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Chemical absorption of carbon dioxide in non-aqueous systems using the amine 2-amino-2-methyl-1-propanol in dimethyl sulfoxide and N-methyl-2-pyrrolidone

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ABSTRACT

Non-aqueous amine systems have been suggested as energy-efficient alternatives to conventional aqueous amine systems in post-combustion carbon capture, as low regeneration temperatures can be achieved. The solubility of CO₂ and heat of absorption in non-aqueous systems were studied using the sterically hindered amine 2-amino-2-methyl-1-propanol (AMP) in the organic solvent dimethyl sulfoxide (DMSO). ¹³C NMR was used to study the product species in solution as CO₂ reacts with AMP in either DMSO or N-methyl-2-pyrrolidone (NMP). The solubility of CO₂ in AMP/DMSO showed that low loadings could be achieved at 80–88 °C, indicating that regeneration can be carried out at lower temperatures than in conventional aqueous systems. Precipitation occurred at 25 wt% AMP in DMSO, increasing the overall capacity of the system. The heat of absorption decreased with increasing temperature, and was explained by physical absorption dominating the absorption mechanism at higher temperatures. This was also confirmed by the results of NMR, as less chemically absorbed species were observed at higher temperatures. The reaction products observed in AMP/DMSO and AMP/NMP were identified as the AMP carbamate, bicarbonate from water impurities, and the AMP carbonate from CO₂ reacting with the hydroxyl group of AMP.

1. Introduction

Due to the increasing concentration of CO₂ in the atmosphere, extensive research in recent years has focused on technologies to control and reduce the emission of anthropogenic CO₂. Post-combustion techniques using aqueous amine absorption for the removal of gaseous CO₂ are among the most developed techniques for carbon capture. These techniques are currently being used in areas such as biogas upgrading, and the production of hydrogen and synthesis gas. Due to the maturity of such techniques, and the possibility of retro-fitting existing industrial plants, post-combustion capture is considered the most promising alternative for carbon capture and storage (CCS) applications [1]. However, drawbacks such as high operating cost, mostly associated with the high amount of energy needed to regenerate the aqueous absorption systems, must be addressed in order to increase their suitability for future large-scale industrial implementation [2].

The energy required for regeneration is partly dependent on the absorption system used, and includes the sensible heat, i.e., the heat

needed to raise the temperature of the solvent to the appropriate regeneration temperature, and the heat of reaction between the amine and CO₂ [3]. Aqueous systems, such as aqueous monoethanolamine (MEA), are also associated with regeneration temperatures above the boiling point of water (120 °C), leading to the requirement of energy to vaporize water in the absorption solution. This has led to growing interest in unconventional absorption solutions that could serve as energy-efficient alternatives to aqueous solutions. Some of the alternatives studied are systems with lower regeneration temperatures and phase-changing systems in which a single-phase system becomes bi-phasic when a new CO₂-rich phase is formed during absorption. This CO₂-rich phase could be separated before regeneration of the solution, thus reducing the total amount of solvent that has to be heated in regeneration.

Several studies have been conducted on non-aqueous absorption systems using the sterically hindered amine 2-amino-2-methyl-1-propanol (AMP) [2,4–9]. In the absence of water, the proposed reaction mechanism for AMP and CO₂ results in the formation of a carbamate

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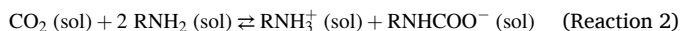
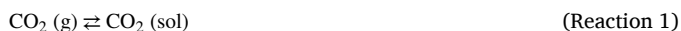
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(Reactions 1–2). Physical absorption of CO₂ takes place (Reaction 1) as the gaseous (g) CO₂ is dissolved in the liquid solution (sol). This is followed by the chemical part of the absorption process as the reaction between AMP and CO₂ takes place (Reaction 2) to form the AMP carbamate. The steric hindrance of this carbamate makes it possible to regenerate the solution at temperatures between 70 and 90 °C [2,10].



In some organic solvents, the AMP carbamate can also induce phase-changing behavior as it is prone to precipitate as solid (s) crystals (Reaction 3).



If alcohols are used as the solvent, additional formation of carbonate species (Reaction 4) will be possible in the presence of a base, such as AMP.



The reaction mechanism for several primary amines, not including AMP, in non-aqueous solutions with both polar and non-polar solvents has been studied by Kortunov et al. [11], using *in situ* nuclear magnetic resonance (NMR) to determine the chemical species in solution during the reaction with CO₂. They found that the choice of solvent played an important role in determining which protonated species were formed in solution during the reaction with CO₂. Polar solvents such as *N*-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO), which were expected to favor the formation of the carbamate species due to their polarity, instead seemed to favor the protonated carbamic acid in solution. The carbonated species formed by AMP in several non-aqueous solutions have also been investigated previously. Barzagli et al. reported the formation of AMP carbamate in non-aqueous ethylene glycol monomethyl ether [9] and diethylene glycol monomethyl ether (DEGMME) [5,9]. In mixtures of AMP with ethylene glycol (EG) + ethanol [12], EG + propanol and EG + DEGMME [8] only small amounts of AMP carbamate were detected, suggesting that the formation of carbonates by the reaction between CO₂ and the organic solvents was promoted. Barzagli et al. [5] also reported on the formation of the AMP carbonate in aqueous solutions of AMP. No NMR studies on the precipitating systems of AMP in DMSO or NMP have been found in the literature. As solids are not detected in conventional NMR, precipitating systems are not ideal for such analysis. However, to be able to validate the reaction mechanism, characterization of the species in solution is needed, and this can be done for precipitating systems at lower amine concentrations where no precipitation occurs, or at low CO₂ loadings prior to precipitation.

In our previous work, we have studied AMP mixed with the organic solvent NMP for use as a bi-phasic absorption system for carbon capture [10,13–15]. The initial idea involves the CO₂ rich AMP carbamate to precipitate in the absorption step, after which some of the NMP can be removed before the regeneration step [16]. Thus, lowering the amount of solvent needed to be heated in the regeneration step. However, since NMP has reproductively toxic properties, we have also performed a screening study to find alternative and less toxic organic solvents, of which AMP in DMSO showed promising absorption behavior at 25 and 40 °C [17]. In order to evaluate the CO₂ absorption performance of AMP in DMSO for carbon capture applications, more comprehensive data on the CO₂ solubility and heat of absorption are needed under both absorption and regeneration conditions. In addition, it is necessary to characterize the species present in the solution under different conditions in order to validate the proposed reaction mechanism (Reactions 1–3).

In this study, we have investigated the absorption behavior of CO₂ in precipitating non-aqueous AMP solutions. The species in solution have

been characterized for both AMP/DMSO and AMP/NMP solutions at 30–80 °C using ¹³C NMR. CO₂ solubility and heat of absorption, in both 10 wt% AMP in DMSO and 25 wt% AMP in DMSO, have been studied using reaction calorimetry at temperatures corresponding to both absorption and regeneration conditions (25–88 °C). Comprehensive vapor–liquid equilibrium data, under both absorption and regeneration conditions, as well as the speciation of reaction products present in the solutions, are presented and the potential use of AMP in DMSO as a non-aqueous precipitating absorption system for carbon capture is discussed.

2. Materials and method

2.1. Materials

The chemicals used in this study are presented in Table 1, together with their purity, chemical structure and supplier. All chemicals were used as received without further purification. The sample mixtures used in this study were prepared gravimetrically in individual containers using a scale with an accuracy of 0.01 g for up to 1200 g.

2.2. Experimental method

2.2.1. Vapor–liquid equilibrium

The experimental procedure used is similar to the procedures used previously, and more detailed information on the experimental setup and data evaluation can be found [13–15,17]. Thus, only a brief description is given here. The samples, together with the experimental conditions, are presented in Table 2.

The experiments were performed in a true heat flow reaction calorimeter (CPA 201 Chemical process Analyzer from ChemiSens AB). The reactor used had a volume of 250 cm³ and about 100 g of solvent mixture was added to reactor before the start of each experiment. The reactor was then evacuated for 10–12 s, using a vacuum pump, at 25 °C. The reactor temperature was then raised to the experimental temperature and the system was left to equilibrate before any CO₂ was added to the reactor. All experiments were performed at constant temperature, controlled using the built-in water bath. The temperature sensors in the reactor and water bath had an accuracy of 2.7 K (at 100 °C). The vapor pressure of amine and organic solvent was assumed to be constant during the experiment, and thus equal to the equilibrium pressure at the experimental temperature before any addition of CO₂. Pure CO₂ was

Table 1

The chemicals used in this study together with their purity, chemical structure and supplier.

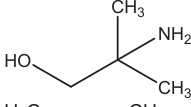
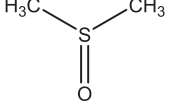
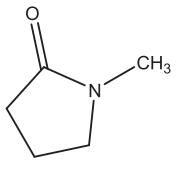
Chemical	Abbreviation	Purity (%)	Chemical structure	Supplier
2-amino-2-methyl-1-propanol	AMP	93–98		Merck
Dimethyl sulfoxide	DMSO	99.9		Merck
Dimethyl sulfoxide-d ₆	DMSO-d ₆	99.9	–	Sigma-Aldrich
<i>N</i> -methyl-2-pyrrolidone	NMP	99.5		Sigma-Aldrich
CO ₂	–	>99.99	–	AGA
¹³ CO ₂	–	99	–	CIL

Table 2

Composition of the absorption solutions used in this study together with the experimental conditions used, in terms of temperature and range of partial pressure of CO₂.

Solution	wt% AMP	wt% DMSO	wt% NMP	Experiment temperature (°C)	P _{CO2} (kPa)
1	10	90	0	25, 40, 50, 60, 70, 80, 88	1.49–375.01
2	25	75	0	50, 60, 70, 80, 88	1.94–336.81
3	2.5	0	97.5	40, 60, 80	22.27–316.94

then injected into the reactor in a series of small doses, each lasting for about 10 s, and each causing an initial total pressure increase of about 0.5 bar. The injection of CO₂ was performed using a Bronkhorst Hi-Tec mass flow controller (MFC), with an accuracy of 0.8%. After each injection, the system was allowed to reach equilibrium, which was assumed to be reached when the change in the total pressure and the true heat flow signals were less than 0.005 bar and 0.02 W for at least 25 and 33 min, respectively. The pressure in the reactor was measured using an Omega pressure transducer with an accuracy of 1.0%. The MFC signal, pressure and true heat flow were measured throughout the experiment, and continuously logged in a computer. A ProFind™ automation script was used to control the temperature and CO₂ dosage, and to determine when equilibrium had been reached.

Two independent experimental runs were performed at each temperature and for each concentration in order to ensure repeatability. Each experiment consisted of 5–8 equilibrium points. The uncertainties in the amount of CO₂ absorbed were determined to be 1.6% for the 10 wt % AMP/DMSO system and 1.3% for the 25 wt% AMP/DMSO system. The uncertainty in the heat of absorption was determined to be 4.0% for 10 wt% AMP/DMSO and 1.9% for 25 wt% AMP/DMSO.

2.2.2. Nuclear magnetic resonance

NMR was used to study product formation as the CO₂ reacted with AMP in the non-aqueous solutions AMP/DMSO and AMP/NMP. Product characterization spectra were collected for the systems at 30 °C, with and without the addition of CO₂, in order to identify product peaks. Experiments were performed at temperatures between 30 and 80 °C to study how the product distribution changed with increasing temperature. The samples and experimental temperatures used in the NMR evaluation are presented in Table 3.

Samples were prepared for ¹³C NMR studies by stirring solutions of AMP in DMSO (2.5 or 10 wt% AMP) or NMP (2.5 wt% AMP) under a ¹³CO₂ atmosphere for 30 min at room temperature. Both solvents contained 5% DMSO-*d*₆ needed for NMR lock and chemical shift reference. After the reaction had been completed, a volume of 600 µl was transferred to a 5 mm NMR tube, which was capped and placed in the NMR magnet.

The product characterization spectra were recorded with a Bruker 500 MHz spectrometer fitted with a 5 mm cryoprobe. Spectra were recorded at 30 °C as the average of 512 scans employing 20-degree pulses, and separated by a 5 s delay. The ¹³C NMR spectra for the experiments in which the temperature was varied were recorded on a Varian 400 MHz spectrometer fitted with a 5 mm AutoXDB probe.

Each spectrum was recorded as the average of 1024 scans employing 20-degree pulses, and separated by a 5 s delay. Spectra were recorded at temperatures of 30, 40, 50, 60, 70 and 80 °C and finally again at 30 °C.

Table 3

Composition of the amine solutions used in this NMR study together with the experimental temperatures used.

Solution	wt% AMP	wt% DMSO	wt% NMP	Experiment temperature (°C)
1	10	90	0	30, 40, 50, 60, 70, 80
2	2.5	97.5	0	30, 40, 50, 60, 70, 80
3	2.5	0	97.5	30, 40, 50, 60, 70, 80

In all NMR experiments, the chemical shifts were referenced to the central peak of the DMSO-*d*₆ multiplet set to 39.5 ppm.

3. Results and discussion

3.1. Solubility of CO₂ in mixtures of AMP and DMSO

The solubility of CO₂, in terms of vapor–liquid equilibrium, was measured in solutions of AMP in DMSO using reaction calorimetry. Two concentrations of AMP were studied, 10 and 25 wt%, at temperatures between 25 and 88 °C, corresponding to both absorption and regeneration conditions.

Solubility data collected for CO₂ in mixtures of 10 wt% AMP in DMSO at temperatures between 25 and 88 °C are presented in Fig. 1. The results show a decrease in the solubility of CO₂ with increasing temperature, which is represented by a higher CO₂ partial pressure at lower loadings with increasing temperature. No precipitation was observed in the 10 wt% AMP/DMSO system under the conditions studied. The capacity of the absorption system, i.e., the difference between rich and lean CO₂ loading, can be estimated from the solubility data at absorption and regeneration conditions (in terms of temperature and partial pressure of CO₂). For the conventional system of 30 wt% aqueous MEA, the rich loading is typically just above 0.5 mol CO₂/mol amine (at 40 °C and 10 kPa CO₂) [18–21] and the lean loading around 0.2 mol CO₂/mol amine (at 120 °C and 10 kPa CO₂) [20–22]. This results in a capacity of slightly above 0.3 mol CO₂/mol amine. If regeneration is performed without stripping gas for 10 wt% AMP/DMSO, this can be represented by the solubility data at 88 °C and 100 kPa, resulting in a lean loading of approximately 0.09 mol CO₂/mol AMP. Absorption is usually performed at 40 °C, and thus in order to achieve a capacity of around 0.3 mol CO₂/mol amine, the incoming gas must have a CO₂ partial pressure of about 50 kPa. If absorption is conducted at 25 °C, a similar capacity is obtained at a CO₂ partial pressure of about 20 kPa. However, additional cooling of the incoming gas will probably be needed in such cases. The temperature of the absorber would also have to be kept as low as possible, in order not to reduce its capacity. The CO₂ partial pressures needed in the incoming gas (20–50 kPa) indicate that the 10 wt% AMP/DMSO system could be suitable for carbon capture in biogas upgrading and industrial CCS.

The solubility of CO₂ in 25 wt% AMP/DMSO obtained in this study at 50–88 °C is presented in Fig. 2, together with the data obtained at 25 and 40 °C in our previous study [17]. A similar trend can be seen to the 10 wt % system, regarding the decreasing solubility with increasing temperature. However, in the 25 wt% AMP/DMSO system, precipitation is observed at the lower temperatures (25–50 °C). This can be seen as a

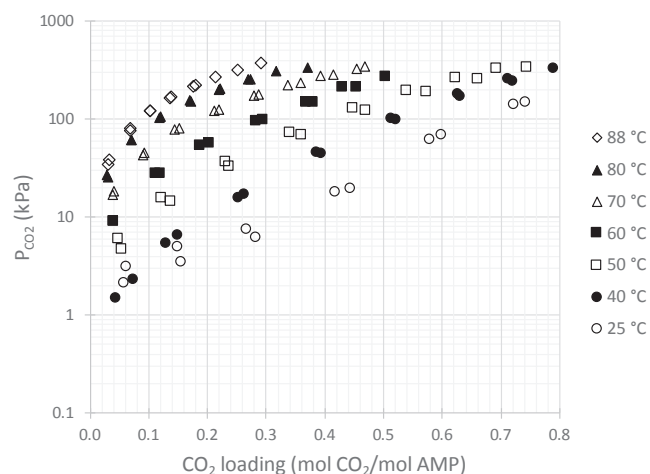


Fig. 1. Solubility of CO₂ in solutions of 10 wt% AMP in DMSO, at temperatures between 25 and 88 °C.

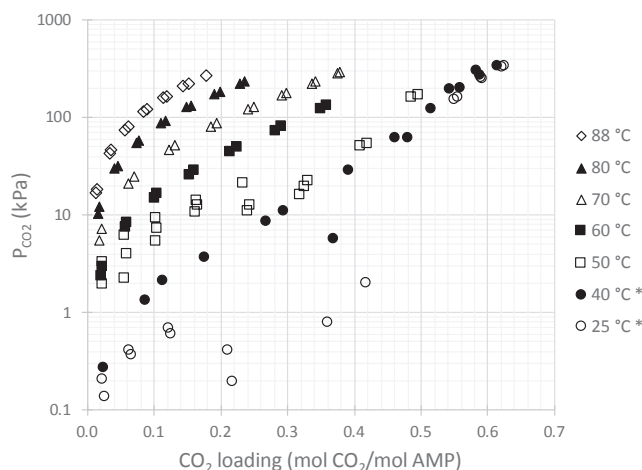


Fig. 2. Solubility of CO₂ in solutions of 25 wt% AMP in DMSO, at 50, 60, 70, 80 and 88 °C. Data obtained in our previous study, at 25 and 40 °C, are included (indicated by an asterisk in the legend) [17].

decrease in pressure, with increased loading, in some data points in the data series for those temperatures. Precipitation drives the equilibrium reactions (Reactions 1–4) further to the right, which allows more CO₂ to be dissolved in the solution. The lower pressure measured after precipitation indicates that the absorption solution is supersaturated prior to precipitation, likely due to slow crystallization kinetics [23]. The pressure will decrease to values closer to true equilibrium after the initial precipitation takes place. It should be noted that if the solution precipitates at higher amine loadings (past 0.5 mol CO₂/mol AMP), and thus a higher partial pressure of CO₂, the decrease of pressure in the solubility data is absent. This is the case for one of the experimental runs at 40 °C. The reason for this is believed to be a combination of the driving force for CO₂ to absorb in the liquid decreasing after its fully chemically loaded, together with the overall pressure in the reactor being higher at this point, and thus a small decrease in pressure becomes less significant. The precipitation point can however still be seen in the heat of absorption data as discussed below in Section 3.2. If precipitation occurs, a higher rich loading is obtained, and the capacity of the system is increased. At 40 °C, and at a CO₂ partial pressure of 10 kPa, the CO₂ loading increases from 0.28 to 0.37 mol CO₂/mol AMP when there is precipitation in the system. If these conditions are used for the absorption, and the regeneration conditions without a stripping gas are represented by 88 °C and 100 kPa, a difference between rich and lean loading of 0.3 mol CO₂/mol AMP can be achieved, based on the solubility data. In the system with 25 wt% AMP in NMP a higher partial pressure of CO₂ is needed to reach a similar capacity at 40 °C [13], indicating that the AMP/DMSO system is more suitable for carbon capture at lower CO₂ partial pressures. Furthermore, if a stripping gas is used during regeneration, even lower lean loadings can be achieved, i.e., below 0.01 mol CO₂/mol AMP at 88 °C and 20 kPa. Also, if it is possible to use a lower absorption temperature of 25 °C, a rich loading of 0.36 mol CO₂/mol AMP can already be achieved at CO₂ partial pressures below 1 kPa. However, in order to determine whether this is feasible, the CO₂ reaction kinetics needs to be evaluated. The reaction kinetics affects the residence time needed in the absorption step and is thus crucial in order to design the absorption system.

The solubility of CO₂ in the AMP/DMSO systems with (25 wt%) and without (10 wt%) precipitation, at absorption and regeneration temperatures is presented in Fig. 3. The lean loading that can be achieved when regeneration is performed at 100 kPa does not differ between the two systems. However, it can clearly be seen that at a CO₂ partial pressure of 10 kPa the rich loading is significantly increased in the 25 wt % AMP/DMSO system, where there is precipitation. This rich loading is almost twice as high as that in the 10 wt% AMP/DMSO system, at

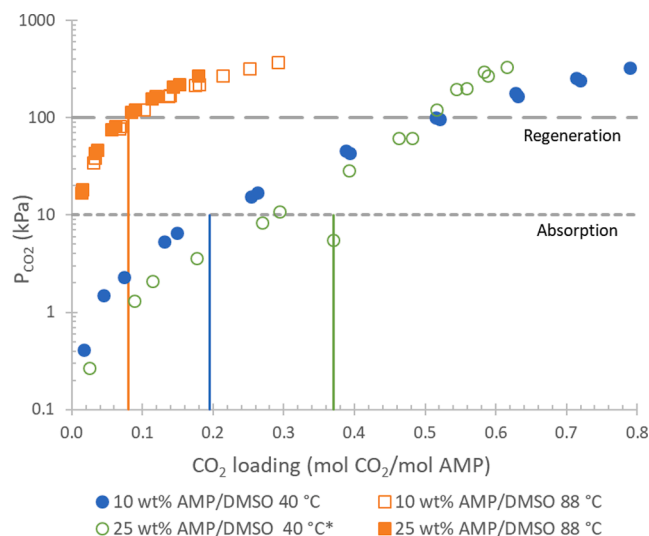


Fig. 3. Comparison of the solubility of CO₂ in 10 wt% and 25 wt% AMP in DMSO at absorption (40 °C) and regeneration (88 °C) temperatures. The CO₂ partial pressure in the absorption step is assumed to be 10 kPa, and regeneration is carried out at atmospheric pressure. The vertical lines indicate the estimated CO₂ loadings that can be achieved for the systems under absorption (green or blue) and regeneration conditions (orange). Data obtained at 40 °C in our previous study are included (indicated by an asterisk in the legend) [17]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

10 kPa. It is thus clear that precipitation is necessary in the AMP/DMSO system in order for it to be competitive with conventional systems, in terms of CO₂ loading capacity. The 25 wt% AMP in DMSO is therefore considered the more interesting alternative as a bi-phasic CO₂ absorption system.

The precipitation of a CO₂ rich phase creates the opportunity to reduce the amount of solvent that goes through the regeneration process, which could lower the amount of energy needed for the CO₂ removal process. However, the precipitation also infers that the capture process needs to be designed to handle the solid precipitate, both in terms of precipitation in the absorbing unit and in terms of fluid transportation. There are pilot designs available for this purpose [24,25] but in order to evaluate the energy requirement, the specific absorption solution needs to be tested. There are also other benefits associated with the AMP/DMSO system, such as the fact that low lean loadings can be achieved without any stripping agent. The lower temperatures needed for regeneration (<90 °C) also allows for the use of excess heat that is more readily available in industry, which could possibly reduce thermal degradation of the amine. As the system is non-aqueous this could reduce corrosion in the absorption unit but further studies are needed to investigate this.

3.2. Heat of absorption of CO₂ in mixtures of AMP and DMSO

The heat of absorption ($-\Delta H_{\text{abs}}$) is another important factor when evaluating absorption systems, as it is an essential part in determining the amount of heat needed to regenerate the system. Heat of absorption includes the heat of dissolution of CO₂ into the liquid system and the heat of reaction between CO₂ and the amine (Reactions 1–3). These are usually exothermic reactions, resulting in heat being released during the absorption process, causing an increase in temperature. The differential heat of absorption obtained from the absorption of CO₂ in 10 wt% AMP in DMSO is presented in Fig. 4. In general, it can be seen that the heat of absorption decreases with increasing CO₂ loading. At low loadings, where chemical absorption dominates the reaction mechanism, the heat released upon the absorption of CO₂ is much higher than for CO₂

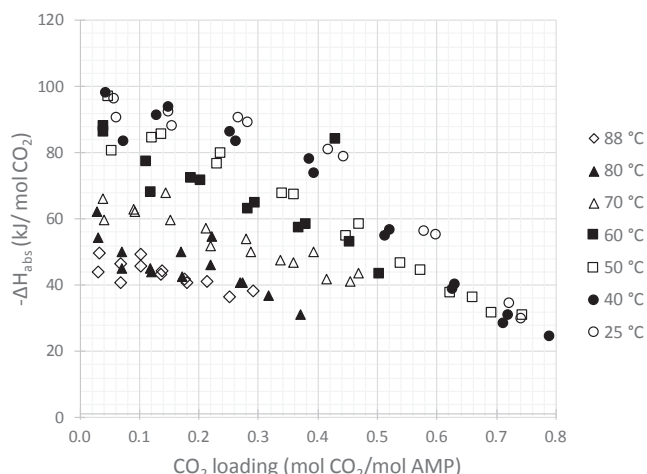


Fig. 4. Differential heat of absorption at different CO_2 loadings for the absorption of CO_2 in the system consisting of 10 wt% AMP in DMSO.

absorption in pure DMSO (i.e. around 10–14 kJ/mol CO_2 in DMSO [17,26,27] where only physical absorption occurs. As the loading approaches its maximum theoretical value of 0.5 mol CO_2 /mol AMP, based on the reaction mechanism (Reactions 1–3), the absorption mechanism will shift towards physical absorption as more amine has reacted, thus causing a decrease in the heat released. Additionally, the heat of absorption decreases with increasing temperature, and the heat released is more than twice as high at 25 °C than at 88 °C for CO_2 absorption in 10 wt% AMP/DMSO.

The same trend, of decreasing heat of absorption with increasing loading and temperature, was seen for the absorption of CO_2 in 25 wt% AMP in DMSO, as shown in Fig. 5. The points at which precipitation occurs can be clearly seen in the heat of absorption data as the points with much higher values, ranging between 140 and 240 kJ/mol CO_2 . Precipitation of the AMP carbamate is an exothermic reaction and, as the absorption solution is supersaturated, more carbamate will precipitate at the same time than in the equilibrium case. Thus, the heat released as precipitation occurs is higher than in the equilibrium case, which gives rise to the high values observed. After the initial precipitation points, the heat of absorption starts to decrease again, and above a loading of 0.5 mol CO_2 /mol AMP, the values approach values that are typical of physical absorption, as in the case of 10 wt% AMP/DMSO.

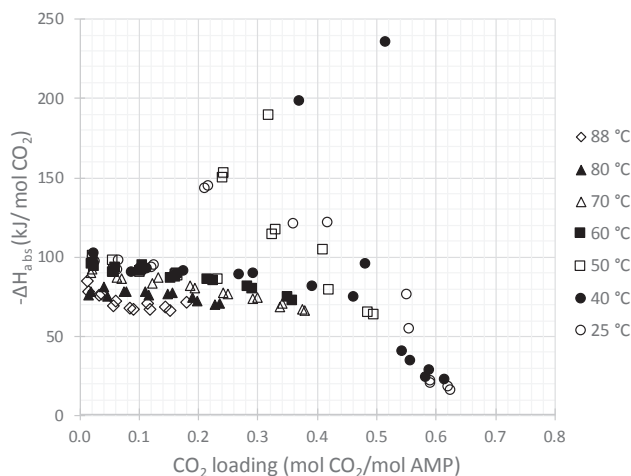


Fig. 5. Differential heat of absorption at different CO_2 loadings for the absorption of CO_2 in the system consisting of 25 wt% AMP in DMSO. Data obtained at 25 and 40 °C in our previous study are included (indicated by an asterisk in the legend) [17].

Decreasing heat of absorption with increasing temperature was also observed in our previous study of 15 and 25 wt% AMP in NMP, in the temperature interval 25–88 °C [13]. In the present study it was verified that this trend is true also at lower amine concentrations (2.5 wt% AMP in NMP) and the data can be found in the Supplementary Material. A similar decreasing trend in heat of absorption has also been reported by Mobley et al. [28] in the non-aqueous system of 2-fluorophenethylamine in 2,2',3,3',4,4',5,5'-octafluoropentanol at 40–120 °C. They speculated that changes in hydrogen bonding around the carbamate, and changing interactions in the aromatic groups, could explain this behavior. In our previous study, we suggested that this decreasing trend could be the result of a larger fraction of the dissolved species being physically absorbed, rather than chemically absorbed, at higher temperatures [13]. Overall, less CO_2 will be absorbed in the system at higher temperatures, but we suggest that the fraction of physically absorbed CO_2 will increase at higher temperatures. This hypothesis is supported by the results obtained in the NMR study for the AMP/DMSO and AMP/NMP systems, discussed below in Section 3.3, showing how the fraction of physically dissolved species increases as the temperature is raised.

The opposite trend has been observed for aqueous MEA, where the heat of absorption increased at higher temperatures [29,30]. In aqueous MEA, CO_2 reacts to form the MEA carbamate, but further reaction to bicarbonate also occurs in aqueous solutions. These reaction products are more stable in solution than the sterically hindered AMP carbamate formed in AMP/DMSO, which affects the temperature required to reverse the reactions for regeneration. The difference in the observed trends, regarding the change in heat of absorption with increasing temperature, between aqueous MEA and non-aqueous AMP could be due to differences in the amount of physically dissolved and chemically reacted CO_2 . The solubility of CO_2 in DMSO is much higher than in water, and since the heat of absorption includes both the heat of dissolution and the heat of reaction, it is likely that the heat of dissolution has a greater effect on the heat of absorption in AMP/DMSO than in aqueous MEA. Even if the heat of reaction resulting from Reactions 1–2 were to increase with temperature for CO_2 in AMP/DMSO, the fraction of physically absorbed CO_2 would still lead to a higher contribution to the measured heat of absorption at higher temperatures.

3.3. NMR speciation of reaction products

In order to study the reaction products formed when CO_2 reacts with AMP in non-aqueous systems, the chemical species in the liquid solutions were characterized with NMR for the systems of 10 wt% AMP in DMSO and 2.5 wt% AMP in either DMSO or NMP. Since solid species are not detected using this technique, a low amine concentration was used in order to avoid precipitation during the analysis.

Fig. 6 shows the ^{13}C NMR spectra covering the product region at 30 °C, obtained for ^{13}C CO_2 absorption in 2.5 wt% AMP in either DMSO or NMP. The AMP/DMSO system shows no peaks in this region before the addition of CO_2 (Fig. 6A), whereas the AMP/NMP system shows several peaks (Fig. 6B). These peaks were assigned to the NMP solvent and its impurities, since no purification of the solvent was performed before the analysis. When CO_2 was added to the systems, peaks corresponding to physically absorbed CO_2 and chemically reacted species appeared. This can be seen for the CO_2 /AMP/DMSO system in Fig. 6C. The broad peak at 124.2 ppm is assigned to physically absorbed CO_2 . The main product peak (160.1 ppm) is assigned to the AMP carbamate resulting from Reactions 1–2. The broadening of the peak suggests an interaction between the different CO_2 species in the system, most likely originating from chemical exchange between the free CO_2 in solution, the AMP carbamate, and the carbamic acid species, also reported for other primary amines [11]. The peak at 158.6 ppm is tentatively assigned to bicarbonate species arising from the reaction between CO_2 and water impurities in the system. Two less intense product peaks at 161.7 and 156.3 ppm can also be seen. The peak at 161.7 ppm is currently left unassigned whereas the peak at 156.3 ppm is tentatively assigned to the

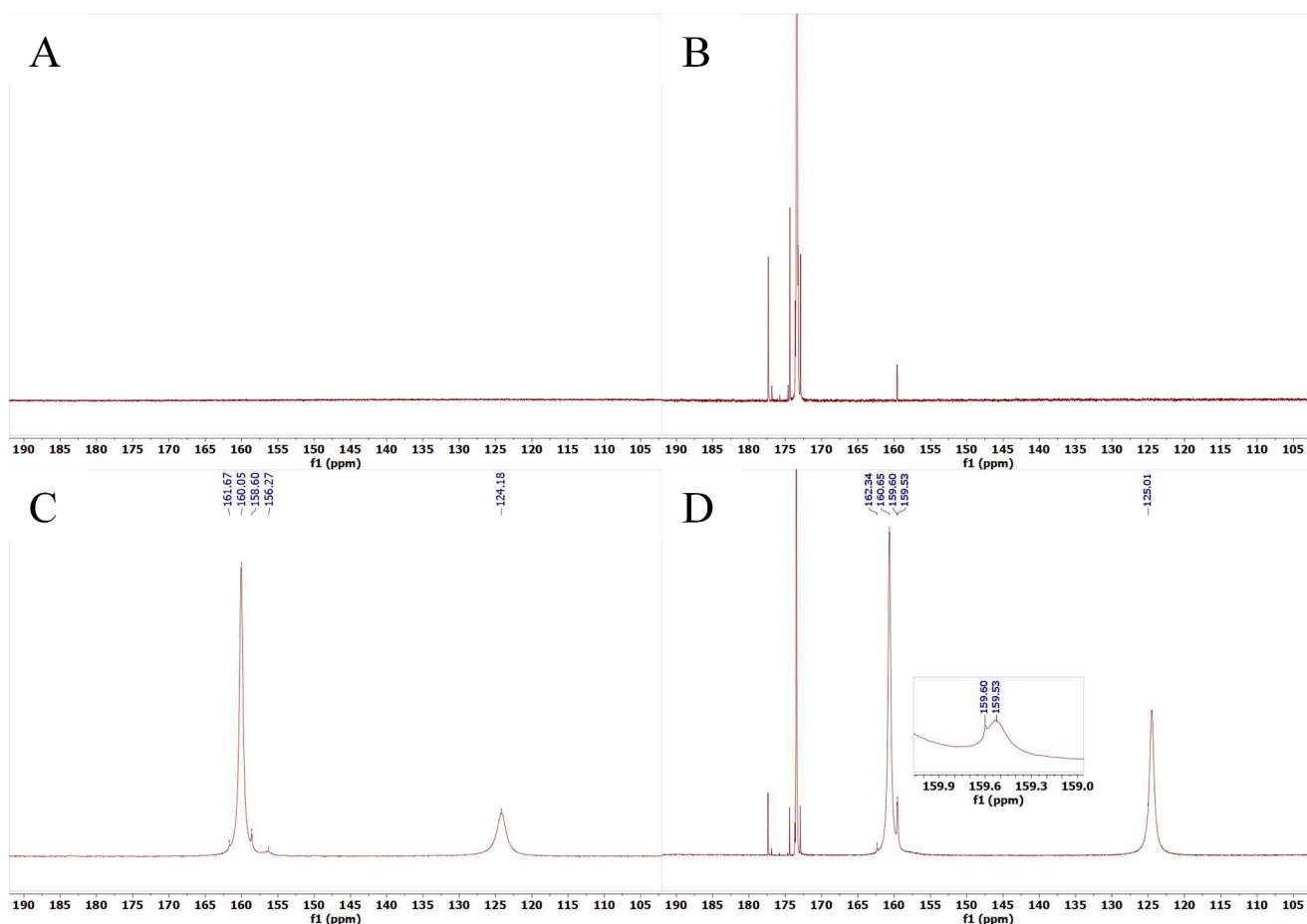


Fig. 6. ^{13}C NMR spectra for non-aqueous 2.5 wt% AMP systems with and without added CO_2 , at 30°C . (A) AMP/DMSO, (B) AMP/NMP, (C) CO_2 /AMP/DMSO, and (D) CO_2 /AMP/NMP.

product in the reaction between CO_2 and the hydroxyl group in the AMP molecule, i.e., the AMP carbonate. The amine group is the more reactive group in the AMP molecule, but previous studies have shown that sterically hindered amines, such as tertiary and secondary amines, can react via the hydroxyl group, which has also been suggested for primary alkanolamines in aqueous solutions [31]. Thus, it is possible that with excess CO_2 , the hydroxyl group will react to form the AMP carbonate as the amount of available amine groups decreases due to reaction with CO_2 . This smaller carbonate peak was not reported in the study by Kortunov et al. [11], where no NMR spectra for alkanolamines were published. Neither was this peak reported in the study by Barzagli et al. [32] in a system of 2-(ethylamino)ethanol in DEGDEE. It may be that, because of its low concentration, and thus low intensity, it is only detectable when using $^{13}\text{CO}_2$, as the product species formed by the reaction with marked CO_2 will give rise to increased signal intensity.

The results were very similar for the CO_2 /AMP/NMP system, as shown in Fig. 6D. In a similar manner, the peak corresponding to physically absorbed CO_2 appears at 125.0 ppm. The large peak at 160.7 ppm is assigned to the carbamate/carbamic acid species in fast exchange, as discussed above. Two overlapping peaks at 159.5 and 159.6 ppm can be seen, the one at 159.6 is assigned to the impurity seen in Fig. 6B, and the one at 159.5 is tentatively assigned to bicarbonate formed from water impurities. The peak at 162.3 ppm remains unidentified. The peak that was tentatively assigned to the AMP carbonate in AMP/DMSO was not detected in AMP/NMP.

In order to study how the systems behave at different temperatures, to obtain a better understanding of how the species in solution change during both absorption and desorption, the CO_2 /AMP/DMSO and CO_2 /AMP/NMP systems were studied at temperatures between 30 and 80°C .

In order to be able to detect the physically dissolved CO_2 in the system, these experiments were carried out using $^{13}\text{CO}_2$.

The ^{13}C NMR spectra obtained for the product region and the region for physically dissolved $^{13}\text{CO}_2$ in 10 wt% AMP/DMSO at temperatures of 30 – 80°C are presented in Fig. 7. Less CO_2 is absorbed in the system at higher temperatures, which can be seen by the integral of the peaks starting to decrease as the temperature is increased. The peak broadening observed as the temperature is increased indicates a higher degree of dynamic interaction between the absorbed CO_2 species in solution, and is a result of the chemical equilibria in Reactions 1–3. At higher temperatures, the exchange between the physically dissolved CO_2 and the chemically reacted species will be faster, since increasing the temperature will drive the equilibrium reactions to the left. This is clearly seen at temperatures above 60°C , as the peaks assigned to the chemically reacted species start to overlap the peak of physically dissolved CO_2 . It can also be seen from these results that CO_2 will still be dissolved in the solution in a closed system at 80°C , as a broad peak is still present at this temperature. A large fraction of the absorbed CO_2 will be physically absorbed or in exchange with physically dissolved species at higher temperatures. This confirms our hypothesis as to why the heat of absorption, i.e., the heat evolved as CO_2 is absorbed by the system, decreases at higher temperatures, as discussed in Section 3.2. The presence of chemically reacted species at 80°C suggests that a stripping gas might be needed to obtain efficient regeneration of the 10 wt% AMP/DMSO system. However, since the CO_2 pressure was not measured during these experiments, further work is required to confirm this.

The distribution of absorbed CO_2 species at temperatures between 30 and 80°C was also measured in 2.5 wt% AMP in DMSO and NMP. Higher concentrations of AMP in NMP were investigated, however, due

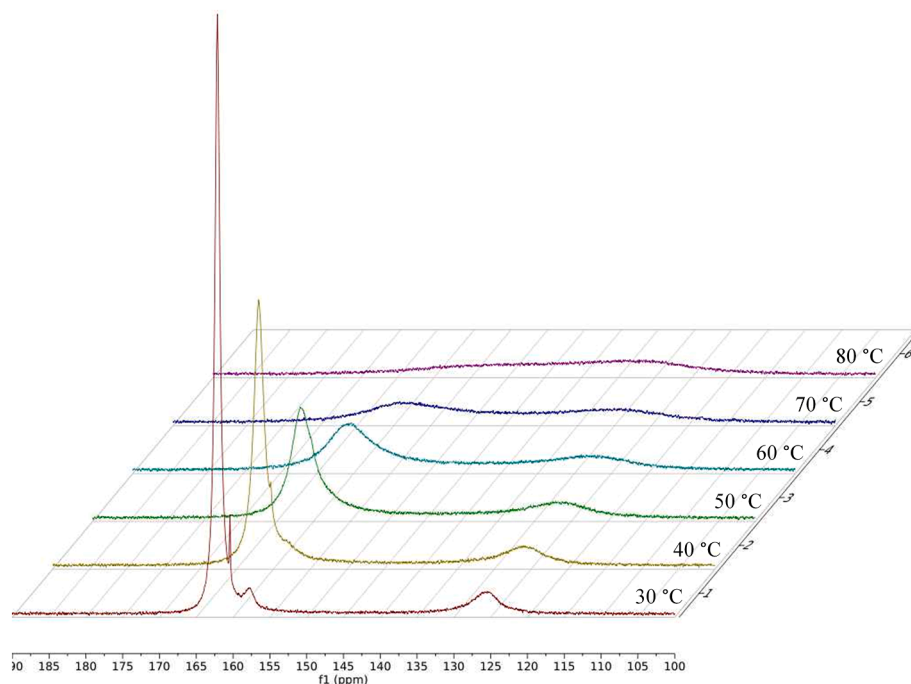


Fig. 7. ^{13}C NMR spectra of product species of $^{13}\text{CO}_2$ in the system consisting of 10 wt% AMP/DMSO at 30–80 °C.

to problems of precipitation before the analysis, a lower concentration of amine was chosen in order to be able to study the liquid species formed (CO_2 solubility data for the 2.5 wt% AMP/NMP system can be found in the Supplementary Material).

The ^{13}C NMR spectra for the product region and the region for physically dissolved $^{13}\text{CO}_2$ in 2.5 wt% AMP/DMSO and 2.5 wt% AMP/NMP at temperatures of 30–80 °C are presented in Fig. 8A and B, respectively. The product peaks in the 2.5 wt% systems appear at similar shifts to those previously observed for the 10 wt% system, indicating that similar reactions also occur when less amine is present. For CO_2 in 2.5 wt% AMP/DMSO there is less interaction between the CO_2 species in solution than in the previously discussed 10 wt% AMP/DMSO system. This can be seen in Fig. 8A, as the peaks representing the chemically reacted species do not show the same degree of broadening or overlapping with the peak from physically dissolved CO_2 , as the corresponding peaks in Fig. 7. The reason for this is probably overall lower amounts of chemically reacted species in solution due to the lower amine concentration. The peaks assigned to the chemically reacted species have almost disappeared at 70 °C, indicating that the system is regenerated above this temperature. This also differs from the

observations for CO_2 in 10 wt% AMP/DMSO, where chemically reacted species were still present at 80 °C. Less CO_2 will be absorbed in systems with lower amine concentrations due to less reaction, and as the experiments were performed in a closed system, the CO_2 partial pressure over the solution will be lower in the 2.5 wt% AMP/DMSO case, probably causing this difference. Characterization of the CO_2 absorption in 2.5 wt% AMP/NMP (Fig. 8B) shows a similar trend to that discussed above for 2.5 wt% AMP/DMSO. However, the solution seems to be regenerated from chemical species at a slightly lower temperature, as the chemically reacted species seem to have essentially disappeared already at 60 °C. In both AMP/DMSO and AMP/NMP the chemically reacted CO_2 species were reformed when the system was cooled to 30 °C, which shows that the reactions are reversible in a closed system. When cooled back to 30 °C after the heating, less CO_2 is dissolved in the liquid again, which is evident from the integrals of the peaks in Fig. 8 (available in the Supplementary Material) that differ between the two measurements at 30 °C. Since the system is closed, this is likely due to CO_2 remaining in the gas phase and mass transfer limitations as the sample is cooled.

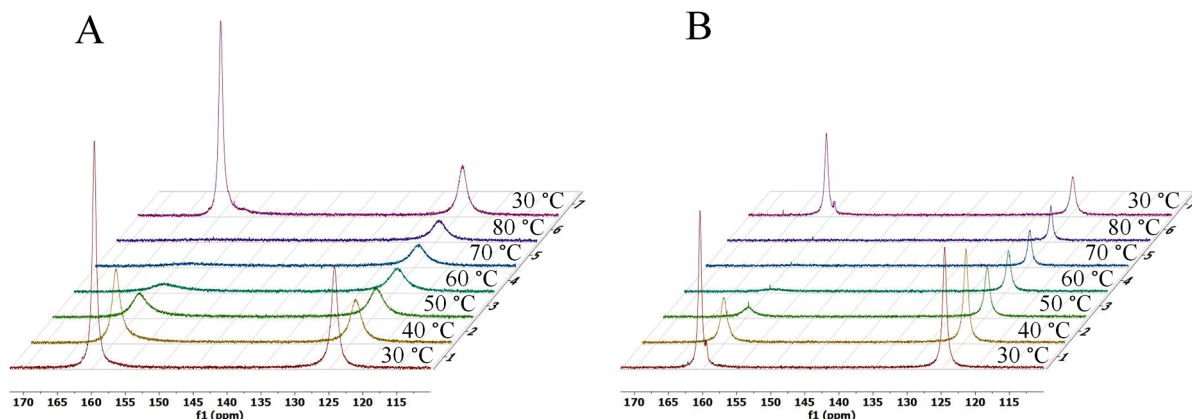


Fig. 8. ^{13}C NMR spectra of product species after the addition of $^{13}\text{CO}_2$ to systems consisting of (A) 2.5 wt% AMP in DMSO and (B) 2.5 wt% AMP in NMP, at 30–80 °C.

4. Conclusions

The solubility of CO₂ and heat of absorption at temperatures between 25 and 88 °C were measured in 10 wt% and 25 wt% AMP in DMSO. Both systems showed low solubility of CO₂ at 88 °C, below 0.1 mol CO₂/mol AMP at 100 kPa, indicating that the AMP/DMSO system can be regenerated at lower temperatures than conventional aqueous systems, and also that low lean loadings can be achieved at high CO₂ partial pressures at those temperatures. The solubility data also showed that the 25 wt% AMP/DMSO system could be used for carbon capture at CO₂ partial pressures down to 1 kPa when using an absorption temperature of 25 °C.

The heat of absorption as CO₂ dissolved and reacted in AMP/DMSO showed a decreasing trend with increasing temperature. We suggest that this is due to a higher fraction of physically absorbed, than chemically absorbed, CO₂ in the AMP/DMSO system at higher temperatures. This was further confirmed using ¹³C NMR, where the products from chemical reactions decreased with temperature, changing the ratio between chemically and physically absorbed CO₂ at higher temperatures. Similar product peaks were identified in both AMP/DMSO and AMP/NMP, indicating a similar reaction mechanism between AMP and CO₂ in both organic solvents. The peaks were assigned to the AMP carbamate/carbamate acid, bicarbonate from water impurities, and the AMP carbonate formed from the reaction of CO₂ with the AMP hydroxyl group. These results suggest that additional reactions, besides the zwitterion mechanism, take place in the chemical absorption of CO₂ in both AMP/DMSO and AMP/NMP.

The AMP/DMSO system is a promising alternative for carbon capture since a reasonable capacity can be obtained without the use of a stripping gas. Furthermore, the lower temperatures needed for CO₂ desorption indicate that low-grade heat could be used for the regeneration step, making it an option for CCS in industry where such heat is readily available. In order to further investigate if the AMP/DMSO system is suitable for CCS applications, the CO₂ reaction kinetics needs to be evaluated.

CRediT authorship contribution statement

Hanna K. Karlsson: Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Hatoon Makhool:** Methodology, Validation, Formal analysis, Investigation, Writing - review & editing. **Magnus Karlsson:** Methodology, Validation, Formal analysis, Investigation, Writing - review & editing. **Helena Svensson:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2020.117789>.

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