



Carbon dioxide solubility in mixtures of methyldiethanolamine with monoethylene glycol, monoethylene glycol–water, water and triethylene glycol

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ABSTRACT

Carbon dioxide solubility in non-aqueous and aqueous mixtures of methyldiethanolamine (MDEA) with monoethylene glycol (MEG) was studied due to the relevance of these solvents for the combined acid gas removal and hydrate control in natural gas treatment. Vapor-liquid equilibrium (VLE) measurements were conducted at temperatures from 303 K to 393 K and pressures up to 600 kPa. In the aqueous solvents, the effect of water content in carbon dioxide solubility was investigated. The absorption capacity of the aqueous solvents decreased with increasing glycol content and decreasing water content, at constant amine concentration. A comparison of the studied systems with concentrated aqueous MDEA was also performed. The non-aqueous solvents were studied in the whole composition range, from pure MDEA to pure MEG. The solubility of carbon dioxide increased with increasing amine content only up to 30–50 wt% MDEA-MEG, upon which it decreased. Water content determination and Nuclear Magnetic Resonance (NMR) analysis were used for the chemical characterization of the systems and explanation of the results. It was found that in the presence of MDEA, a chemical reaction occurs between carbon dioxide and MEG. A theory based on MEG autoprotolysis is proposed which is further supported by supplementary VLE data obtained in blends of MDEA and triethylene glycol.

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1. Introduction

1.1. Literature review

Primary downstream processes in natural gas production are the removal of acid gases, namely carbon dioxide (CO₂) and hydrogen sulfide (H₂S), and the removal of water in order to meet pipeline transportation specifications, gas quality specifications and environmental requirements. Acid gases in the presence of water are highly corrosive and can jeopardize the safety of operations, both in terms of the personnel's wellbeing as well as equipment failure. The same applies in the event of hydrate formation if excess of water is present, which can lead to pipeline clogging and, in extreme cases, production shut-down [1].

In offshore gas and oil wells, non-regenerative chemicals, called scavengers, are commonly used to control hydrogen sulfide content in natural gas. However, they are not ideal since their use imposes space, weight and disposal requirements which are not friendly for offshore/subsea application [2], and they cannot treat

high H₂S concentrations. A typical example is triazine, which is injected directly into the gas stream and is able to treat hydrogen sulfide at concentrations not higher than 200×10^{-6} ppmv [3]. As a result, fields are abandoned or not even produced due to high H₂S content. In addition, oil and gas fields experience reservoir souring, i.e. increase in sulfur content, due to EOR (Enhanced Oil Recovery) activities such as water injection [4]. Maintaining production and safe operation in increasingly sour fields is an important industrial challenge.

A solution to the problematic high H₂S concentrations in production wells is the development of a regenerative process where hydrogen sulfide and water content can be removed simultaneously. Despite the fact that the employment of a regenerative solvent requires additional equipment for its regeneration, it could enable trouble-free operations and extend the life of the field. Aqueous methyldiethanolamine (MDEA) and aqueous monoethylene glycol (MEG) are regenerative solutions traditionally used today for the selective removal of H₂S over CO₂ and for hydrate control, respectively. MDEA is a tertiary amine whose aqueous solutions have significantly higher reaction rates with H₂S than with CO₂. Therefore, mixtures of MDEA-MEG as well as highly concentrated

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MDEA are promising candidates for the combined removal of H₂S and water vapor.

The concept of a gas treating process for combined acid gas and water vapor removal from natural gas was conceived already in 1930s and was first patented in 1939 by Hutchinson [5]. Process improvements were suggested in the following years [6–8] and the amine-glycol process found wide acceptance in the gas processing industry. An aqueous mixture of monoethanolamine (MEA) and either diethylene (DEG) or triethylene glycol (TEG) was used for the simultaneous absorption of acid gas and water from natural gas [9]. In spite of many advantages, severe corrosion was encountered and the process was eventually abandoned. However, MEA is known for its corrosivity issues, thus its substitution with another amine and/or the decrease in water content can potentially eliminate this problem. The years that followed until today, many researchers have studied blended aqueous and non-aqueous amine-glycol solvents, mainly in the framework of water-lean solvents, which can potentially have increased absorption capacity and reduced regeneration heating duties [10–20]. The majority of the literature studies concerns MEA and diethanolamine (DEA) and few sources were found for MDEA-glycol systems [16,17,19].

Wanderley and co-workers [20] studied vapor-liquid equilibrium and mass transfer in MDEA – MEG – H₂O among other solvents, promising for CO₂ capture in biogas upgrading. They observed that the solubility of CO₂ decreased compared to aqueous MDEA, and they underlined the fact that higher CO₂ partial pressure than in aqueous MDEA was also accompanied by faster reaction rates for the same CO₂ pressure. Eimer [19] and Xu et al. [16] focused on the selectivity of H₂S over CO₂ with non-aqueous or water-lean MDEA-containing solvents. Eimer [19] investigated the performance of a mixture composed of MDEA and TEG aiming for the combined selective removal of H₂S over CO₂ and dehydration. It was found that the reaction rate of H₂S in the combined solvent decreases with increasing glycol content. High viscosity promotes low absorption rate and this is one of the main reasons why, in this study, we consider the far less viscous MEG as a more suitable glycol than TEG for this multifunctional solvent. Moreover, following a first screening of potential diluents which showed increased H₂S selectivity in MDEA – MEG compared to aqueous MDEA, Xu et al. [16] measured the solubility of CO₂ and H₂S in aqueous and non-aqueous MDEA – MEG blends. They concluded that the carbon dioxide solubility significantly decreases in MDEA – MEG than MDEA – H₂O, while the solubility of H₂S is only slightly lower.

1.2. Aim of this work

Successful process development relies on accurate data and/or models to describe the physical properties, thermodynamic behavior and system kinetics. The first step for the evaluation of a complex multicomponent system, such as the combined hydrogen sulfide and hydrate control process, is the study of its subsystems. The aim of this work is to describe and understand the thermodynamic behavior of the subsystems CO₂ – MDEA – MEG and CO₂ – MDEA – MEG – H₂O. Since carbon dioxide is generally present in natural gas with hydrogen sulfide, investigating this system is of equal importance as the absorption of H₂S in the proposed solvent.

This work includes two main studies: a) an extensive study of the vapor-liquid equilibrium (VLE) behavior of CO₂ – MDEA – MEG systems in the whole composition range from pure MEG to pure MDEA, and b) a study of CO₂ – MDEA – MEG – H₂O systems with focus on the effect of water content in the system and a comparison with highly concentrated amine solutions, *i.e.* 70 wt% and 90 wt% MDEA – H₂O. The measurements were performed at CO₂ pressures up to 600 kPa and temperatures from 303 to 393 K.

We further investigated our VLE results through Karl-Fischer titration (for the non-aqueous systems), Nuclear Magnetic Resonance (NMR) spectroscopy, and comparison with MDEA – TEG systems in order to understand the underlying phenomena and identify possible chemical reactions undergone during the absorption of CO₂ into aqueous and non-aqueous MDEA-glycol blends. Density measurements were also performed as part of the VLE data processing.

2. Materials and methods

2.1. Materials

Table 1 contains information for the chemicals used in this work. They were used as received from the supplier without further purification. Deionized water was used for preparation of the aqueous mixtures. The solutions were prepared gravimetrically in a METTLER PM1200 scale with an accuracy of 1×10^{-6} kg, they were sealed and let under magnetic stirring for at least 8 h to ensure homogeneous solutions. Amine analysis by means of acid-base titration was performed in order to verify the MDEA concentration in the studied systems.

2.2. Experimental methods

2.2.1. Vapor-liquid equilibrium measurements

Two similar setups were used to conduct the vapor-liquid equilibrium (VLE) measurements, named VLE-1 and VLE-2. The main components of the setups are a glass reactor and a storage cylinder for CO₂ of ca. 1×10^{-3} m³ volume each, whose pressure and temperature are monitored. Measurements can be conducted at temperature range of (303 – 393) K (accuracy ± 0.1 K) and pressures (0 – 600) kPa (accuracy ± 0.9 kPa). The setups' description and instrumentation are provided in detail by Hartono et al. [21] Experiments were performed in two different ways, either at multiple temperatures with one CO₂ loading or at one temperature and multiple loadings.

Each experiment started by evacuating the reactor. The solvent was introduced and the reactor was set again to vacuum to eliminate possible air introduced with the solvent. The exact amount of solvent introduced was known by weighing the solvent holder, before and after charging the reactor. For measurements performed at multiple temperatures with one CO₂ loading, the temperature was set to automatically increase from 303 to 393 K with a step of 10 K. At 393 K, CO₂ was injected to the maximum pressure of the reactor and the temperature was decreased in reversed steps until 303 K. For the measurements performed under isothermal conditions and multiple loadings, once equilibrium was reached at the desired temperature, CO₂ was added. After each system equilibration, more CO₂ was added manually until the pressure inside the reactor was close to 600 kPa. Equilibrium in every temperature level, both for the vapor pressure of the solution and the CO₂-solvent equilibrium, required approximately (4–8) hours. The system was under constant stirring (ca. 500 rpm) and equilibrium was assumed when the temperature and pressure of the reactor were constant for 5 min.

The pressure and temperature were recorded every 5 s during the experiment, which lasted (3–4) days. The calculations are based on mass balances; the solvent is added from a beaker whose weight before and after the reactor filling is measured. The temperature, volume and pressure of the CO₂ storage vessel are known, and thus the amount of gas before and after the CO₂ loading of the solvent can be calculated. The amount of carbon dioxide in the vessel was calculated using Peng-Robinson equation of state [22]. The equilibrium pressure was calculated according to Eq. (1):

Table 1
Chemical Sample Table.

Component	UIPAC name	CAS	Supplier	Mass fraction purity as stated by supplier
N-methyldiethanolamine (MDEA)	2-[2-hydroxyethyl(methyl) amino] ethanol)	105-59-9	Sigma-Aldrich	≥0.99
monoethylene glycol (MEG)	ethane-1,2-diol	107-21-1	Sigma-Aldrich	0.998
triethylene glycol (TEG)	2-[2-(2-hydroxyethoxy) ethoxy]ethanol	112-27-6	Sigma-Aldrich	≥0.985
carbon dioxide	carbon dioxide	124-38-9	AGA	0.99999
water	oxidane	–	–	–

$$P_{\text{CO}_2} = P_{\text{tot}} - P_{\text{res}} \quad (1)$$

where P_{CO_2} : partial pressure of CO_2 , P_{tot} : total pressure inside the reactor and P_{res} : residual pressure inside the reactor before CO_2 addition. Amine analysis was performed in the end of every experiment to verify that the amine concentration remained the same (within 2% error). CO_2 analysis was also performed in most of the experiments to confirm our mass balance-based calculations. The average absolute relative deviation (AARD), calculated according to Eq. (2), is 4% for all the experiments, excluding those in pure H_2O , MEG and TEG where the very low values of carbon dioxide absorbed leads to large relative deviations. However, the results from those experiments are compared to and found in agreement with values reported in the literature in Section 3.

$$\text{AARD}[\%] = \frac{100}{\text{NP}} \sum_{i=1}^{\text{NP}} \left| \frac{x_i^{\text{calc}} - x_i^{\text{exp}}}{x_i^{\text{exp}}} \right| \quad (2)$$

where x stands for any property whose relative deviations were calculated in this work, and NP stands for number of points.

For the non-aqueous systems, the Henry's constant was calculated according to Eq. (3). c_{CO_2} denotes the concentration of CO_2 in the solvent and the Henry's constant H is expressed in $\text{kPa} \cdot \text{m}^3 \cdot \text{kmol}^{-1}$. For the aqueous systems, the loading α , expressed in mol CO_2 per mol MDEA, was calculated and reported.

$$H = \frac{P_{\text{CO}_2}}{c_{\text{CO}_2}} \quad (3)$$

The experimental apparatuses and procedure were validated by measuring the solubility of carbon dioxide in pure water and comparing our results to the correlation provided by Carroll et al. [23], as formulated by Penttilä et al. [24] (Fig. 1). The experiments were repeated two times and conducted both before and during the experimental campaigns to ensure good quality data. The validation measurements are presented in Table A.1. The AARD between

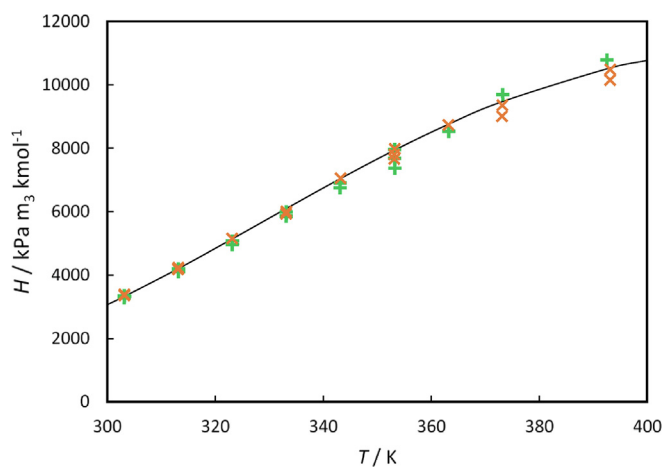


Fig. 1. Henry's constant for CO_2 in water as a function of temperature. (+) Measurements in VLE-1, (X) Measurements in VLE-2, (—) Correlation by Penttilä et al. [24].

measured and literature values was always lower than 3% for both VLE-1 and VLE-2, and the repeatability was found to be within 3% as well.

2.2.2. Density measurements

An Anton Paar Density Meter DMA 4500 M was used to measure the density of the solutions used in this work, when not reported in the literature. The knowledge of the density as a function of temperature was necessary in order to calculate the volume of the solution inside the reactor, assuming that pressure effect is negligible. Calibration and validation of the apparatus was performed according to Hartono et al. [25] and Skylogianni et al. [26] An average absolute relative deviation of 0.01% was found for two repeated measurements.

2.2.3. Karl-Fischer titration

The presence of water in the MDEA-glycol systems was studied through Karl-Fischer titration measurements using a METHROM 831 KF coulometer. Coulometric Karl-Fischer titration is an established method for water content determination as low as a few ppm. The AARD in this work is 11%.

2.2.4. NMR experiments

NMR is a powerful non-invasive analytical technique for chemical analyses. Interpretation of the NMR spectra leads to the identification of the chemical structures of the molecules, including unknown products and/or side-products, and in proper performed NMR experiments the species can also be quantified [27].

In this study, qualitative ^1H , ^{13}C and 2D NMR experiments were performed on selected liquid samples after CO_2 absorption to identify reaction products formed upon the addition of carbon dioxide. In particular, ^{13}C NMR spectra show the signals belonging to all the CO_2 -derivatives formed upon the addition of CO_2 , like e.g. amine carbonate, alkyl carbonate, bicarbonate and carbonate which all contain carbon ($-\text{C}$) nuclei in their structure [28].

Each sample was inserted in an NMR tube, together with a coaxial insert containing deuterated benzene (C_6D_6) for locking and referencing. The NMR experiments were performed at 300 K on a Bruker 600 MHz Avance III HD equipped with a 5-mm cryogenic CP-TCI z-gradient probe. The qualitative ^{13}C NMR spectra shown in this work were all obtained with a standard decoupling acquisition sequence with 30-degree pulse angle and Nuclear Overhauser Effect (NOE) growth (zgpg30), using a recycle delay time of 2 s and 1024 scans.

2.3. Modeling methods

Vapor-liquid equilibrium of CO_2 with aqueous MDEA and aqueous MDEA-MEG was modeled employing the so-called "soft model", proposed by Bröder et al. [29]. It is a purely empirical correlation which is described by Eqs. (4)–(7).

$$\ln(P_{\text{CO}_2}) = A \ln \alpha + k_1 + \frac{B}{(1 + k_2 \exp(-k_3))} \quad (4)$$

where A, B are parameters and k_1 , k_2 and k_3 are temperature-dependent coefficients:

$$k_1 = k_{1,a} \ln\left(\frac{1}{T}\right) + k_{1,b} \quad (5)$$

$$k_2 = \exp\left(\frac{k_{2,a}}{T} + k_{2,b}\right) \quad (6)$$

$$k_3 = \frac{k_{3,a}}{T} + k_{3,b} \quad (7)$$

P_{CO_2} is expressed in kPa, α in mol CO₂/mol MDEA and T in K in the fitted model.

The model can predict the CO₂ partial pressures based only on temperature and loading and it has been employed in the past to successfully describe amine-containing reactive systems [29–31]. The VLE data were fitted to the correlation by minimizing the sum of the relative least square error and for each system, a different set of parameters is proposed. The binary systems, for which one or two points are obtained per temperature, were not possible to be described with the model due to the limited number of data.

3. Results and discussion

3.1. Analysis of the water content

As we investigate several non-aqueous blends, it was decided to use Karl-Fischer titration for the quantification of the water present. Analysis was performed both before and after the VLE experiments for selected non-aqueous systems studied in this work. For all the systems titrated, low water amount was found before the experiment equal or lower than 0.1 wt% H₂O. The detailed water concentrations and corresponding uncertainties are given in [Supporting Information](#) (Section C). It is important to note here that water was also detected in pure MEG samples even though we purchased anhydrous ethylene glycol. This signifies that some humidity was absorbed through the solution's contact with the atmosphere during solution preparation and experiment preparation.

Higher water contents were detected after the experiment was concluded. The increased water content after the experiment indicates that humidity must have remained in the reactors or in the condenser on the top of the reactor even after their thorough cleaning and drying. The observed water content was typically below 0.2 wt% while the maximum water content was observed for pure MDEA (0.5 wt%) in the end of the experiment. The impact of the detected water is discussed on the following sections.

3.2. MDEA – MEG mixtures

Carbon dioxide absorption in pure MEG, pure MDEA and their blends was investigated and the data obtained are presented in the [Appendix](#) (Table A.2). The measurements are reported with their respective uncertainties, calculated using the Law of propagation of uncertainty, according to the uncertainty analysis provided in [Supporting Information](#) (Section E). As explained in the experimental procedure, the solubility of a fixed CO₂ amount was measured at temperatures from 303 K to 393 K. The densities of the MDEA – MEG blends, required for the data processing, were calculated using the model proposed by Skylogianni et al. [26]. Density measurements of indicative systems, which were conducted to verify the model results, demonstrated maximum ARD of 1% (Section B of [Supporting Information](#)).

Several authors have reported P - T - x data for the binary system CO₂ – MEG. [Fig. 2](#) and [Fig. 3](#) show the mole fraction of CO₂ in the liquid phase against pressure at 323 K and 373 K, respectively. Literature data are also available at the studied temperatures 303 K, 333 K and 343 K and a graphical comparison can be found at [Sup-](#)

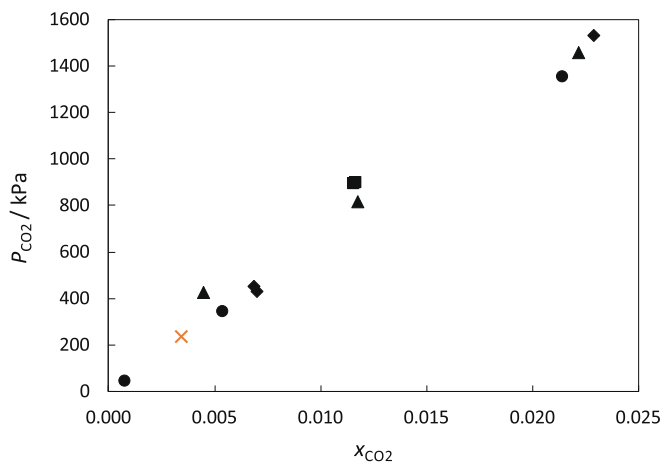


Fig. 2. Carbon dioxide solubility in MEG expressed in mole fraction (x_{CO_2}) as a function of pressure at 323 K. (■) Zheng et al. (1999) [32], (▲) Galvao and Francescconi (2010) [33], (●) Jou et al. (1990) [34], (◆) Wise and Chapoy (2017) [35], (×) This work.

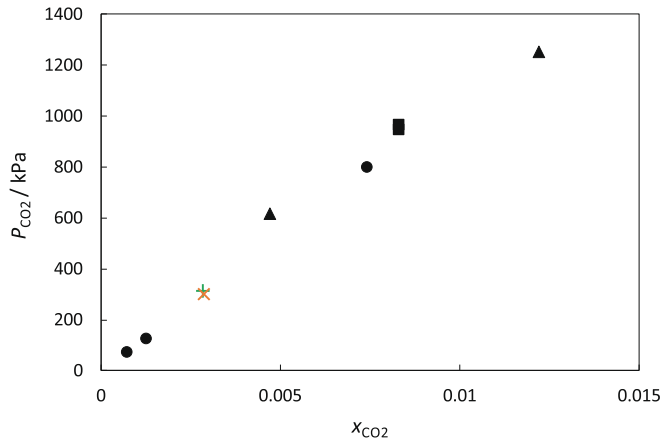


Fig. 3. Carbon dioxide solubility in MEG expressed in mole fraction (x_{CO_2}) as a function of pressure at 373 K. (■) Zheng et al. (1999) [32], (▲) Galvao and Francescconi (2010) [33], (●) Jou et al. (1990) [34], (×) This work (A), (+) This work (B).

porting Information (Figs. S.1–S.3). It is observed that the data obtained in this work are in line with those reported in the literature. The Henry's constant values are plotted as a function of temperature in [Fig. 4](#) for all studied blends, from pure MEG to pure MDEA.

As illustrated in [Fig. 4](#), Henry's constant increases with temperature, thus the solubility of CO₂ into the solvent decreases, for both unitary and binary solvents studied in this work. This is explained by the higher kinetic energy with temperature resulting to the escape of gas molecules from the liquid and in the gas phase. Moreover, it is shown that the Henry's constant of CO₂ in MEG is higher than the Henry's constant of CO₂ in MDEA. The uncertainties calculated have an average deviation from their corresponding properties of 7%. It was found that Henry's constant has higher sensitivity to the amount of CO₂ absorbed in the solvent, due to the propagation of errors in its calculation (Eq. S.24 in [Supporting Information](#)). Therefore, the experiments with low CO₂ uptake are expected to have the highest uncertainty in Henry's constant. These experiments include mainly those experiments performed with a single loading.

An unexpected behavior was observed for the mixtures of the glycol with the amine: the solubility of carbon dioxide in mixtures

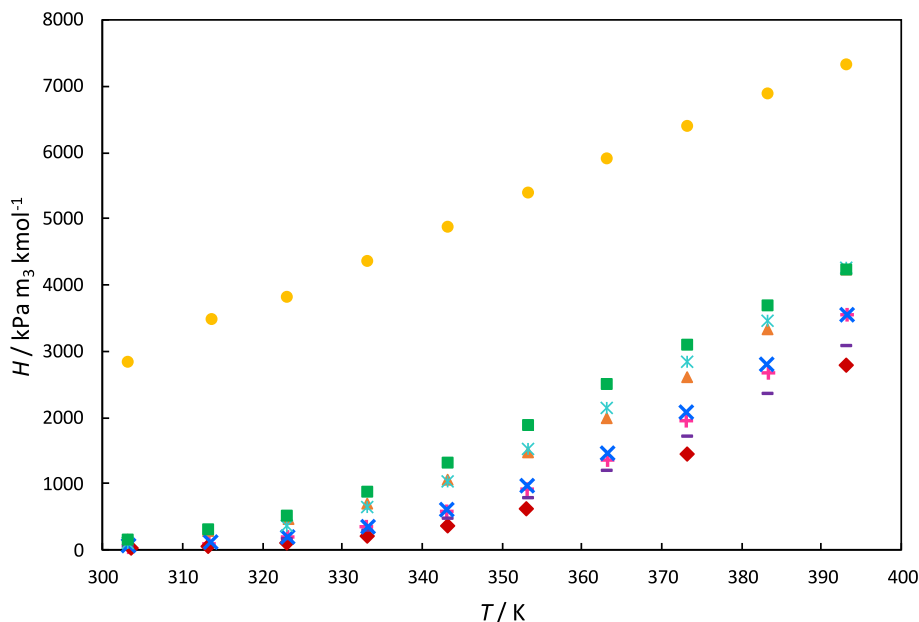


Fig. 4. Henry's constant as a function of temperature for pure MEG, pure MDEA and their blends as measured in this work. (●) Pure MEG, (▲) 5 wt% MDEA – 95 wt% MEG, (+) 10 wt% MDEA – 90 wt% MEG, (◆) 30 wt% MDEA – 70 wt% MEG, (—) 50 wt% MDEA – 50 wt% MEG, (×) 70 wt% MDEA – 30 wt% MEG, (⊕) 90 wt% MDEA – 10 wt% MEG, (■) Pure MDEA.

of MDEA – MEG is higher than it is in its individual components. The measurements for selected blends of MDEA – MEG were repeated in order to confirm the observed trends. To be specific, the CO_2 solubility measurements were conducted twice in the blends of 5 wt% MDEA – 95 wt% MEG, 10 wt% MDEA – 90 wt% MEG, 30 wt% MDEA – 70 wt% MEG and 50 wt% MDEA – 50 wt% MEG as well as in pure MEG. Good repeatability was found with AARD equal to 4%. The repeated measurements are given in the Appendix (Table A.4).

In addition, we can observe that as amine is added in MEG, initially the solubility of carbon dioxide increases. Between 30 and 50 wt% MDEA content, a transition occurs, after which addition of amine leads to lower CO_2 solubility. As a result, the Henry's constant of CO_2 is similar in a rich-amine system and a lean-amine system, for example in 70 wt% MDEA – 30 wt% MEG system and 10 wt% MDEA – 90 wt% MEG system. This behavior indicates the presence of chemical effects for CO_2 – MDEA – MEG systems. Therefore, the solubility of CO_2 in MDEA – MEG may not be only physical as initially assumed.

No chemical reactions are indeed expected between CO_2 and neither pure MEG nor pure MDEA. MDEA is a tertiary amine which cannot react with carbon dioxide in the absence of water [9,36]. In order to gain an understanding of the phenomena observed, we conducted isothermal VLE experiments at 313 K and 343 K for the systems CO_2 – MEG and CO_2 – MDEA. CO_2 solubility in 50 wt% MDEA – 50 wt% MEG was also measured at constant temperature in order to provide more insights. The results of this study are reported in Table A.3. The data obtained at 313 K are plotted in Fig. 5 while a similar plot of the data at 343 K can be found in Supporting Information (Fig. S.4).

A linear relation between the partial pressure of a gas and its solubility in a solvent denotes that only physical absorption occurs, according to the simplified form of Henry's Law for ideal systems. In that case, the $H_{\text{gas,solvent}}$, i.e. the slope, is constant and a strong function of temperature. The linearity is assessed using the coefficient of determination, R^2 . It is clear that the P - x relation is linear for pure MEG with R^2 equal to almost unity, i.e. 0.9995 and 0.9998 for 313 K and 373 K, respectively. This indicates that there

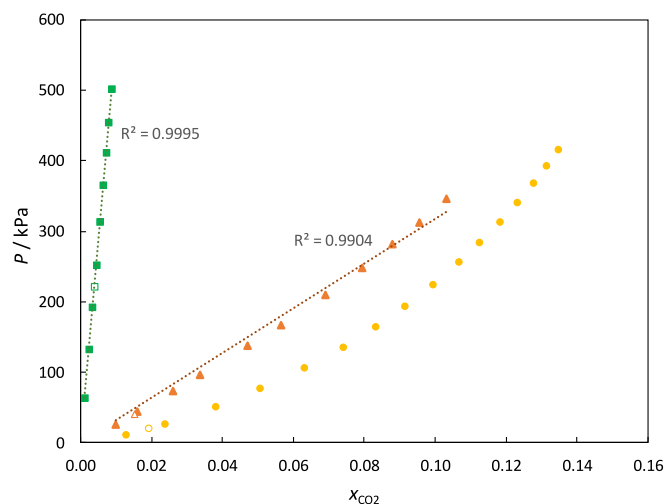


Fig. 5. Partial pressure of CO_2 as a function of CO_2 solubility in pure MEG, pure MDEA and their 50 – 50 wt% blend at 313 K. Filled symbols denote isothermal experiment (Table A.3) and hollow symbols denote previous experiment (Table A.2); (■) MEG, (▲) MDEA, (●) 50 wt% MDEA – 50 wt% MEG. Dotted lines are linear trend lines; the linearity between P and x for pure MEG and pure MDEA is assessed through the coefficient of determination, R^2 .

are no chemical effects. For pure MDEA, a linear relation can be also seen at the studied conditions with a coefficient of determination 0.9904 and 0.9982 for 313 K and 373 K, respectively. One could, however, argue that some chemical effects might be present since the coefficient of determination for MDEA data is lower and also some curvature can be observed with a naked eye, particularly at 313 K (Fig. 5). A non-linear relationship between the partial pressure of carbon dioxide and its solubility in a 50 wt% MDEA – 50 wt% MEG blend is also pronounced in the same figure.

Chemical absorption of carbon dioxide into pure MDEA or blends of MDEA-MEG could take place if water is present in the system. Some amounts of water were detected by Karl-Fischer titration in our samples, as presented in Section 3.1. Although

the presence of small amount of water can explain the noticed chemical effects in pure MDEA, it does not explain the interesting behavior of increased CO₂ solubility up to (30 – 50) wt% MDEA-MEG and decreased solubility as the amine content further rises. For this reason, we also conducted NMR experiments to identify the species present in our loaded systems and further understand the system chemistry. The NMR results follow the VLE results for the aqueous systems.

3.3. MDEA – MEG – H₂O mixtures

Solubility measurements of carbon dioxide into aqueous solutions of MDEA – MEG were performed with MDEA concentration in the solution kept constant at 30 wt% while the water content varied from 10 wt% to 50 wt% (Table A.6). Similar to the MDEA – MEG study, the densities, which are necessary for the data treatment, were found in the literature [26]. Comparison between experimental and literature values at selected temperatures revealed 0.3% maximum absolute relative deviation (Section B of Supporting Information).

The partial pressure of CO₂ as a function of CO₂ loading at 313 K and 343 K is shown in Fig. 6 for the 30 wt% MDEA – 60 wt% MEG – 10 wt% H₂O studied mixture. The increase in loading as temperature decreases, at constant pressure, is justified by the exothermic nature of the reaction of CO₂ with aqueous MDEA. One can also observe the good repeatability between two experiments, one with multiple pressurizations under isothermal conditions and one with single CO₂ pressurization and temperature variation, which was performed for repeatability checks and to provide data points in several temperatures (Table A.5). These remarks are also valid for the additional aqueous mixtures studied in this work, as shown in Supporting Information (Figs. S.5 and S.6).

The effect of water content is illustrated in Fig. 7 and Fig. 8 for 313 K and 343 K, respectively. At 313 K, our measurements are compared with the data points reported by Shen and Li [37] and Xu et al. [16] for a 30 wt% MDEA – H₂O system, for non-aqueous and aqueous MDEA – MEG blends. Although the data produced in this work for the ternary systems cover partial pressures up to 500 kPa, the y axis of Fig. 7 extends up to 140 kPa, in order for the data points at low partial pressures and loadings to be shown distinctly. The same figure covering pressures in the whole range

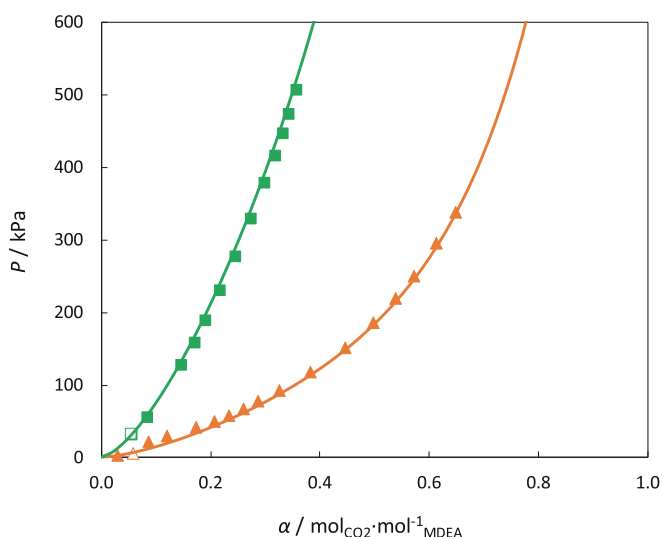


Fig. 6. Partial pressure of CO₂ as a function of CO₂ loading in a solution of 30 wt% MDEA – 60 wt% MEG – 10 wt% H₂O. Filled symbols denote isothermal experiment (Table A.6) and hollow symbols denote repeated experiment with a single loading (Table A.5). (▲) 313.2 K, (■) 343.2 K.

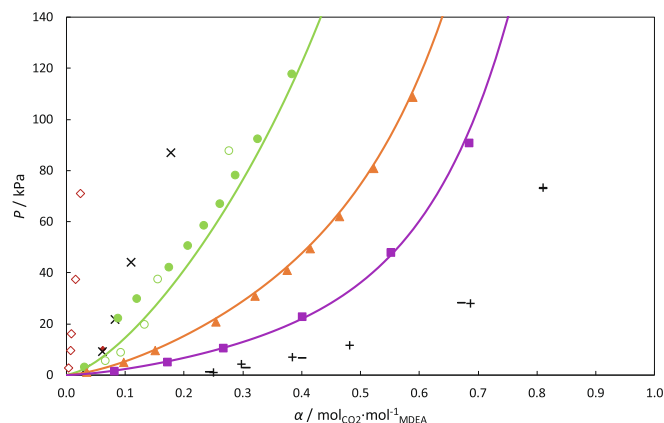


Fig. 7. Partial pressure of CO₂ as a function of CO₂ loading in MDEA (1) – MEG (2) – H₂O (3) blends at 313 K. 30 wt% MDEA – 70 wt% MEG: (◆) This work and (◇) data from Xu et al. [16], 30 wt% MDEA – 65 wt% MEG – 5 wt% H₂O: (×) Xu et al. [16], 30 wt% MDEA – 60 wt% MEG – 10 wt% H₂O: (●) This work and (○) Xu et al. [16], 30 wt% MDEA – 40 wt% MEG – 30 wt% H₂O: (▲) This work, 30 wt% MDEA – 20 wt% MEG – 50 wt% H₂O: (■) This work, 30 wt% MDEA – 70 wt% H₂O: (+) Xu et al. [16] and (–) Shen and Li [37]. The lines represent model estimations.

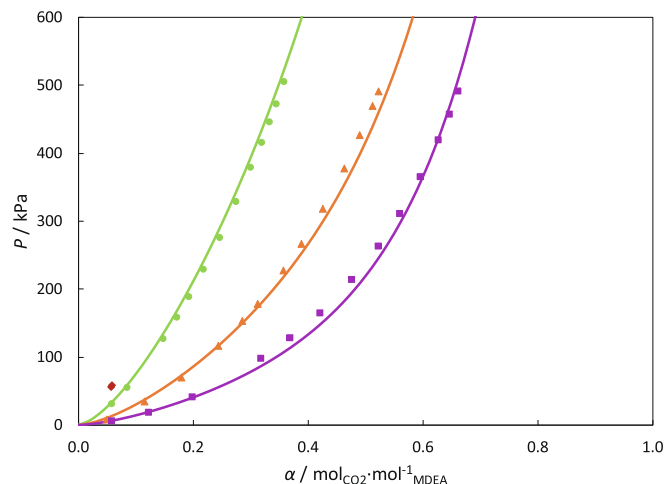


Fig. 8. Partial pressure of CO₂ as a function of CO₂ loading in MDEA (1) – MEG (2) – H₂O (3) blends at 343 K as measured in this work. (◆) 30 wt% MDEA – 70 wt% MEG, (●) 30 wt% MDEA – 60 wt% MEG – 10 wt% H₂O, (▲) 30 wt% MDEA – 40 wt% MEG – 30 wt% H₂O, (■) 30 wt% MDEA – 20 wt% MEG – 50 wt% H₂O. The lines represent model estimations.

of this study can be found in Supporting Information (Fig. S.7). We notice that the CO₂ solubility in aqueous blends of MDEA – MEG is lower than the one in aqueous MDEA. The higher the water content, the higher loading at constant pressure, as shown for both 313 K and 343 K. For example, at pressure ca. 50 kPa and 313 K, the loading is approximately 0.20, 0.41 and 0.55 at water compositions 10 wt%, 30 wt% and 50 wt% respectively and constant amine content (30 wt%).

The presence of glycol and its substitution with water therefore leads to lower solution loadings. On the one hand, the physical solubility of CO₂ into pure MEG is higher than the one in water. For example, at 323 K, $H_{CO_2, water} = 5000 \text{ kPa} \cdot \text{m}^3 \cdot \text{kmol}^{-1}$ while $H_{CO_2, MEG} = 3800 \text{ kPa} \cdot \text{m}^3 \cdot \text{kmol}^{-1}$ approximately. On the other hand, the carbon dioxide uptake from MDEA due to the reaction in the presence of water is much larger than the one due to dissolution in the solvent. We can confidently say that this behavior of decreasing solution loading with increasing glycol content is true as the water content decreases down to 10 wt%. Interestingly, the data point

obtained for the 30 wt% MDEA – 70 wt% MEG system at 313 K in the first experimental campaign coincides with the measurements performed in the presence of 10 wt% water (30 wt% MDEA – 60 wt% MEG – 10 wt% H₂O). At 343 K and Fig. 8 though, employment of 30 wt% MDEA – 70 wt% MEG solution yields indeed lower amine loadings. NMR analysis was therefore decided to be performed also for the aqueous systems.

As far as the comparison with literature data on MDEA – MEG – H₂O and 30 wt% MDEA – 70 wt% is concerned, some disagreements can be observed. For the non-aqueous system, a significant deviation can be seen between the measured solubility and the literature one. Xu et al. [16] state that they performed Karl-Fischer titration but they do not inform the amount of detected water in their systems. Lower water content in Xu et al.'s samples than in ours, could explain the observed deviations. Moreover, at amine loadings lower than 0.15 mol CO₂/mol MDEA, our data for a 30 wt% MDEA – 60 wt% MEG – 10 wt% H₂O system fall together with literature data for a 30 wt% MDEA – 65 wt% MEG – 5 wt% H₂O system. Our measurements were performed twice demonstrating a maximum ARD of 6% at 303 K and the uncertainties of the data obtained in this study are low and cannot explain the deviations from the literature.

The solid lines in Figs. 6–8 are model estimations using the so-called “soft model”, as described in Section 2.3. In the aforementioned figures, it can be seen that the model yields accurate predictions of the VLE data. The AARD is 9% for the systems 30 wt% MDEA – 60 wt% MEG – 10 wt% H₂O and 30 wt% MDEA – 20 wt% MEG – 50 wt% H₂O while for the system 30 wt% MDEA – 40 wt% MEG – 30 wt% H₂O, whose number of data points is higher than the other two systems, the AARD is 4%. The AARDs for the 70 wt% aqueous MDEA and for the 90 wt% aqueous MDEA investigated in the next section, are 3% and 5%, respectively. The model parameters are presented in Appendix B.

3.4. Comparison with highly concentrated MDEA solutions

After investigating the effect of water and after observing the effect of MEG concentration in CO₂ loading of the non-aqueous solvent, as described in Section 3.2, we decided to investigate the outcome of substituting glycol with amine. In this framework, CO₂ solubility measurements were conducted in 70 wt% MDEA – 30 wt% H₂O and in 90 wt% MDEA – 10 wt% H₂O. Similar to the experiments with aqueous MDEA – MEG, the experiments were performed at 313 K and 343 K. The obtained data are reported in Appendix A (Table A.7). At constant pressure, higher CO₂ loadings are achieved with 70 wt% aqueous MDEA than with 90 wt% aqueous MDEA. Thus, increasing amine concentrations in the solvent leads to lower absorption capacities and the CO₂ capture by the aqueous MDEA seems to be limited by water availability.

A comparison was performed between the amine and amine-glycol systems with constant water content, i.e. 10 wt% and 30 wt% water. Fig. 9 shows the results of the comparison between 30 wt% MDEA – 60 wt% MEG – 10 wt% H₂O and 90 wt% MDEA – 10 wt% H₂O in terms of CO₂ absorbed per kg of solution in order to give a more perceptible sense of the capacity of the solvent. One can observe that at constant pressure, the glycol-containing system demonstrates similar or better performance than the MDEA-H₂O system in terms of CO₂ removed per kg of solution. Although CO₂ solubility in MDEA is higher than in MEG, some additional reactivity is observed in the aqueous MDEA – MEG system, at same water content, in line with previous observations. At 313 K, this behavior is shown for pressures lower than 200 kPa. For the systems with 30 wt% water however, aqueous MDEA outperforms the glycol-containing system (Fig. S.8 in Supporting Information). It is worth mentioning that non-aqueous systems, i.e. 90 wt% MDEA – 10 wt% MEG and 70 wt% MDEA – 30 wt%

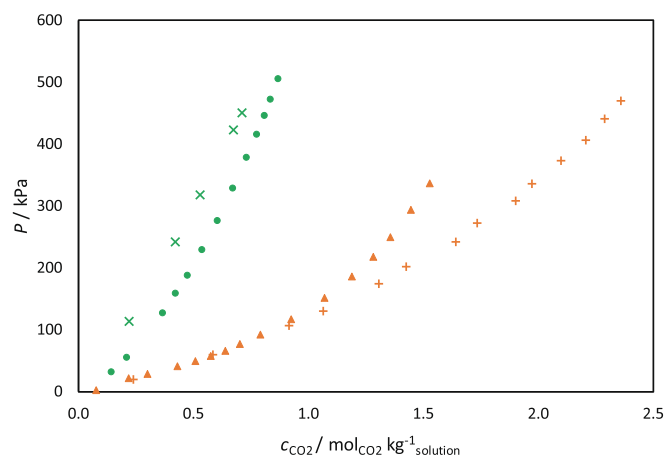
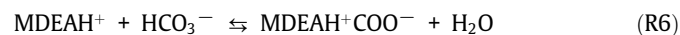
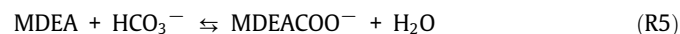
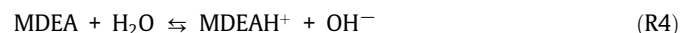
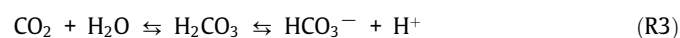
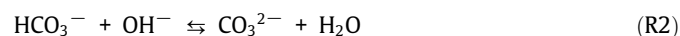


Fig. 9. Partial pressure of CO₂ as a function of CO₂ liquid phase concentration in 30 wt% MDEA – 60 wt% MEG – 10 wt% H₂O and 90 wt% MDEA – 10 wt% H₂O. (▲) denotes data obtained at 313 K with MDEA – MEG – H₂O system; (+) 313 K with MDEA – H₂O system; (●) 343 K with MDEA – MEG – H₂O system and (×) 343 K with MDEA – H₂O system.

MEG, yield lower CO₂ concentrations than their aqueous counterparts.

3.5. Chemical characterization by NMR spectroscopy

Small amounts of water were detected in our non-aqueous systems signifying a possible reaction with carbon dioxide, due to the amine protonation by the water which is present. The reactions taking place in CO₂ – MDEA – H₂O systems are listed below. Reactions R. 1 to R. 4 are usually considered in the description of chemical equilibrium, however, there are several studies in literature showing that aqueous tertiary amines can react with CO₂ to form alkyl carbonate [38,39]. Behrens et al. [40] showed by means of NMR analysis that, in CO₂ – MDEA – H₂O system, more than 10 mol% of the absorbed CO₂ is in the form of MDEA carbonate (MDEACOO⁻) (Reactions R. 5 and R. 6).



With the aim of identifying possible chemical products deriving from the addition of CO₂ in the VLE measurements of pure MEG, pure MDEA, non-aqueous MDEA – MEG blends (5 wt% MDEA – 95 wt% MEG and 50 wt% MDEA – 50 wt% MEG) and aqueous MDEA – MEG blends (30 wt% MDEA – 60 wt% MEG – 10 wt% H₂O and 30 wt% MDEA – 20 wt% MEG – 50 wt% H₂O), ¹H and ¹³C NMR experiments were performed, together with 2D NMR experiments. The interpretation of the spectra and their comparison allowed the structural characterization of the species in the solutions.

Fig. 10 shows the ¹³C NMR spectra and the signal assignment of the species at equilibrium in pure MEG, pure MDEA and 50 wt% MDEA – 50 wt% MEG in the presence of CO₂. In the up field region of the ¹³C NMR spectra, which here spans from ca. (40 to 70) × 10⁻⁶, the signals belonging to carbons nuclei –CH₂ and CH₃

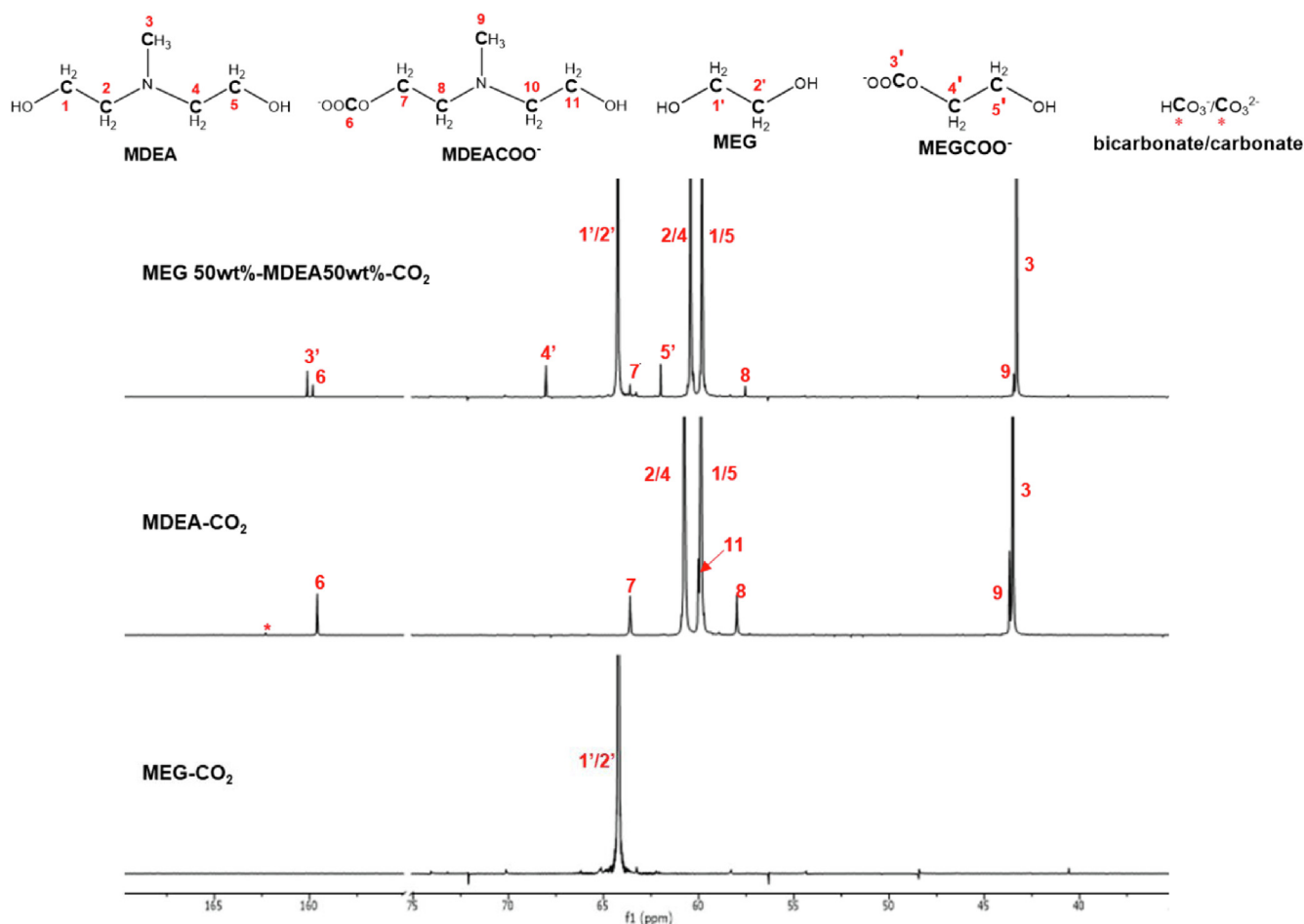


Fig. 10. ^{13}C NMR spectra of CO_2 loaded pure MEG, pure MDEA, and 50 wt% MDEA – 50 wt% MEG.

of MDEA, MEG and their derivatives are resonating. In the downfield region, here spanning from ca. $(155 \text{ to } 170) \times 10^{-6}$, the nuclei of the carbonyl carbons in the alkyl carbonates (R-O-COO^-) and bicarbonate/carbonate ($\text{HCO}_3^-/\text{CO}_3^{2-}$) are found. The downfield region is therefore very representative of the formation of CO_2 -derivatives in the samples under study. It is worth mentioning that, in the ^{13}C NMR spectra, the carbons of HCO_3^- and CO_3^{2-} appear with a common signal at an averaged chemical shift. This is due to the fact that they are two species in equilibrium, and the proton exchange between them (R. 2) is faster than the NMR time scale. The same is true for the amine and its protonated form (such as shown in R. 4 and R. 6) [41].

Looking at the species content, we observe that in CO_2 -MDEA system, in addition to MDEA itself, MDEA carbonate (MDEACOO^-) is formed, together with negligible traces of $\text{HCO}_3^-/\text{CO}_3^{2-}$. These reaction products may be the result of the presence of water traces which start a series of reactions (R. 1 to R. 6). On the contrary, in CO_2 -MEG system, neither MEG is chemically reacting with carbon dioxide nor $\text{HCO}_3^-/\text{CO}_3^{2-}$ is formed. Interestingly, in the presence of MDEA, MEG is reacting to CO_2 , giving MEG carbonate (MEGCOO^-). This is even formed in the presence of only 5 wt% MDEA (Fig. S.11 in the Supporting Information). With regard to the electroneutrality, it would be expected that the protonated form of MDEA (MDEAH^+) would act as counterion of the alkyl carbonates and $\text{HCO}_3^-/\text{CO}_3^{2-}$.

In Fig. 11, the comparison of the downfield region in the ^{13}C NMR spectra of the MEG – MDEA blends in water are reported (Full spectra are available in Fig. S.12 of the Supporting Information). In

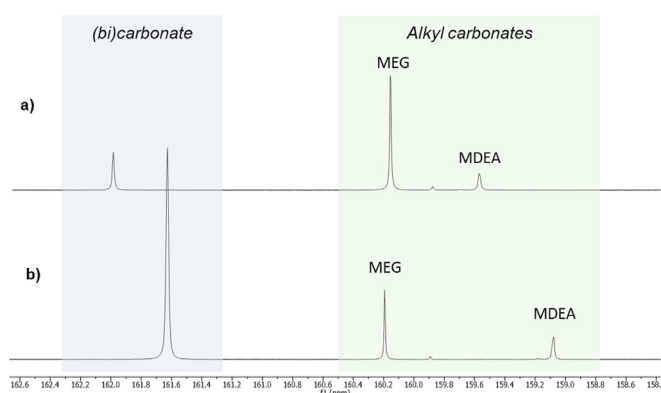


Fig. 11. Downfield region of the ^{13}C NMR spectra of CO_2 loaded a) 30 wt% MDEA – 60 wt% MEG – 10 wt% H_2O and b) 30 wt% MDEA – 20 wt% MEG – 50 wt% H_2O ; (bi)carbonate stands for $\text{HCO}_3^-/\text{CO}_3^{2-}$.

the presence of water, consistent amounts of bicarbonate/carbonate are formed, and the intensity of the peak is proportional to the amount of water in the sample. In the alkyl carbonates region, the carbonyl carbon belonging to MEG and MDEA carbonates are found, and the presence of additional weak signals may suggest the formation of additional MEG- CO_2 and MDEA- CO_2 derivatives, like e.g. MEG dicarbonate ($\text{MEG}(\text{COO}^-)_2$) and/or MDEA dicarbonate ($\text{MDEA}(\text{COO}^-)_2$). However, due to weakness and/or overlapping of these signals in the spectra, these compounds were not identified.

3.6. Hypothesis on reaction mechanisms of MEG with CO₂ in the presence of MDEA and comparison with TEG

The NMR results can explain the behavior of CO₂ – MDEA – MEG system as illustrated in Fig. 4. The solubility of carbon dioxide into MDEA – MEG is higher than in pure MEG or pure MDEA because of the chemical reaction taking place between CO₂ and MEG in the presence of MDEA. This may be the result of autoprotolysis of MEG in the alkaline environment created by the amine [42]. The absence of MEGCOO⁻ in MEG-CO₂ system indicates that, in the presence of MDEA, the hydroxyl group (-OH) of MEG is more prone to lose its proton, and it is then available to chemically bind carbon dioxide. As a result, in MDEA – MEG blends, both MDEA carbonate and MEG carbonate are formed. The chemical absorption of carbon dioxide into monoethylene glycol is a trade-off between the amount of amine available to offer the basicity required for MEG to autoprotolyze and the amount of MEG available for autoprotolysis.

The solvent composition between 30 and 50 wt% MDEA where we observed the reduced CO₂ solubility upon addition of amine, is probably the limits of this trade-off. From that point towards leaner-in-glycol systems, smaller amount of MEG autoprotolyzes and therefore the Henry's constant increases, for a given temperature. Moreover, the overlapping data for 30 wt% MDEA – 60 wt% MEG – 10 wt% H₂O and 30 wt% MDEA – 70 wt% MEG discussed earlier can be attributed to the CO₂ – MEG reaction and MEG carbonate formation in the MDEA – MEG system which is probably in the same extent as the combined MEG carbonate and MDEA carbonate formation in the aqueous system.

Barzagli et al. [43] have also reported the presence of the glycol carbonate in their studies of CO₂ solubility into non-aqueous MDEA – MEG – propanol systems and discussed the ability of alcohols to absorb carbon dioxide when in the presence of a base. For these phenomena to take place, only tertiary amines should serve as a base. If a primary or a secondary amine was used, the glycol carbonate formation would be hindered by the stable carbamate formation. On the contrary, tertiary amines cannot form carbamates, making them ideal for selective removal of hydrogen sulfide over carbon dioxide, since H₂S can react directly with the amine. The increased reactivity of MDEA – MEG blends for the selective removal of H₂S over CO₂ is also discussed by Dag Eimer [42].

The degree of autoprotolysis of a compound is informed by its dissociation constant (autoprotolysis constant, K_{ap}). The higher the K_{ap} (the lower the $pK_{ap} = -\log_{10}(K_{ap})$), the higher the tendency of releasing a proton from the -OH group. As suggested by Eimer [42], amine-MEG mixtures should have higher reactivity than amine-TEG blends, due to the lower pK_{ap} value of MEG. The pK_{ap} values for MEG and TEG are approximately 16 and 18.5, respectively [42]. Thus, the degree of autoprotolysis in TEG is lower than that in MEG and, it would be expected that the solubility of CO₂ in MDEA – TEG mixtures would be lower than in MDEA – MEG mixtures at the same concentrations.

To confirm this theory, we performed an additional VLE experimental campaign for the system CO₂ – MDEA – TEG. The VLE data for the TEG-containing systems are presented in Table A.8 in the Appendix and the required for the data processing measured densities can be found in Table S.1 in the Supporting Information. Available literature data for the density of pure TEG were compared with our measurements (Fig. 12). The obtained experimental points follow the behavior of the literature data, except for the data of Sagdeev et al. [44] and Tawfik and Teja [45], which are consistently higher than the rest of the data. The uncertainties reported by the different authors in most cases are higher than the deviations observed. These deviations can be attributed to the different chemical purity as well as to possible unwanted humidity absorption from the air due to the high hygroscopicity of TEG. However,

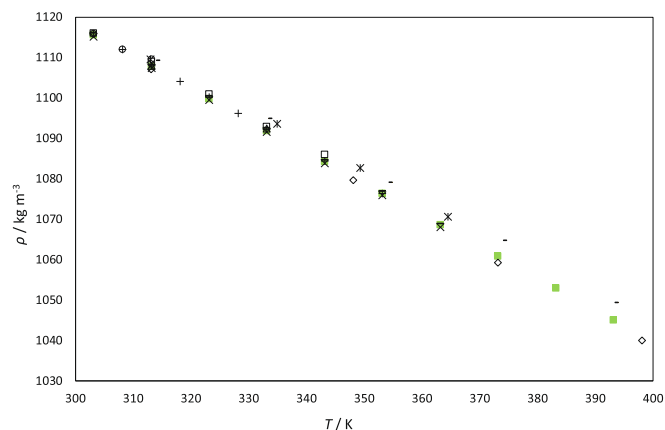


Fig. 12. Density of pure TEG as a function of temperature at atmospheric pressure. (x) Pereira et al. (2019) [46], (—) Crespo et al. (2017) [47], (✱) Sagdeev et al. (2011) [44], (□) Tsai et al. (2009) [48], (○) Sastry et al. (2008) [49], (+) Valtz et al. (2004) [50], (◇) Steele et al. (2002) [51], (Δ) Kumagai et al. (1993) [52], (-) Tawfik and Teja (1989) [45], (■) This work.

the calculated absolute relative deviations (ARD) are low, ranging from 0.01% to 0.15%.

In this study of TEG-containing systems, we first measured the carbon dioxide solubility in pure TEG and compared our results with literature values [53,54] (Fig. 13). It is observed that the obtained data are in good agreement with the literature. Moreover, Tan et al. [18] reported Henry's constant of CO₂ in pure TEG. Their data agree with the measured Henry's constants in this work, and any small deviations observed are well within experimental uncertainty. A graphical comparison is provided in Supporting Information (Fig. S.10).

Moreover, we studied MDEA – TEG blends in two different compositions, 30 wt% MDEA – 70 wt% TEG and 50 wt% MDEA – 50 wt% TEG. These compositions were selected in order to allow for a direct comparison with MDEA – MEG mixtures at same amine weight fraction.

The following figure (Fig. 14) depicts Henry's constant as a function of temperature and composition in MDEA – MEG and

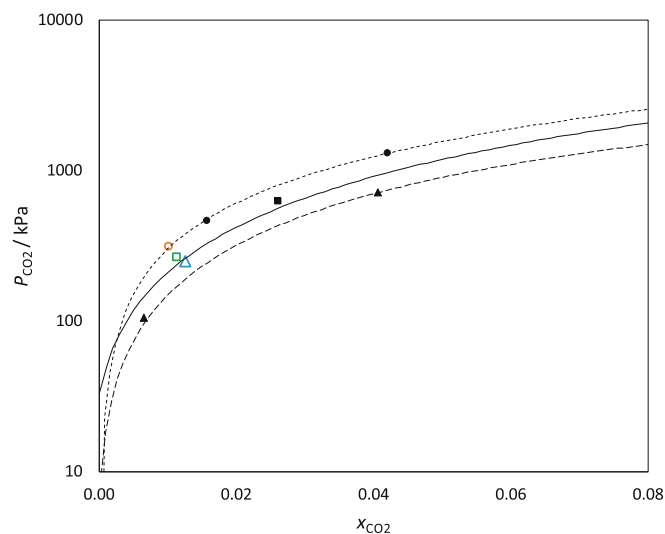


Fig. 13. Partial pressure of CO₂ as a function of CO₂ solubility and temperature in pure TEG. Triangles denote 323 K, squares denote 343 K and circles denote 373 K. Filled symbols are literature values; (●), (▲) from Jou et al. [53] and (■) from Wise and Chapoy [54]. Hollow symbols are data obtained in this work. Tendency curves are drawn: dashed line (---) for 323 K, solid line (—) for 343 K and dotted line (····) for 373 K.

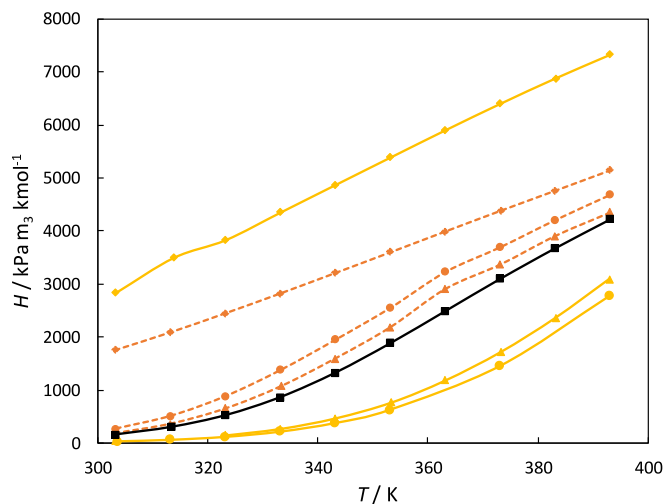


Fig. 14. Henry's constants as a function of temperature for MDEA – MEG and MDEA – TEG systems. Tendency curves are drawn: (—•—, dashed dot line) MEG-containing systems, (....., dotted line) TEG-containing systems. (◆) Pure glycol, (●) 30 wt% MDEA – 70 wt% glycol, (▲) 50 wt% MDEA – 50 wt% glycol, (■) Pure MDEA.

MDEA – TEG systems. Henry's constant is higher in MDEA – TEG blends than MDEA – MEG blends, while it is lower in pure TEG than in pure MEG. These results are therefore in agreement with the theory, since the degree of autoprotolysis of TEG is lower than that of MEG, leading to lower CO_2 solubility. In addition to this, the Henry's constant values in MDEA – TEG blends lie between the Henry's constants in pure TEG and pure MDEA suggesting that CO_2 is absorbed mainly physically in the solvent. However, some chemical effects are also present as indicated by the results of an isothermal experiment at 313 K for the 50 wt% MDEA – 50 wt% TEG system where a non-linear relation between P - x is pronounced (Fig. S.9). Based on the NMR data obtained in this study, there is no formation of TEG carbonate (TEGCOO^-) in CO_2 – TEG system, as it was also observed in CO_2 – MEG. In CO_2 – MDEA – TEG systems, MDEACOO^- was found, but the presence of TEGCOO^- was not clear. Due to overlapping signals and crowded-signals spectra, some low-intensity signals were not assigned, but it is expected that the correspondent molecules would be in negligible amounts. Therefore, the chemical effects observed in MDEA – TEG systems are mainly due to the reaction of CO_2 with MDEA in the presence of water traces. All relevant spectra are available in [Supporting Information](#) (Fig. S.13).

The findings of this work are important for the industrial application of an MDEA – MEG mixture for the combined hydrogen sulfide removal and hydrate control. For a successful design and trouble-free operations, the knowledge of the amount of co-absorbed carbon dioxide into the solvent through the known aqueous amine mechanism as well as through its reaction with MEG is necessary. The importance of this work lies in the need to account for the CO_2 absorbed in the glycol as well in the amine during solvent regeneration. As proven from the data presented for CO_2 – MDEA – TEG systems, these implications are in a significantly lesser extent in the systems using TEG.

4. Conclusions

Aqueous and non-aqueous solvents composed by MDEA and MEG are promising for the simultaneous H_2S removal and hydrate

control in natural gas. Since CO_2 co-exists with H_2S in natural gas streams, the solubility of carbon dioxide in non-aqueous and aqueous MDEA – MEG systems was investigated in this work.

VLE data were obtained at temperatures from 303 K to 393 K and pressures up to 600 kPa. It was found that the absorption capacity of the aqueous solvents decreases with increasing glycol content and substitution of water, at constant amine concentration. Increasing amine content up to 90 wt% in aqueous MDEA systems, also leads to lower solvent CO_2 loadings.

In the non-aqueous solvents, a transition phase was observed at compositions between 30 and 50 wt% MDEA – MEG. CO_2 solubility increases with amine concentration up to this transition area, after which the solubility starts decreasing. This behavior is attributed to the CO_2 capture through chemical reaction of CO_2 with MEG in the presence of MDEA, as a result of MEG autoprotolysis in the alkaline environment of the amine. This theory is supported by supplementary VLE data obtained for MDEA – TEG systems.

NMR experiments proved the formation of glycol carbonate, both in non-aqueous and aqueous MDEA – MEG blends. MDEA carbonate was also identified both in single and blended MDEA, which is probably due to the small amounts of water found in our non-aqueous solvents. The CO_2 solubility in aqueous blends of MDEA – MEG is generally higher than the one in their non-aqueous counterparts. However, similar absorption capacities can be observed for aqueous systems containing less than 10 wt% water and non-aqueous systems.

The CO_2 uptake by the glycol demonstrated in this work is important knowledge for the application of aqueous or non-aqueous MDEA – MEG mixtures for the combined removal of H_2S and hydrate control, and specifically for the solvent regeneration.

CRedit authorship contribution statement

Eirini Skylogianni: Conceptualization, Investigation, Validation, Writing - original draft, Writing - review & editing. **Cristina Perinu:** Investigation, Writing - review & editing. **Blanca Y. Cervantes Gameros:** Investigation. **Hanna K. Knuutila:** Conceptualization, Investigation, 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

All VLE data obtained in this work are presented in this section.

Table A.1

Measured mole fraction solubility x_{CO_2} and Henry's constant H for CO_2 in water as a function of temperature T and pressure (total pressure P_{tot} , residual pressure P_{res} and their difference, CO_2 partial pressure P_{CO_2}).^a

T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	H	$u(H)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	H	$u(H)$
K	kPa	kPa	kPa		$\cdot 10^2$	kPa $\text{m}^3 \text{kmol}^{-1}$		K	kPa	kPa	kPa		$\cdot 10^2$	kPa $\text{m}^3 \text{kmol}^{-1}$	
VLE 1								VLE 2							
303.1	200.3	4.6	195.7	0.108	0.015	3281	454	303.1	168.2	5.3	162.9	0.087	0.006	3389	512
313.2	224.0	7.6	216.4	0.096	0.015	4108	648	313.2	188.6	8.7	180.0	0.077	0.006	4234	727
323.2	247.0	12.4	234.6	0.086	0.015	4952	873	323.2	209.3	13.6	195.6	0.069	0.006	5145	992
333.2	271.4	19.5	251.8	0.079	0.015	5854	1141	343.2	255.8	32.3	223.5	0.058	0.006	7046	1645
343.1	298.1	30.5	267.7	0.073	0.015	6748	1435	353.2	284.5	48.5	236.0	0.055	0.006	7981	2013
353.2	329.6	46.6	283.0	0.068	0.015	7679	1770	363.2	318.8	71.9	246.9	0.053	0.006	8733	2328
363.2	366.4	69.4	297.1	0.065	0.015	8527	2100	313.2	167.2	8.0	159.2	0.069	0.013	4203	798
303.1	230.5	4.6	225.9	0.122	0.016	3345	442	333.2	206.4	20.6	185.8	0.057	0.013	6001	1401
313.2	256.5	7.8	248.6	0.108	0.016	4196	637	353.1	256.4	47.8	208.6	0.050	0.013	7802	2129
323.2	281.6	12.8	268.8	0.097	0.016	5074	866	373.1	330.3	101.7	228.5	0.046	0.014	9359	2860
333.2	307.9	20.4	287.5	0.088	0.016	5988	1135	393.2	445.7	199.7	246.0	0.045	0.015	10481	3496
343.2	336.2	31.4	304.8	0.081	0.017	6904	1432	303.2	143.9	5.3	138.6	0.075	0.014	3362	640
353.2	369.4	46.9	322.5	0.075	0.017	7956	1813	313.1	160.6	8.6	152.0	0.066	0.014	4183	905
364.7	414.1	69.4	344.7	0.067	0.016	9618	2514	333.2	196.8	21.3	175.5	0.054	0.014	5935	1584
303.2	138.9	4.3	134.6	0.073	0.016	3325	722	353.1	244.1	48.5	195.6	0.047	0.015	7656	2383
313.2	155.2	7.5	147.7	0.065	0.016	4153	1027	373.1	315.5	102.9	212.6	0.044	0.015	9011	3099
333.2	190.2	20.2	170.0	0.053	0.016	5868	1784	393.1	429.8	201.1	228.7	0.043	0.016	10154	3829
353.3	235.8	47.6	188.2	0.047	0.016	7374	2554	-	-	-	-	-	-	-	-
373.2	308.9	100.1	208.8	0.041	0.017	9689	4035	-	-	-	-	-	-	-	-
392.5	411.6	188.1	223.5	0.040	0.018	10783	4814	-	-	-	-	-	-	-	-

^a Standard uncertainties are reported (level of confidence 0.68). Standard uncertainty for temperature is $u(T) = 0.1$ K, for total and residual pressure is $u(P_{\text{tot}}) = u(P_{\text{res}}) = 0.9$ kPa and for CO_2 pressure is $u(P_{\text{CO}_2}) = 1.3$ kPa.

Table A.2

Measured mole fraction solubility x_{CO_2} , loading α and Henry's constant H for CO_2 in MDEA (1) – MEG (2) blends as a function of weight fraction w of unloaded solvent, temperature T and pressure (total pressure P_{tot} , residual pressure P_{res} and their difference, CO_2 partial pressure P_{CO_2}).^a

w_1	$u(w_1)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	α	$u(\alpha)$	H	$u(H)$		
		K	kPa	kPa	kPa			$\text{mol}_{\text{CO}_2} \text{mol}_{\text{MDEA}}^{-1}$		kPa $\text{m}^3 \text{kmol}^{-1}$			
0.000	0.000	303.2	200.5	2.3	198.2	0.0039	0.0004	-	-	2835	284		
		313.7	223.8	2.5	221.3	0.0036	0.0004	-	-	3498	389		
		323.2	236.8	2.8	234.0	0.0035	0.0004	-	-	3833	440		
		333.2	253.9	3.1	250.8	0.0033	0.0004	-	-	4355	530		
		343.2	270.4	3.5	266.9	0.0031	0.0004	-	-	4875	624		
		353.2	286.3	3.9	282.4	0.0030	0.0004	-	-	5393	720		
		363.2	301.7	4.5	297.2	0.0029	0.0004	-	-	5907	820		
		373.1	317.2	5.5	311.7	0.0028	0.0004	-	-	6406	918		
		383.2	332.8	7.1	325.7	0.0028	0.0004	-	-	6886	1013		
		393.2	348.7	9.6	339.1	0.0027	0.0004	-	-	7333	1100		
		0.050	0.001	303.2	42.9	1.8	41.1	0.0141	0.0005	0.535	0.024	166	8
				313.1	66.2	1.9	64.3	0.0132	0.0005	0.501	0.024	279	13
323.2	97.6			2.0	95.6	0.0121	0.0005	0.458	0.024	457	22		
333.1	134.0			2.2	131.8	0.0108	0.0005	0.411	0.023	709	38		
343.2	173.2			2.4	170.8	0.0096	0.0005	0.363	0.023	1048	63		
353.2	212.5			2.8	209.7	0.0084	0.0006	0.318	0.023	1479	103		
363.2	250.1			3.4	246.7	0.0074	0.0006	0.279	0.023	2001	161		
373.1	285.4			4.4	281.0	0.0065	0.0006	0.246	0.023	2610	241		
383.1	319.2			5.8	313.4	0.0058	0.0006	0.217	0.023	3321	352		
393.2	354.4			8.1	346.4	0.0050	0.0006	0.190	0.024	4239	521		
0.100	0.001			303.2	10.7	1.9	8.8	0.0096	0.0004	0.178	0.008	53	6
				313.2	18.8	2.2	16.5	0.0094	0.0004	0.174	0.008	103	7
		323.2	32.1	2.5	29.7	0.0091	0.0004	0.168	0.008	193	11		
		333.1	52.3	2.8	49.5	0.0086	0.0004	0.159	0.008	342	19		
		343.2	79.9	3.5	76.4	0.0080	0.0004	0.147	0.008	575	33		
		353.1	113.6	4.6	109.0	0.0073	0.0004	0.134	0.009	909	58		
		363.1	151.3	5.9	145.4	0.0065	0.0004	0.120	0.009	1365	97		
		373.1	190.6	8.0	182.6	0.0058	0.0004	0.106	0.009	1948	158		
		383.3	230.1	10.8	219.3	0.0051	0.0005	0.094	0.009	2667	248		
		393.2	266.9	15.2	251.7	0.0044	0.0005	0.081	0.009	3557	386		
		0.300	0.001	303.5	7.8	2.3	5.5	0.0114	0.0004	0.063	0.003	32	5
				313.1	12.6	2.5	10.1	0.0112	0.0004	0.062	0.003	60	6
323.1	21.7			2.7	19.0	0.0110	0.0005	0.061	0.003	115	7		
333.2	36.8			2.9	33.9	0.0106	0.0005	0.059	0.003	214	11		
343.1	59.3			3.2	56.1	0.0101	0.0005	0.056	0.003	376	19		
353.1	90.0			3.7	86.4	0.0094	0.0005	0.052	0.003	627	33		
373.2	169.2			6.0	163.3	0.0078	0.0005	0.043	0.003	1454	92		

(continued on next page)

Table A.2 (continued)

w_1	$u(w_1)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	α	$u(\alpha)$	H	$u(H)$
		K	kPa	kPa	kPa					$\text{mol}_{\text{CO}_2} \text{mol}_{\text{MDEA}}^{-1}$	$\text{kPa m}^3 \text{kmol}^{-1}$
0.500	0.002	393.2	257.4	11.1	246.3	0.0063	0.0005	0.035	0.003	2780	226
		303.1	13.0	2.1	11.0	0.0200	0.0006	0.060	0.002	41	4
		323.2	39.9	2.3	37.5	0.0188	0.0007	0.056	0.002	151	6
		333.2	65.9	2.5	63.4	0.0177	0.0006	0.053	0.002	274	11
		343.2	101.5	2.7	98.9	0.0162	0.0006	0.048	0.002	471	20
		353.3	145.0	2.9	142.1	0.0144	0.0006	0.043	0.002	767	36
		363.1	192.3	3.3	189.0	0.0126	0.0006	0.037	0.002	1178	64
		373.2	239.7	4.0	235.7	0.0109	0.0006	0.032	0.002	1713	109
		383.2	283.9	5.3	278.6	0.0095	0.0007	0.028	0.002	2353	176
		393.1	324.3	7.3	317.0	0.0083	0.0007	0.024	0.002	3084	268
0.700	0.003	303.2	10.9	2.4	8.6	0.0132	0.0006	0.024	0.001	56	6
		313.6	21.1	2.6	18.5	0.0129	0.0006	0.024	0.001	126	9
		323.2	30.9	3.0	28.0	0.0125	0.0006	0.023	0.001	198	11
		333.2	50.4	3.2	47.2	0.0119	0.0006	0.022	0.001	355	19
		343.2	77.4	3.6	73.8	0.0110	0.0006	0.020	0.001	605	34
		353.2	110.7	4.0	106.8	0.0099	0.0006	0.018	0.001	975	61
		363.2	147.2	4.6	142.5	0.0089	0.0006	0.016	0.001	1472	103
		373.1	183.8	5.6	178.2	0.0079	0.0006	0.014	0.001	2090	166
		383.2	218.2	7.2	211.0	0.0070	0.0006	0.013	0.001	2796	252
		393.1	249.8	9.6	240.2	0.0063	0.0006	0.012	0.001	3549	358
0.900	0.005	303.1	18.5	1.6	16.8	0.0162	0.0006	0.0200	0.001	107	7
		323.2	53.9	2.0	51.9	0.0147	0.0007	0.0181	0.001	370	19
		333.2	83.4	2.1	81.2	0.0135	0.0007	0.0166	0.001	635	35
		343.2	119.0	2.3	116.7	0.0122	0.0007	0.0149	0.001	1024	62
		353.2	156.7	2.6	154.1	0.0108	0.0007	0.0132	0.001	1535	105
		363.2	192.5	3.1	189.5	0.0096	0.0007	0.0118	0.001	2139	166
		373.2	224.9	3.7	221.1	0.0085	0.0007	0.0104	0.001	2840	251
		383.2	253.3	4.8	248.5	0.0079	0.0007	0.0097	0.001	3465	333
		393.1	278.1	6.4	271.7	0.0071	0.0007	0.0087	0.001	4260	460
		1.000	0.006	303.1	25.0	2.6	22.4	0.0160	0.0007	0.016	0.001
313.3	42.9			2.8	40.1	0.0152	0.0007	0.015	0.001	302	17
323.2	67.2			3.0	64.2	0.0141	0.0007	0.014	0.001	525	30
333.2	98.4			3.2	95.2	0.0128	0.0007	0.013	0.001	868	54
343.2	132.5			3.4	129.2	0.0114	0.0007	0.012	0.001	1331	93
353.2	165.6			3.5	162.1	0.0102	0.0008	0.010	0.001	1888	149
363.2	195.2			3.8	191.4	0.0092	0.0008	0.009	0.001	2494	219
373.2	221.0			4.3	216.7	0.0085	0.0008	0.009	0.001	3103	300
383.2	243.3			5.0	238.3	0.0079	0.0008	0.008	0.001	3681	383
393.1	263.2			6.1	257.2	0.0075	0.0007	0.008	0.001	4224	466

^a Standard uncertainties are reported (level of confidence 0.68). Standard uncertainty for temperature is $u(T) = 0.1$ K, for total and residual pressure is $u(P_{\text{tot}}) = u(P_{\text{res}}) = 0.9$ kPa and for CO_2 pressure is $u(P_{\text{CO}_2}) = 1.3$ kPa.

Table A.3

Measured mole fraction solubility x_{CO_2} , loading α and Henry's constant H for CO_2 in MDEA (1) – MEG (2) blends as a function of weight fraction w of unloaded solvent and pressure (total pressure P_{tot} , residual pressure P_{res} and their difference, CO_2 partial pressure P_{CO_2}) at temperatures of 313 K and 343 K.^a

w_1	$u(w_1)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	α	$u(\alpha)$	H	$u(H)$
		K	kPa	kPa	kPa					$\text{mol}_{\text{CO}_2} \text{mol}_{\text{MDEA}}^{-1}$	$\text{kPa m}^3 \text{kmol}^{-1}$
0.000	0.000	313.1	66.0	2.2	63.8	0.0011	0.0005	–	–	3188	1560
		313.2	133.9	2.2	131.7	0.0023	0.0008	–	–	3187	1074
		313.1	194.3	2.2	192.1	0.0034	0.0008	–	–	3158	737
		313.2	254.4	2.2	252.1	0.0045	0.0008	–	–	3145	572
		313.2	315.8	2.2	313.5	0.0056	0.0008	–	–	3157	480
		313.2	367.8	2.2	365.6	0.0065	0.0009	–	–	3173	436
		313.1	413.6	2.2	411.4	0.0072	0.0009	–	–	3186	407
		313.1	456.6	2.2	454.4	0.0079	0.0009	–	–	3209	387
		313.1	503.9	2.2	501.7	0.0087	0.0009	–	–	3219	366
		343.2	61.9	2.9	59.1	0.0007	0.0005	–	–	4663	3299
		343.1	113.3	2.9	110.4	0.0014	0.0007	–	–	4663	2502
		343.2	152.4	2.9	149.5	0.0018	0.0007	–	–	4667	1865
		343.2	200.0	2.9	197.1	0.0024	0.0007	–	–	4676	1437
		343.2	251.5	2.9	248.7	0.0030	0.0007	–	–	4691	1169
		343.2	305.1	2.9	302.3	0.0037	0.0008	–	–	4721	999
		343.2	348.7	2.9	345.9	0.0042	0.0008	–	–	4704	897
		343.1	400.2	2.9	397.4	0.0048	0.0008	–	–	4701	809
		343.1	455.3	2.9	452.5	0.0055	0.0008	–	–	4739	750
		343.2	505.3	2.9	502.4	0.0061	0.0009	–	–	4742	703
		343.1	548.2	2.9	545.4	0.0066	0.0009	–	–	4738	669

Table A.3 (continued)

w_1	$u(w_1)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	α	$u(\alpha)$	H	$u(H)$
		K	kPa	kPa	kPa				$\text{mol}_{\text{CO}_2} \text{mol}_{\text{MDEA}}^{-1}$	$\text{kPa m}^3 \text{kmol}^{-1}$	
0.500	0.002	313.1	14.1	2.1	11.9	0.0129	0.0006	0.038	0.002	70	6
		313.1	29.4	2.1	27.2	0.0238	0.0008	0.071	0.003	86	4
		313.1	53.4	2.1	51.2	0.0380	0.0009	0.115	0.003	99	4
		313.1	78.7	2.1	76.5	0.0505	0.0009	0.155	0.004	110	3
		313.2	108.2	2.1	106.0	0.0631	0.0010	0.197	0.005	121	3
		313.2	137.8	2.1	135.6	0.0739	0.0010	0.233	0.005	130	3
		313.2	167.1	2.1	164.9	0.0833	0.0010	0.265	0.006	139	3
		313.2	196.0	2.1	193.9	0.0916	0.0011	0.294	0.006	147	3
		313.2	226.6	2.1	224.5	0.0994	0.0011	0.322	0.007	156	4
		313.2	258.6	2.1	256.4	0.1066	0.0012	0.349	0.007	164	4
		313.1	286.7	2.1	284.6	0.1126	0.0012	0.371	0.007	172	4
		313.2	314.8	2.1	312.6	0.1182	0.0013	0.391	0.008	179	4
		313.2	342.3	2.1	340.2	0.1231	0.0014	0.410	0.008	186	4
		313.2	370.0	2.1	367.9	0.1276	0.0014	0.427	0.008	193	4
		313.2	395.0	2.1	392.8	0.1315	0.0015	0.442	0.009	199	4
313.2	417.4	2.1	415.2	0.1348	0.0015	0.455	0.009	204	5		
1.000	0.006	313.1	27.9	2.3	25.6	0.0099	0.0010	0.010	0.001	296	34
		313.1	45.8	2.3	43.6	0.0161	0.0014	0.016	0.002	309	30
		313.1	75.1	2.3	72.8	0.0259	0.0017	0.027	0.002	318	23
		313.1	98.3	2.3	96.0	0.0337	0.0019	0.035	0.002	320	20
		313.2	139.8	2.3	137.5	0.0472	0.0020	0.050	0.002	323	16
		313.2	169.4	2.3	167.1	0.0565	0.0021	0.060	0.003	324	15
		313.1	211.6	2.3	209.3	0.0689	0.0021	0.074	0.003	329	13
		313.1	250.4	2.3	248.2	0.0796	0.0021	0.086	0.003	334	13
		313.2	284.1	2.3	281.8	0.0881	0.0022	0.097	0.003	339	12
		313.2	315.3	2.3	313.0	0.0956	0.0022	0.106	0.004	344	12
		313.1	349.2	2.3	346.9	0.1031	0.0023	0.115	0.004	351	12
		343.1	58.2	4.3	54.0	0.0059	0.0011	0.006	0.001	1078	198
		343.2	101.7	4.3	97.4	0.0103	0.0015	0.010	0.002	1110	164
		343.1	130.2	4.3	125.9	0.0132	0.0018	0.013	0.002	1120	159
		343.2	173.2	4.3	169.0	0.0174	0.0020	0.018	0.002	1132	140
		343.2	222.9	4.3	218.6	0.0222	0.0022	0.023	0.002	1144	124
		343.1	247.8	4.3	243.6	0.0248	0.0024	0.025	0.003	1138	122
		343.2	301.9	4.3	297.6	0.0298	0.0026	0.031	0.003	1150	111
		343.2	351.0	4.3	346.8	0.0344	0.0027	0.036	0.003	1159	105
		343.2	372.5	4.3	368.3	0.0364	0.0029	0.038	0.003	1160	106

^a Standard uncertainties are reported (level of confidence 0.68). Standard uncertainty for temperature is $u(T) = 0.1$ K, for total and residual pressure is $u(P_{\text{tot}}) = u(P_{\text{res}}) = 0.9$ kPa and for CO_2 pressure is $u(P_{\text{CO}_2}) = 1.3$ kPa.

Table A.4

Measured mole fraction solubility x_{CO_2} , loading α and Henry's constant H for CO_2 in MDEA (1) – MEG (2) – H_2O (3) blends in two repeated experiments as a function of weight fraction w of unloaded solvent, temperature T and pressure (total pressure P_{tot} , residual pressure P_{res} and their difference, CO_2 partial pressure P_{CO_2}).^a Experiment A denotes the first experiment, also tabulated in Table A.2 for MDEA-MEG systems and in Table A.5 for MDEA-MEG- H_2O system. Experiment B is the repeated experiment.

w_1	$u(w_1)$	w_2	$u(w_2)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	α	$u(\alpha)$	H	$u(H)$
				K	kPa	kPa	kPa				$\text{mol}_{\text{CO}_2} \cdot \text{mol}_{\text{MDEA}}^{-1}$	$\text{kPa m}^3 \text{kmol}^{-1}$	
0.000	0.000	1.000	0.006	Experiment A									
				303.2	200.5	2.3	198.2	0.0039	0.0004	–	–	2835	284
				313.7	223.8	2.5	221.3	0.0036	0.0004	–	–	3498	389
				323.2	236.8	2.8	234.0	0.0035	0.0004	–	–	3833	440
				333.2	253.9	3.1	250.8	0.0033	0.0004	–	–	4355	530
				343.2	270.4	3.5	266.9	0.0031	0.0004	–	–	4875	624
				353.2	286.3	3.9	282.4	0.0030	0.0004	–	–	5393	720
				363.2	301.7	4.5	297.2	0.0029	0.0004	–	–	5907	820
				373.1	317.2	5.5	311.7	0.0028	0.0004	–	–	6406	918
				383.2	332.8	7.1	325.7	0.0028	0.0004	–	–	6886	1013
				393.2	348.7	9.6	339.1	0.0027	0.0004	–	–	7333	1100
				Experiment B									
				303.2	207.2	2.0	205.2	0.0042	0.0006	–	–	2749	376
				313.2	223.1	2.2	220.9	0.0039	0.0006	–	–	3222	478
				333.2	252.7	2.6	250.1	0.0034	0.0006	–	–	4217	720
353.2	280.0	3.7	276.3	0.0031	0.0006	–	–	5183	977				
373.2	306.7	5.7	300.9	0.0029	0.0006	–	–	6139	1251				
393.2	334.8	10.9	323.9	0.0027	0.0006	–	–	6991	1495				
0.050	0.001	0.950	0.001	Experiment A									
				303.2	42.9	1.8	41.1	0.0141	0.0005	0.535	0.024	166	8
313.1	66.2	1.9	64.3	0.0132	0.0005	0.501	0.024	279	13				

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Table A.4 (continued)

w_1	$u(w_1)$	w_2	$u(w_2)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	α	$u(\alpha)$	H	$u(H)$
				K	kPa	kPa	kPa			$\text{mol}_{\text{CO}_2} \cdot \text{mol}_{\text{MDEA}}^{-1}$		$\text{kPa m}^3 \text{ kmol}^{-1}$	
				323.2	97.6	2.0	95.6	0.0121	0.0005	0.458	0.024	457	22
				333.1	134.0	2.2	131.8	0.0108	0.0005	0.411	0.023	709	38
				343.2	173.2	2.4	170.8	0.0096	0.0005	0.363	0.023	1048	63
				353.2	212.5	2.8	209.7	0.0084	0.0006	0.318	0.023	1479	103
				363.2	250.1	3.4	246.7	0.0074	0.0006	0.279	0.023	2001	161
				373.1	285.4	4.4	281.0	0.0065	0.0006	0.246	0.023	2610	241
				383.1	319.2	5.8	313.4	0.0058	0.0006	0.217	0.023	3321	352
				393.2	354.4	8.1	346.4	0.0050	0.0006	0.190	0.024	4239	521
				Experiment B									
				313.2	64.5	16.7	62.8	0.0128	0.0005	0.487	0.023	281	13
				323.2	96.5	17.6	94.8	0.0117	0.0005	0.445	0.023	467	22
				333.2	133.8	19.8	131.8	0.0105	0.0005	0.398	0.023	732	39
				343.2	173.6	22.5	171.4	0.0093	0.0005	0.351	0.023	1088	66
				353.2	214.0	27.6	211.2	0.0081	0.0005	0.307	0.023	1546	109
				363.2	252.6	35.1	249.1	0.0071	0.0006	0.268	0.023	2104	172
				373.2	288.4	45.3	283.9	0.0062	0.0006	0.236	0.023	2750	259
				383.1	321.3	61.6	315.1	0.0056	0.0006	0.209	0.023	3463	371
				393.1	352.4	84.9	343.9	0.0050	0.0006	0.188	0.023	4248	513
0.100	0.001	0.900	0.001	Experiment A									
				303.2	10.7	1.9	8.8	0.0096	0.0004	0.178	0.008	53	6
				313.2	18.8	2.2	16.5	0.0094	0.0004	0.174	0.008	103	7
				323.2	32.1	2.5	29.7	0.0091	0.0004	0.168	0.008	193	11
				333.1	52.3	2.8	49.5	0.0086	0.0004	0.159	0.008	342	19
				343.2	79.9	3.5	76.4	0.0080	0.0004	0.147	0.008	575	33
				353.1	113.6	4.6	109.0	0.0073	0.0004	0.134	0.009	909	58
				363.1	151.3	5.9	145.4	0.0065	0.0004	0.120	0.009	1365	97
				373.1	190.6	8.0	182.6	0.0058	0.0004	0.106	0.009	1948	158
				383.3	230.1	10.8	219.3	0.0051	0.0005	0.094	0.009	2667	248
				393.2	266.9	15.2	251.7	0.0044	0.0005	0.081	0.009	3557	386
				Experiment B									
				303.2	13.0	2.2	10.8	0.0108	0.0004	0.200	0.009	58	5
				323.2	40.1	2.6	37.4	0.0102	0.0004	0.188	0.008	218	11
				343.2	97.4	3.2	94.2	0.0088	0.0004	0.163	0.008	639	33
				353.2	135.8	3.6	132.1	0.0080	0.0004	0.148	0.008	996	56
0.300	0.001	0.700	0.001	Experiment A									
				303.5	7.8	2.3	5.5	0.0114	0.0004	0.063	0.003	32	5
				313.1	12.6	2.5	10.1	0.0112	0.0004	0.062	0.003	60	6
				323.1	21.7	2.7	19.0	0.0110	0.0005	0.061	0.003	115	7
				333.2	36.8	2.9	33.9	0.0106	0.0005	0.059	0.003	214	11
				343.1	59.3	3.2	56.1	0.0101	0.0005	0.056	0.003	376	19
				353.1	90.0	3.7	86.4	0.0094	0.0005	0.052	0.003	627	33
				373.2	169.2	6.0	163.3	0.0078	0.0005	0.043	0.003	1454	92
				393.2	257.4	11.1	246.3	0.0063	0.0005	0.035	0.003	2780	226
				Experiment B									
				303.2	7.5	2.4	5.1	0.0120	0.0005	0.067	0.003	28	5
				323.2	22.7	3.0	19.7	0.0116	0.0005	0.064	0.003	113	7
				343.2	62.5	3.9	58.7	0.0106	0.0005	0.059	0.003	376	19
				353.1	94.8	4.7	90.1	0.0098	0.0005	0.054	0.003	628	33
0.500	0.002	0.500	0.002	Experiment A									
				303.1	13.0	2.1	11.0	0.0200	0.0006	0.060	0.002	41	4
				323.2	39.87	2.3	37.5	0.0188	0.0007	0.056	0.002	151	6
				333.2	65.9	2.5	63.4	0.0177	0.0006	0.053	0.002	274	11
				343.2	101.5	2.7	98.9	0.0162	0.0006	0.048	0.002	471	20
				353.3	145.0	2.9	142.1	0.0144	0.0006	0.043	0.002	767	36
				363.1	192.3	3.3	189.0	0.0126	0.0006	0.037	0.002	1178	64
				373.2	239.7	4.0	235.7	0.0109	0.0006	0.032	0.002	1713	109
				383.2	283.9	5.3	278.6	0.0095	0.0007	0.028	0.002	2353	176
				393.1	324.3	7.3	317.0	0.0083	0.0007	0.024	0.002	3084	268
				Experiment B									
				303.1	12.5	2.1	10.4	0.0197	0.0006	0.059	0.002	39	4
				313.1	22.3	2.2	20.1	0.0192	0.0006	0.057	0.002	79	4
				323.1	38.9	2.2	36.6	0.0185	0.0006	0.055	0.002	150	7
				343.2	100.4	2.5	98.0	0.0160	0.0006	0.048	0.002	470	20
				353.1	144.4	2.7	141.6	0.0144	0.0006	0.043	0.002	766	36
				363.2	193.2	3.2	190.0	0.0126	0.0006	0.037	0.002	1182	63
				373.2	242.9	4.1	238.8	0.0110	0.0006	0.032	0.002	1727	107
				383.1	288.8	5.5	283.4	0.0096	0.0006	0.028	0.002	2372	171
				393.1	330.9	7.7	323.2	0.0084	0.0007	0.025	0.002	3100	259

Table A.4 (continued)

w_1	$u(w_1)$	w_2	$u(w_2)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	α	$u(\alpha)$	H	$u(H)$
				K	kPa	kPa	kPa			$\text{mol}_{\text{CO}_2} \cdot \text{mol}_{\text{MDEA}}^{-1}$		$\text{kPa m}^3 \text{ kmol}^{-1}$	
0.300	0.001	0.400	0.001	Experiment A									
				303.1	5.3	3.3	2.0	0.0065	0.0002	0.066	0.003	11	5
				313.1	8.5	5.4	3.0	0.0064	0.0002	0.066	0.003	17	5
				323.2	13.8	8.6	5.1	0.0064	0.0002	0.066	0.003	29	5
				343.2	36.5	21.1	15.4	0.0062	0.0003	0.064	0.003	92	7
				353.2	57.9	31.9	26.0	0.0061	0.0002	0.062	0.003	162	9
				363.1	89.1	46.7	42.4	0.0058	0.0002	0.059	0.003	277	15
				373.2	133.0	66.4	66.5	0.0054	0.0002	0.056	0.003	467	25
				383.2	190.6	94.2	96.5	0.0050	0.0002	0.051	0.003	740	42
				393.1	262.1	131.6	130.5	0.0046	0.0002	0.047	0.003	1112	68
				Experiment B									
				313.4	7.9	5.3	2.6	0.0049	0.0002	0.050	0.002	19	7
				323.1	12.4	8.7	3.7	0.0048	0.0002	0.050	0.002	28	7
				333.1	19.8	13.7	6.0	0.0048	0.0002	0.049	0.002	46	7
				343.2	31.5	21.2	10.4	0.0048	0.0002	0.049	0.002	81	8
				353.1	49.6	32.0	17.6	0.0047	0.0002	0.048	0.002	142	10
				363.1	75.9	47.2	28.7	0.0045	0.0002	0.046	0.002	240	15
				373.2	113.7	67.3	46.4	0.0043	0.0002	0.044	0.002	409	24
				383.2	164.7	94.3	70.4	0.0041	0.0002	0.042	0.002	667	7
				393.2	230.9	131.7	99.2	0.0038	0.0002	0.038	0.002	1022	41

^a Standard uncertainties are reported (level of confidence 0.68). Standard uncertainty for temperature is $u(T) = 0.1$ K, for total and residual pressure is $u(P_{\text{tot}}) = u(P_{\text{res}}) = 0.9$ kPa and for CO_2 pressure is $u(P_{\text{CO}_2}) = 1.3$ kPa.

Table A.5

Measured mole fraction solubility x_{CO_2} , loading α and Henry's constant H for CO_2 in MDEA (1) – MEG (2) – H_2O (3) blends as a function of weight fraction w of unloaded solvent, temperature T and pressure (total pressure P_{tot} , residual pressure P_{res} and their difference, CO_2 partial pressure P_{CO_2}).^a

w_1	$u(w_1)$	w_2	$u(w_2)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	α	$u(\alpha)$	H	$u(H)$
				K	kPa	kPa	/kPa			$\text{mol}_{\text{CO}_2} \text{ mol}_{\text{MDEA}}^{-1}$		$\text{kPa m}^3 \text{ kmol}^{-1}$	
0.300	0.001	0.599	0.001	303.2	5.5	2.4	3.1	0.0084	0.0003	0.059	0.002	19	6
				313.0	9.0	3.5	5.5	0.0083	0.0003	0.059	0.002	35	6
				323.1	15.3	5.1	10.2	0.0082	0.0003	0.058	0.002	65	6
				333.2	26.0	7.5	18.5	0.0080	0.0003	0.057	0.002	121	8
				343.2	43.1	11.1	32.0	0.0078	0.0003	0.055	0.002	219	12
				353.2	68.7	16.3	52.4	0.0074	0.0003	0.052	0.002	380	19
				363.2	103.2	23.7	79.5	0.0069	0.0003	0.049	0.003	622	33
				373.2	147.5	33.9	113.7	0.0063	0.0003	0.045	0.003	979	56
				383.2	199.9	47.7	152.2	0.0057	0.0003	0.040	0.003	1468	95
				393.1	257.7	66.3	191.4	0.0051	0.0004	0.036	0.003	2080	153
0.300	0.001	0.400	0.001	303.1	5.3	3.3	2.0	0.0065	0.0002	0.066	0.002	11	5
				313.1	8.5	5.4	3.0	0.0064	0.0002	0.066	0.002	17	5
				323.2	13.8	8.6	5.1	0.0064	0.0002	0.066	0.002	29	5
				343.2	36.5	21.1	15.4	0.0062	0.0002	0.064	0.002	92	7
				353.2	57.9	31.9	26.0	0.0061	0.0002	0.062	0.002	162	9
				363.1	89.1	46.7	42.4	0.0058	0.0002	0.059	0.002	277	15
				373.2	133.0	66.4	66.5	0.0054	0.0002	0.056	0.002	467	25
				383.2	190.6	94.2	96.5	0.0050	0.0002	0.051	0.002	740	42
				393.1	262.1	131.6	130.5	0.0046	0.0002	0.047	0.002	1112	68
0.300	0.002	0.200	0.002	303.1	5.1	4.2	1.0	0.0067	0.0003	0.048	0.003	8	7
				313.1	8.1	6.9	1.2	0.0067	0.0003	0.048	0.003	9	7
				323.1	12.8	11.0	1.8	0.0067	0.0003	0.048	0.003	14	7
				343.2	31.8	26.9	4.9	0.0067	0.0003	0.047	0.003	40	8
				353.1	48.8	40.5	8.3	0.0066	0.0003	0.047	0.003	69	8
				363.1	73.3	59.6	13.6	0.0065	0.0003	0.046	0.003	116	10
				373.2	108.4	85.9	22.5	0.0063	0.0003	0.045	0.003	199	14
				383.2	156.8	121.1	35.7	0.0061	0.0003	0.043	0.003	329	22
				393.1	221.4	168.0	53.4	0.0058	0.0004	0.041	0.003	522	36

^a Standard uncertainties are reported (level of confidence 0.68). Standard uncertainty for temperature is $u(T) = 0.1$ K, for total and residual pressure is $u(P_{\text{tot}}) = u(P_{\text{res}}) = 0.9$ kPa and for CO_2 pressure is $u(P_{\text{CO}_2}) = 1.3$ kPa.

Table A.6

Measured mole fraction solubility x_{CO_2} , loading α and Henry's constant H for CO_2 in MDEA (1) – MEG (2) – H_2O (3) blends as a function of weight fraction w of unloaded solvent and pressure (total pressure P_{tot} , residual pressure P_{res} and their difference, CO_2 partial pressure P_{CO_2}) at temperatures of 313 K and 343 K.^a

w_1	$u(w_1)$	w_2	$u(w_2)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	α	$u(\alpha)$	H	$u(H)$
				K	kPa	kPa	kPa	–		mol _{CO₂}	mol _{MDEA} ⁻¹	kPa m ³	kmol ⁻¹
0.300	0.001	0.599	0.001	313.2	8.1	5.1	3.0	0.0044	0.0005	0.031	0.004	36	12
				313.2	27.2	5.1	22.1	0.0123	0.0007	0.088	0.005	93	7
				313.1	34.8	5.1	29.7	0.0168	0.0008	0.120	0.006	91	6
				313.1	47.1	5.1	42.0	0.0242	0.0009	0.175	0.007	89	4
				313.1	55.6	5.1	50.5	0.0285	0.0009	0.207	0.008	90	4
				313.1	63.6	5.1	58.5	0.0322	0.0010	0.234	0.009	92	4
				313.1	72.0	5.1	67.0	0.0357	0.0010	0.261	0.010	95	4
				313.1	83.3	5.1	78.2	0.0392	0.0011	0.288	0.011	100	4
				313.1	97.4	5.1	92.3	0.0442	0.0011	0.326	0.011	105	4
				313.2	122.6	5.1	117.5	0.0516	0.0010	0.383	0.012	113	4
				313.2	156.5	5.1	151.4	0.0596	0.0010	0.446	0.013	125	4
				313.2	191.3	5.1	186.2	0.0661	0.0010	0.498	0.013	138	4
				313.2	224.1	5.1	219.0	0.0711	0.0010	0.539	0.014	150	4
				313.2	254.7	5.1	249.6	0.0751	0.0010	0.572	0.015	161	4
				313.2	300.0	5.1	295.0	0.0801	0.0010	0.614	0.015	178	5
				313.2	342.6	5.1	337.6	0.0844	0.0010	0.650	0.016	192	5
				343.2	42.8	11.1	31.6	0.0081	0.0005	0.058	0.004	206	14
				343.1	66.9	11.1	55.8	0.0119	0.0006	0.085	0.005	249	15
				343.2	137.9	11.1	126.8	0.0205	0.0007	0.148	0.006	324	14
				343.2	169.7	11.1	158.6	0.0238	0.0008	0.172	0.007	349	15
				343.1	199.6	11.1	188.5	0.0266	0.0009	0.192	0.008	370	16
				343.2	240.7	11.1	229.6	0.0301	0.0009	0.218	0.009	396	16
				343.2	287.3	11.1	276.2	0.0338	0.0010	0.246	0.010	423	17
				343.1	340.2	11.1	329.1	0.0375	0.0010	0.275	0.010	452	17
				343.1	389.9	11.1	378.8	0.0408	0.0010	0.300	0.011	477	18
				343.2	427.0	11.1	415.9	0.0434	0.0011	0.319	0.011	491	18
				343.1	457.5	11.1	446.4	0.0451	0.0011	0.333	0.012	506	19
				343.2	484.1	11.1	473.0	0.0466	0.0011	0.344	0.013	518	19
				343.1	517.1	11.1	506.0	0.0484	0.0011	0.358	0.013	533	20
0.300	0.001	0.400	0.001	313.1	6.5	5.5	1.0	0.0034	0.0003	0.034	0.003	11	10
				313.1	10.3	5.5	4.8	0.0095	0.0004	0.097	0.004	18	4
				313.2	15.0	5.5	9.5	0.0146	0.0004	0.151	0.005	23	2
				313.1	26.2	5.5	20.7	0.0243	0.0004	0.254	0.006	30	2
				313.1	36.2	5.5	30.7	0.0306	0.0004	0.321	0.007	36	1
				313.2	46.5	5.5	40.9	0.0356	0.0005	0.376	0.008	41	1
				313.1	54.8	5.5	49.3	0.0391	0.0005	0.414	0.009	45	1
				313.1	67.5	5.5	62.0	0.0436	0.0005	0.464	0.009	50	1
				313.1	86.4	5.5	80.8	0.0489	0.0005	0.523	0.010	58	1
				313.1	114.2	5.5	108.6	0.0547	0.0005	0.589	0.011	69	1
				313.1	148.4	5.5	142.8	0.0599	0.0005	0.648	0.011	82	2
				313.2	189.3	5.5	183.8	0.0644	0.0006	0.701	0.012	98	2
				313.1	219.8	5.5	214.3	0.0671	0.0006	0.731	0.012	110	2
				313.1	273.7	5.5	268.2	0.0707	0.0006	0.774	0.013	130	2
				313.1	325.8	5.5	320.2	0.0733	0.0007	0.805	0.013	149	3
				313.2	381.3	5.5	375.7	0.0756	0.0007	0.832	0.014	169	3
				313.2	427.5	5.5	421.9	0.0771	0.0007	0.850	0.014	186	3
				313.2	477.7	5.5	472.1	0.0785	0.0007	0.867	0.014	204	4
				313.2	513.3	5.5	507.7	0.0794	0.0007	0.878	0.015	217	4
				343.1	29.2	20.3	8.9	0.0048	0.0003	0.049	0.004	70	9
				343.1	55.4	20.3	35.0	0.0111	0.0004	0.114	0.005	117	6
				343.1	91.4	20.3	71.1	0.0173	0.0005	0.179	0.006	152	6
				343.1	137.5	20.3	117.2	0.0233	0.0005	0.243	0.007	184	6
				343.1	173.5	20.3	153.2	0.0272	0.0006	0.285	0.008	206	6
				343.2	199.8	20.3	179.5	0.0298	0.0006	0.312	0.009	220	7
				343.2	248.2	20.3	227.9	0.0339	0.0006	0.357	0.010	244	7
				343.2	287.4	20.3	267.1	0.0368	0.0006	0.388	0.011	263	7
				343.1	339.7	20.3	319.4	0.0402	0.0006	0.426	0.011	287	8
				343.2	397.8	20.3	377.5	0.0435	0.0006	0.462	0.012	312	8
				343.2	447.1	20.3	426.8	0.0459	0.0007	0.489	0.013	333	9
				343.1	490.3	20.3	470.0	0.0480	0.0007	0.513	0.013	350	9
				343.1	512.0	20.3	491.7	0.0488	0.0007	0.523	0.014	360	10
0.300	0.002	0.200	0.002	313.2	8.2	6.8	1.4	0.0061	0.0002	0.082	0.003	6	4
				313.1	11.7	6.8	4.9	0.0128	0.0003	0.173	0.005	11	2
				313.2	17.2	6.8	10.4	0.0197	0.0003	0.267	0.006	15	1
				313.1	29.4	6.8	22.6	0.0293	0.0003	0.402	0.007	21	1
				313.1	54.6	6.8	47.8	0.0399	0.0003	0.553	0.008	33	1
				313.1	97.5	6.8	90.7	0.0490	0.0004	0.685	0.009	50	1
				313.1	155.9	6.8	149.1	0.0550	0.0005	0.775	0.010	73	1
				313.1	220.3	6.8	213.5	0.0587	0.0005	0.830	0.011	98	2
				313.2	292.1	6.8	285.3	0.0613	0.0006	0.870	0.011	125	2

Table A.6 (continued)

w_1	$u(w_1)$	w_2	$u(w_2)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	α	$u(\alpha)$	H	$u(H)$
				K	kPa	kPa	kPa	–		mol_{CO_2}	$\text{mol}_{\text{MDEA}}^{-1}$	kPa m^3	kmol^{-1}
				313.2	379.6	6.8	372.8	0.0634	0.0006	0.901	0.012	157	2
				313.1	440.6	6.8	433.8	0.0645	0.0006	0.918	0.012	179	3
				313.1	501.8	6.8	495.0	0.0654	0.0006	0.931	0.013	202	3
				343.2	32.2	26.6	5.6	0.0043	0.0002	0.058	0.003	38	6
				343.1	45.0	26.6	18.4	0.0091	0.0003	0.122	0.005	59	4
				343.2	67.8	26.6	41.2	0.0147	0.0003	0.198	0.006	80	3
				343.1	124.3	26.6	97.7	0.0233	0.0004	0.318	0.007	119	4
				343.2	154.9	26.6	128.3	0.0270	0.0004	0.369	0.007	135	3
				343.2	192.0	26.6	165.4	0.0306	0.0004	0.420	0.008	152	3
				343.2	240.7	26.6	214.1	0.0345	0.0004	0.476	0.009	174	4
				343.2	290.3	26.6	263.7	0.0378	0.0004	0.523	0.010	195	4
				343.2	338.3	26.6	311.7	0.0404	0.0004	0.560	0.010	216	4
				343.2	391.9	26.6	365.3	0.0429	0.0004	0.596	0.011	237	5
				343.2	446.5	26.6	419.9	0.0450	0.0004	0.627	0.011	259	5
				343.1	484.5	26.6	457.9	0.0463	0.0004	0.647	0.012	274	5
				343.1	518.1	26.6	491.5	0.0474	0.0004	0.662	0.012	288	6

^a Standard uncertainties are reported (level of confidence 0.68). Standard uncertainty for temperature is $u(T) = 0.1$ K, for total and residual pressure is $u(P_{\text{tot}}) = u(P_{\text{res}}) = 0.9$ kPa and for CO_2 pressure is $u(P_{\text{CO}_2}) = 1.3$ kPa.

Table A.7

Measured mole fraction solubility x_{CO_2} , loading α and Henry's constant H for CO_2 in MDEA (1) – H_2O (3) blends as a function of weight fraction w of unloaded solvent and pressure (total pressure P_{tot} , residual pressure P_{res} and their difference, CO_2 partial pressure P_{CO_2}) at temperatures of 313 K and 343 K.^a

w_1	$u(w_1)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	α	$u(\alpha)$	H	$u(H)$
		K	kPa	kPa	kPa			mol_{CO_2}	$\text{mol}_{\text{MDEA}}^{-1}$	kPa m^3	kmol^{-1}
0.700	0.006	313.1	9.3	5.1	4.2	0.0089	0.0003	0.034	0.004	20	4
		313.2	27.4	5.1	22.3	0.0416	0.0004	0.166	0.007	22	1
		313.2	51.2	5.1	46.1	0.0674	0.0008	0.277	0.009	27	1
		313.1	81.3	5.1	76.2	0.0935	0.0014	0.396	0.012	31	1
		313.1	117.0	5.1	111.9	0.1119	0.0020	0.483	0.013	38	1
		313.2	162.3	5.1	157.2	0.1283	0.0026	0.564	0.015	45	1
		313.1	197.8	5.1	192.7	0.1373	0.0030	0.610	0.016	51	1
		313.1	261.8	5.1	256.7	0.1495	0.0036	0.674	0.017	62	1
		313.1	307.9	5.1	302.8	0.1558	0.0040	0.708	0.017	70	1
		313.1	353.9	5.1	348.9	0.1611	0.0042	0.736	0.018	77	1
		313.1	423.3	5.1	418.2	0.1672	0.0046	0.770	0.019	88	1
		313.1	477.1	5.1	472.0	0.1710	0.0048	0.791	0.020	97	1
		343.1	87.0	23.2	63.8	0.0208	0.0003	0.081	0.001	131	3
		343.1	163.7	23.2	140.5	0.0365	0.0003	0.145	0.002	161	2
		343.1	239.6	23.2	216.5	0.0491	0.0005	0.198	0.003	182	2
		343.1	310.5	23.2	287.4	0.0590	0.0006	0.241	0.003	199	2
		343.1	371.3	23.2	348.1	0.0665	0.0007	0.273	0.004	212	2
		343.2	425.9	23.2	402.8	0.0721	0.0008	0.298	0.004	225	3
		343.1	467.7	23.2	444.5	0.0763	0.0009	0.317	0.005	234	3
		343.2	499.6	23.2	476.4	0.0794	0.0010	0.331	0.005	240	3
0.900	0.006	313.1	25.0	4.2	20.8	0.0179	0.0005	0.032	0.001	83	4
		313.2	65.1	4.2	60.9	0.0437	0.0007	0.079	0.002	98	3
		313.1	111.6	4.2	107.3	0.0678	0.0010	0.126	0.003	108	2
		313.1	134.5	4.2	130.2	0.0785	0.0012	0.148	0.003	112	2
		313.1	178.7	4.2	174.4	0.0956	0.0015	0.183	0.003	121	2
		313.2	206.7	4.2	202.4	0.1039	0.0018	0.201	0.004	128	2
		313.1	247.0	4.2	242.8	0.1189	0.0022	0.234	0.004	132	2
		313.1	277.5	4.2	273.2	0.1253	0.0025	0.248	0.004	140	2
		313.1	313.7	4.2	309.4	0.1368	0.0029	0.275	0.005	143	2
		313.2	340.4	4.2	336.2	0.1415	0.0031	0.286	0.005	150	2
		313.1	377.5	4.2	373.3	0.1500	0.0035	0.306	0.005	155	2
		313.1	410.6	4.2	406.4	0.1571	0.0038	0.323	0.005	160	2
		313.2	445.0	4.2	440.8	0.1627	0.0041	0.337	0.006	166	2
		313.2	474.4	4.2	470.2	0.1674	0.0044	0.349	0.006	172	3
		343.1	78.7	13.5	65.2	0.0051	0.0005	0.009	0.001	946	103
		343.2	127.0	13.5	113.6	0.0166	0.0007	0.029	0.001	505	24
		343.1	150.9	13.5	137.4	0.0195	0.0008	0.035	0.002	518	25
		343.1	255.9	13.5	242.5	0.0317	0.0009	0.057	0.002	557	19
		343.1	332.2	13.5	318.8	0.0398	0.0009	0.072	0.002	578	18
		343.1	404.1	13.5	390.6	0.0471	0.0010	0.086	0.003	593	17
		343.1	436.3	13.5	422.9	0.0502	0.0010	0.092	0.003	600	17
		343.1	464.5	13.5	451.0	0.0529	0.0011	0.097	0.003	606	18
		343.1	488.8	13.5	475.3	0.0551	0.0011	0.101	0.003	612	18

^a Standard uncertainties are reported (level of confidence 0.68). Standard uncertainty for temperature is $u(T) = 0.1$ K, for total and residual pressure is $u(P_{\text{tot}}) = u(P_{\text{res}}) = 0.9$ kPa and for CO_2 pressure is $u(P_{\text{CO}_2}) = 1.3$ kPa.

Table A.8

Measured mole fraction solubility x_{CO_2} , loading a and Henry's constant H for CO_2 in MDEA (1) – TEG (4) blends as a function of weight fraction w of unloaded solvent, temperature T and pressure (total pressure P_{tot} , residual pressure P_{res} and their difference, CO_2 partial pressure P_{CO_2}).^a

w_1	$u(w_1)$	T	P_{tot}	P_{res}	P_{CO_2}	x_{CO_2}	$u(x_{\text{CO}_2})$	α	$u(\alpha)$	H	$u(H)$		
		K	kPa	kPa	kPa			mol _{CO₂}	mol _{1MDEA} ⁻¹	kPa m ³ kmol ⁻¹			
0.000	0.000	303.1	192.5	2.3	190.3	0.0143	0.0010	–	–	1761	136		
		313.1	212.2	2.3	209.9	0.0134	0.0011	–	–	2095	174		
		323.1	231.3	2.4	228.9	0.0126	0.0011	–	–	2454	219		
		333.1	249.6	2.6	247.1	0.0119	0.0011	–	–	2829	269		
		343.2	267.3	2.7	264.6	0.0113	0.0011	–	–	3216	324		
		353.2	284.3	3.0	281.3	0.0108	0.0011	–	–	3606	382		
		363.1	300.7	3.3	297.3	0.0103	0.0011	–	–	3997	443		
		373.2	316.7	3.7	313.0	0.0100	0.0011	–	–	4389	506		
		383.2	332.2	4.3	327.8	0.0097	0.0011	–	–	4767	568		
		393.1	347.5	5.0	342.5	0.0095	0.0011	–	–	5148	632		
		0.300	0.003	303.2	57.3	2.4	54.9	0.0256	0.0010	0.075	0.003	267	13
				313.1	95.0	2.5	92.5	0.0228	0.0010	0.067	0.003	510	26
323.1	139.8			2.5	137.2	0.0198	0.0010	0.057	0.003	883	50		
333.1	183.8			2.5	181.3	0.0169	0.0010	0.049	0.003	1377	92		
343.2	222.6			2.5	220.1	0.0146	0.0010	0.042	0.003	1951	151		
353.2	255.1			2.6	252.5	0.0129	0.0010	0.037	0.003	2557	226		
363.1	282.0			2.8	282.0	0.0115	0.0011	0.033	0.003	3231	323		
373.2	304.9			3.1	301.8	0.0109	0.0011	0.031	0.003	3702	395		
383.2	325.2			3.8	321.4	0.0102	0.0011	0.029	0.003	4216	480		
393.2	343.7			4.6	339.1	0.0098	0.0011	0.028	0.003	4692	561		
0.500	0.003			303.1	44.7	2.3	42.4	0.0279	0.0011	0.051	0.002	183	10
				313.2	77.7	2.5	75.2	0.0253	0.0011	0.047	0.002	362	20
		323.2	119.5	2.6	116.9	0.0221	0.0011	0.041	0.002	649	40		
		333.2	165.1	2.8	162.2	0.0189	0.0011	0.034	0.002	1068	75		
		343.2	207.2	3.2	204.1	0.0161	0.0012	0.029	0.002	1595	131		
		353.2	243.3	3.5	239.8	0.0139	0.0012	0.025	0.002	2186	207		
		363.2	273.4	4.4	273.4	0.0121	0.0012	0.022	0.002	2909	317		
		373.2	298.8	5.3	293.5	0.0113	0.0012	0.021	0.002	3371	395		
		383.1	320.7	6.5	314.3	0.0105	0.0013	0.019	0.002	3910	494		
		393.1	339.6	8.3	331.3	0.0101	0.0013	0.018	0.002	4354	578		
		313.1	57.4	1.6	55.7	0.0186	0.0011	0.034	0.002	367	26		
		313.1	104.3	1.6	102.7	0.0329	0.0015	0.061	0.003	376	22		
		313.1	158.2	1.6	156.5	0.0485	0.0014	0.091	0.004	383	17		
		313.2	213.3	1.6	211.7	0.0634	0.0013	0.121	0.004	390	15		
		313.1	263.8	1.6	262.2	0.0759	0.0013	0.147	0.004	398	14		
		313.2	303.9	1.6	302.3	0.0855	0.0013	0.168	0.005	403	14		
		313.2	344.1	1.6	342.5	0.0944	0.0013	0.187	0.005	410	13		
		313.1	375.4	1.6	373.7	0.1010	0.0014	0.202	0.005	415	13		
		313.1	406.5	1.6	404.9	0.1072	0.0014	0.215	0.005	421	13		
		313.2	431.9	1.6	430.3	0.1120	0.0015	0.226	0.006	426	13		
		313.2	473.3	1.6	471.6	0.1196	0.0015	0.244	0.006	433	14		
		313.1	505.1	1.6	503.5	0.1250	0.0016	0.256	0.006	440	14		
		313.1	528.3	1.6	526.7	0.1289	0.0017	0.265	0.006	444	14		

^a Standard uncertainties are reported (level of confidence 0.68). Standard uncertainty for temperature is $u(T) = 0.1$ K, for total and residual pressure is $u(P_{\text{tot}}) = u(P_{\text{res}}) = 0.9$ kPa and for CO_2 pressure is $u(P_{\text{CO}_2}) = 1.3$ kPa.

Appendix B

The parameters for the so-called “soft model” used to describe the VLE data in the aqueous systems studied in this work are pre-

sented in Table B.1. Reference is made to equations Eqs. (4)–(7). The parameters are given with their significant numbers.

Table B.1

Model parameters (Eq. (4)).

Systems	Parameters							
	A	B	$k_{1,a}$	$k_{1,b}$	$k_{2,a}$	$k_{2,b}$	$k_{3,a}$	$k_{3,b}$
30 wt% MDEA – 60 wt% MEG – 10 wt% H ₂ O	1.487	10.16	–17.924	–96.8894	–10	1.77	29	3.55
30 wt% MDEA – 40 wt% MEG – 30 wt% H ₂ O	1.496	10.24	–19.004	–104.0863	–10	1.56	–199	3.91
30 wt% MDEA – 20 wt% MEG – 50 wt% H ₂ O	1.480	10.12	–19.686	–108.8514	–10	1.27	55	2.86
70 wt% MDEA – 30 wt% H ₂ O	1.241	10.03	–20.083	–109.9550	–10	1.39	55	3.45
90 wt% MDEA – 10 wt% H ₂ O	–0.296	10.03	–18.919	–108.7841	–10	–1.04	55	0.52

Appendix C. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jct.2020.106176>.

References

- [1] M. Stewart, K. Arnold, Part 1 - Gas Sweetening, Gulf Professional Publishing, 2011, pp. 1–140.
- [2] O. Økland, S. Davies, R.M. Ramberg, H. Rognø, Steps to the Subsea Factory. in OTC-24307-MS (Offshore Technology Conference, 2013). doi: 10.4043/24307-MS.
- [3] GATEkeeper. H₂S scavenging: Using Triazine, 2014.
- [4] M.G. Lioliou, J. Sandrod, M. Stipanicev, Ø. Birketveit, Qualification and field performance of subsea H₂S scavenger injection, 2017.
- [5] A.J.L. Hutchinson, Process for treating gases, 1939.
- [6] E.R. McCartney, Gas purification and dehydration process, 1948.
- [7] W.F. Chapin, Purification and dehydration of gases, 1950.
- [8] E.R. McCartney, Extraction of acidic impurities and moisture from gases, 1951.
- [9] A.L. Kohl, R.B. Nielsen, Chapter 2 - Alkanolamines for Hydrogen Sulfide and Carbon Dioxide Removal, in: Gas Purification, Gulf Professional Publishing, 1997, pp. 40–186.
- [10] B.B. Woertz, Experiments with solvent-amine-water for removing CO₂ from gas, Can. J. Chem. Eng. 50 (1972) 425–427.
- [11] K. Sridharan, M.M. Sharma, New systems and methods for the measurement of effective interfacial area and mass transfer coefficients in gas–liquid contactors, Chem. Eng. Sci. 31 (1976) 767–774.
- [12] C. Alvarez-Fuster, N. Midoux, A. Laurent, J.C. Charpentier, Chemical kinetics of the reaction of CO₂ with amines in pseudo m–nth order conditions in polar and viscous organic solutions, Chem. Eng. Sci. 36 (1981) 1513–1518.
- [13] M.H. Oyevaar, H.J. Fontein, K.R. Westerterp, Equilibria of carbon dioxide in solutions of diethanolamine in aqueous ethylene glycol at 298 K, J. Chem. Eng. Data 34 (1989) 405–408.
- [14] J.-H. Song, S.-B. Park, J.-H. Yoon, H. Lee, K.-H. Lee, Solubility of Carbon Dioxide in Monoethanolamine + Ethylene Glycol + Water and Monoethanolamine + Poly(ethylene glycol) + Water at 333.2 K, J. Chem. Eng. Data 42 (1997) 143–144.
- [15] I.L. Leites, Thermodynamics of CO₂ solubility in mixtures monoethanolamine with organic solvents and water and commercial experience of energy saving gas purification technology, Energy Convers. Manage. 39 (1998) 1665–1674.
- [16] H.-J. Xu, C.-F. Zhang, Z.-S. Zheng, Selective H₂S Removal by Nonaqueous Methyl-diethanolamine Solutions in an Experimental Apparatus, Ind. Eng. Chem. Res. 41 (2002) 2953–2956.
- [17] S.-W. Park, J.-W. Lee, B.-S. Choi, J.-W. Lee, Absorption of carbon dioxide into non-aqueous solutions of N-methyl-diethanolamine, Korean J. Chem. Eng. 23 (2006) 806–811.
- [18] J. Tan, H. Shao, J. Xu, L. Du, G. Luo, Mixture absorption system of monoethanolamine–triethylene glycol for CO₂ capture, Ind. Eng. Chem. Res. 50 (2011) 3966–3976.
- [19] D. Eimer, Simultaneous removal of water and hydrogen sulphide from natural gas, NTNU, 1994.
- [20] R.R. Wanderley, Y. Yuan, G.T. Rochelle, H.K. Knuutila, CO₂ solubility and mass transfer in water-lean solvents, Chem. Eng. Sci. 202 (2019) 403–416.
- [21] A. Hartono, O. Juliussen, H.F. Svendsen, Solubility of N₂O in Aqueous Solution of Diethylenetriamine, J. Chem. Eng. Data 53 (2008) 2696–2700.
- [22] D.-Y. Peng, D.B. Robinson, A new two-constant equation of state, Ind. Eng. Chem. Fund. 15 (1976) 59–64.
- [23] J.J. Carroll, J.D. Slupsky, A.E. Mather, The solubility of carbon dioxide in water at low pressure, J. Phys. Chem. Ref. Data 20 (1991) 1201–1209.
- [24] A. Penttilä, C. Dell’Era, P. Uusi-Kyyny, V. Alopaeus, The Henry’s law constant of N₂O and CO₂ in aqueous binary and ternary amine solutions (MEA, DEA, DIPA, MDEA, and AMP), Fluid Phase Equilib. 311 (2011) 59–66.
- [25] A. Hartono, E.O. Mba, H.F. Svendsen, Physical properties of partially CO₂ loaded aqueous monoethanolamine (MEA), J. Chem. Eng. Data 59 (2014) 1808–1816.
- [26] E. Skylogianni, R.R. Wanderley, S.S. Austad, H.K. Knuutila, Density and viscosity of the nonaqueous and aqueous mixtures of methyl-diethanolamine and monoethylene glycol at temperatures from 283.15 to 353.15 K, J. Chem. Eng. Data 64 (2019) 5415–5431.
- [27] C. Perinu, B. Arstad, K.-J. Jens, NMR spectroscopy applied to amine–CO₂–H₂O systems relevant for post-combustion CO₂ capture: A review, Int. J. Greenhouse Gas Control 20 (2014) 230–243.
- [28] C. Perinu, B. Arstad, K.-J. Jens, ¹³C NMR Experiments and Methods used to Investigate Amine–CO₂–H₂O Systems, Energy Proc. 37 (2013) 7310–7317.
- [29] P. Bröder, K.G. Lauritsen, T. Mejdell, H.F. Svendsen, CO₂ capture into aqueous solutions of 3-methylaminopropylamine activated dimethyl-monoethanolamine, Chem. Eng. Sci. 75 (2012) 28–37.
- [30] A. Hartono et al., Characterization of 2-piperidineethanol and 1-(2-hydroxyethyl)pyrrolidine as strong bicarbonate forming solvents for CO₂ capture, Int. J. Greenhouse Gas Control 63 (2017) 260–271.
- [31] I.M. Bernhardsen, A.A. Trollebø, C. Perinu, H.K. Knuutila, Vapour-liquid equilibrium study of tertiary amines, single and in blend with 3-(methylamino)propylamine, for post-combustion CO₂ capture, J. Chem. Thermodyn. 138 (2019) 211–228.
- [32] D.-Q. Zheng, W.-D. Ma, R. Wei, T.-M. Guo, Solubility study of methane, carbon dioxide and nitrogen in ethylene glycol at elevated temperatures and pressures, Fluid Phase Equilib. 155 (1999) 277–286.
- [33] A.C. Galvão, A.Z. Francesconi, Solubility of methane and carbon dioxide in ethylene glycol at pressures up to 14 MPa and temperatures ranging from (303 to 423) K, J. Chem. Thermodyn. 42 (2010) 684–688.
- [34] F.-Y. Jou, R.D. Deshmukh, F.D. Otto, A.E. Mather, Vapour-liquid equilibria of H₂S and CO₂ and ethylene glycol at elevated pressures, Chem. Eng. Commun. 87 (1990) 223–231.
- [35] M. Wise, A. Chapoy, Phase Behaviour of CO₂ in Monoethylene Glycol between 263.15–343.15 K and 0.2–40.3 MPa: An Experimental and Modelling Approach, J. Chem. Eng. Data 62 (2017) 4154–4159.
- [36] J.M. Campbell, Amine-based processes. in Gas Conditioning and Processing vol. 4, 1998.
- [37] K.P. Shen, M.H. Li, Solubility of carbon dioxide in aqueous mixtures of monoethanolamine with methyl-diethanolamine, J. Chem. Eng. Data 37 (1992) 96–100.
- [38] C. Perinu, I.M. Bernhardsen, D.D.D. Pinto, H.K. Knuutila, K.-J. Jens, NMR Speciation of Aqueous MAPA, Tertiary Amines, and Their Blends in the Presence of CO₂: Influence of pK_a and Reaction Mechanisms, Ind. Eng. Chem. Res. 57 (2018) 1337–1349.
- [39] M. Nitta, K. Hayashi, Y. Furukawa, H. Sato, Y. Yamanaka, ¹³C-NMR study of acid dissociation constant (pK_a) effects on the CO₂ absorption and regeneration of aqueous tertiary alkanolamine–piperazine blends, Energy Procedia 63 (2014) 1863–1868.
- [40] R. Behrens et al., Monoalkylcarbonate Formation in Methyl-diethanolamine–H₂O–CO₂, Ind. Eng. Chem. Res. 56 (2017) 9006–9015.
- [41] C. Perinu, B. Arstad, A.M. Bouzga, J.A. Svendsen, K.J. Jens, NMR-Based Carbamate Decomposition Constants of Linear Primary Alkanolamines for CO₂ Capture, Ind. Eng. Chem. Res. 53 (2014) 14571–14578.
- [42] D. Eimer, Gas treating: Absorption Theory and Practice, John Wiley & Sons Inc., 2014.
- [43] F. Barzagli, S. Lai, F. Mani, Novel non-aqueous amine solvents for reversible CO₂ capture, Energy Procedia 63 (2014) 1795–1804.
- [44] D.I. Sagdeev, M.G. Fomina, G.Kh. Mukhamedzyanov, I.M. Abdulgatov, Experimental study of the density and viscosity of polyethylene glycols and their mixtures at temperatures from 293K to 473K and at atmospheric pressure, J. Chem. Thermodyn. 43 (2011) 1824–1843.
- [45] W.Y. Tawfik, A.S. Teja, The densities of polyethylene glycols, Chem. Eng. Sci. 44 (1989) 921–923.
- [46] M.F.V. Pereira, H.M.N.T. Avelino, F.J.P. Caetano, J.M.N.A. Fareira, Viscosity of liquid diethylene, triethylene and tetraethylene glycols at moderately high pressures using a vibrating wire instrument, Fluid Phase Equilib. 480 (2019) 87–97.
- [47] E.A. Crespo et al., New measurements and modelling of high pressure thermodynamic properties of glycols, Fluid Phase Equilib. 436 (2017) 113–123.
- [48] C.-Y. Tsai, A.N. Soriano, M.-H. Li, Vapour pressures, densities, and viscosities of the aqueous solutions containing (triethylene glycol or propylene glycol) and (LiCl or LiBr), J. Chem. Thermodyn. 41 (2009) 623–631.
- [49] N.V. Sastry, R.R. Thakor, M.C. Patel, Thermophysical Properties for Diethylene Glycol + Nitrobenzene and Triethylene Glycol + (Chloro-, Bromo-, Nitro-) Benzene Systems at Different Temperatures, Int. J. Thermophys. 29 (2008) 610–618.
- [50] A. Valtz, M. Teodorescu, I. Wichterle, D. Richon, Liquid densities and excess molar volumes for water + diethylene glycolamine, and water, methanol, ethanol, 1-propanol + triethylene glycol binary systems at atmospheric pressure and temperatures in the range of 283.15–363.15 K, Fluid Phase Equilib. 215 (2004) 129–142.
- [51] W.V. Steele, R.D. Chirico, S.E. Knipmeyer, A. Nguyen, Measurements of Vapour Pressure, Heat Capacity, and Density along the Saturation Line for ε-Caprolactam, Pyrazine, 1,2-Propanediol, Triethylene Glycol, Phenyl Acetylene, and Diphenyl Acetylene, J. Chem. Eng. Data 47 (2002) 689–699.
- [52] A. Kumagai, H. Mochida, S. Takahashi, Liquid viscosities and densities of HFC-134a+glycol mixtures, Int. J. Thermophys. 14 (1993) 45–53.
- [53] F.-Y. Jou, R.D. Deshmukh, F.D. Otto, A.E. Mather, Vapourliquid equilibria for acid gases and lower alkanes in triethylene glycol, Fluid Phase Equilib. 36 (1987) 121–140.
- [54] M. Wise, A. Chapoy, Carbon dioxide solubility in Triethylene Glycol and aqueous solutions, Fluid Phase Equilib. 419 (2016) 39–49.