

# Heat of Absorption of CO<sub>2</sub> in Phase Change Solvents: DEEA and MAPA

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## Abstract

Heat of absorption of CO<sub>2</sub> in phase change solvents containing 2-(diethylamino)ethanol (DEEA) and 3-(methylamino)propylamine (MAPA) were measured as a function of CO<sub>2</sub> loading at different temperatures using a commercially available reaction calorimeter. The tested systems were aqueous single amines (5M DEEA, 2M MAPA and 1M MAPA) and aqueous amine mixtures (5M DEEA + 2M MAPA and 5M DEEA + 1M MAPA) which give two liquid phases on reacting with CO<sub>2</sub>. All parallel experiments have shown good repeatability. The measurements were taken isothermally at three temperatures in the industrially important temperature range of 40-120°C. The measured differential heat of absorption values were converted into integral values by integration. Heats of absorption of CO<sub>2</sub> in aqueous single amines were affected by changing the solvent composition (large difference in concentrations) and CO<sub>2</sub> feed pressure simultaneously. In addition to these two parameters, it also depends on temperature and the type of amine used. Tertiary alkanolamine (DEEA) has shown greater dependency on these parameters compared to the diamine (MAPA) containing both primary and secondary amine functional groups. In aqueous amine mixtures, heats of absorption depend on CO<sub>2</sub> loading, temperature and composition of the constituent amines in the mixture. All measured heat of absorption data were compared with 30 mass% MEA used as a base case.

Keywords: Heat of absorption, Calorimeter, Post combustion capture, Phase change solvents, 2-(diethylamino)ethanol (DEEA), 3-(methylamino)propylamine (MAPA)

## 1. Introduction

Amine scrubbing is one of the most common post-combustion CO<sub>2</sub> capture technologies available today. Due to its extensive use in different industrial applications e.g. CO<sub>2</sub> removal from reformer gases, natural gas sweetening etc.<sup>1</sup>, it has been considered as the most feasible route for the post-combustion capture. These amine scrubbing processes selectively absorb CO<sub>2</sub> from the flue gases and release a high-purity CO<sub>2</sub>

offgas stream upon heating in a stripper which is suitable for storage without any further treatment. However, it is well known that these processes are energy intensive.<sup>2,3</sup> Innovative process design and technological improvements are necessary in order to reduce the high capital cost and energy requirements for the capture processes.<sup>4</sup> Besides this, It is also essential to develop solvent systems with improved energy efficiency while retaining the desirable properties of fast reaction rate, high loading and cyclic capacities, low solvent degradation, low corrosiveness and being environmental friendly etc. For energy efficient solvent systems, besides reasonable heat of absorption, the equilibrium temperature sensitivity should also be high in order to reduce the need for stripping steam.<sup>5</sup>

Single amine solvent systems for CO<sub>2</sub> capture were extensively studied and reported in the open literature. Primary and secondary amines are very reactive towards CO<sub>2</sub> as they form carbamates. They have high heats of reaction and fast reaction rates.<sup>6</sup> Consequently, high energy is required for the solvent regeneration. Tertiary amines, on the other hand, form bicarbonates due to base catalysis of CO<sub>2</sub> hydration.<sup>7</sup> They have low heats of reaction leading to low energy requirements for the reaction reversion. These amines generally have high CO<sub>2</sub> loading capacity and low reaction rate.<sup>8,9</sup> Each type of amine group is associated with its own merits and demerits. Therefore, amine blends have become an attractive choice in order to exploit the favorable properties of both amine types. Various amine blends (e.g. MEA + MDEA) have been studied and reported in the literature.<sup>26,27</sup>

Recently, a new class of mixed amine solvent systems is emerging, which may be called as phase change solvents. They have shown a potential to reduce the solvent regeneration energy. These phase change solvents either form precipitates on CO<sub>2</sub> absorption such as the Alstom chilled ammonia process (CAP)<sup>10</sup> or make a liquid-liquid split e.g. the DMX<sup>TM</sup> process<sup>11,12</sup> and Thermomorphic Biphasic Solvents (TBS) systems.<sup>13</sup> The TBS systems, after CO<sub>2</sub> absorption, regenerate at relatively lower temperature of 80°C compared to the regeneration temperature of conventional alkanolamine solutions (~120°C). They give liquid-liquid split upon heating and agitating during the regeneration and become single phase during absorption. The main advantage of these systems is lower regeneration temperature which can be achieved without using steam.<sup>14-16</sup> In the DMX<sup>TM</sup> process, on the other hand, the single phase solvent splits into two liquid phases after CO<sub>2</sub> absorption. The CO<sub>2</sub> lean phase recycles back to the absorber without regeneration and only the CO<sub>2</sub> rich phase goes to the stripper for thermal regeneration. Therefore, the energy consumption for solvent regeneration can be lowered due to reduced flow rate of the liquid in the stripper.<sup>11</sup>

In the present 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 (see Fig. 1). Therefore, we can exploit the favorable properties of amines by blending DEEA and MAPA. Their mixtures have an additional benefit of making liquid-liquid split when reacted with CO<sub>2</sub>. Previous studies have shown that the single phase aqueous blends of DEEA-MAPA turn into two liquid phases upon CO<sub>2</sub> absorption with an upper phase lean in CO<sub>2</sub> and the lower phase rich in CO<sub>2</sub>.<sup>17</sup> If only the lower phase is regenerated, these blends have the potential to reduce the energy requirements for the solvent regeneration.

Heat of absorption is an important parameter to design unit operations in the gas treating processes. The energy requirements for solvent regeneration in the capture process are directly related to it. The magnitude of heat of absorption gives a direct measure of heat requirements in the stripper.<sup>18</sup> Experimental data in the literature<sup>19-23</sup> have shown a difference of about 25-30% between the enthalpy of

absorption at 40°C (absorption condition) and 120°C (desorption condition). Therefore, the effect of temperature on heat of absorption is an important parameter to be determined which is generally ignored and a constant value of enthalpy of absorption is assumed both for the absorption and desorption conditions.<sup>1</sup> Direct calorimetric measurements give accurate heat of absorption values, reflecting the combined effect of heat due to the reaction between solvent and CO<sub>2</sub>, and the physical dissolution of gas in the solvent. Since, it is possible to perform the heat of absorption measurements isothermally in the calorimeters, temperature dependency can be observed.

The main objective in this work is to measure the heats of absorption of CO<sub>2</sub> in aqueous DEEA, MAPA and their mixtures. Since, these phase change solvent systems are relatively new, no heat of absorption data were found in the literature except some data published by Kim.<sup>23</sup> However, these data do not cover the concentration range where liquid-liquid phase split occurs. Therefore, an important objective in this work is to measure the data for the aqueous amine mixtures of DEEA-MAPA within the target concentration range where the solvent systems give two liquid phases. The experimental measurements for the solutions with different amine compositions were made by using a reaction calorimeter as a function of CO<sub>2</sub> loading in the temperature range of 40-120°C.

## 2. Experimental section

DEEA (purity ≥ 99%), MAPA (purity 99%) and MEA (purity ≥ 99%) were purchased from Sigma-Aldrich. All chemicals were clear liquids at room temperature. Carbon dioxide (CO<sub>2</sub>) was purchased from AGA (a member of The Linde Group, Linde AG) with purity ≥ 99.99%. The amine solutions were made with deionized water using an analytical balance. All chemicals were used as received with no further purification.

The amine systems studied in this work with experimental conditions of temperature and pressure are listed in Table 1. The experimental setup is given schematically in Fig. 2. The details of reaction calorimeter, working procedure and experimental uncertainties have already been described elsewhere<sup>21,23</sup>. A very brief description of the setup and the procedure is given here.

The reaction calorimeter (model CPA 122) used in this work is a stainless steel reactor from ChemiSens AB - Lund, Sweden. The volume of the reactor is 2000 cm<sup>3</sup> and it has a mechanical agitator. The insulated jacketed reactor is suitable for working in a temperature range of -20 to 200°C and pressure range of -1 to 100 bar. All the units are connected to a computer through a control device (VRC200) which records heat production rate (online Heat Balance), reactor and jacket temperatures, CO<sub>2</sub> storage cylinders and reactor pressure, stirring speed and other operating parameters as a functions of time.

Before starting the experiment, the reactor was evacuated to a pressure between 40-50 mbar and then filled with CO<sub>2</sub> to a pressure of ~ 3 bar and then evacuated again. This CO<sub>2</sub> flushing was done in order to ensure the complete removal of any inert gas present in the reactor. After evacuation about 1200-1500 cm<sup>3</sup> of amine solution was fed into the reactor from an amine solution feed bottle. The solution was then heated at a preset temperature and the system was allowed to reach the equilibrium. When the change in temperature or pressure of the reactor is respectively within ±0.01°C or ±0.01 bar, the system was assumed to be at equilibrium. Also at equilibrium, no heat transfer took place between the outer heating jacket of

the reactor and the reaction system inside the reactor i.e.  $\Delta T = T_{in}^{jacket} - T_{out}^{jacket} = constant$ . Once the equilibrium is ensured, about 0.1-0.3 mol of CO<sub>2</sub> was injected into the reactor via a pre-calibrated mass flow controller from CO<sub>2</sub> storage cylinders by monitoring their pressure difference. The injected CO<sub>2</sub> got absorbed in the amine solution and produced heat. The thermostat medium (reactor jacket) added or removed heat from the system to keep the isothermal conditions in the reactor. All the operating parameters were logged against time. The system took about 60-90 min (with some exceptions where it took more time) to reach the new equilibrium and the reactor was fed again with CO<sub>2</sub> for another cycle. The reactor was continuously fed with CO<sub>2</sub> until no more gas could enter in it at a preset pressure (the absorption rate nearly became zero). The temperature and pressure of the reactor and CO<sub>2</sub> storage cylinders were recorded before and after every CO<sub>2</sub> feeding cycle. The amount of CO<sub>2</sub> added to the reactor in each feeding cycle was calculated from the Peng-Robinson equation of state by using the data of pressure difference in the CO<sub>2</sub> storage cylinders (recorded earlier). The heat released in each feeding cycle was determined by integration of the heat flux curve. Finally, the ratio of heat released in a given feeding cycle ( $Q_{total}$ ) to the amount of CO<sub>2</sub> absorbed ( $n_{CO_2}$ ) gave the molar heat of absorption for that feeding cycle.

The heats of absorption measurements were taken isothermally at three different temperatures 40, 80 and 120°C. The initial total pressure at a given temperature before feeding any CO<sub>2</sub> to the reactor at the start of each experiment was the amine plus water vapor pressure and it changes after each CO<sub>2</sub> feeding cycle to a maximum final total pressure (amine + water vapors + CO<sub>2</sub>) of 6 bar during the last feeding (CO<sub>2</sub> feed pressure). In calculations, it is assumed that the initial total pressure (amine + water vapors) remains constant. Previous work by Kim and Svendsen<sup>21</sup> found no effect of CO<sub>2</sub> feed pressure while performing experiments at different feed pressures of 3 and 10 bar. However, higher loadings could be achieved at very high CO<sub>2</sub> feed pressures. The CO<sub>2</sub> was injected in the reactor in several small steps by keeping a low loading span (about 0.015-0.07 mol CO<sub>2</sub>·(mol amine)<sup>-1</sup>) which gives differential heat of absorption values that are semi-differential in loading (integral within each feeding interval). These differential heats of absorption values were then converted into integral values by integration.

The main uncertainty sources in the measured heat of absorption data were the calculated amount of CO<sub>2</sub> fed to the reactor from CO<sub>2</sub> storage cylinders, the change of CO<sub>2</sub> amount in the gas phase of the reactor and integration of the heat flux curves to calculate the heat released in each CO<sub>2</sub> feeding cycle (for details see Kim and Svendsen<sup>21</sup> and Kim<sup>23</sup>). The uncertainty can be determined as<sup>21</sup>:

$$\frac{\sigma_{\Delta H_{abs}}}{\Delta H_{abs}} = \sqrt{\left(\frac{\sigma_{Q_{total}}}{Q_{total}}\right)^2 - \left(\frac{\sigma_{n_{CO_2}}}{n_{CO_2}}\right)^2} \quad (1)$$

As described earlier, the amount of CO<sub>2</sub> injected to the reactor in each feeding cycle was calculated from the Peng-Robinson equation of state. However, it may also be taken from the pre-calibrated mass flow controller readings. Kim and Svendsen<sup>21</sup> reported an estimated uncertainty of ±1.2% for the amount of CO<sub>2</sub> fed to the reactor based on difference between the two methods. The main uncertainty in integrating the heat flux curves stems from selection of the integration borders and setting of the baseline. Since the baseline was not very stable, the heat flux curves were integrated by using the trapezoidal method with the assumption of linear change in the baseline. Also, each curve was integrated thrice and an average value of

heat released was used in the calculations. The uncertainty in the amount of released heat was then determined to be  $\pm 1.7\%$ . Finally, the estimated uncertainty in the molar heat of absorption was  $\pm 2.1\%$ .

### 3. Results and Discussion

Aqueous solutions of single amines (5M DEEA, 2M MAPA and 1M MAPA) and amine mixtures (5M DEEA + 2M MAPA and 5M DEEA + 1M MAPA) were studied in this work in the temperature range of 40-120°C. The selected composition of amine blends gave two liquid phases upon CO<sub>2</sub> absorption. The experimental measurements of heat of absorption of CO<sub>2</sub> were carried out with 30 mass% MEA solution and used as a reference case to compare with the systems studied in this work. The results for 30 mass% MEA at temperatures 40, 80 and 120°C are presented in Fig. 3 which shows a good agreement in the data measured in this work, feed pressure 6 bar, and from Kim<sup>23</sup>, feed pressure 3 bar. No effect of CO<sub>2</sub> feed pressure was observed on heat of absorption.

**DEEA:** The differential enthalpies of absorption of CO<sub>2</sub> in 5M (~61.1 mass%) DEEA solutions were measured in the temperature ranging from 40-120°C and converted to integral values by integration. The results are given in Tables 2a-2c. These measurements were taken at a CO<sub>2</sub> feed pressure of 6 bar and compared with 32 and 37 mass% DEEA data from Kim<sup>23</sup> (CO<sub>2</sub> feed pressure of 3 bar). The results are shown in Fig. 4 which shows disagreement between the two sets of data except at 40°C up to CO<sub>2</sub> loading of 0.35 mol CO<sub>2</sub>.(mol DEEA)<sup>-1</sup>. The repeatability in this work is fairly good whereas there is some scatter in Kim's data (at 80 and 120°C). Experimental data shows that the heat of absorption is dependent on temperature i.e. increases by increasing the temperature. However, CO<sub>2</sub> loading capacity, on the other hand, decreases significantly by increasing the temperature e.g. the loading capacity at 120°C decreases by an order of magnitude from the values at 40°C at the given experimental conditions in this work. This can make DEEA a potential candidate for energy efficient CO<sub>2</sub> absorbent. Differential heats of absorption values are almost constant for 5M DEEA at 40°C up to the saturation loading point of ~ 0.9 mol CO<sub>2</sub>.(mol amine)<sup>-1</sup> in this work. However, it shows strong dependency on CO<sub>2</sub> loading at 80 and 120°C.

According to Kim and Svendsen<sup>21</sup>, amine concentration has almost negligible effect on heat of absorption. Contrary to this, Merkley et al.<sup>24</sup> reported that the heat of absorption of CO<sub>2</sub> has dependency on the concentration of amine (MDEA) in the solution. However, there is an agreement between Kim and Merkley that the heat of absorption is independent of partial pressure of CO<sub>2</sub> above the solution. But, this may only be true when one parameter (solvent concentration) is fixed and the other parameter (CO<sub>2</sub> feed pressure) is changed as can be seen in Fig. 3 where 30 mass% MEA (fixed concentration) is used for two different feed pressures i.e. 6 bar (this work) and 3 bar (Kim's work). Similarly, there is no effect on heat of absorption by fixing the second parameter (CO<sub>2</sub> feed pressure) and changing the first one (solvent concentration). This can be seen in the results of MAPA where no effect on heat of absorption was observed when two different concentration of MAPA, 2M (~17.9 mass%) and 1M (~8.9 mass%), were tested at a fixed CO<sub>2</sub> feed pressure of 6 bar (see Fig. 10). It can also be seen that Kim's findings of negligible concentration effect on heat of absorption may only be valid for small changes in concentration of the solvent e.g. a difference of only 5 mass% between 37 mass% and 32 mass% DEEA solutions. But this may not be true if higher changes in solvent concentration are used e.g. 5M (~61.1 mass%) DEEA used in this work compared to 32 mass% and 37 mass% DEEA from Kim. After this discussion, one can argue that changing both parameters, solvent

concentration (large difference in concentration) and CO<sub>2</sub> feed pressure, simultaneously can affect the heat of absorption. This argument can explain the disagreement between two sets of data presented in Fig. 4 in which a comparison is given for different concentrations of DEEA tested at different CO<sub>2</sub> feed pressures.

**MAPA:** For MAPA, the differential heats of absorption of CO<sub>2</sub> were measured in 2M (~17.9 mass%) and 1M (~8.9 mass%) MAPA solutions at a CO<sub>2</sub> feed pressure of 6 bar and temperatures 40, 80 and 120°C. These results along with the integrated heat of absorption values are given respectively in Tables 3a-3c and Tables 4a-4c for 2M and 1M MAPA. The experimental data from this work are compared with 3 and 8 mass% MAPA (feed pressure of 3 bar) data from Kim<sup>23</sup> as presented in Fig. 5 and Fig. 6 for 2M and 1M MAPA respectively. A very good repeatability can be seen in our results. However, there is large scatter in Kim's data except for the results at 40°C. Since MAPA is a diamine, a high CO<sub>2</sub> loading is achieved. The heats of absorption show an increase with increase in the temperature. Contrary to DEEA, MAPA shows high CO<sub>2</sub> loading capacity at higher temperatures. It can also be noticed that the differential heat of absorption is almost constant up to a loading of ~1 mol CO<sub>2</sub>.(mol amine)<sup>-1</sup> (the saturation point). After the saturation loading point is reached, the carbamate reversion reaction starts to take place. This can be indicated by a relatively sharp drop in the heat of absorption after the saturation point. Very high heats of absorption values can be seen for lower CO<sub>2</sub> loadings at 120°C. This effect was reproduced in all parallel experiments as well as for all the single amine systems studied (5M DEEA, 2M MAPA, 1M MAPA and 30 mass% MEA). Kim and Svendsen<sup>21</sup> also reported this effect for single amine solvent systems. The reason for this behavior is not clear, so these points were omitted in calculating the integral heat of absorption. However, this effect was not observed in the amine mixture systems studied in this work.

The two sets of data in Fig. 5 and Fig. 6 have fairly good agreement at low CO<sub>2</sub> loadings. It can be seen that 1M (~8.9 mass%) MAPA results from this work and 8 mass% MAPA from Kim have comparatively better agreement which support our argument as discussed earlier. However, 3 mass% MAPA from Kim also shows a fairly good agreement at lower loadings and temperatures 40 and 80°C. This may be explained by the different effect for different types of amines. For example, Merkley et al.<sup>24</sup> reported solvent concentration dependency of the heat of absorption of CO<sub>2</sub> when MDEA, a tertiary alkanolamine, is used. On the other hand, Kim and Svendsen<sup>21</sup> reported negligible effect of solvent concentration on heat of absorption by using MEA (primary amine) and AEEA (diamine, both primary and secondary amine functionalities). Our results for DEEA (tertiary alkanolamine) and MAPA (diamine, both primary and secondary amine functionalities), and taking into account the earlier discussed argument, are consistent both with Merkley and Kim. Thus, for the studied systems in this work, it can be postulated that the heat of absorption of CO<sub>2</sub> with single amine solutions can be affected by changing solvent composition (maybe large concentration differences) and CO<sub>2</sub> feed pressure simultaneously in combination with type of amine used. However, further experimental investigations are proposed to see the effect of these parameters on heat of absorption.

Heat of absorption results can also be presented as integral values per mole of amine in the solution against CO<sub>2</sub> loading. Mathonat et al.<sup>25</sup> have used this representation to measure the solubility limit of CO<sub>2</sub> in 30 mass% MEA solution when the heat of absorption (kJ.(mol MEA)<sup>-1</sup>) data are measured at very high CO<sub>2</sub> loadings ( $\alpha = 4$  mol CO<sub>2</sub>.(mol MEA)<sup>-1</sup>). The results of our work are presented in Fig. 7 for 5M DEEA, 2M MAPA and 1M MAPA in the temperature range of 40-120°C. It may be seen that the integral values heat of absorption first increases almost linearly with CO<sub>2</sub> loading as an almost straight line until the saturation

point is reached and then the slope of the line decreases. The heat of absorption is constant along this straight line. It can also be seen that the slope of the line increases with temperature which indicates that the heat of absorption increases with temperature. The slopes of these lines give the values of heats of absorption in  $\text{kJ} \cdot (\text{mol CO}_2)^{-1}$  which are similar to the measured values. For example, the calculated slopes of the lines for 2M MAPA give values of 84.9, 101.7 and 122.8  $\text{kJ} \cdot (\text{mol CO}_2)^{-1}$  for 40, 80 and 120°C respectively, which are similar to the measured values.

**Amine mixtures:** The measured data for heat of absorption of  $\text{CO}_2$  in 5M DEEA + 2M MAPA (~ 63.5 mass% DEEA + 19.1 mass% MAPA) and 5M DEEA + 1M MAPA (~62 mass% DEEA + 9.3 mass% MAPA) at 6 bar  $\text{CO}_2$  feed pressure in the temperature range 40-120°C are given in Tables 5a-5c and Tables 6a-6c respectively. For simplicity, 5M DEEA + 2M MAPA and 5M DEEA + 1M MAPA are abbreviated as 5D2M and 5D1M respectively. The results for 5D2M and 5D1M are presented in Fig. 8 and Fig. 9 respectively and compared with the data from Kim<sup>23</sup> measured at 3 bar  $\text{CO}_2$  feed pressure. The results indicate that the heat of absorption of  $\text{CO}_2$  in amine mixtures is a function of temperature and  $\text{CO}_2$  loading. This functionality is more pronounced in 5D1M than in 5D2M. Our results again show very good repeatability. The differential heat of absorption data for amine mixtures is very scarce in the literature. Kim and Svendsen<sup>22</sup> reported that the heat of absorption profile against loading depends on the composition of the amine mixture. This can also be seen in comparison of our results with Kim's data (Fig. 8 and Fig. 9).

In the selected concentration range, these amine blends give two liquid phases upon  $\text{CO}_2$  absorption. However, the two liquid phases may become one phase again above a certain  $\text{CO}_2$  loading. This was observed when fully loaded amine mixtures, at the given experimental conditions, were taken out from the calorimeter after finishing the experiments. The loaded amine mixtures were transferred into a separating funnel and analyzed visually for the two phases at 25°C.

Table 7 gives an overview of maximum loading achieved against final total pressure in the reactor at the end of experiments along with number of phases formed and volume percentages of upper and lower phases (at 25°C) for all the experiments of amine mixtures in the temperature range of 40-120°C. Both 5D2M and 5D1M systems gave one viscous phase at 40°C. However, 5D2M system gave two phases at 80 and 120°C with upper phase/ lower phase volume% of around 50/50 ( $\alpha = 0.44$ ) and 64/36 ( $\alpha = 0.31$ ) respectively. 5D1M, on the other hand, gave one phase at 80°C and two phases at 120°C with upper phase/ lower phase volume% of around 67/33 ( $\alpha = 0.23$ ). It was observed that the lower phase rich in  $\text{CO}_2$  was relatively more viscous compared to the upper phase lean in  $\text{CO}_2$ . The parallel experiments gave similar results for all cases. These results show that the volume of relatively viscous lower phase ( $\text{CO}_2$  rich phase) increases with increase in  $\text{CO}_2$  loading and become one  $\text{CO}_2$  rich viscous phase after certain loading as shown by results of 5D2M and 5D1M systems at 40°C. 5D1M system has shown relatively lower heat of absorption compared to 5D2M (Fig. 8 and Fig. 9). However, it becomes one phase from two liquid phases at certain loading above  $\alpha = 0.23$ . The phase change behavior of these solvents as a function of  $\text{CO}_2$  loading and possibly other parameters requires further examination in order to find the critical  $\text{CO}_2$  loading range where these solvents give two liquid phases at a reasonably high loading in combination with low heat of absorption of  $\text{CO}_2$  for the solvent system.

An overall comparison of differential enthalpies of absorption of  $\text{CO}_2$  for all the studied systems and 30 mass% MEA (base case) at 40, 80 and 120°C is given in Fig. 10. 2M and 1M MAPA solutions have similar heats of absorption as that of 30 mass% MEA at 40°C but these values are higher at temperatures 80 and

120°C. However, high CO<sub>2</sub> loading were achieved in both 2M and 1M MAPA solutions compared to 30 mass% MEA which is obviously due to the presence of two amine functionalities on the MAPA molecules. On the other hand, 5M DEEA, a tertiary alkanolamine, has shown the lowest heat of absorption (as expected) among all the studied systems. It can also be seen that DEEA shows the lowest absorption capacity at 120°C which indicates that less energy may be needed for reaction reversion between DEEA and CO<sub>2</sub> in the stripper.

In amine mixtures, primary and secondary amines are expected to react first with CO<sub>2</sub> due to their fast reaction rates followed by the tertiary amines which have comparatively slower reaction rate. This can be seen at temperature 40°C in Fig. 10. Both 5D2M and 5D1M systems show that MAPA reacts first in the mixture due to its fast reaction rate and its values are close to that of single MAPA solution values and then DEEA start reacting and reaches close to values of single DEEA solution. The length of this transition and consequently the heat of absorption depends on the concentration of the promoter (MAPA in this case) i.e. increases by increasing the amount of promoter. Therefore, 5D1M has shown relatively lower heat of reaction compared to 5D2M. However, at higher temperatures, MAPA appears to be the main reacting component in the emulsion due to low CO<sub>2</sub> absorption capacity of DEEA at higher temperatures especially at 120°C. Therefore, both 5D2M and 5D1M systems have almost the same heat of absorption at 120°C but lower than the single MAPA solutions values. On comparison with 30 mass% MEA, 5D2M has slightly higher heats of absorption and 5D1M has the same as that of 30 mass% MEA at 40°C and lower loadings. However, it drops quickly with increase in loading. These mixtures have high loading capacities compared to 30 mass% MEA at 40°C. However, they show much lower absorption capacities at 120°C compared to 30 mass% MEA.

It can also be noticed that the mixtures have shown relatively low CO<sub>2</sub> absorption capacities compared to the constituent amines when they were used as single solvents. This can be due to some interaction between the amine molecules which reduces the CO<sub>2</sub> absorption capacity of these mixtures. It was also observed that the CO<sub>2</sub> loaded amine mixtures were relatively more viscous than the original unloaded feed solutions when they were taken out from the calorimeter after finishing the experiments. This increase in viscosity during CO<sub>2</sub> absorption may have an effect on CO<sub>2</sub> absorption capacity.

#### **4. Conclusions**

Heat of absorption of CO<sub>2</sub> in phase change solvents containing DEEA and MAPA were measured as a function of CO<sub>2</sub> loading at different temperatures using a commercially available reaction calorimeter. The tested systems were 5M DEEA, 2M MAPA, 1M MAPA, 5M DEEA + 2M MAPA and 5M DEEA + 1M MAPA. The selected amine composition in the mixtures gave two liquid phases on reacting with CO<sub>2</sub>. All experiments were repeated and have shown good repeatability. The measurements were taken isothermally over an industrially important temperature range of 40-120°C. The measured differential heat of absorption values were converted into integral values by integration. Since CO<sub>2</sub> was injected in the reactor in several small steps by keeping a low loading span, the measured enthalpy of absorption data are semi-differential in loading. Heat of absorption is a function of temperature i.e. increases with temperature.



For the studied solvent systems, the heat of absorption of CO<sub>2</sub> in single amine solutions can be affected by changing the solvent composition (large difference in concentration) and CO<sub>2</sub> feed pressure simultaneously in combination with type of amine used. This effect is more pronounced in tertiary alkanolamine (DEEA) compared to diamine (MAPA) consisting of primary and secondary amine functional groups. However, further experimental investigations are proposed to fully understand the relationship of these parameters on heat of absorption. In aqueous amine mixtures, heat of absorption depends on CO<sub>2</sub> loading, temperature and composition of the constituent amines in the mixture.

DEEA showed the lowest heat of absorption among all the studied systems and MAPA has values close to that of 30 mass% MEA. 5D1M has shown lower heat of absorption compared to 5D2M system. However, it becomes one liquid phase at certain loading above  $\alpha = 0.23 \text{ mol CO}_2 \cdot (\text{mol amine})^{-1}$ . Further experimental work is suggested to fully investigate the phase change behavior of these solvent systems against CO<sub>2</sub> loading.

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## Nomenclature

### Symbols

$\Delta H_{abs}$  heat of absorption ( $\text{kJ}\cdot\text{mol}^{-1}$ )

$Q_{total}$  heat (kJ)

$n_{CO_2}$   $\text{CO}_2$  absorbed (mol)

### Greek symbols

$\alpha$   $\text{CO}_2$  loading ( $\text{mol CO}_2\cdot(\text{mol amine})^{-1}$ )

### Subscripts

*diff* differential

*int* integral

## References

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Table 1: List of amine systems studied in this work.

Amine	CAS No.	Concentration	T/ °C	P/ kPa
<b>Aqueous single amines</b>				
2-(Diethylamino)ethanol (DEEA)	100-37-8	5M (~61.1 mass%)	40, 80, 120	600
3-(Methylamino)propylamine (MAPA)	6291-84-5	2M (~17.9 mass%), 1M (~8.9 mass%)	40, 80, 120	600
Monoethanolamine (MEA)	141-43-5	30 mass%	40, 80, 120	600
<b>Aqueous amine mixtures*</b>				
DEEA+MAPA	-	5M + 2M ~(63.5 mass% + 19.1 mass%)	40, 80, 120	600
DEEA+MAPA	-	5M + 1M ~(62 mass% + 9.3 mass%)	40, 80, 120	600

\* The selected concentrations of amine mixtures give liquid-liquid split on CO<sub>2</sub> absorption.

Table 2a: Heat of absorption of CO<sub>2</sub> with 5M (~61.1 mass%) DEEA solutions at 40°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> ·(mol DEEA) <sup>-1</sup>	kJ·(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ·(mol DEEA) <sup>-1</sup>	kJ·(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>40°C (1)</b>			
0.045	55.308	2.483	55.308
0.090	56.643	5.051	55.979
0.136	56.387	7.653	56.117
0.182	56.840	10.239	56.298
0.226	57.720	12.798	56.577
0.271	57.917	15.364	56.796
0.314	58.840	17.939	57.081
0.358	58.481	20.497	57.252
0.401	59.019	23.053	57.443
0.447	61.369	25.861	57.845
0.489	55.916	28.197	57.680
0.530	59.760	30.657	57.841
0.576	56.532	33.264	57.736
0.622	56.852	35.888	57.671
0.668	56.200	38.454	57.570
0.712	56.024	40.941	57.474
0.755	55.889	43.330	57.384
0.798	55.430	45.725	57.278
0.840	55.720	48.037	57.201
0.880	56.687	50.309	57.178
0.918	48.924	52.156	56.838
0.954	45.837	53.814	56.421
0.975	39.473	54.652	56.052
0.987	28.674	54.986	55.729
0.990	15.863	55.044	55.582
<b>40°C (2)</b>			
0.039	56.271	2.213	56.271
0.101	59.384	5.902	58.177
0.164	59.601	9.649	58.722
0.224	59.287	13.214	58.873
0.284	59.276	16.754	58.958
0.362	60.532	21.453	59.296
0.438	60.197	26.049	59.453
0.513	61.098	30.619	59.693
0.598	58.315	35.560	59.497
0.679	59.998	40.463	59.558
0.759	56.886	45.015	59.276
0.837	57.898	49.523	59.148
0.893	55.957	52.651	58.948
0.949	51.510	55.524	58.511
0.983	47.319	57.129	58.125

1.005	42.780	58.080	57.786
1.020	32.980	58.556	57.434
1.031	11.818	58.695	56.915
1.038	25.315	58.867	56.708

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Table 2b: Heat of absorption of CO<sub>2</sub> with 5M (~61.1 mass%) DEEA solutions at 80°C

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> ·(mol DEEA) <sup>-1</sup>	kJ·(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ·(mol DEEA) <sup>-1</sup>	kJ·(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>80°C (1)</b>			
0.041	82.234	3.404	82.234
0.104	76.961	8.224	79.059
0.144	71.997	11.121	77.089
0.185	68.304	13.915	75.148
0.225	67.683	16.615	73.825
0.265	64.020	19.177	72.345
0.304	64.368	21.680	71.324
0.342	64.509	24.144	70.564
0.380	62.049	26.492	69.716
0.418	63.592	28.894	69.162
0.454	64.166	31.217	68.764
0.493	59.476	33.561	68.022
0.508	54.382	34.355	67.629
0.517	48.745	34.804	67.293
0.526	45.989	35.200	66.945
<b>80°C (2)</b>			
0.038	83.516	3.179	83.516
0.077	81.271	6.364	82.377
0.134	73.045	10.498	78.431
0.189	69.458	14.316	75.819
0.243	67.747	17.995	74.016
0.296	66.372	21.528	72.643
0.348	64.918	24.849	71.506
0.398	65.072	28.116	70.693
0.447	65.222	31.335	70.089
0.485	59.956	33.631	69.290
0.502	58.808	34.599	68.946
0.515	53.724	35.286	68.568
0.525	47.610	35.757	68.172



Table 2c: Heat of absorption of CO<sub>2</sub> with 5M (~61.1 mass%) DEEA solutions at 120°C

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> ·(mol DEEA) <sup>-1</sup>	kJ·(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ·(mol DEEA) <sup>-1</sup>	kJ·(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>120°C (1)</b>			
0.035	105.415	3.658	105.415
0.066	85.232	6.337	95.822
0.098	68.455	8.523	86.911
0.111	67.899	9.396	84.707
<b>120°C (2)</b>			
0.015	265.834	4.044	<i>a</i>
0.029	120.766	5.680	120.766
0.050	90.659	7.595	102.428
0.066	77.082	8.814	94.485
0.081	71.615	9.942	89.049
0.095	65.490	10.799	85.161
0.104	61.474	11.369	82.680
0.111	54.825	11.752	80.645
<b>120°C (3)</b>			
0.017	230.233	3.932	<i>a</i>
0.032	100.768	5.450	100.768
0.050	84.614	6.962	92.001
0.069	65.880	8.221	82.414
0.088	63.383	9.403	77.392
0.100	57.493	10.106	74.457
0.107	52.535	10.486	72.697

<sup>a</sup> The first point was omitted from the integration.

Table 3a: Heat of absorption of CO<sub>2</sub> with 2M (~17.9 mass%) MAPA solutions at 40°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> .(mol MAPA) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ.(mol MAPA) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>40°C (1)</b>			
0.084	84.454	7.058	84.454
0.214	84.960	18.170	84.763
0.384	86.232	32.768	85.411
0.549	86.115	46.989	85.623
0.749	85.756	64.161	85.658
0.943	83.169	80.324	85.146
1.094	66.493	90.369	82.571
1.184	41.694	94.103	79.479
1.365	34.758	99.877	73.144
1.455	31.210	102.665	70.570
1.532	29.883	104.982	68.511
1.584	26.683	106.369	67.139
<b>40°C (2)</b>			
0.081	84.460	6.851	84.460
0.205	85.667	17.463	85.190
0.368	85.369	31.419	85.269
0.530	84.582	45.103	85.060
0.686	85.252	58.373	85.103
0.838	83.227	71.040	84.763
0.988	78.644	82.840	83.833
1.134	56.241	91.050	80.282
1.288	36.930	96.744	75.093
1.416	33.339	101.008	71.323
1.504	31.485	103.782	68.990
1.572	29.383	105.781	67.275

Table 3b: Heat of absorption of CO<sub>2</sub> with 2M (~17.9 mass%) MAPA solutions at 80°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> .(mol MAPA) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ.(mol MAPA) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>80°C (1)</b>			
0.083	100.290	8.293	100.290
0.209	107.061	21.803	104.381
0.334	103.525	34.739	104.060
0.456	102.939	47.343	103.759
0.577	102.800	59.735	103.559
0.696	100.438	71.744	103.023
0.813	101.300	83.567	102.776
0.935	99.670	95.696	102.372
1.079	78.804	107.095	99.213
1.200	64.735	114.929	95.737
1.273	52.209	118.722	93.253
1.327	43.070	121.051	91.209
1.359	39.274	122.313	89.982
<b>80°C (2)</b>			
0.086	99.184	8.561	99.184
0.218	99.504	21.640	99.377
0.387	100.111	38.594	99.698
0.553	100.749	55.325	100.014
0.716	101.394	71.835	100.328
0.876	96.749	87.335	99.673
1.033	90.819	101.552	98.331
1.195	63.743	111.883	93.639
1.302	46.593	116.882	89.763
1.351	38.885	118.797	87.908

Table 3c: Heat of absorption of CO<sub>2</sub> with 2M (~17.9 mass%) MAPA solutions at 120°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> .(mol MAPA) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ.(mol MAPA) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>120°C (1)</b>			
0.072	208.383	15.075	<i>a</i>
0.154	149.583	27.259	<i>a</i>
0.276	108.512	40.529	108.512
0.397	102.917	52.924	105.736
0.514	103.108	65.013	104.880
0.631	106.652	77.506	105.315
0.755	102.335	90.252	104.698
0.876	108.432	103.311	105.321
0.995	107.568	116.102	105.639
1.104	91.328	126.064	103.996
1.137	97.930	129.262	103.794
1.151	69.934	130.300	103.290
<b>120°C (2)</b>			
0.082	214.410	17.620	<i>a</i>
0.172	149.657	31.105	<i>a</i>
0.295	102.375	43.670	102.375
0.455	110.371	61.284	106.894
0.615	105.361	78.213	106.338
0.767	103.262	93.861	105.554
0.913	103.216	108.987	105.092
1.066	84.982	121.949	101.659
1.104	67.054	124.514	100.239
1.121	63.449	125.571	99.593

<sup>a</sup> The first two points were omitted from the integration.

Table 4a: Heat of absorption of CO<sub>2</sub> with 1M (~8.9 mass%) MAPA solutions at 40°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> .(mol MAPA) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ.(mol MAPA) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>40°C (1)</b>			
0.175	82.522	14.433	82.522
0.438	84.859	36.728	83.925
0.710	85.402	59.957	84.491
0.984	80.390	82.013	83.348
1.231	56.607	95.997	77.981
1.389	38.287	102.055	73.460
1.544	33.919	107.318	69.488
1.684	30.291	111.559	66.230
1.813	27.579	115.112	63.484
1.875	23.669	116.563	62.181
<b>40°C (2)</b>			
0.153	86.100	13.210	86.100
0.387	86.365	33.393	86.260
0.618	85.195	53.093	85.862
0.845	82.543	71.763	84.973
1.063	72.255	87.571	82.356
1.253	44.098	95.953	76.554
1.423	35.085	101.907	71.610
1.563	31.616	106.331	68.029
1.678	28.863	109.663	65.335
1.766	26.395	111.968	63.410

Table 4b: Heat of absorption of CO<sub>2</sub> with 1M (~8.9 mass%) MAPA solutions at 80°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> .(mol MAPA) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ.(mol MAPA) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>80°C (1)</b>			
0.177	107.384	18.957	107.384
0.440	107.009	47.136	107.160
0.705	105.463	75.067	106.522
0.959	101.754	100.931	105.258
1.196	68.895	117.259	98.052
1.365	49.593	125.654	92.043
1.452	40.664	129.191	88.965
1.495	37.598	130.913	87.595
<b>80°C (2)</b>			
0.173	110.238	19.118	110.238
0.408	106.952	44.215	108.348
0.659	103.691	70.212	106.576
0.908	103.849	96.138	105.827
1.146	73.234	113.561	99.062
1.342	57.308	124.789	92.968
1.418	41.648	127.926	90.241
1.481	36.335	130.235	87.929

Table 4c: Heat of absorption of CO<sub>2</sub> with 1M (~8.9 mass%) MAPA solutions at 120°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> .(mol MAPA) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ.(mol MAPA) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>120°C (1)</b>			
0.176	145.357	25.615	<i>a</i>
0.345	115.542	45.153	115.542
0.512	114.746	64.223	115.148
0.674	113.206	82.644	114.513
0.838	114.962	101.462	114.624
0.995	107.413	118.314	113.242
1.136	96.384	131.967	110.755
1.227	83.689	139.517	108.431
1.252	66.190	141.211	107.426
<b>120°C (2)</b>			
0.189	148.542	28.062	<i>a</i>
0.387	118.273	51.480	118.273
0.574	115.920	73.210	117.129
0.796	111.549	97.964	115.090
1.022	104.885	121.640	112.325
1.186	85.301	135.627	107.881
1.216	74.261	137.865	106.895
<b>120°C (3)</b>			
0.186	141.748	26.435	<i>a</i>
0.370	110.821	46.816	110.821
0.569	114.161	69.456	112.554
0.764	115.783	92.084	113.647
0.959	107.144	112.962	112.006
1.139	95.286	130.078	108.852
1.204	80.204	135.312	107.014
<b>120°C (4)</b>			
0.186	140.740	26.247	<i>a</i>
0.388	114.894	49.420	114.894
0.594	117.798	73.688	116.361
0.785	110.203	94.670	114.401
0.967	102.806	113.424	111.691
1.166	91.103	131.572	107.505
1.206	57.394	133.883	105.527

<sup>a</sup> The first point was omitted from the integration.

Table 5a: Heat of absorption of CO<sub>2</sub> with 5M (~63.5 mass%) DEEA + 2M (~19.1 mass%) MAPA solutions at 40°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> .(mol amine) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ.(mol amine) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>40°C (1)</b>			
0.024	93.781	2.208	93.781
0.060	92.799	5.603	93.184
0.109	93.049	10.111	93.124
0.156	90.380	14.419	92.287
0.202	91.678	18.658	92.148
0.247	89.347	22.678	91.638
0.292	84.490	26.425	90.552
0.335	71.434	29.505	88.091
0.385	61.814	32.571	84.701
0.434	60.713	35.558	81.981
0.481	59.334	38.341	79.770
0.527	61.201	41.150	78.152
0.565	57.655	43.374	76.753
0.595	53.045	44.978	75.549
0.620	51.361	46.244	74.587
0.642	52.540	47.401	73.831
0.666	50.273	48.605	72.983
0.689	50.513	49.764	72.235
0.712	50.194	50.912	71.527
0.729	49.155	51.746	71.006
<b>40°C (2)</b>			
0.044	95.994	4.247	95.994
0.098	94.813	9.347	95.346
0.151	93.574	14.333	94.722
0.203	91.823	19.072	93.985
0.253	90.508	23.636	93.293
0.304	80.994	27.769	91.231
0.359	65.582	31.369	87.312
0.416	62.631	34.928	83.941
0.470	61.766	38.267	81.392
0.522	62.399	41.503	79.505
0.570	56.463	44.197	77.575
0.609	53.936	46.328	76.042
0.637	51.792	47.783	74.973
0.668	50.239	49.346	73.822
0.695	49.919	50.683	72.902
0.720	49.945	51.926	72.108
0.743	47.984	53.018	71.369



Table 5b: Heat of absorption of CO<sub>2</sub> with 5M (~63.5 mass%) DEEA + 2M (~19.1 mass%) MAPA solutions at 80°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> .(mol amine) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ.(mol amine) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>80°C (1)</b>			
0.024	96.510	2.357	96.510
0.059	99.535	5.821	98.287
0.107	98.509	10.496	98.386
0.153	98.461	15.063	98.409
0.199	99.037	19.590	98.553
0.243	96.877	23.882	98.248
0.286	89.741	27.747	96.967
0.327	72.132	30.705	93.854
0.372	58.078	33.326	89.518
0.408	53.531	35.253	86.345
0.432	50.128	36.450	84.343
0.439	43.960	36.746	83.723
<b>80°C (2)</b>			
0.026	96.160	2.523	96.160
0.068	98.445	6.676	97.569
0.114	99.104	11.223	98.185
0.161	98.027	15.824	98.139
0.204	98.846	20.064	98.288
0.247	96.202	24.164	97.927
0.288	88.720	27.849	96.601
0.328	72.346	30.748	93.641
0.368	56.360	32.982	89.627
0.406	51.756	34.949	86.080
0.427	49.840	35.997	84.296
0.437	45.667	36.449	83.422

Table 5c: Heat of absorption of CO<sub>2</sub> with 5M (~63.5 mass%) DEEA + 2M (~19.1 mass%) MAPA solutions at 120°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> .(mol amine) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ.(mol amine) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>120°C (1)</b>			
0.027	106.295	2.819	106.295
0.066	106.755	6.997	106.569
0.108	103.682	11.352	105.443
0.152	102.077	15.853	104.465
0.189	98.215	19.543	103.225
0.228	90.906	23.036	101.146
0.264	83.033	26.069	98.643
0.299	67.864	28.434	95.057
0.306	45.542	28.757	93.910
<b>120°C (2)</b>			
0.030	104.153	3.154	104.153
0.057	103.700	5.908	103.941
0.087	101.320	8.922	103.041
0.115	100.475	11.814	102.401
0.145	96.829	14.637	101.277
0.175	96.336	17.552	100.421
0.206	94.771	20.512	99.565
0.235	92.943	23.217	98.745
0.264	81.932	25.600	96.894
0.291	70.254	27.487	94.436
0.307	60.522	28.468	92.646
0.312	41.102	28.658	91.884

Table 6a: Heat of absorption of CO<sub>2</sub> with 5M (62 mass%) DEEA + 1M (9.3 mass%) MAPA solutions at 40°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> .(mol amine) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ.(mol amine) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>40°C (1)</b>			
0.027	84.892	2.331	84.892
0.068	86.119	5.833	85.624
0.121	83.830	10.289	84.838
0.173	79.747	14.398	83.320
0.223	72.200	18.017	80.820
0.271	66.710	21.244	78.304
0.320	62.025	24.240	75.844
0.374	59.883	27.518	73.510
0.427	58.907	30.631	71.703
0.481	58.428	33.792	70.211
0.531	58.220	36.677	69.092
0.579	57.468	39.451	68.123
0.626	57.699	42.173	67.338
0.680	55.901	45.170	66.436
0.732	53.753	47.986	65.529
0.765	53.562	49.740	65.016
0.795	52.848	51.343	64.552
0.825	51.164	52.872	64.068
0.852	49.498	54.207	63.607
0.873	46.505	55.192	63.192
<b>40°C (2)</b>			
0.032	86.089	2.729	86.089
0.077	87.170	6.640	86.723
0.135	84.177	11.533	85.624
0.191	77.842	15.950	83.317
0.255	69.563	20.385	79.881
0.318	64.963	24.442	76.948
0.386	61.413	28.642	74.196
0.455	58.762	32.698	71.855
0.522	59.226	36.690	70.226
0.592	58.605	40.754	68.864
0.651	58.397	44.204	67.914
0.711	56.919	47.647	66.979
0.766	54.649	50.634	66.099
0.808	54.123	52.890	65.481
0.844	52.090	54.795	64.901
0.879	47.368	56.456	64.202
0.901	41.829	57.375	63.657

Table 6b: Heat of absorption of CO<sub>2</sub> with 5M (62 mass%) DEEA + 1M (9.3 mass%) MAPA solutions at 80°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> .(mol amine) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ.(mol amine) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>80°C (1)</b>			
0.031	105.657	3.316	105.657
0.078	99.871	8.019	102.185
0.137	92.526	13.388	98.079
0.187	84.460	17.658	94.398
0.234	73.415	21.115	90.179
0.279	66.903	24.127	86.426
0.320	63.064	26.731	83.415
0.366	59.878	29.472	80.473
0.407	59.479	31.900	78.367
0.435	59.096	33.523	77.150
0.453	54.144	34.515	76.219
0.463	47.750	34.987	75.610
<b>80°C (2)</b>			
0.032	103.277	3.287	103.277
0.079	99.173	7.988	100.822
0.133	93.888	13.072	98.006
0.184	85.765	17.443	94.622
0.227	78.208	20.815	91.510
0.274	66.835	23.914	87.333
0.321	63.264	26.925	83.769
0.364	60.278	29.472	81.040
0.405	58.603	31.872	78.768
0.438	58.131	33.824	77.187
0.457	50.498	34.767	76.096

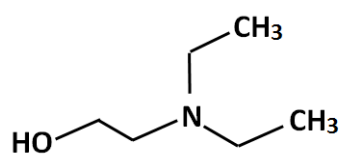
Table 6c: Heat of absorption of CO<sub>2</sub> with 5M (62 mass%) DEEA + 1M (9.3 mass%) MAPA solutions at 120°C.

$\alpha$	$\Delta H_{diff}$	$\Delta H_{int}$	$\Delta H_{int}$
mol CO <sub>2</sub> .(mol amine) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>	kJ.(mol amine) <sup>-1</sup>	kJ.(mol CO <sub>2</sub> ) <sup>-1</sup>
<b>120°C (1)</b>			
0.031	106.259	3.278	106.259
0.061	105.608	6.444	105.938
0.091	97.901	9.391	103.277
0.120	99.274	12.298	102.302
0.149	96.555	15.034	101.206
0.175	92.281	17.514	99.839
0.206	79.016	19.953	96.723
0.223	67.273	21.109	94.459
0.230	49.177	21.423	93.199
<b>120°C (2)</b>			
0.030	109.350	3.271	109.350
0.062	106.447	6.666	107.852
0.096	99.872	10.071	105.015
0.128	102.432	13.345	104.370
0.163	96.051	16.675	102.595
0.195	81.435	19.318	99.072
0.220	64.126	20.921	95.102
0.227	47.212	21.254	93.614

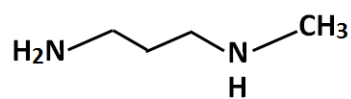
Table 7: Volume distribution in upper and lower phases

T	5M DEEA + 2M MAPA				5M DEEA + 1M MAPA			
	$\alpha$	Final $P_{total}$	No. of phases	UP/LP*	$\alpha$	Final $P_{total}$	No. of phases	UP/LP*
$^{\circ}C$	$\text{mol CO}_2 \cdot (\text{mol amine})^{-1}$	kPa		$\text{vol}\% \cdot (\text{vol}\%)^{-1}$	$\text{mol CO}_2 \cdot (\text{mol amine})^{-1}$	kPa		$\text{vol}\% \cdot (\text{vol}\%)^{-1}$
40 (1)	0.729	265.6	1	-	0.873	235.9	1	-
40 (2)	0.743	288.1	1	-	0.901	266.9	1	-
80 (1)	0.439	556.6	2	50/50	0.463	568.9	1	-
80 (2)	0.437	543.1	2	50.2/49.8	0.457	550.9	1	-
120 (1)	0.306	589.2	2	64.3/35.7	0.230	582.9	2	67.1/32.9
120 (2)	0.312	584.5	2	64.1/35.9	0.227	582.3	2	67.2/32.8

\*UP = upper phase and LP = lower phase



DEEA



MAPA

Fig. 1: Structures of DEEA and MAPA.

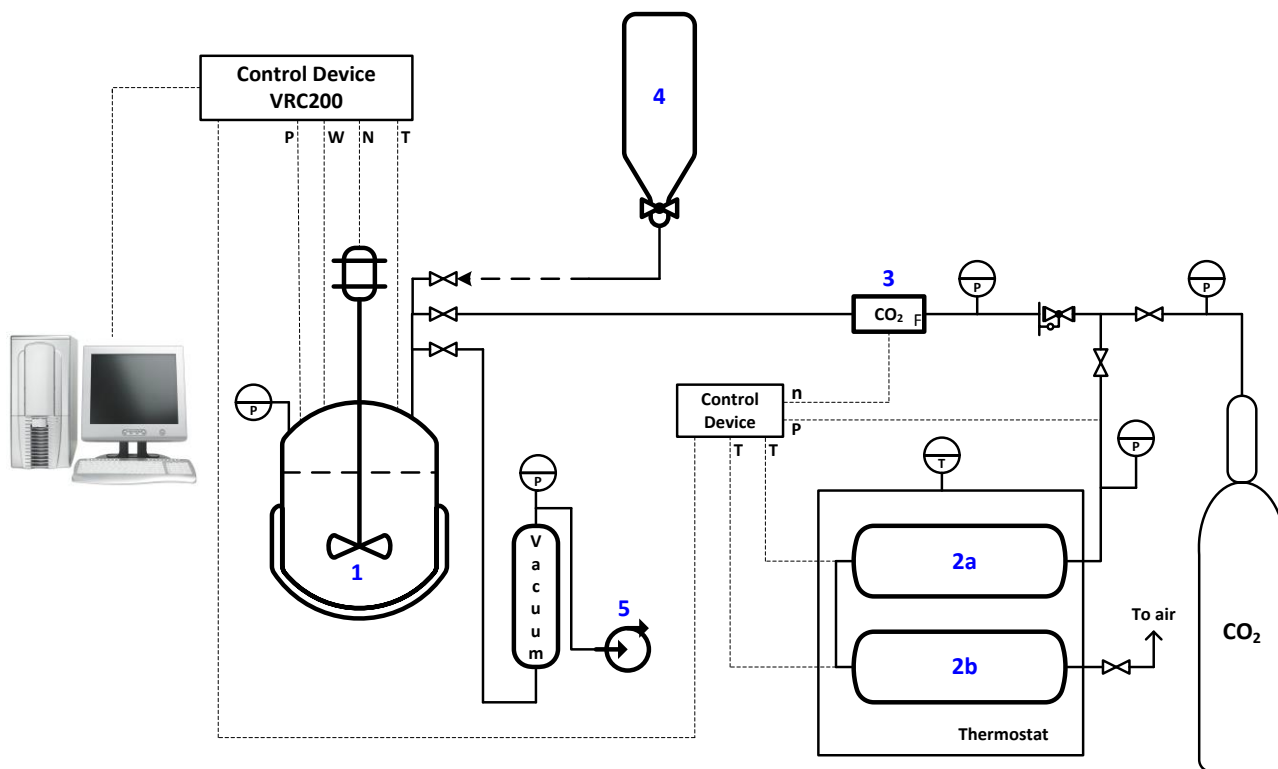


Fig. 2: Experimental setup for measuring heat of absorption: 1 - reaction calorimeter; 2a, 2b - CO<sub>2</sub> storage cylinders; 3 - CO<sub>2</sub> mass flow controller; 4 - amine solution feed bottle; 5 - vacuum pump.



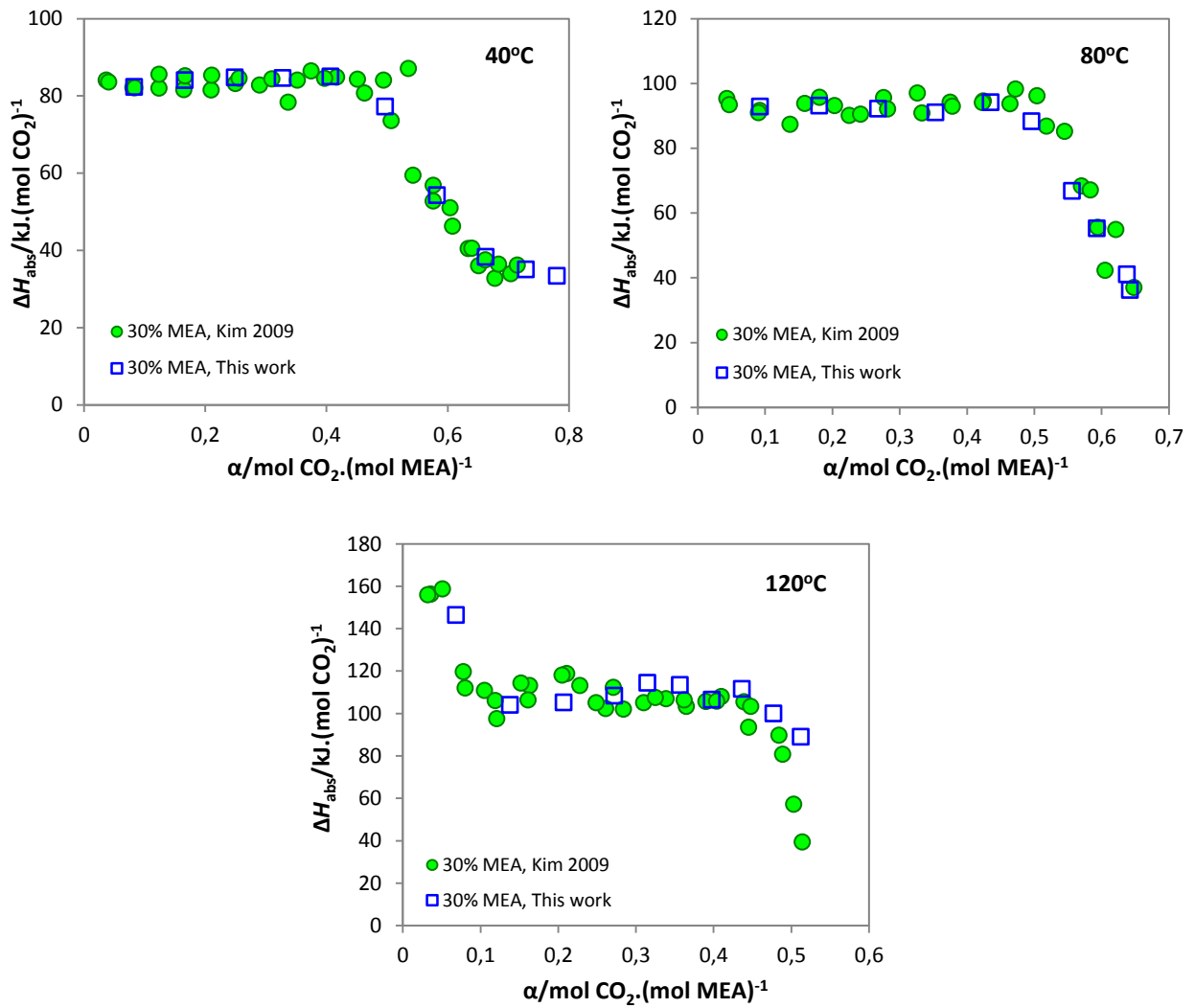


Fig. 3: Differential enthalpy of absorption of CO<sub>2</sub> with 30 mass% MEA at 40, 80 and 120°C.

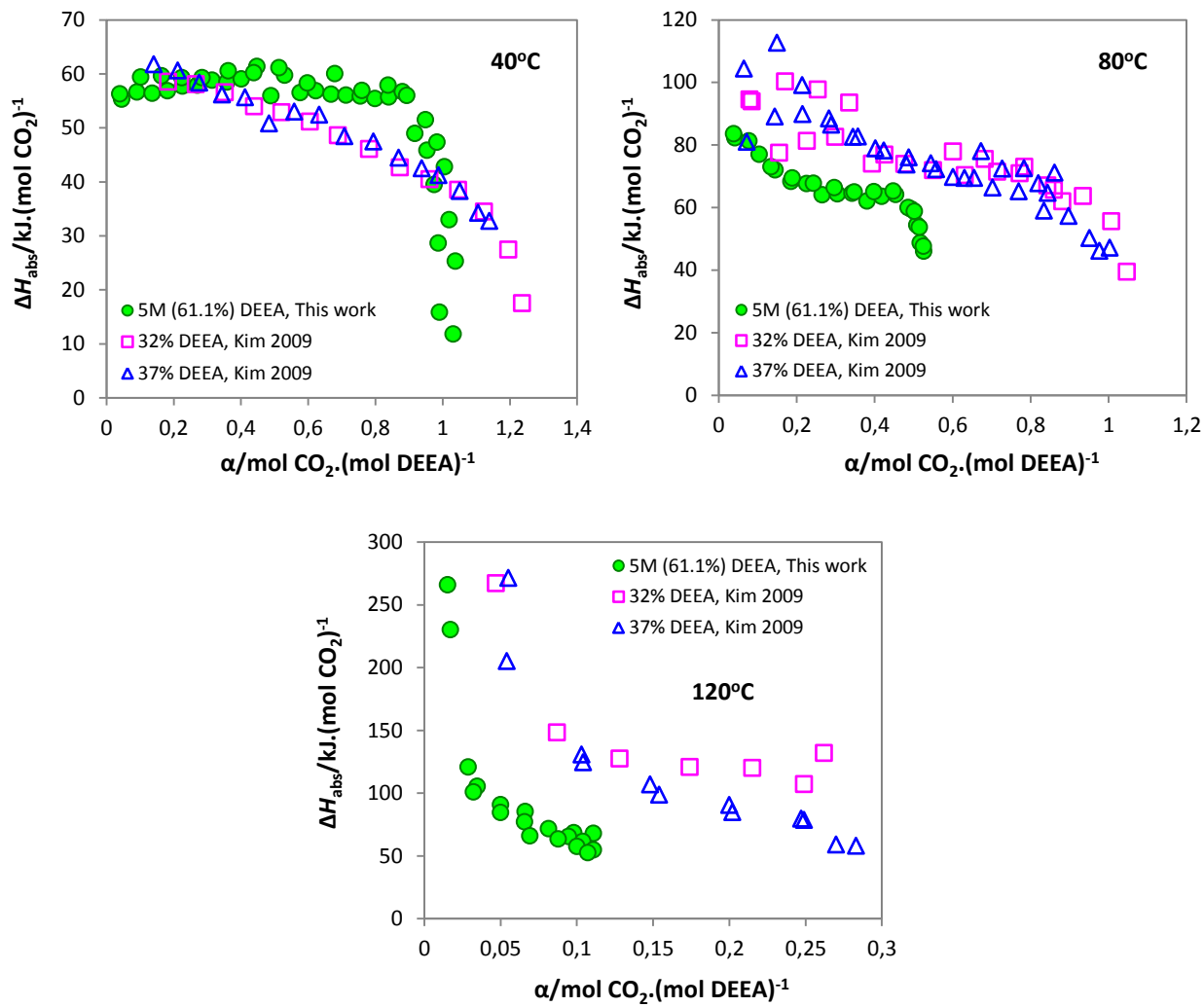


Fig. 4: Differential enthalpy of absorption of CO<sub>2</sub> with 5M (61.1 mass%) DEEA at 40, 80 and 120°C.

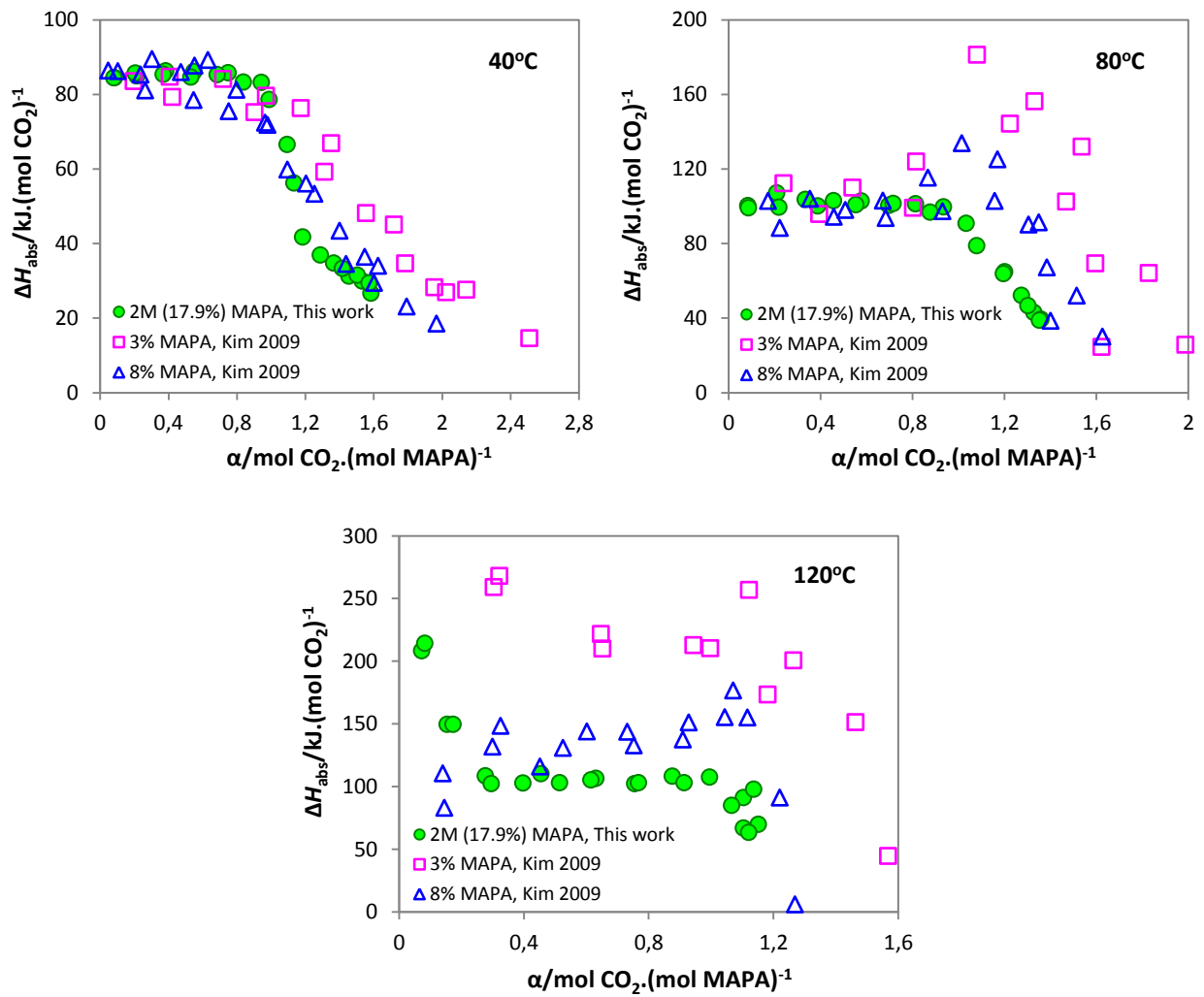


Fig. 5: Differential enthalpy of absorption of CO<sub>2</sub> with 2M (17.9 mass%) MAPA at 40, 80 and 120°C.

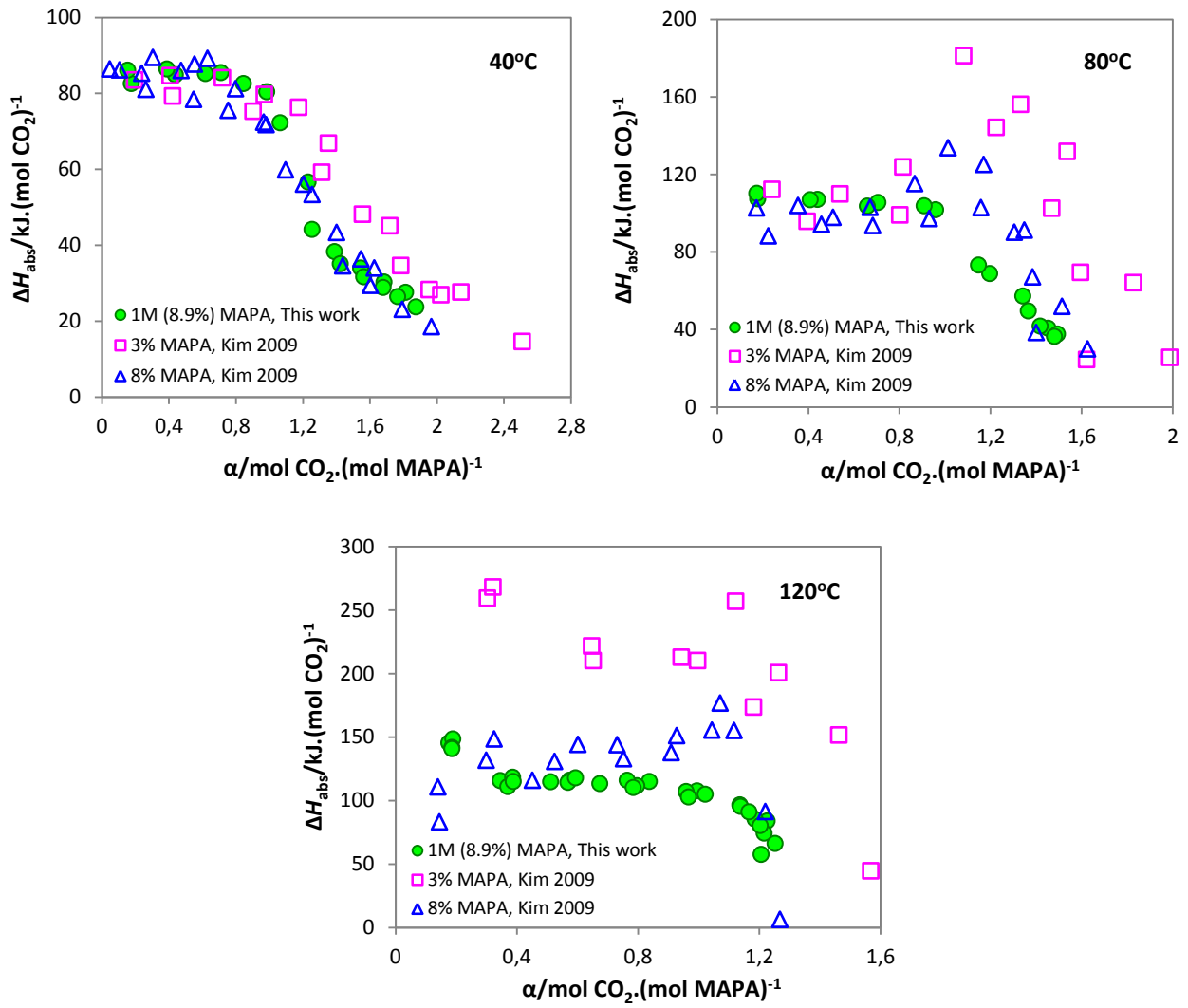


Fig 6: Differential enthalpy of absorption of  $\text{CO}_2$  with 1M (8.9 mass%) MAPA at 40, 80 and 120°C.

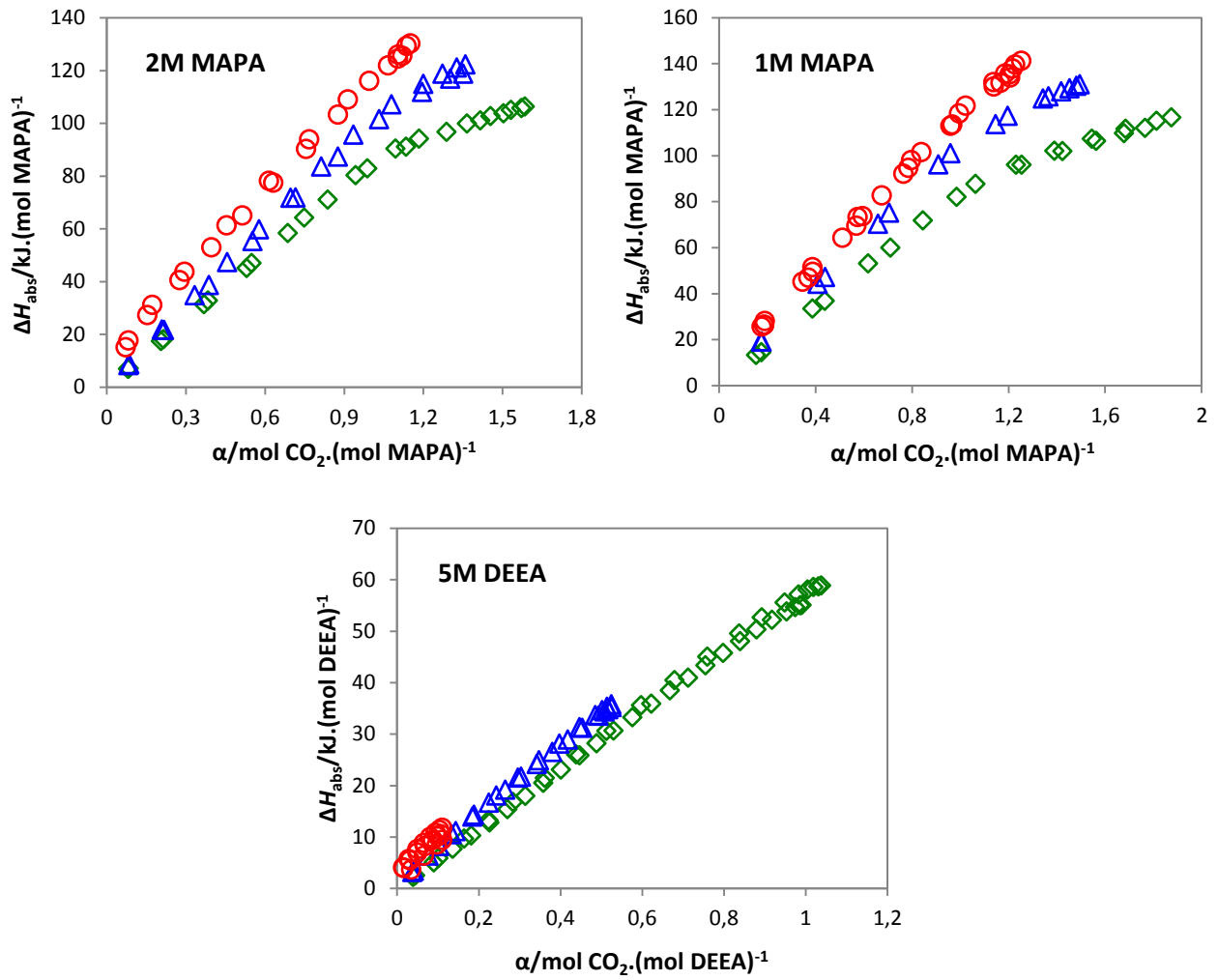


Fig. 7: Integral heat of absorption of CO<sub>2</sub> with 5M DEEA, 2M MAPA and 1M MAPA at temperatures 40°C (◇), 80°C (△) and 120°C (○).

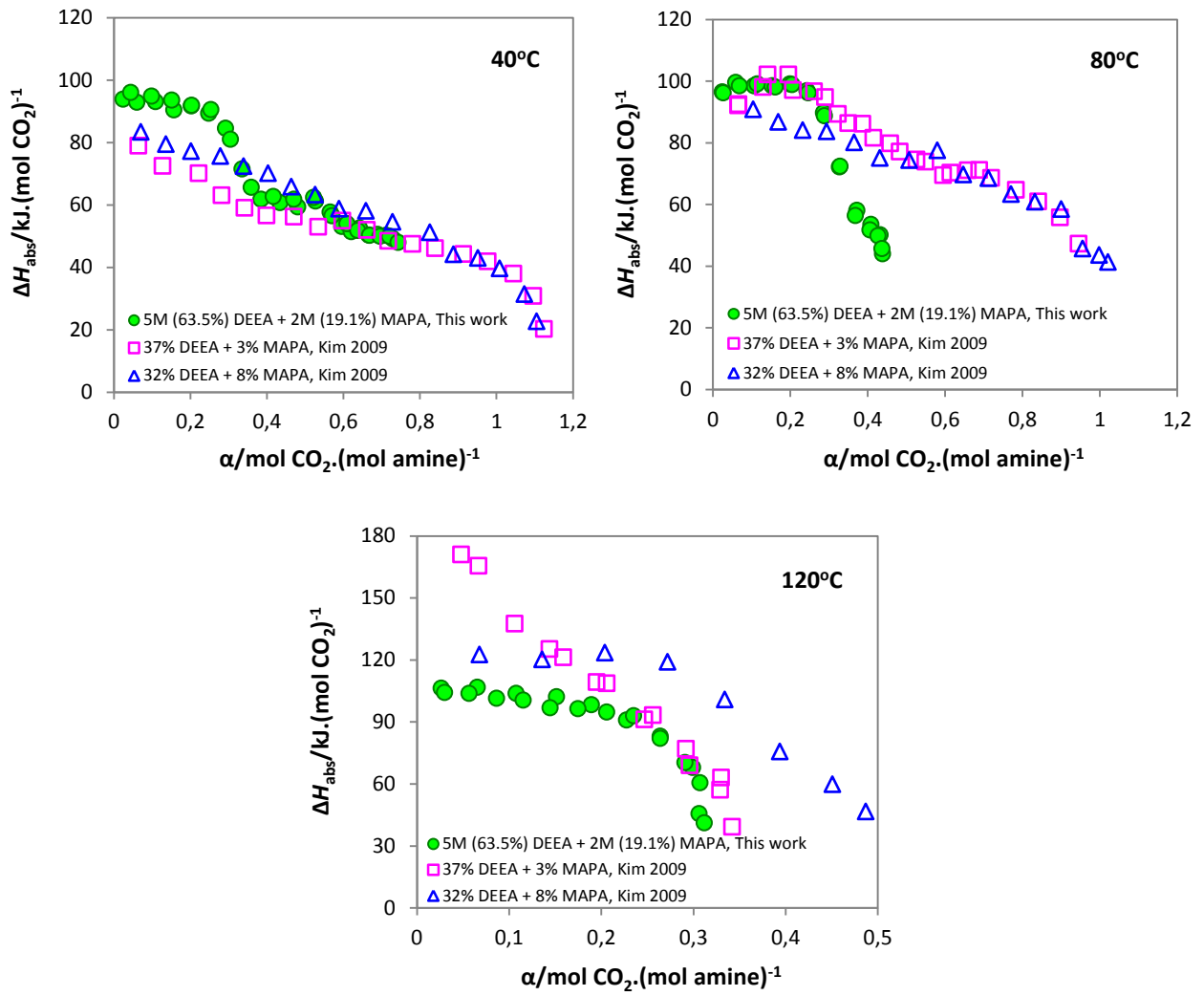


Fig. 8: Differential enthalpy of absorption of CO<sub>2</sub> with 5M (63.5 mass%) DEEA + 2M (19.1 mass%) MAPA at 40, 80 and 120°C.

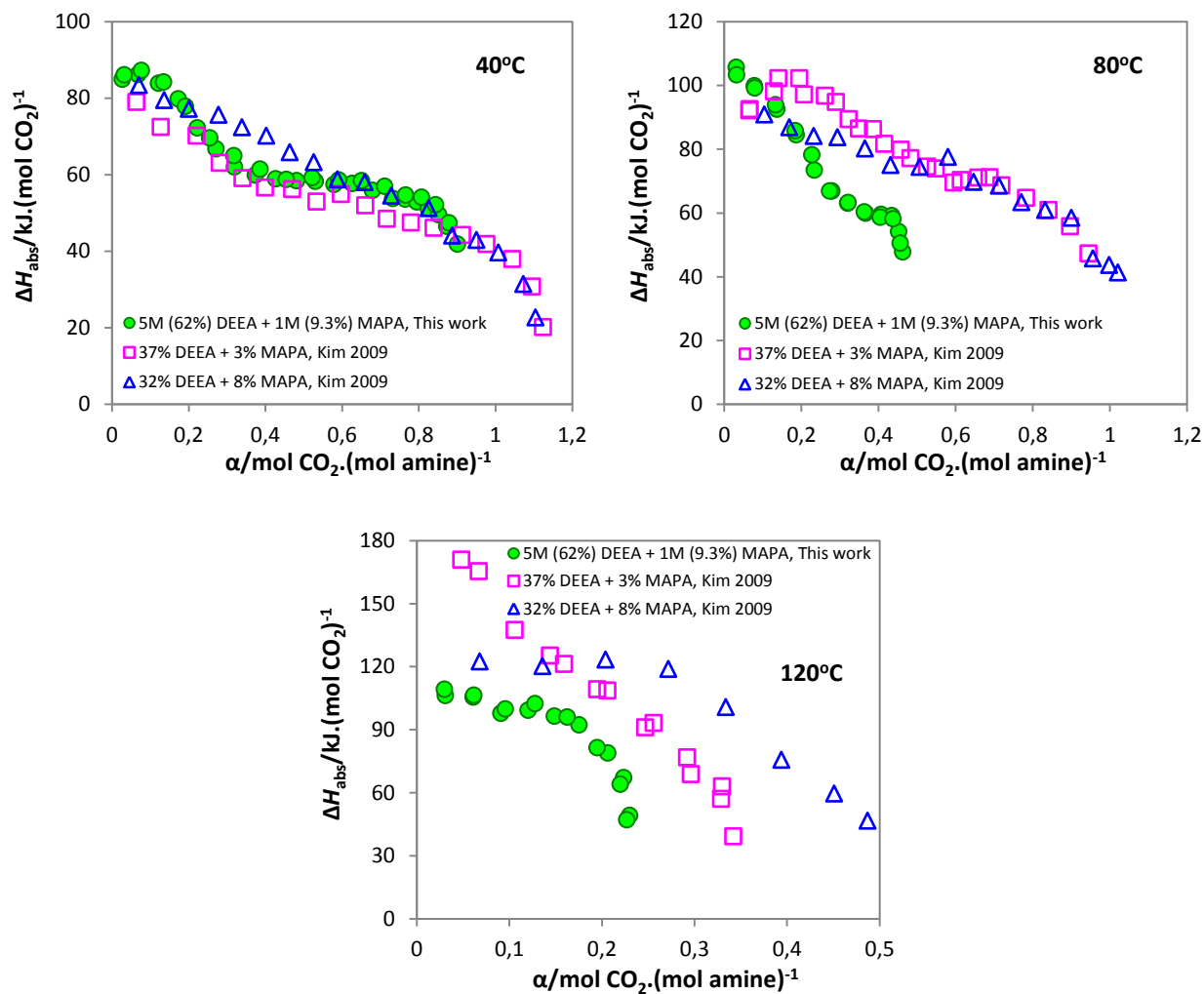


Fig. 9: Differential enthalpy of absorption of CO<sub>2</sub> with 5M (62 mass%) DEEA + 1M (9.3 mass%) MAPA at 40, 80 and 120°C.

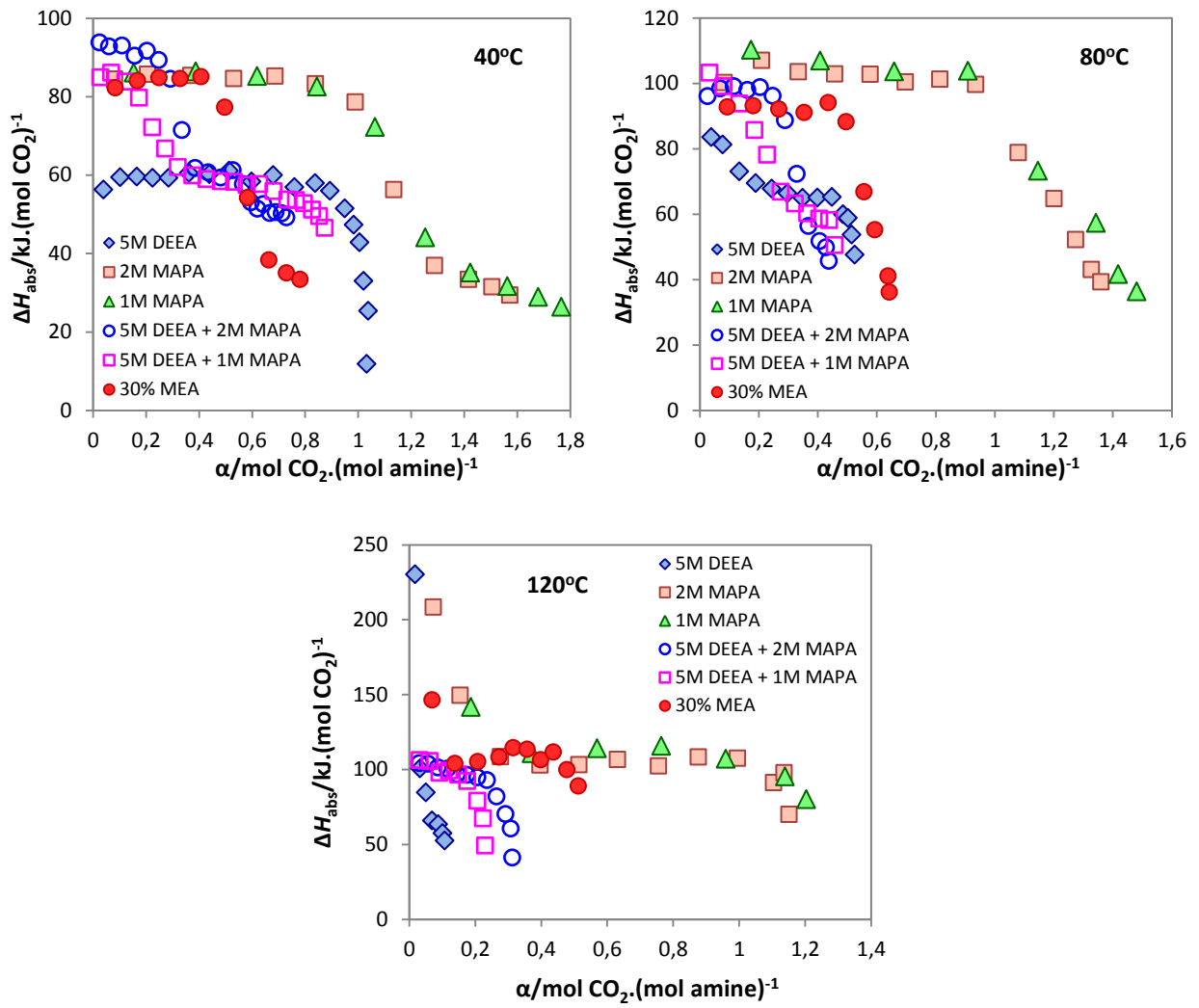


Fig. 10: Overall comparison of differential enthalpy of absorption of CO<sub>2</sub> for all studied systems and 30 mass% MEA at 40, 80 and 120°C.