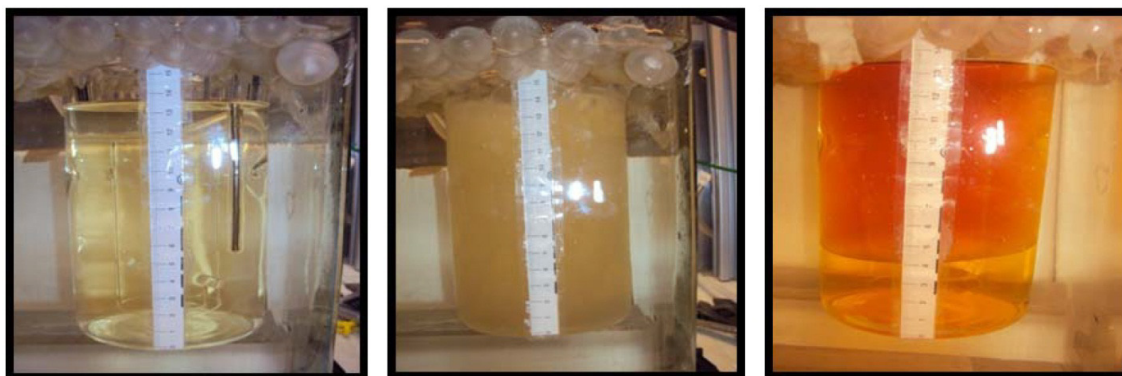


Fig. 1: Single phase amine mixture of DEEA and MAPA before starting the CO₂ loading experiment (left), during the experiment (centre) and two liquid phases with an upper phase lean in CO₂ and the lower phase rich in CO₂ after the experiment (right) [8].

2. Experimental Section

2.1. Materials

The chemicals used in this work were Carbon dioxide, CO₂ (AGA, 99.99%); 2-(Diethylamino)ethanol, DEEA (Sigma-Aldrich, 99%) and 3-(Methylamino)propylamine, MAPA (Sigma-Aldrich, 99%). All chemicals were used as received with no further purification. The amine solutions were prepared from deionized water using analytical balance.

2.2. Working Procedure

The schematic diagram of the experimental setup is given in Fig. 2. The reaction calorimeter and working procedure have already been described in details by Kim and Svendsen [10], only a brief overview is given here.

A reaction calorimeter (model CPA 122) was used for the measurements in this work. It is a mechanically agitated stainless steel reactor with a volume 2000 cm³ from ChemiSens AB, Sweden. The well-insulated jacketed reactor is suitable for working in a pressure range from -1 to 100 bar and temperatures from -20 to 200°C. It is connected to the CO₂ storage cylinders through a CO₂ mass flow controller. A vacuum pump is also attached to the reactor. The whole system is connected to a computer for data acquisition via a control device (VRC200). The system continuously measures heat production rate (online Heat Balance in real time), reactor and jacket temperatures, CO₂ storage cylinders and reactor pressure, stirring speed and other parameters. All operating parameters were recorded as function of time as illustrated in Fig 3.

First the reactor was evacuated and flushed with CO₂ in order to ensure the complete removal of any inert gas present in the reactor. After evacuation about 1200-1500 cm³ of amine solution was fed into the reactor from an amine solution feed bottle and heated to a set temperature. The system was then allowed to reach equilibrium by ensuring that no change in reactor temperature (within ±0.01°C) or pressure (within ±0.01 bar) took place. When the system attained equilibrium, ~0.1-0.3 mol of CO₂ was fed into the reactor through the mass flow controller monitored by the pressure difference in the CO₂ storage cylinders. The system was then allowed to reach a new equilibrium before the next CO₂ feeding sequence could take place. The feeding process was continued until no more CO₂ could enter the reactor at a set

pressure (the absorption rate equals zero). An example can be seen in Fig. 3 with different parameters (heat flux curve, reactor temperature and pressure and CO₂ flow in the reactor) recorded as a function of time for one complete experiment. The pressure and temperature in the reactor and CO₂ storage cylinders were recorded before and after each feeding. The amount of heat added or removed from the system by the thermostat medium used to keep the system at constant temperature was also recorded.

The experiments were conducted in an isothermal mode while the total pressure inside the reactor varied from the amine plus water vapor pressure before the first feeding of CO₂ at the start of experiment to a maximum total pressure (amine + water vapor + CO₂) of 6 bar during the last feeding (CO₂ feed pressure), see pressure equilibria in Fig. 3. Previous work by Kim and Svendsen [10] found no effect of CO₂ feed pressure while performing experiments at feed pressures of 3 and 10 bar. However, higher loadings could be achieved at higher CO₂ feed pressure. The CO₂ was injected in the reactor in several small steps by keeping a low loading span (about 0.015-0.07 mol CO₂/ mol amine) which gives differential heat of absorption values that are semi-differential in loading (integral within each feeding interval). The measurements were taken isothermally at three different temperatures, 40, 80 and 120°C. The Peng-Robinson equation of state was used to calculate the amount of CO₂ added into the reactor from the pressure difference in the CO₂ storage cylinders before and after each CO₂ feeding. The heat released in each interval was determined by integration of the heat flux curve. The molar heats of absorption were then calculated from the ratio of heat released in a feeding interval to the amount of CO₂ absorbed. The measurements were performed for aqueous solutions of 5M DEEA, 2M MAPA and their mixture, 5M DEEA + 2M MAPA, at three different temperatures 40, 80 and 120°C.

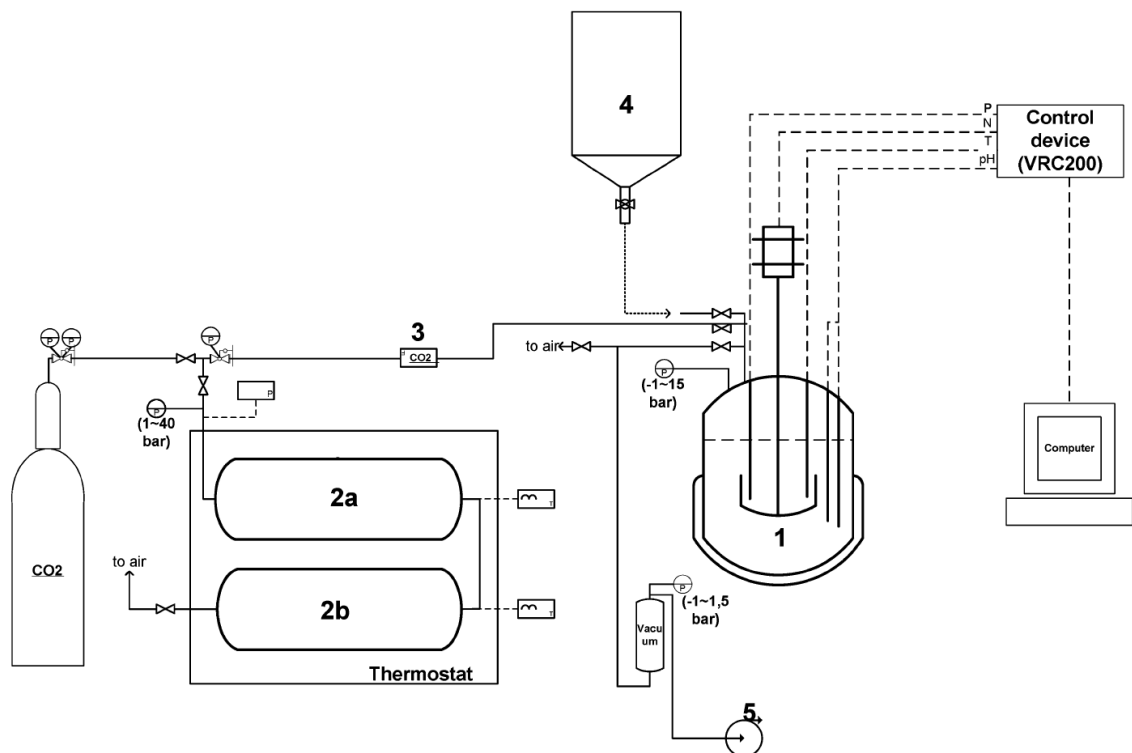


Fig. 2: Experimental setup for measuring heat of absorption: 1 - reaction calorimeter; 2a, 2b - CO₂ storage cylinders; 3 - CO₂ mass flow controller; 4 - amine solution feed bottle; 5 - vacuum pump [10].

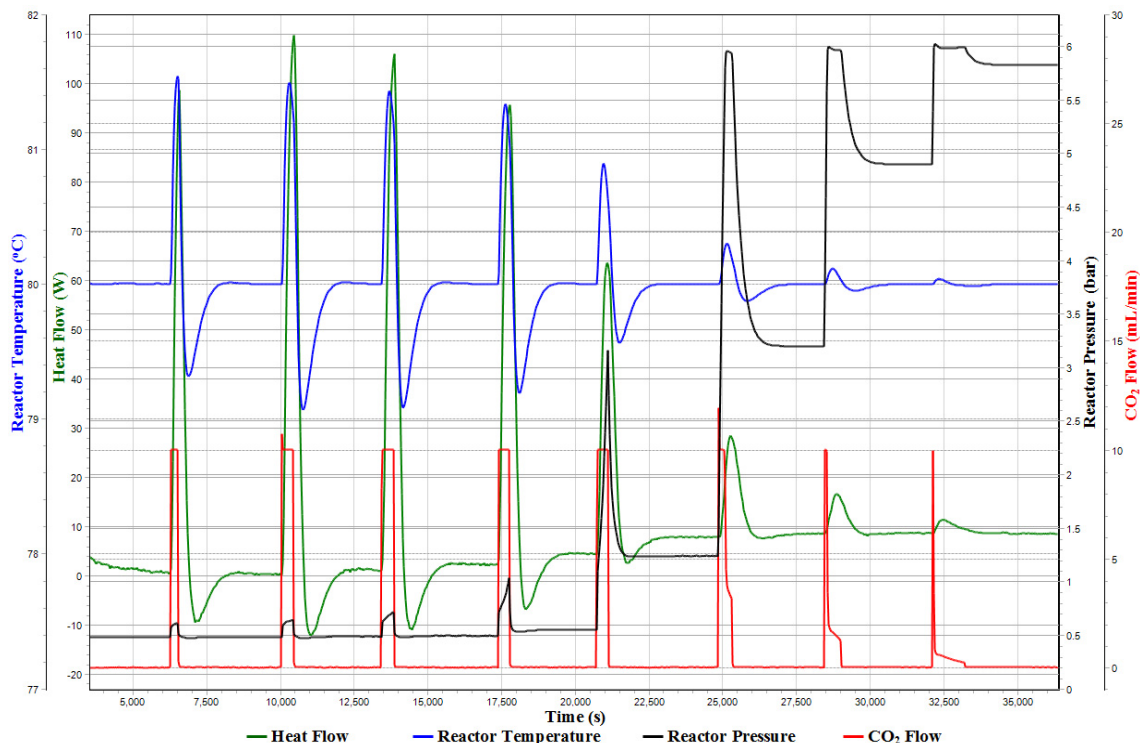


Fig. 3: An example of different parameters (heat flux curve, reactor temperature and pressure and CO₂ flow in the reactor) recorded as function of time from start to end of one experiment.

3. Results and Discussion

3.1. 5M DEEA

The differential enthalpies of absorption of CO₂ in 5M DEEA solutions were measured at three different temperatures, 40, 80 and 120°C. These measurements were taken at a CO₂ feed pressure of 6 bar and the results are presented in Fig. 4. The results show that heat of absorption is a function of temperature, increases by increasing temperature. However, CO₂ loading capacity, on the other hand, decreases significantly with increase in temperature e.g. the loading capacity at 120°C is an order of magnitude lower than the values at 40°C at the given experimental conditions. This can make DEEA a potential candidate for energy efficient CO₂ absorbent. It can also be noticed that the differential heats of absorption values are almost constant for 5M DEEA at 40°C up to the saturation loading point of ~ 0.9 mol CO₂/ mol amine. However, it shows strong dependency on CO₂ loading at 80 and 120°C.

3.2. 2M MAPA

For MAPA, the differential heats of absorption of CO₂ were measured with 2M MAPA concentration at a CO₂ feed pressure of 6 bar and temperatures 40, 80 and 120°C. The experimental results are illustrated in Fig. 5. A high CO₂ loading is achieved with 2M MAPA solutions due to presence of both the primary and the secondary amine functional groups on the MAPA molecules. The heat of absorption shows an increase with increase in the temperature. However, MAPA shows a high CO₂ loading capacity

at higher temperatures contrary to DEEA. It can also be noticed that the differential heat of absorption is almost constant up to a loading of ~ 1 mol CO₂/ mol amine (the saturation point). Once the saturation loading point is reached, the carbamate reversion reaction starts taking place. This is evident from a relatively sharp drop in the heat of absorption after the saturation point. Very high values of heat of absorption can be seen for the lower CO₂ loadings at 120°C in MAPA results. This effect can also be noticed in DEEA results shown earlier in Fig 4. Kim and Svendsen also reported this effect for single amine solvent systems [10]. The reason for this behavior is not clear. However, this effect was not observed in the amine mixture (5M DEEA + 2M MAPA) studied in this work (see Fig. 6) which is similar to the Kim and Svendsen results for different amine mixtures [10].

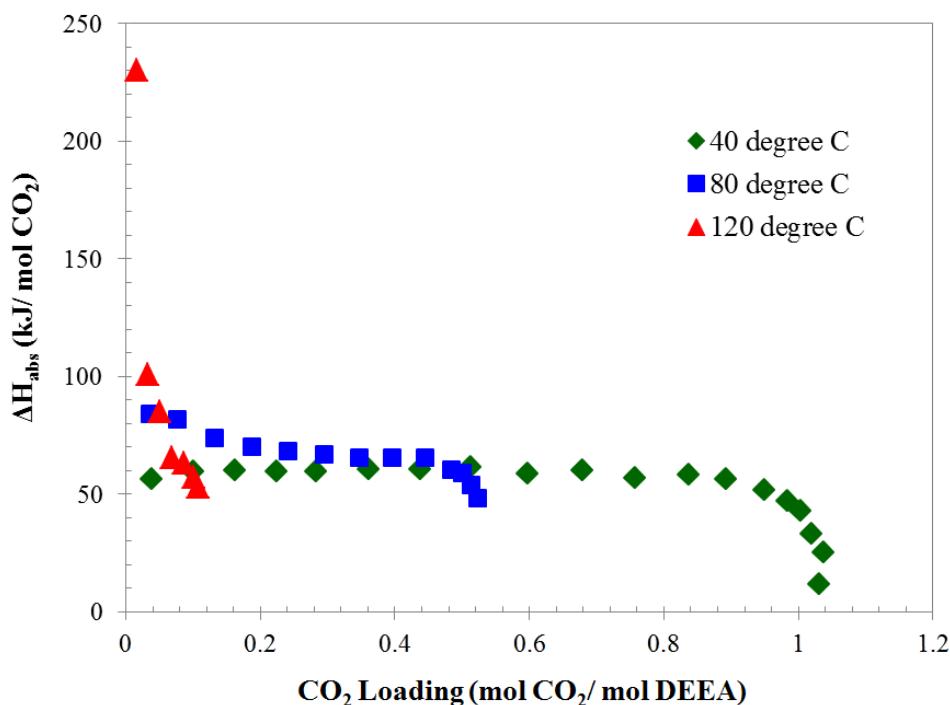


Fig. 4: Differential enthalpy of absorption of CO₂ with 5M DEEA at 40, 80 and 120°C.

3.3. 5M DEEA + 2M MAPA

The heat of absorption results for CO₂ with 5M DEEA + 2M MAPA at 6 bar CO₂ feed pressure and in the temperature range 40-120°C are presented in Fig. 6. It can be seen that the heat of absorption of CO₂ with amine mixture is a function of CO₂ loading and temperature. The differential heats of absorption data for amine mixtures are very scarce in the literature. Kim and Svendsen [11] reported that the heat of absorption profile against loading depends on the composition of the amine mixture and this can also be seen in our results in Fig. 6. This mixture gave two liquid phases when reacted with CO₂. At the end of the experiment, the fully loaded amine mixture was taken out of the reactor and transferred to a separating funnel to check the formation of these phases as given in Fig. 7. It was observed that the volume ratio of the two phases depends on the total CO₂ loading in the mixture i.e. the higher the CO₂ loading the more volume will be in the lower phase.

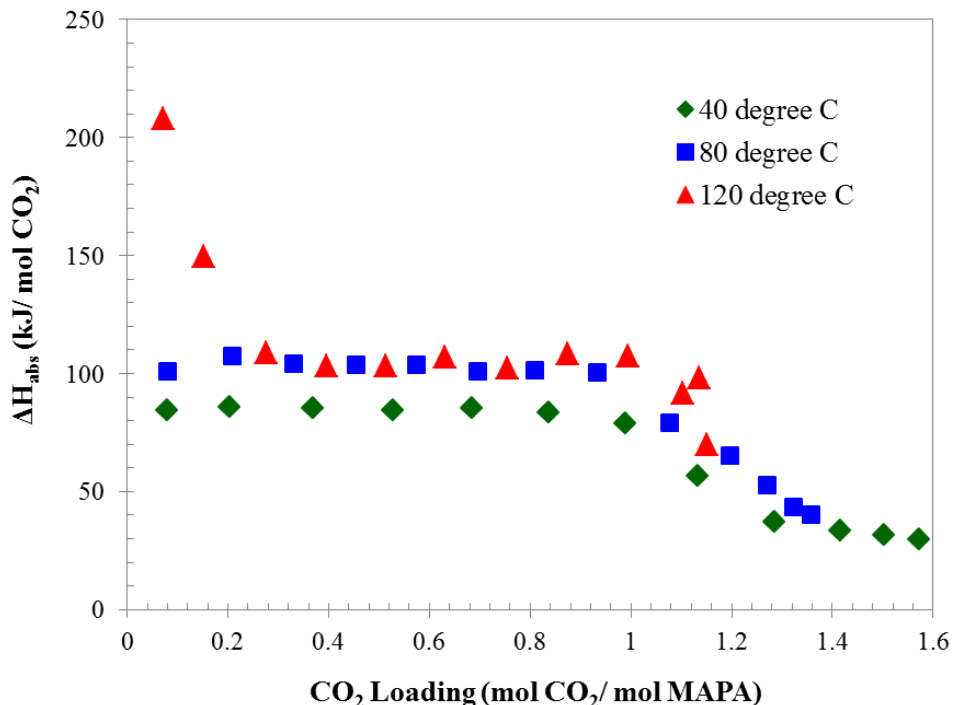


Fig. 5: Differential enthalpy of absorption of CO_2 with 2M MAPA at 40, 80 and 120°C.

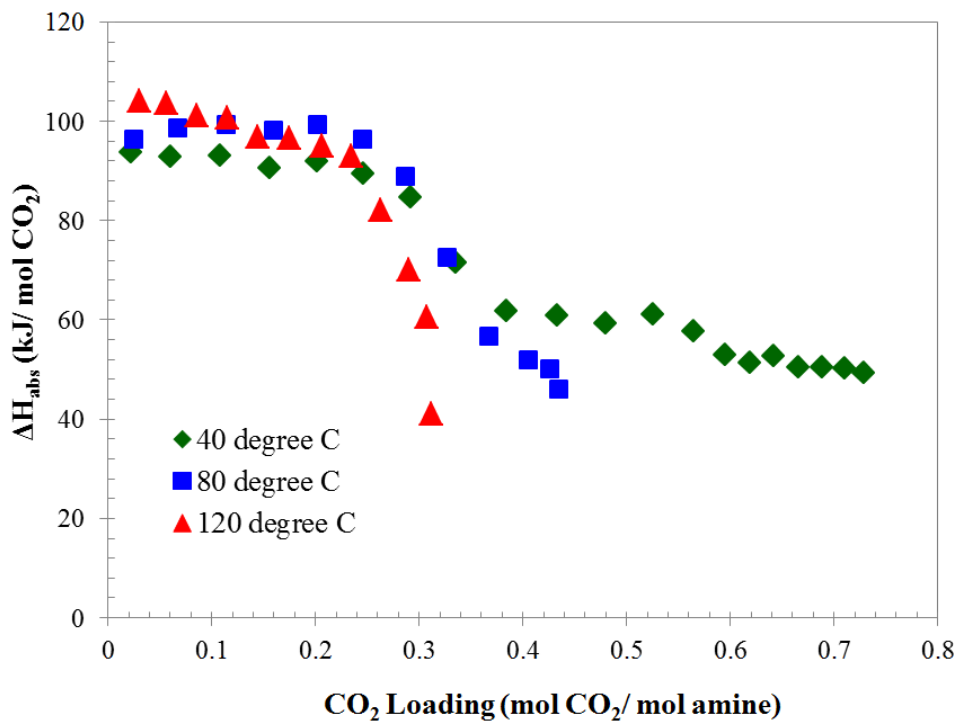


Fig. 6: Differential enthalpy of absorption of CO_2 with 5M DEEA + 2M MAPA at 40, 80 and 120°C.

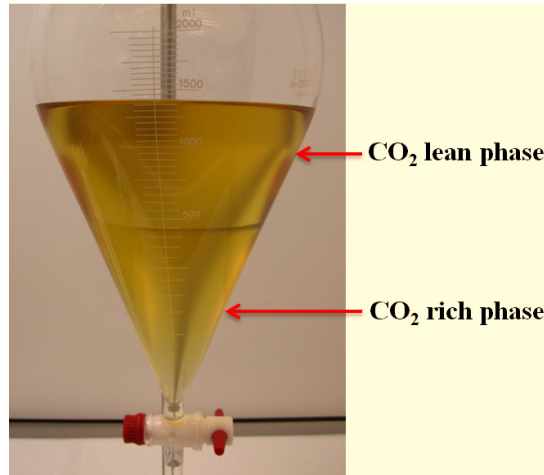


Fig. 7: Two liquid phases after the experiment.

3.4. Overall Comparison

Fig. 8 and Fig. 9 give an overall comparison of differential enthalpy of absorption of CO₂ for all the studied systems and 30% MEA (base case) at absorption (40°C) and desorption (120°C) conditions respectively. Since, 30% MEA has constant value of heat of absorption up to its saturation point (0.5 mol CO₂/amol amine) an average value is used for the comparison.

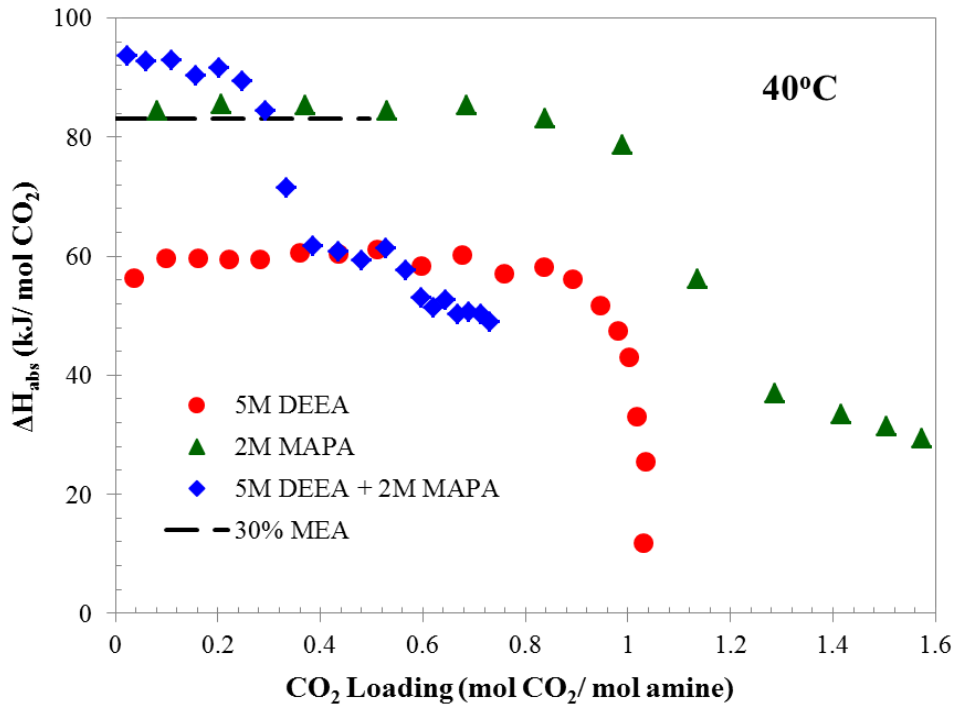


Fig. 8: Overall comparison of differential enthalpy of absorption of CO₂ for all the studied systems and 30% MEA (base case) up to a CO₂ loading of 0.5 mol CO₂/amol amine at 40°C.

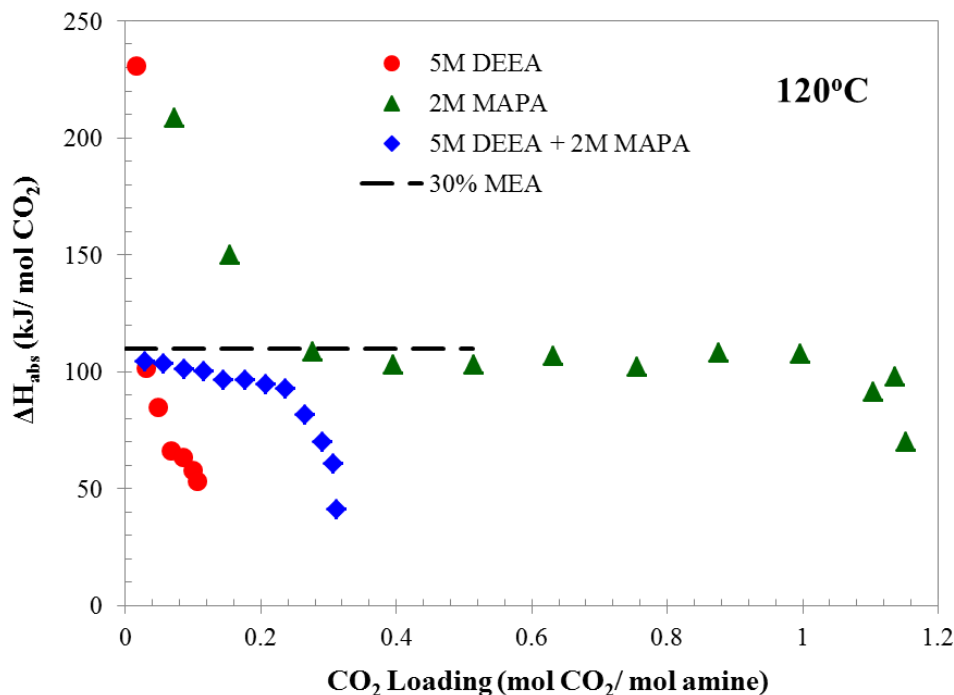


Fig. 9: Overall comparison of differential enthalpy of absorption of CO₂ for all the studied systems and 30% MEA (base case) up to a CO₂ loading of 0.5 mol CO₂/amol amine at 120°C.

2M MAPA has similar heats of absorption as that of 30% MEA at 40°C but the values are higher at temperatures 80 and 120°C. However, high CO₂ loadings were achieved in 2M MAPA solutions compared to 30% MEA which is due to the presence of both primary and secondary amine functional groups on the MAPA molecules. 5M DEEA (a tertiary alkanolamine), on the other hand, shows the lowest heat of absorption amongst all the studied systems in this work. It can also be noticed that DEEA shows the lowest absorption capacity at 120°C which indicates that less energy may be needed for reaction reversion between DEEA and CO₂ in the stripper.

In amine mixtures, the primary and secondary amines are expected to react first due to their fast reaction rates followed by the tertiary amines which have comparatively low reaction rate. This can be seen at temperature 40°C in Fig. 8. It can be noticed that MAPA reacts first in the mixture due to its fast reaction rate and its values are a little higher to that of single MAPA solution values and then DEEA start reacting and reaches close to values of single DEEA solution. However, MAPA appears to be the main reacting component in the mixture at higher temperatures due to low CO₂ absorption capacity of DEEA at higher temperatures especially at 120°C. It can also be noticed that the mixture system has lower heat of absorption values than the single MAPA solution values at 120°C. On comparison with 30% MEA, the mixture system has slightly higher heats of absorption at 40°C at lower loadings. However, it drops quickly with increase in loading. This mixture has high loading capacity compared to 30% MEA at 40°C. However, it shows much lower absorption capacity at 120°C compared to 30% MEA which makes this system an attractive choice in terms of energy efficiency. It can also be noticed that the amine mixture studied in this work has shown relatively lower CO₂ absorption capacity compared to the constituent amines when they were used as single solvents. This may be due to some interaction between the amines that reduces the CO₂ absorption capacity of this mixture.

4. Conclusions

Heats of absorption of CO₂ in phase change solvents were measured as a function of temperature, CO₂ loading and solvent composition using a commercially available reaction calorimeter CPA 112 from ChemiSens AB, Sweden. The measurements were taken for aqueous solutions of 2-(diethylamino)ethanol (DEEA), 3-(methylamino)propylamine (MAPA) and their mixture. The tested compositions were 5M DEEA, 2M MAPA and their mixture, 5M DEEA + 2M MAPA which gives two liquid phases on reacting with CO₂. Experimental measurements were also carried out for 30% MEA used as a base case. The measurements were taken isothermally at three different temperatures 40, 80 and 120°C at a CO₂ feed pressure of 600 kPa. Due to relatively large size of the reactor, it was possible to feed CO₂ in several small steps by keeping a low loading span, which gave heat of absorption values that are semi-differential in loading. In aqueous single amine solutions, heat of absorption increases with increase in temperature and depends on the type of amine used. DEEA, a tertiary amine, has lower heat of absorption compared to the diamine MAPA with primary and secondary amine groups. For amine mixtures, heat of absorption is a function of CO₂ loading and temperature. The heat of absorption against CO₂ loading depends on the composition of the amines in the mixture. All the measured data in this work were compared with 30% MEA at absorption (40°C) and desorption (120°C) conditions. DEEA has shown the lowest heat of absorption among all the studied systems and MAPA has values close to that of 30% MEA. The measured heats of absorption data can be used for designing the unit operations and for thermodynamic modeling of CO₂ absorption-desorption system when aqueous blends of DEEA-MAPA are used as solvents.

Acknowledgements

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