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Evaluation of the effect of water on CO₂ absorption in AMP and DMSO systems

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ABSTRACT

Non-aqueous precipitating amine systems for carbon capture allows for CO₂ desorption at lower temperatures than conventional aqueous amine systems and can potentially reduce the energy requirement for regeneration. In this work, the influence of water accumulation that may arise from humid gases entering the absorption column was investigated for absorption systems containing 2-amino-2-methyl-1-propanol (AMP) and dimethyl sulfoxide (DMSO). The physical solubility of CO₂ decreased with increasing water concentration, as expected from the lower solubility of CO₂ in water than in DMSO. The CO₂ loading capacity was increased with the addition of water, resulting from formation of bicarbonate with water present in the system. Low lean loadings of 0.1 mol CO₂/mol AMP and precipitation was observed in 23 wt% AMP/DMSO with 9 wt% added water, suggesting that some water accumulation might be tolerable while still maintaining the desired properties of the absorption system. NMR was used to study the CO₂ reaction products at 30–88 °C. The results suggested that 88 °C can be used for regeneration of the system even with water accumulated in the system. At 80 °C formation of the tentatively assigned species 4,4-dimethyl-1,3-oxazolidin-2-one was observed, indicating that thermal degradation of AMP may occur above this temperature.

1. Introduction

To mitigate global climate change it may be necessary to create CO₂ sinks, which can offset emissions that cannot be fully eliminated from other sources [1]. To achieve this, implementation of carbon capture and storage (CCS) and creating negative emissions through Bio Energy CCS (BECCS) can be employed. Post-combustion techniques using aqueous amine absorption for the removal of gaseous CO₂ is considered one of the most promising technologies for carbon capture, due to the maturity of the technology and the possibility of *retro*-fitting to existing plants [2]. One of the main reasons why these technologies are not implemented is the high capture cost, which is primarily associated with the energy requirement of the process related to regeneration of the absorption liquid [3].

One approach suggested to reduce the energy requirements is replacing water in the amine solution with organic solvents, in so called non-aqueous solvents (NAS) [4], making it possible to use similar process design and infrastructure as for conventional aqueous systems. This would alter the physical properties of the solution and can result in a solution with lower heat capacity, decreased vaporization, and higher

solubility of CO₂, potentially leading to a more energy efficient alternative [5,6]. The use of organic solvents also affect the reactions taking place in the solution, and less stable reaction products, which can be regenerated at lower temperatures, can be formed when combining sterically hindered amines in NASs [7]. This could make it possible to utilize excess heat to supply the energy needed for regeneration [8]. Absorption systems that can utilize already existing excess heat for the regeneration of the absorption liquid are of interest as they make use of an available resource and may alleviate a major obstacle to the implementation of CCS and BECCS. Reaction products with low stability typically also precipitate in NASs due to their limited solubility in the solution [9–11]. Since the reaction products precipitate, the equilibrium is shifted which counteracts solvent saturation and enables more CO₂ to be dissolved in the solution, thus increasing the solvent capacity [8,12,13]. However, one drawback of NASs is associated with the presence of unavoidable water, which may be absorbed from the humid flue gas that enters the capture process. As many organic solvents are hygroscopic, it is likely that water from the treated gas will be absorbed in the solution and potentially accumulate over time. This will affect the reaction mechanism of the system and may result in the formation of

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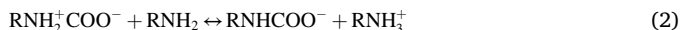
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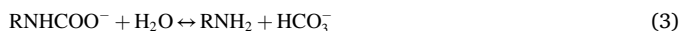
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reaction products that require higher temperatures to regenerate [14].

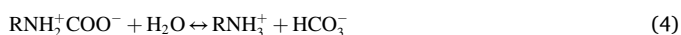
In aqueous solutions of 2-amino-2-methyl-1-propanol (AMP) the reaction between CO₂ and AMP has been suggested to proceed through the zwitterion mechanism [15], in which CO₂ reacts with AMP to form a zwitterion which then reacts further with AMP to produce a carbamate, according to reactions (1) and (2):



As AMP is a sterically hindered amine, steric effects reduce the stability of the carbamate, which is further hydrolysed to produce bicarbonate, according to reaction (3):



It has also been suggested that if the amine is sterically hindered, the zwitterion formed in reaction (1) reacts more readily with water to produce bicarbonate [15], according to reaction (4):



Another suggested mechanism, which recent studies show is more likely for AMP [16], proposes that the reaction proceeds through a termolecular mechanism in which AMP reacts simultaneously with CO₂ and a base (i.e. water or AMP) to produce a carbamate, according to reaction (5):



In non-aqueous solutions of AMP the reactions above with water cannot occur but the solvent may act as the base in reaction (2) or (5), yielding reaction products such as alkyl carbonate [7]. If the solvent is not involved in the reactions, previous work has shown [8,12,13] that AMP reacts to form a carbamate that precipitates in the solution. This has been further investigated and confirmed through ¹³C NMR-analysis of the solid precipitate, where carbamate crystals with two different crystal structures were identified [17]. ¹³C NMR-analysis of the liquid phase also showed the presence of predominantly carbamate, with only traces of bicarbonate, likely due to water impurities in the solvent, and a possible additional reaction product not yet identified but most likely being the AMP carbonate [12]. This product was present in solutions of AMP in dimethyl sulfoxide (DMSO), but not detected in solutions of AMP in N-methyl-2-pyrrolidone (NMP). Results also showed that the heat of absorption decreased at higher temperatures, indicating that the relative amounts of reaction products and physically absorbed CO₂ likely changed in the liquid phase as a function of temperature [13]. The results of the ¹³C NMR-analysis of the liquid phase also supported this hypothesis, with a shift from chemical reaction products in the solution towards physically dissolved CO₂ at higher temperatures [12].

As DMSO is a highly hygroscopic solvent it is very likely that water will be absorbed from the treated gas in a non-aqueous solution of AMP/DMSO, and possibly accumulate over time. Previous studies have shown that the amount of water that may be absorbed in 100 g DMSO at high relative humidity and 22 °C can exceed 180 g over a period of 70 days [18]. Whether the water content of AMP/DMSO in a carbon capture process will achieve a steady state value over time is not yet known. However, studies of several water-lean solvents have shown that water interacts differently with each solvent and that water-lean solvents may be water tolerant [4]. A recent study on 2-ethylhexylan-1-amine (EHA) and DMSO showed that when 5 % water was present in the solvent, during continuous absorption and desorption cycles, water was evaporated and the performance of the solvent became closer to that of non-aqueous EHA/DMSO, which indicates that a steady state water content may be possible to achieve when using DMSO as a solvent [19].

The aim of this study was to evaluate how water accumulation in the non-aqueous solvent AMP/DMSO would affect the solvent, in terms of

changes in solubility of CO₂, heat of absorption of CO₂, and reaction products formed. A preliminary evaluation of the amount of water absorbed in solutions of AMP/DMSO over time was performed. The effect of water addition, to the non-aqueous solvent AMP/DMSO, on solubility of CO₂ and heat of absorption of CO₂ in these mixtures was investigated using reaction calorimetry. As a change in solubility of CO₂ and/or heat of absorption is likely caused by different reactions taking place in the solvent, the formed reaction products were also studied using nuclear magnetic resonance.

2. Materials and method

2.1. Materials

The samples used in this work consisted of approximately 100 g of absorption solution, prepared gravimetrically by mixing 2-amino-2-methyl-1-propanol (AMP) (93–98 %, Merck) and dimethyl sulfoxide (DMSO) (99.9 %, Merck), used as received without further purification. For the samples containing water, deionized water was added to the mixed absorption solutions. A scale with an accuracy of 0.01 g for up to 1200 g was used to prepare the sample mixtures. The gases used were pure CO₂ (>99.99 %, AGA), N₂O (>99.99 %, AGA) or ¹³CO₂ (99 %, Cambridge Isotope Laboratories, Andover, USA).

2.2. Experimental method

2.2.1. Absorption of water

To investigate the hygroscopicity of DMSO and blends of AMP in DMSO, a preliminary evaluation of the amount of water absorbed in these solutions was performed. Two beakers containing DMSO and 25 wt% AMP in DMSO were placed in an enclosed space. The enclosed space was kept at approximately 80 % relative humidity at room temperature (20 °C). These conditions were achieved by placing an additional beaker filled with water in the enclosed space and letting the atmosphere equilibrate. After stable conditions had been reached, the beakers containing DMSO and AMP/DMSO were placed in the enclosed space and the weight of the solution was measured at set intervals. The weight increase of the solution was assumed to be caused by the absorption of water into the solution sample, as DMSO has a very low vapor pressure at 20 °C (0.55 hPa [20]) and evaporation of DMSO was considered negligible. The weight of the solution samples was monitored over a time period of 20 days.

To further assess the possible equilibrium content of water that might be reached, a sample of 46.98 g was placed in an enclosed space at 21–22 °C with 86–89 % relative humidity over a time period of 46 days. The weight increase and water content of the sample was then assessed over a time period of 8 days to ascertain whether or not equilibrium had been reached.

2.2.2. Reaction calorimetry

A true heat flow reaction calorimeter (CPA 201, Chemical Process Analyzer from ChemiSens AB) was used to determine the solubility of either N₂O or CO₂ in the investigated solutions. The experimental set-up and method used in this work, are similar to that used in our previous work [8,12,13,21,22] and will thus only be described briefly.

To determine solubility of CO₂ or N₂O in the amine solutions, the samples were loaded into a stirred batch reactor (250 cm³) before the experiment. The sample was then evacuated at 25 °C for about 10–12 s. The temperature was then raised to the experimental temperature and the system was allowed to equilibrate, to obtain the baseline conditions for each experimental run. CO₂ or N₂O was injected in a series of small doses using a mass flow controller (MFC), each dosing causing a pressure increase of about 0.5 bar. After each injection the system was allowed to equilibrate before the next injection. Equilibrium was defined as the change in total pressure and the true heat flow signal being less than 0.005 bar and 0.02 W, respectively, for no less than 28 min. The MFC

signal, pressure and true heat flow were continuously logged throughout the experiment. Two individual experimental runs were made at each experimental condition to ensure repeatability.

The absorbed amount of CO₂ or N₂O ($n_{i,abs}$) in the liquid phase was obtained from the collected data according to Eq. (6),

$$n_{i,abs} = n_{i,in} - \frac{P_i \cdot V}{RT} \quad (6)$$

where $n_{i,in}$ is the total amount of gas added to the reactor, P_i is the partial pressure of the gas above the solution. The CO₂ loading (α) was estimated using Eq. (7), where $n_{0,AMP}$ is the initial amount of AMP in the solution.

$$\alpha = \frac{n_{CO_2,abs}}{n_{0,AMP}} \quad (7)$$

The sample mixtures evaluated in this work are presented in Table 1, along with the experimental conditions in terms of gases used, initial CO₂ loading and temperatures studied.

Solubility of CO₂ in 25 wt% AMP in DMSO solutions with added water was studied in order to investigate the influence of water on the absorption of CO₂. For mixtures 24AD5W and 23AD9W, either 5 or 10 g of deionized water was added to 100 g of mixed 25AD before the experiment (the time of addition varied between the different experimental runs). For the 10AD2W and 10AD4W mixtures, the amount of water added was chosen so as to achieve approximately the same molar ratio of AMP to water as in the 24AD5W and 23AD9W mixtures, respectively.

Henry's constant (H_i) was obtained according to Eq. (8), where P_i is the partial pressure of either N₂O or CO₂ in the gas phase and x_i is the molar fraction of N₂O or CO₂ in the liquid phase.

$$H_i = \frac{P_i}{x_i} \quad (8)$$

Henry's constant for both CO₂ (H_{CO_2}) and N₂O (H_{N_2O}) in DMSO was obtained from solubility data according to Eq. (8). These were then used together with experimentally obtained values of H_{N_2O} in AMP/DMSO mixtures to estimate H_{CO_2} in AMP/DMSO mixtures using Eq. (9). A minimum of 6 data points were used to obtain both H_{CO_2} and H_{N_2O} . Estimations of H_{CO_2} by using Eq. (9), were made for mixtures 25AD, 10AD, 10AD2W and 10AD4W.

$$H_{CO_2,AMP+DMSO} = \frac{H_{CO_2,DMSO}}{H_{N_2O,DMSO}} \cdot H_{N_2O,AMP+DMSO} = \frac{1}{R_H} \cdot H_{N_2O,AMP+DMSO} \quad (9)$$

The dielectric constant of AMP/DMSO in the studied non-aqueous and aqueous blends at 40 °C was estimated using the linear correlation in Equation (10) [23]. Here ϵ_{mix} is the dielectric constant in the mixture, m_i is mass fraction of each component and ϵ_i is the dielectric constant of each component.

$$\epsilon_{mix} = \sum_{i=1}^n m_i \cdot \epsilon_i \quad (10)$$

Table 1

Sample mixtures used in this study, along with gases tested, experimental temperatures and pressures (P_i).

Abbreviation	AMP [wt %]	DMSO [wt %]	H ₂ O [wt %]	Gas	Temperature [°C]	P_i [kPa]
DMSO	0	100	0	CO ₂ , N ₂ O	40, 60, 88	34–370
25AD	25	75	0	N ₂ O	40, 60, 88	42–305
24AD5W	24	71	5	CO ₂	40, 88	42–297
23AD9W	23	68	9	CO ₂	40, 88	1.1–258
10AD	10	90	0	N ₂ O	40, 88	0.4–194
10AD2W	10	88	2	N ₂ O	40, 88	47–381
10AD4W	10	86	4	N ₂ O	40, 88	43–391
						44–389

The values for the pure substances at 40 °C were taken from literature and are listed in Table 2, together with the estimated values for the mixtures.

The average uncertainties for the calorimetric experiments were calculated and determined to be as follows: in pure DMSO the calculated uncertainty for absorbed amount of gas was determined to be 2.8 % and 3.5 % for CO₂ and N₂O, respectively; for the systems with 10 wt% AMP the uncertainty in absorbed amount of N₂O was determined to be 3.7 %, and in 25AD it was determined to be 3.4 %; the uncertainty for absorbed amount of CO₂ and heat of absorption was determined to be 1.3 % and 1.6 %, respectively, for the systems 24AD5W and 23AD9W.

2.2.3. Nuclear magnetic resonance

Nuclear magnetic resonance NMR was used to study product formation and dynamics as the CO₂ reacted with AMP in the aqueous (2 wt % or 4 wt %) solutions of AMP/DMSO.

Samples were prepared for ¹³C NMR studies by stirring solutions of AMP (10 wt%) in DMSO, containing either 2 wt% or 4 wt% water, under a ¹³CO₂ atmosphere for 30 min at room temperature. Both solvents contained 5 wt% DMSO-*d*₆ needed for NMR lock, shim and chemical shift reference. After the completed reaction, a volume of 600 μl was transferred to a 5 mm NMR tube, which was capped and placed in the NMR magnet.

The ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer fitted with a 5 mm AutoXDB probe. Spectra were recorded as the average of 512 scans employing 20-degree pulses separated by a 5 s delay. The spectra were recorded at temperatures of 30, 40, 50, 60, 70, 80 and 88 °C and finally again at 30 °C. The chemical shifts of the spectra recorded at 30 °C were referenced to the central resonance of the DMSO-*d*₆ multiplet set to 39.5 ppm.

3. Results and discussion

The aim of this work was to evaluate the influence of water on non-aqueous precipitating amine absorption systems. The hygroscopic properties of organic solvents, in this work DMSO, will most likely result in accumulation of water in the absorption system when exposed to a humid environment. How much water that is accumulated, depends largely on the humidity of the incoming gas that needs to be cleaned. In produced biogas the water content is typically at the level of saturation, which corresponds to approximate values of 5–10 % [24] if no drying is implemented before the upgrading process. The following results and discussion look in to how the solubility of CO₂ and distribution of CO₂ reaction products changes with water content.

3.1. Hygroscopic properties of DMSO + AMP/DMSO

DMSO is a highly hygroscopic organic solvent in which water will accumulate when exposed to a humid environment. Thus, the water accumulation in solutions of AMP and DMSO in a humid environment was studied to investigate how the composition of the absorption

Table 2

Dielectric constant of DMSO, AMP and water at 40 °C from literature, and dielectric constant for the mixtures used in the N₂O analogy at 40 °C (estimated from Equation (10)).

Solution	Dielectric constant(ϵ_i)	Reference
DMSO	44.64	(Płowaś et al., 2013)
AMP	19.69	(Hsieh et al., 2007)
H ₂ O	73.29	(Płowaś et al., 2013)
25AD	38.4	Eq. (10)
10AD	42.1	Eq. (10)
10AD2W	42.7	Eq. (10)
10AD4W	43.3	Eq. (10)

solution will change over time.

The results regarding the hygroscopicity of DMSO or mixtures of AMP/DMSO and amount of water absorbed from humid air over time is shown in Fig. 1a). The graph shows that the water content of the solution increases over time in a close to linear fashion. Over the time period of 20 days the water content of the solutions of DMSO and AMP/DMSO increased from 0 wt% to 14.0 and 13.8 wt% respectively. The absorption of water in the solutions was close to identical and AMP is therefore not considered to affect the absorption behaviour of water into the solvent DMSO. The amount of water absorbed in the solution was relatively low compared to other results reported in literature regarding the hygroscopicity of DMSO. LeBel et al. [18] reported a weight increase of slightly above 60 g H₂O/100 g DMSO, over a time period of 20 days at a relative humidity of 81 %, which is considerably higher than the weight increase of 16 g H₂O/100 g DMSO determined in the current work at comparable conditions. Waybright et al. [25] reported the percent water due to water absorption, at 18–20 °C and a relative humidity of 40 %, for 10 to 20 mL samples of DMSO to reach slightly above 25 % after 6–7 days, which is also considerably higher than the values obtained in the current work. Even though a higher relative humidity (80 %) was used in the current work, the water content only reached 14 wt% over a time period of 20 days. The study of LeBel et al. [18] did not reach the same results at similar conditions as Waybright et al. [25], but instead reported a weight increase of 10 and 20 g H₂O/100 g of DMSO at a relative humidity of 32 and 53 % respectively, over approximately 7 days, which is slightly lower than the values reported by Waybright et al. [18,25] The reason for this discrepancy may be due to the absorption rate being highly affected by the mass transfer area available for water absorption and the ratio between the mass transfer area and sample volume. Although this ratio is not reported in the literature, the values probably lie in the region of 2–1 in the study by Waybright et al. [25], as compared to the area to volume ratio of approximately 0.4 in the current work. Waybright et al. [25] also reports that weight gain, expressed as a percentage of the solvent weight, is greater for smaller volumes, which likely have a higher area to volume ratio. The current work employed a larger sample volume (approximately 180 g) than that used by Waybright et al. (10–20 mL) [25], which could explain the lower water content reached in the current work as compared to those previously reported in literature.

The results of the equilibrium water content in a DMSO sample showed that equilibrium water content had not been reached during the investigated time. The results are shown in Fig. 1b), and the data shows

that the water content increased to above 55 wt% over a period of 46 days and continued to increase slightly over the following 8 days. The rate of absorption is markedly lower after 46 days compared to the initial rate of absorption in the solutions of DMSO and AMP/DMSO previously investigated.

3.2. Physical solubility

One of the potential benefits of using organic instead of aqueous amine solutions for carbon capture, is the significantly higher physical solubility of CO₂ found in many organic solvents compared to water. With increased physical solubility, the mass transfer into the liquid solution is enhanced which can result in a higher rate of absorption, even though the rate of reaction might be lower. The Henry's constant for CO₂ in water [26] is significantly higher than for DMSO, resulting in water having a lower physical solubility of CO₂. If water is accumulated in the absorption system, it is natural to assume that if the concentration reaches significant levels, the water content will cause the physical solubility of CO₂ in the solution to decrease over time. The effect of this might be that the conditions used for the absorption and regeneration steps of the removal process will have to be changed with increasing operating time. To investigate how severe such a decrease in physical solubility might be, Henry's constant for CO₂ in AMP/DMSO/H₂O solutions was determined using reaction calorimetry. The physical solubility of CO₂, in both non-aqueous AMP/DMSO and AMP/DMSO/H₂O solutions, was estimated using the N₂O analogy according to Eq. (7).

Solubility data for both N₂O and CO₂ in DMSO, and for N₂O in the solutions 25AD and 10AD (25 and 10 wt% AMP in DMSO), was collected at temperatures of 40, 60 (only 25 wt%) and 88 °C. Henry's constant (H_i) in DMSO was obtained according to Eq. (8). The experimental solubility data, from which the constants are derived, can be found in the [supplementary material](#). A comparison of the experimentally determined Henry's constant for CO₂ in DMSO was made to values reported in literature, summarized in Table 3. Overall, the values of Henry's constant, for CO₂ in DMSO, obtained in this study are similar to those reported in the literature, as can be seen in Table 3. The values differ less than 10 % from previously reported Henry's constant values, except for those reported in [27], which are significantly higher than the other Henry's constant values reported in literature and obtained in this work.

The experimentally obtained Henry's constants for N₂O and CO₂, are shown in Table 4. As expected, the general trend shows higher values of Henry's constant for both gases with increasing temperature, which is

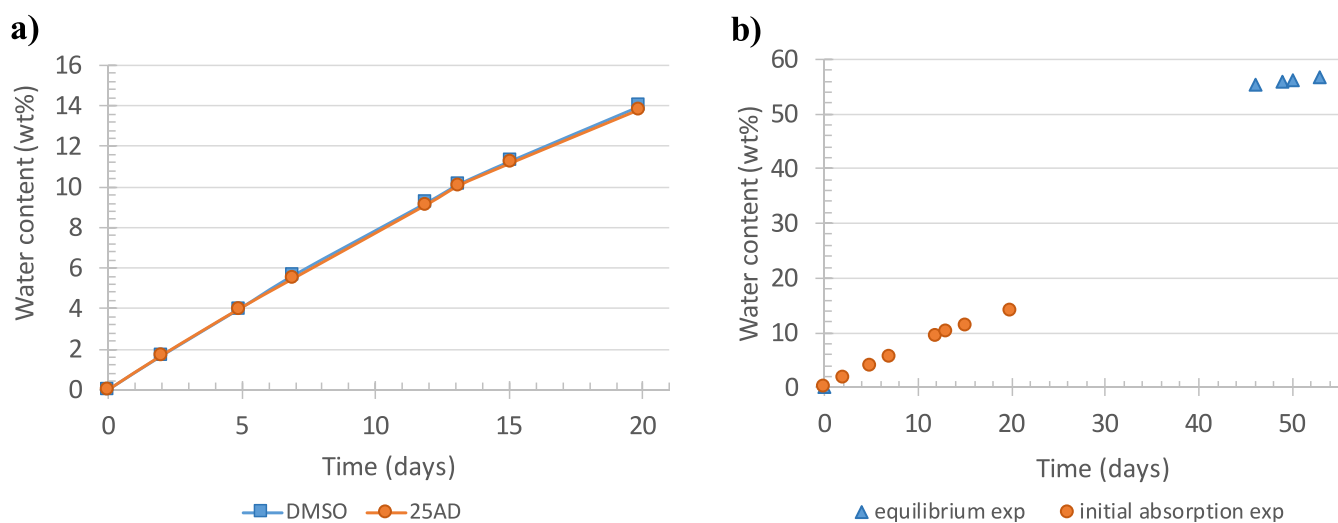


Fig. 1. (a) Water content in solutions of DMSO (blue) and 25 wt% AMP in DMSO (orange) caused by absorption of water from humid air displayed as a function of time. (b) Water content in solutions of DMSO for initial absorption experiment (orange) and solutions of DMSO for equilibrium experiment (blue), caused by absorption of water from humid air displayed as a function of time.

Table 3

Values of Henry's constant (H_{CO_2}) obtained for CO_2 in DMSO, compared with values from literature.

Temperature (°C)	H_{CO_2} (MPa)	Reference
35	16.58	[27]
40	13.07	This work
	14.361	[288]
	12.77	
45	19.48	[27]
55	21.92	[27]
60	16.89	This work
	18.273	[28]
80	23.002	[28]
88	22.10	This work

Table 4

Henry's constant for N_2O and CO_2 in DMSO and mixtures of 10 and 25 wt% AMP in DMSO, at temperatures of 40, 60 and 88 °C.

Temperature (°C)	DMSO		10AD	25AD
	H_{CO_2} (MPa)	H_{N_2O} (MPa)	H_{N_2O} (MPa)	H_{N_2O} (MPa)
40	13.07	18.50	18.32	16.89
60	16.89	23.58	–	22.19
88	22.10	29.12	27.88	26.79

translated to lower solubility of both N_2O and CO_2 with increasing temperature. Similarly to water, N_2O has a slightly lower solubility in DMSO than CO_2 .

The N_2O analogy was used to estimate the physical solubility of CO_2 in the amine containing solutions. The estimated values of Henry's constant, obtained using Eq. (9), are listed in Table 5, together with the ratio H_{N_2O}/H_{CO_2} in DMSO (R_H). There is a slight decrease in Henry's constant for CO_2 with increasing amine concentration, meaning that the physical solubility of CO_2 increases with amine concentration under the conditions tested. This trend differs from what was observed for AMP/NMP systems in our previous work [26], where a slight increase of Henry's constant could be observed for CO_2 in solutions of 15 and 25 wt % AMP in NMP (15AN and 25AN). At 40 °C Henry's constant for CO_2 in 15AN and 25AN was estimated to be 10.04 and 10.51 MPa, respectively. The difference in the physical solubility of CO_2 in 25AD and 25AN could stem from differences in solvent interactions with the dissolved carbonated species. A possibility is that the value of R_H , which is assumed to be constant when using the N_2O -analogy, changes with the addition of AMP to solvents, as the polarity of the mixture is altered. Thus, this might affect the solubility of the two gases differently due to CO_2 being more polar than N_2O , which is further discussed at the end of this section. The change in polarity, often expressed through the dielectric properties, might be different when AMP is added to DMSO than for addition to NMP. Overall, the values of H_{CO_2} in 25AD were slightly higher than what was obtained for 25AN, indicating lower physical solubility of CO_2 in 25AD. This agrees with Henry's constant for CO_2 in the pure solvents (13.07 MPa for DMSO and 8.85 MPa for NMP [26], at 40 °C). Although the physical solubility of CO_2 is slightly lower in 25AD than in 25AN, the chemical solubility of CO_2 has been shown to be slightly higher in 25AD than in 25AN, at low partial pressures of CO_2 [12,13].

Table 5

R_H values in DMSO together with estimated H_{CO_2} in mixtures of 10 and 25 wt% AMP in DMSO.

Temperature (°C)	R_H (-)	H_{CO_2} (MPa)	
	DMSO	10AD	25AD
40	1.42	12.94	11.93
60	1.40	–	15.89
88	1.32	21.16	20.33

Solutions of AMP in DMSO with added water were also tested to evaluate how the physical solubility is affected by possible water accumulating in non-aqueous solutions over time. Estimated values of Henry's constant for CO_2 in systems containing 10 wt% AMP with added water corresponding to 2 wt% (10AD2W) and 4 wt% (10AD4W) were tested at 40 and 88 °C. The experimental value of Henry's constant for N_2O , together with the estimated Henry's constant for CO_2 , are presented in Table 6. As water has a significantly lower physical solubility of CO_2 than DMSO, the value of H_{CO_2} increases with water content.

If the physical solubility of CO_2 , in an absorption solution, decreases over time, as water is accumulated, this could influence the rate of absorption as the mass transfer rates could then also decrease. This might mean that the contact time between the gas and the liquid absorption system needs to be increased as water is accumulated in the system, as the conditions in the absorption column are altered.

The N_2O -analogy is commonly used for aqueous amine absorption systems to estimate the physical solubility of CO_2 , but have also been used for water lean solutions [29]. However, the validity of the N_2O -analogy has been discussed for concentrated amine systems [30]. The basis of this discussion is the change of the polar properties of a solution, here further expressed through the dielectric constant, as the amine concentration is increased. CO_2 , being more polar than N_2O , is more soluble in polar solvents which can be seen in Table 4 as the ratio of H_{N_2O}/H_{CO_2} , R_H , being above unity. The value of R_H must be constant for the N_2O analogy to be valid. However, because of the difference in polarity between CO_2 and N_2O , R_H might change due to the change of dielectric constant as the concentration of added amine is increased. In aqueous systems the change in dielectric constant with amine concentration can be quite large since the difference in dielectric constant between water (approx. 78 at 25 °C, [31]) and amines (approx. 34 for MEA at 25 °C, [32]) is high. Monteiro et al. [30] reported a 16 % decrease in the dielectric constant of 5 M aqueous MEA compared to pure water at 25 °C, and that the N_2O analogy might be valid in this case. The validity of the N_2O -analogy for different simulated water–ethanol blends was studied by Kohns et al. [33] by looking at how the R_H ratio changes with the composition of the mixture. They found that the R_H ratio showed a significant decreasing trend with increasing ethanol concentration. At 50 °C the R_H ratio decreased from approximately 1.4 in pure water, to 1.2 at an ethanol mole fraction of about 0.2 (corresponding to approx. mass fraction of 0.4) at 50 °C. The dielectric constant for ethanol–water mixtures at these conditions (a mass fraction of 0.4 and 50 °C) is about 30 % less than that of pure water [34]. This suggests that the N_2O -analogy cannot be used, at least not within the entire composition range, for mixtures of water and ethanol. For the non-aqueous AMP/DMSO solutions studied in this work, the dielectric constant at 40 °C was roughly estimated to be 6 % and 14 % lower for 10AD and 25AD, respectively, compared to pure DMSO. For the systems containing water, the dielectric constant was roughly estimated to be 4 % and 3 % lower for 10AD2W and 10AD4W, respectively, compared to pure DMSO at 40 °C. These variations are relatively low which suggests that the approximation with the N_2O -analogy might be valid for the studied systems. However, further determination of experimental values of the dielectric constant of the solutions are needed to get a more accurate value for the dielectric constants in the mixtures. From the previous discussion it is reasonable to assume that the larger the difference in dielectric properties of the mixture components are, the more deviation from the N_2O -analogy can be assumed. For the solvents used in this

Table 6

H_{N_2O} and estimated H_{CO_2} in mixtures of 10 wt% AMP in DMSO with added water corresponding to 2 and 4 wt%.

Temperature (°C)	10AD2W		10AD4W	
	H_{N_2O} (MPa)	H_{CO_2} (MPa)	H_{N_2O} (MPa)	H_{CO_2} (MPa)
40	20.51	14.49	23.61	16.68
88	33.80	25.65	37.04	28.11

work, the difference in dielectric constants for the pure components is similar to that of the aqueous MEA case, with AMP having a dielectric constant of about half of that of DMSO.

3.3. Chemical solubility

Besides the change in physical CO₂ solubility, there will also be a change in the overall chemical reactions when water is accumulated in non-aqueous AMP/DMSO. Amines that form sterically hindered carbamates upon reaction with CO₂, favor further reaction to bicarbonate in aqueous solutions. Further reaction to bicarbonate will potentially mean that a higher rich loading is achieved but, at the same time, mean that less AMP-carbamate will be present in the solution compared to a non-aqueous case. A side effect of this might be that precipitation of the AMP-carbamate will not occur under the new conditions. From our previous work we found that for AMP/DMSO systems, precipitation is needed in order for the cyclic capacity to be high enough to be comparable to that of conventional aqueous systems such as MEA [12]. To evaluate the effect of water present in the solution on the cyclic capacity, the solubility of CO₂ in AMP/DMSO/H₂O systems were therefore investigated at 40 and 88 °C, representing absorption and regeneration conditions.

In Fig. 2, CO₂ solubility in 25AD solutions with either 5 or 10 g (5 and 9 wt%) added water are shown and compared to our previous data of non-aqueous 25AD. The added amount of water corresponds to approximate AMP/H₂O molar ratios of 1:1 and 1:2 for 5 g (24AD5W) and 10 g (23AD9W) water, respectively. As expected, the addition of water allows for higher CO₂-loadings, as the additional reaction to bicarbonate is possible to some extent in these solutions. For non-aqueous 25AD, the cyclic capacity was estimated to approximately 0.3 mol CO₂/mol AMP with rich and lean loadings of just above 0.37 (40 °C, 20 kPa) and 0.07 (88 °C, 100 kPa) mol CO₂/mol AMP, respectively. The change

in observed loadings with the addition of water is more apparent at 40 °C, where the loading is increased with approximately 0.05–0.1 mol CO₂/mol AMP at 20 kPa. At 88 °C and 100 kPa the change is smaller, approximately 0.02 mol CO₂/mol AMP, providing similar or slightly higher cyclic capacity to that of the non-aqueous case, within the studied temperature range.

Precipitation was still observed in both experimental runs using 23AD9W at 40 °C, and in one run for 24AD5W at 40 °C. For 24AD5W with precipitation, the solubility of CO₂ was slightly lower, and more similar to the non-aqueous 25AD, than the run without precipitation and the other tested water containing solutions. Precipitation of the AMP carbamate results in less AMP available in solution. This implies that less basic species will be available to accept protons from bicarbonate formation. When precipitation was absent in 24AD5W, there was no significant difference in solubility between 23AD9W and 24AD5W at 40 °C, as can be seen in Fig. 2. This could be the result of less carbamate precipitation overall due to more bicarbonate formation at higher water content. It might also be that the higher water content in 23AD9W enables higher solubility of CO₂, even with similar precipitation amount, as the autoionization of water frees proton accepting species. It should also be noted that the composition of the precipitate was not evaluated in these experiments and that bicarbonate precipitation cannot be ruled out.

Although a higher loading can be achieved in the systems containing water, which suggests that further reaction to bicarbonate takes place at the tested water concentrations, precipitation could still be observed in the solutions. This suggests that accumulation of water might not be an immediate problem for precipitating AMP/DMSO solutions. The cyclic capacity is not severely affected between the temperatures 40–88 °C, suggesting that low regeneration temperatures below 100 °C can still be used even with some water present in the system.

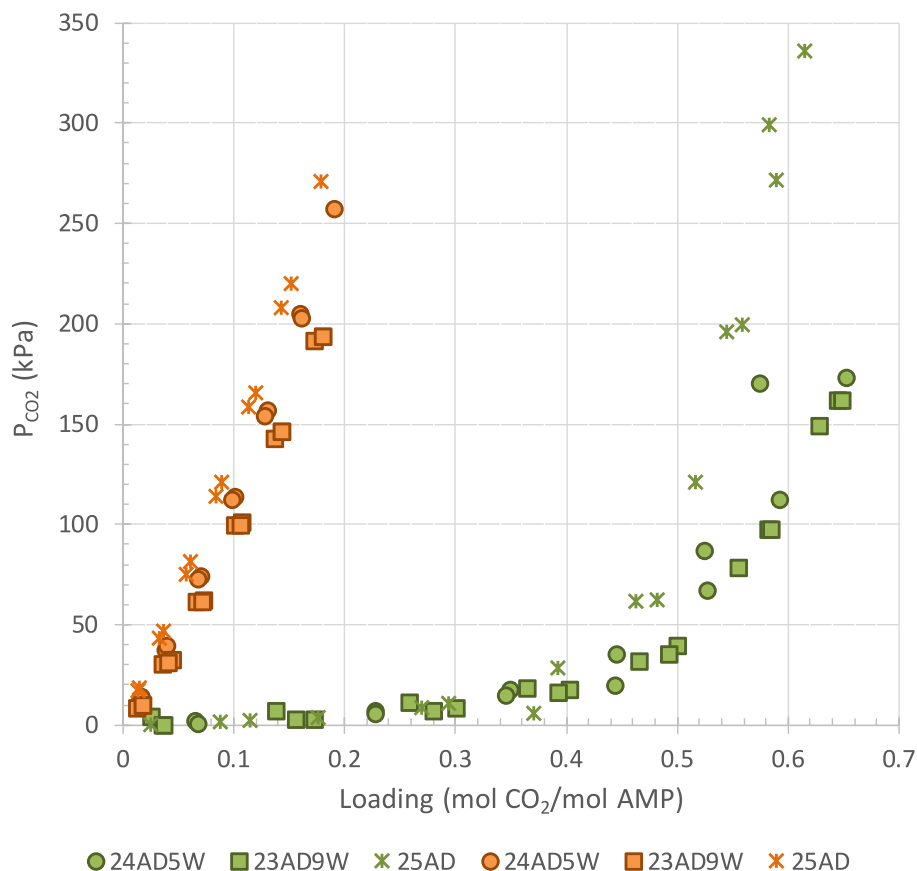


Fig. 2. Solubility data for CO₂ absorption in 25AD (Karlsson et al., 2021), 24AD2W and 23AD9W at 40 °C (green) and 88 °C (orange).

3.4. Heat of absorption

The heat of absorption for 25AD [12], 24AD5W and 23AD9W at 40 and 88 °C are shown in Fig. 3. In general, a similar trend can be seen for the samples with added water and the non-aqueous solutions, with lower heat of absorption at 88 °C than at 40 °C. There is no significant difference between the non-aqueous system and the systems with added water in terms of when precipitation occurs. The points of precipitation, where the heat of absorption is significantly higher (around and above 200 kJ/mol CO₂), occurred at a loading of 0.44 mol CO₂/mol AMP in the 24AD5W and between 0.49 and 0.55 mol CO₂/mol AMP for the 23AD9W solutions. This is similar to the loadings at which precipitation occurs in non-aqueous 25AD, 0.37–0.52 mol CO₂/mol AMP. As discussed in previous publications [12,13,22], the high heat of absorption observed at the point of precipitation indicates that the solvent is supersaturated with AMP-carbamate prior to precipitation. As precipitation occurs, a larger amount of AMP-carbamate will precipitate at once, due to the supersaturation, than in an equilibrium case. The overlapping of the loading regions where precipitation occurs for 25AD, 24AD5W and 23AD9W, suggests that the tested solutions are similarly prone to supersaturation. More data is needed to determine whether a higher water content leads to precipitation at higher loadings.

The rapid decrease in heat of absorption after a loading of 0.5 mol CO₂/mol AMP, observed for the non-aqueous system, as a result of the system reaching its maximum theoretical loading, is not as pronounced for the systems containing water. As the sterically hindered carbamate will further react to bicarbonate, the maximum loading will be increased. This will result in a slower decrease in heat of absorption up to the new theoretical maximum capacity.

3.5. NMR

The distribution of reaction products in 10AD with either 2 or 4 wt% water was studied using ¹³C NMR at 30–88 °C. As can be seen in Fig. 4a), three main reaction products are formed with CO₂ absorption at 30 °C in 10AD2W. In agreement with our previous work [12], the signals are assigned the AMP-carbamate (161.3 ppm), bicarbonate (159.5 ppm) and tentatively the AMP-carbonate (156.5 ppm). A broad resonance corresponding to physically dissolved CO₂ can also be seen at 124.5 ppm. As

the temperature is increased (Fig. 5), the signals corresponding to CO₂ reaction products starts to broaden and decrease in intensity as the equilibrium reactions start to shift towards desorption (spectra showing the full bicarbonate resonance can be found in supplementary information). Based on the NMR-results, the bicarbonate species appear to require a higher regeneration temperature compared to the AMP-carbamate. This can be seen as the resonance at 161.3 ppm corresponding to the AMP-carbamate, is practically gone at temperatures of 60 °C whereas the bicarbonate resonance (159.5 ppm) is still visible. Both products are however regenerated at 80–88 °C, with no distinct product signals present in the sample. A new resonance at 158.1 ppm appears at 80 °C. This product seems to be irreversibly formed and is still present after the sample was cooled to 30 °C after heating (Fig. 4b). This product was not observed in our previous study of non-aqueous 10AD, which investigated the product distribution in non-aqueous solutions of 10 wt% AMP in DMSO at temperatures up to 80 °C [12]. The species is tentatively assigned to one of the possible side reactions that might occur, where 4,4-dimethyl-1,3-oxazolidin-2-one (DMOZD) is formed by ring closure of the AMP carbamate. The signal broadening arising from species interactions makes it hard to determine at which temperature this species is first formed, but it becomes distinguishable in the NMR spectra at 80 °C. A repeat run of the sample resulted in an increase of the signal. DMOZD is reported in literature as both a thermal and oxidative degradation product of AMP [35–38]. The studies in literature were performed in aqueous solutions of AMP and predominantly at temperatures above 100 °C, to represent the stripper and reboiler temperatures used in conventional amine scrubbing. Matin et al. [36] found the formation rate of DMOZD in aqueous AMP to increase with temperature, amine concentration and CO₂ loading. The lower rich loadings achieved in non-aqueous AMP solutions, in combination with the potential to use lower regeneration temperatures of 88 °C, could thus reduce the formation rate of DMOZD compared to aqueous AMP solutions. This is supported by the results obtained in our previous study [12], where the product was not observed in non-aqueous solutions of AMP in DMSO. Wang et al. [38] also reported DMOZD formation at lower temperatures of 80 °C in an oxidative environment. The distribution of oxidative degradation products was reported to vary with temperature. At 80 °C and an oxygen partial pressure of 250 kPa another ring product, 4,4-dimethyl-1,3-oxazolidine, was found to be a major degradation product of aqueous AMP, whereas at above 100 °C further reaction to 2,4-lutidine dominated. In order to verify the formation of DMOZD and to evaluate the severity of AMP degradation at conditions suitable for CO₂ absorption in non-aqueous AMP solutions, further experimental evaluation is needed.

Similar results, in terms of CO₂ containing species observed in 10AD2W at 40–88 °C, were observed in 10AD4W, showed in the supplementary information (Fig. B1). The main difference is the higher intensity observed for the bicarbonate resonance, due to more bicarbonate formation resulting from a higher water content. The NMR spectra for both 10AD2W and 10AD4W confirms the trends seen in the solubility data with higher CO₂ solubility with added water. With increasing bicarbonate formation at lower temperatures there will also be more chemically reacted species left in the solution at higher temperatures. However, at 88 °C the majority of the CO₂ in solution is physically dissolved.

4. Conclusions

In this work the influence of water accumulation in non-aqueous AMP/DMSO mixtures, on CO₂ absorption, was studied. It is difficult to assess the possible rate of absorption of water in non-aqueous AMP/DMSO solutions in a full-scale process, as the rate is likely highly dependent on the mass transfer area and thus case specific. The physical solubility of CO₂ in mixtures of AMP/DMSO and AMP/DMSO/H₂O were estimated using the N₂O analogy. As expected, the physical solubility of CO₂ decreases as the water content increases, as a result of the much

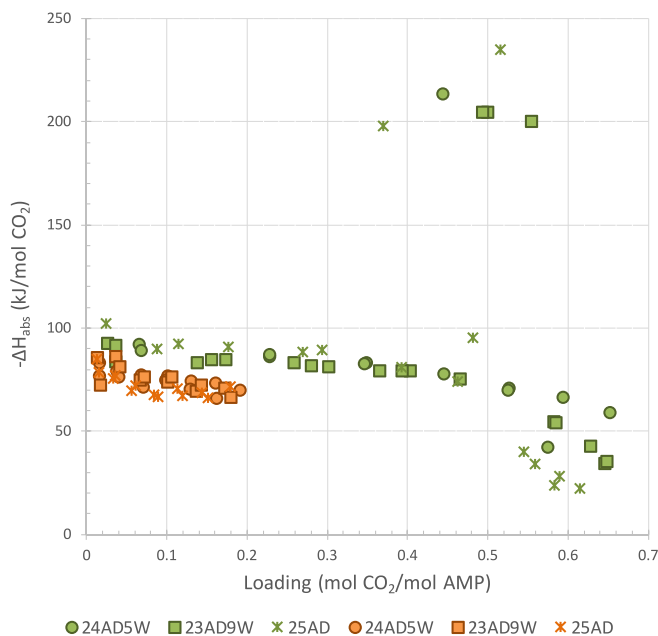


Fig. 3. Heat of absorption for CO₂ in 25AD (Karlsson et al., 2021), 24AD2W and 23AD9W at 40 °C (green) and 88 °C (orange).

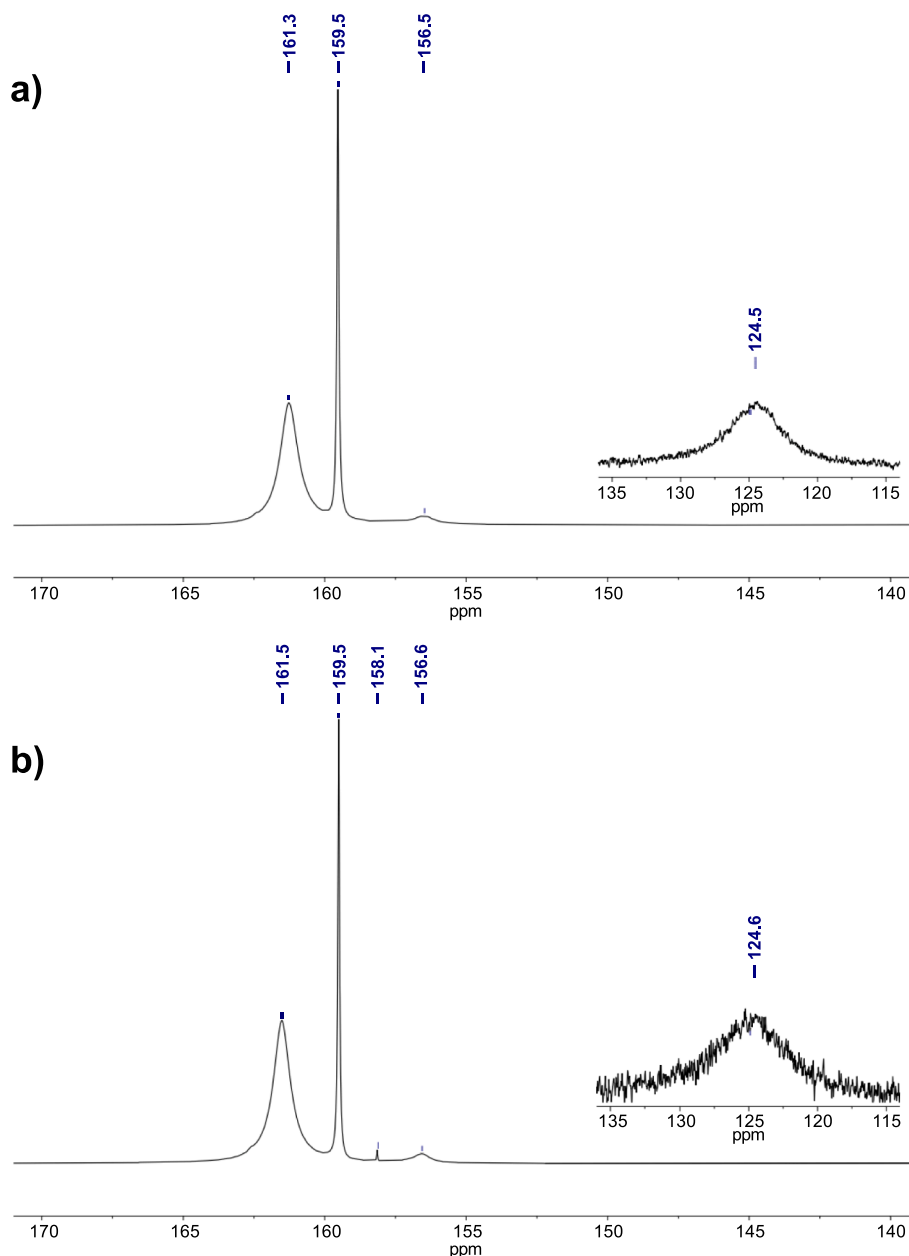


Fig. 4. ^{13}C NMR spectra for CO_2 in 10AD2W showing shift region for reaction products and physically dissolved CO_2 at 30 °C. a) Before heating to 88 °C. b) After heating to 88 °C and returning to 30 °C.

lower physical solubility of CO_2 in water than in DMSO. The physical solubility of CO_2 increases with increasing amine concentration.

The addition of water to AMP/DMSO resulted in a shift in the equilibrium solubility towards increased CO_2 loading and chemically absorbed CO_2 at both 40 and 88 °C. This is a result of bicarbonate formation, enabled in the presence of water. The shift towards higher CO_2 loadings was more apparent at 40 °C than at 88 °C, and a reasonable cyclic capacity of above 0.3 mol CO_2 /mol AMP was still achieved in the solutions with added water. This suggests that regeneration temperatures of around 88 °C could be used for the studied AMP/DMSO/ H_2O systems. Precipitation was still observed in the systems with water present, suggesting that some water content, at least up to 9 wt% is tolerable in precipitating 25AD systems. The increasing bicarbonate formation was also confirmed with ^{13}C NMR, where it could be seen that that most chemically absorbed species were regenerated at 88 °C and the remaining species present in the solution was predominantly physically absorbed CO_2 . At 80 °C and above, a new species appeared which is

tentatively assigned to the amine degradation product DMOZD, formed from ring closure of the AMP carbamate. Further experimental studies are needed to investigate the severity of amine degradation at conditions appropriate for absorption and regeneration of AMP/DMSO absorption systems.

CRediT authorship contribution statement

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

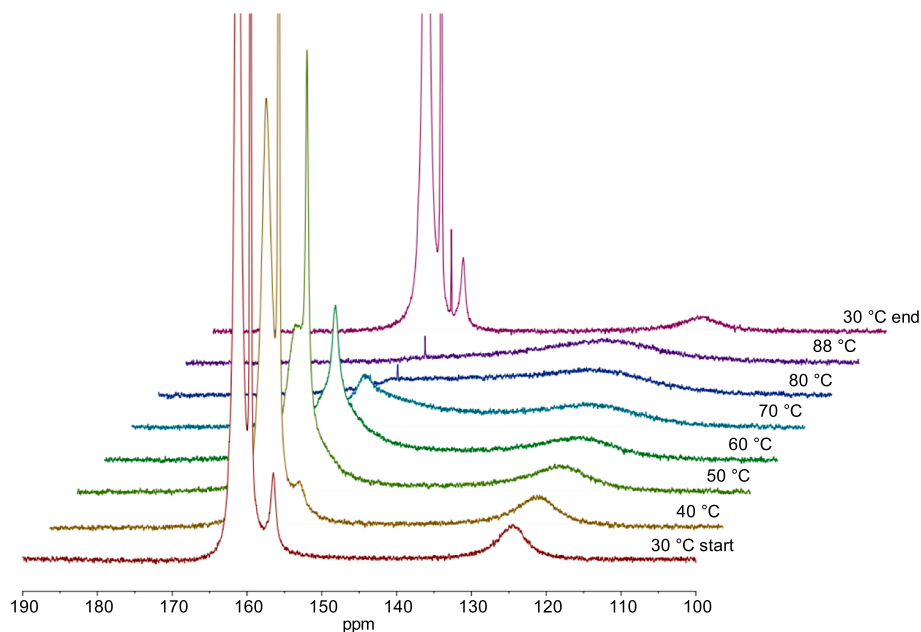


Fig. 5. ^{13}C NMR spectra for CO_2 in 10AD2W showing shift region for reaction products and physically dissolved CO_2 at 30–88 °C and again at 30 °C after the temperature ramp.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2024.126858>.

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