



CO₂ Solubility in diethylenetriamine (DETA) and triethylenetetramine (TETA) aqueous mixtures: Experimental investigation and correlation using the CPA equation of state

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ABSTRACT

CO₂ capture is of profound significance to mitigate emissions from fossil fuel combustion. Absorption technologies represent a mature approach for post-combustion CO₂ capture, and, in this direction, the development of new solvent systems, alternative to aqueous ethanolamine (MEA) solutions that are currently used, has attracted significant research interest. Among the solvents that have been suggested, polyamines, such as diethylenetriamine (DETA) and triethylenetetramine (TETA), represent interesting candidates for use in amine mixture solvents. This work presents new high pressure experimental data for the solubility of CO₂ in aqueous DETA and TETA solutions. The former system is investigated using two experimental techniques in order to expand the investigated pressure range. In addition, the obtained new experimental data are used to parameterize the Cubic-Plus-Association Equation of State (CPA EoS), which, in turn, coupled with the pseudo-chemical reaction approach, is used to satisfactorily describe the VLE behavior of the studied systems.

1. Introduction

Carbon dioxide, which is emitted from fossil fuel combustion contributes significantly to global warming. It is believed that global warming causes disruption of the environmental balance provoking extreme weather conditions, drought, animal extinction etc. For this reason, the Carbon Capture Utilization and/or Storage (CCUS) scheme has been suggested, which, however, constitute a major engineering challenge, since it should apply safe, environmentally friendly and efficient technologies that will not significantly increase the energy cost.

Among the most promising methods for CO₂ capture, solvent-based absorption using amines in post-combustion mode seems to be a financially feasible option, as the process is well-known and easy to implement in industrial settings [1]. Therefore, amine-based carbon capture technology attracted significant interest, while there are intensive re-

search efforts for the development of novel solvents that will replace ethanolamine (MEA) in the conventional process [2].

In this work, aqueous mixtures of diethylenetriamine (DETA) and triethylenetetramine (TETA) are investigated. DETA and TETA are considered polyamines with multiple functional groups as shown in Table 1. DETA's molecule has three amine groups (two primary and one secondary), while TETA possesses one more secondary amine group (two primary and two secondary). Due to that, they are expected to exhibit high CO₂ absorption capacity, while the existence of only primary and secondary amine groups renders them absorption activators, according to the classification proposed by Zhang [3].

CO₂ absorption kinetics in DETA aqueous solutions were investigated by Hartono et al. [4], who found that the reaction rates increase with increasing DETA concentration and temperature. Hartono et al. [5] studied the main species formed in DETA aqueous solutions upon CO₂ dissolution and found that 24 species may potentially be formed.

Abbreviations: AMP, 2-Amino-2-methyl-1-propanol; BDA, 1,4-Butanediamine; BDMAEE, Bis (2-dimethylaminoethyl); CHAP, *N*-cyclohexyl-1,3-propanediamine (also known as S1N); CPA, Cubic plus association equation of state; DEAPD, 3-(diethylamino)-1,2-propanediol; DEEA, Diethylethanolamine; DETA, Diethylenetriamine; DMBA, *N,N*-dimethylbutylamine; DMCA, *N,N*-dimethylcyclohexylamine; EOS, Equation of state; MAPA, 3-Methylaminopropylamine; MCA, *N*-Methylcyclohexylamine; MDEA, Methyl diethanolamine; MEA, Ethanolamine; PEG(200), Polyethylene glycol(200); PMDETA, *N,N,N',N''*-Pentamethyldiethylenetriamine; TMPDA, *N,N,N',N'*-Tetramethyl-1,3-propanediamine; TETA, Triethylenetetramine; TSP, Sodium phosphate tribasic; VLE, Vapor – Liquid Equilibrium; VLLE, Vapor – Liquid – Liquid Equilibrium.

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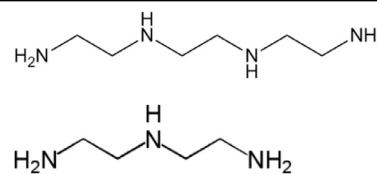
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Table 1
Structure of DETA and TETA.

Name	Structure
TETA, (Mw 146.23) Triethylenetetramine	$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-NH_2$
DETA, (Mw 103.17) Diethylenetriamine	$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2$

**Table 2**
Literature studies regarding mixtures that contain DETA or TETA.

Amine(s)	References
TETA	[17-19]
DETA	[4,5,8,14,18,20-24]
DETA Blends	
DEEA-DETA	[7,10,25]
DETA-MDEA-AMP	[26]
DETA-PMDETA	[9,27]
DETA-Sulfolane	[11,14]
TETA Blends	
TETA-AMP, TETA-AMP-EtOH	[28]
TETA-BDMAEE, TETA-PMDETA, TETA-DEAPD	[15]
TETA-DEEA	[7,15,25,29-31]
TETA-DMCA	[15,16,32]
TETA-EtOH	[28,33]
TETA-PEG200	[34]
TETA- PMDETA	[35]
TETA-TSP	[36]

However, carbamate, dicarbamate, and HCO_3^-/CO_3^{2-} are the main species formed in the system.

As recently reviewed by Papadopoulos et al. [6], such polyamines were suggested for use in combination with lipophilic amines, in mixed solvents that present phase change behavior, i.e. the phase separation in one CO_2 rich and one CO_2 lean liquid phase upon increase of temperature. The main advantage of such solvents is the relatively lower regeneration energy need compared to non-phase change solvents, since only the CO_2 rich phase needs thermal regeneration.

In this direction, Ye et al. [7] investigated 50 amine mixtures to verify their potential as phase-change solvents. The absorption activators included mainly linear or cyclic amines, whereas the regeneration activators were either *N,N*-dimethyl cyclohexylamine (DMCA) or 2-(diethylamino)-ethanol (DEEA). Ye et al. [8] suggested and investigated the aqueous mixture of DETA and pentamethyldiethylenetriamine (PMDETA). PMDETA contains three tertiary amino groups and was used due to its high CO_2 loading capacity. Two liquid phases occurred as the CO_2 loading of the DETA-PMDETA blend reached the value of 0.2 mol mol^{-1} . Such system achieved approximately 35% higher CO_2 loading capacity compared to 5M MEA. As DETA concentration increased, the volume of the CO_2 rich phase and the CO_2 loading was also increased [8]. Subsequently, Zhou et al. [9] investigated various mixtures of PMDETA and DETA with respect to CO_2 capture capacity and reaction mechanism. They concluded that the upper phase mainly contains PMDETA, while DETA is the absorption accelerator, but also contributes to the CO_2 absorption capacity of the mixture.

Wang et al. [10] suggested the use of DETA-DEEA aqueous solution as a new phase change solvent, reporting that liquid-liquid separation occurred when the mixed solution of 1M DETA and 4M DEEA absorbed a sufficient amount of CO_2 . Their kinetic analysis revealed that temperature and CO_2 loading significantly affect the total mass transfer coefficient, while changes in gas flow rate had only minor effect.

Other investigated mixtures of DETA, summarized in Table 2, include mixtures with MDEA and AMP, as well as nonamine solvents, such as sulfolane. DETA/sulfolane mixture was examined by Luo et al.

[11] as a potential biphasic solvent system, since sulfolane has been previously used as an aprotic polar solvent for the physical absorption of acid gases [12,13]. It is reported that sulfolane changes the VLE equilibrium, but does not affect the DETA- CO_2 reaction mechanism. Subsequently, Wang et al. [14] investigated the kinetic behaviour, the CO_2 absorption rate and the theoretical regeneration energy requirements of DETA/sulfolane. In CO_2 absorption, sulfolane behaves as an inert solvent, as substitute of water, and it is separated from the CO_2 rich phase. The sensible heat and vaporization heat are found to be substantially decreased by 59% and 12%, respectively, and the total heat duty by 19%.

In the same direction, TETA was investigated as a constituent of various aqueous solutions that contain amine blends and present phase change behavior, which are summarized in Table 2. In more detail, Zhang et al. [15] experimentally studied the CO_2 absorption capacity and phase separation behavior of various TETA mixtures with other amines, including DMCA, DEEA and PMDETA. Their results reveal that the TETA/DMCA aqueous system showed high cyclic capacity, favorable phase separation behavior, and low regeneration heat needs.

Shen et al. [16] experimentally investigated 10 primary/secondary amines and 8 tertiary amines with different alkalinity (pKa) and hydrophobicity (log P) in terms of absorption capacity, VLE and kinetic behavior. Experimental data are also exploited for theoretical prediction of the regeneration energy requirements for solvent mixtures of TETA with various amines, including DEEA and DMCA.

Literature studies regarding the CO_2 loading of aqueous mixtures that contain DETA and/or TETA are summarized in Table 2.

While the above works pertain mainly to experimental measurements, the derived data may be exploited for the development of predictive models. The latter are needed in order to determine the impact of the investigated solvents on the economic and operating performance of the absorption and desorption processes, through process simulation and optimization. The modeling of CO_2 absorption in aqueous amine solutions is a very demanding task, since it requires the simultaneous modeling of chemical equilibria and phase behavior. For this reason mainly empirical models are used, with the most popular ones being the Kent-Eisenberg model [37,38] and its modifications [39].

The rigorous use of equation of state models, which is very important in modeling the physical absorption of gases in liquid solvents, is not easy, since the chemical interactions are the dominating phenomena in such aqueous amine solutions. It requires the knowledge of the equilibrium constants, which are usually obtained by adjusting three or four parameters to the experimental data, on top of the other pure and binary parameters of the model. However, if models are adequately parameterized, satisfactory correlations are obtained [40,41].

The complexity of the underlying phenomena, the difficulties in attaining experimental data, and often their lack thereof, is mainly compensated by the introduction of important simplifications. The most popular one is to account for chemical interactions in the same way as strong specific interactions (such as the hydrogen bonding ones) are accounted for. Using such pseudo-chemical reaction approach, Rodriguez et al. [42] used the SAFT-VR model to correlate the absorption of CO_2 in aqueous amine solutions. More recently, a group contribution (GC) approach, based on the SAFT- γ equation of state, was used and produced

Table 3
Chemicals used in this work.

Product Name	Abbreviation	CAS-number	Purity	Supplier
Carbon dioxide	CO ₂	124-38-9	99.9 (vol%)	Air Liquide
Diethylenetriamine	DETA	111-40-0	99%	Sigma Aldrich
Triethylenetetramine	TETA	112-24-3	97%	Sigma Aldrich

Table 4
CO₂ loading of DETA aqueous mixtures obtained by the chemical analysis of loaded solutions.

Temperature ^a , T/K	CO ₂ Partial Pressure, P/kPa	Loading, α / mol CO ₂ per mol amine	Final amine content (on water basis), %wt.
313.15	10.1	1.32 ± 0.08	33.0 ± 0.6
	15.2	1.36 ± 0.08	29.8 ± 0.5
	31.4	1.41 ± 0.09	29.0 ± 0.5
	81.0	1.43 ± 0.09	31.2 ± 0.5
333.15	30.4	1.23 ± 0.08	30.1 ± 0.5
	51.7	1.42 ± 0.09	31.2 ± 0.5
363.15	30.4	0.85 ± 0.05	32.1 ± 0.5
	50.7	1.10 ± 0.08	32.1 ± 0.5
	70.9	1.19 ± 0.08	31.5 ± 0.5

^a Temperature stability ±0.10 K at 313 K and ±0.80 K at 363 K

very satisfactory predictions for the solubility of CO₂ in amine solutions and their phase behavior [43]. A similar approach was also used in the work of Papadopoulos et al. [44], in which SAFT- γ -Mie enabled the efficient prediction of the phase-behavior of phase-change solvents. In the same direction, Leontiadis et al. [45] used the CPA model that is based in the SRK EoS, while Wang et al. [46] used the PR-CPA, for modeling the solubility of CO₂ in aqueous alkanolamine solutions.

In this work, a 30% wt. DETA aqueous solution was experimentally investigated in terms of CO₂ solubility at 313, 333 and 363 K using two experimental techniques, in order to expand the investigated pressure range. Subsequently, a 30% wt. TETA aqueous solution was experimentally studied at 313 and 333 K. Such measurements were prompted by the available literature data, which are dubious and scarce. The new data are valuable for the parameterization of thermodynamic models that allow the rational design of the relevant separation processes. In this direction, the CPA equation of state [47–48], coupled with the pseudo-chemical reaction approach, was parameterized and used to correlate the Vapor-Liquid Equilibrium of the investigated systems.

2. Materials and methods

The materials used in this work are shown in Table 3. They were used as received without further purification.

The DETA solutions were initially investigated in an apparatus that enables experiments between 1 and 100 kPa of CO₂ partial pressure and involves chemical analysis of the liquid phase after the experiment. This pressure range was then expanded through experiments in a second apparatus that uses a pressure decay method and allows experiments in the 10 – 2000 kPa pressure range. TETA solutions were studied using only the latter experimental method.

The first method and the relevant experimental apparatus, which is presented in Fig. S1 of the ESI, are described in detail by Tzirakis et al. [49]. Briefly, CO₂ and N₂ gas mixtures of known composition pass through a series of four gas wash bottles immersed in a temperature-controlled water bath (temperature stability during experiments around ±0.1 K at 313 K and ±0.8 K at 363 K). The first gas wash bottle contains de-ionized water in order to compensate vaporization losses. The second gas wash bottle contains the aqueous amine solution, while the last two bottles are used as traps to collect potential amine losses. The system is held at constant temperature, with a constant gas flow rate for sufficient time, estimated through preliminary experiments, to ensure saturation of the liquid solvent. Subsequently, the composition of the liquid phase

is measured using the BaCl₂ and an acid titration method, for estimating the gas and the amine content, respectively, as described by Tzirakis et al. [49].

The pressure decay method and the relevant apparatus, which is shown in Fig. S2 of the ESI, are described in detail by Leontiadis et al. [45]. Briefly, a weighted amount of CO₂ (3–5 g depending on the experiment, maximum error ± 0.002 g) is added in a high-pressure cell containing a known amount of liquid solvent (around 25 g, maximum error ±0.002 g). It is assumed that equilibrium is reached upon stabilization of pressure for at least 1 h, while the absorbed CO₂ is calculated through the mass balance equations, knowing the pressure and temperature conditions and the volume of the vapor phase [45]. The volume of the cell (152.2 ± 1.6 cm³ at 298.15 K) was measured at all experimental temperatures by monitoring the pressure after the addition of known amounts of CO₂. The needed CO₂ density was obtained from NIST [50]. The cell is immersed inside a water bath of constant temperature (temperature stability of 0.1K). The temperature and the pressure inside the equilibrium cell are monitored using a Pt-100 (±0.01 K) thermometer and a pressure transducer (WIKA A-10, ± 0.5%), respectively.

According to this procedure the total pressure of the vapor phase is measured. For estimating the partial CO₂ pressure, the vapor pressure of the aqueous solution was subtracted from the total pressure. Such approximation is often used in similar experimental studies [45,51,52]. Since the investigated solutions are not highly volatile, such correction is not significant at relatively high pressures (higher than 1 bar at the studied temperatures).

In all cases, the uncertainties of the loading values denote the most probable error, calculated through propagation of errors, considering the uncertainties of all the measurements (weights of the materials, volumes used in the titration, volume of the cell, densities etc.) [45,49].

3. Experimental results

3.1. DETA results

Considering the DETA systems, measurements were performed at 313 and 333 K with both experimental techniques, as well as at 363 K using only the chemical analysis method, since the pressure decay method is not recommended at high temperatures due to potential significant solvent vaporization. All measurements were performed starting from a 30 % wt. aqueous amine solution. The experimental results are presented in Tables 4 and 5.

Table 5
Loading of 30.0 ± 0.1 %wt. aqueous DETA solutions obtained by pressure decay method.

Temperature ^a , T/K	CO ₂ Partial Pressure ^b , P/kPa	Loading, α / mol CO ₂ per mol amine
313.15	10.0	1.21 ± 0.06
	10.0	1.25 ± 0.06
	21.0	1.38 ± 0.05
	29.1	1.44 ± 0.05
	45.1	1.47 ± 0.04
	93.1	1.52 ± 0.03
	210.1	1.60 ± 0.03
	212.1	1.60 ± 0.03
	541.1	1.68 ± 0.04
	619.1	1.67 ± 0.06
333.15 K	16.2	1.20 ± 0.06
	16.2	1.24 ± 0.06
	47.4	1.36 ± 0.05
	66.4	1.41 ± 0.05
	89.4	1.43 ± 0.04
	150.5	1.48 ± 0.03
	297.6	1.54 ± 0.03
	297.6	1.54 ± 0.03
	662.6	1.60 ± 0.04
	713.6	1.59 ± 0.06

^a Standard uncertainty in temperature $u(T) = 0.10$ K

^b Standard uncertainty in total pressure $u(p) = 0.005 \cdot P$.

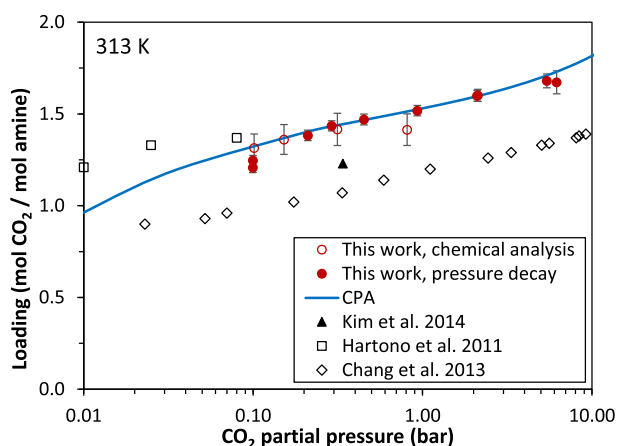


Fig. 1. Solubility of CO₂ in aqueous DETA solutions at 313 K. Experimental data (points) [18,22,53] and CPA correlations (line).

The obtained data are compared with available literature values at Figs. 1 and 2. It is observed that there are significant differences between the available literature data sets.

As shown in Figure 1, the available literature data for DETA aqueous solutions at 313 K include the data reported by Hartono et al. [22] for 2.5M solution, as well as the data of Chang et al. [53] and Kim et al. [18] for 30% wt. solutions. It is observed that there are significant differences between the available literature data sets, which indicate the experimental difficulties in such measurements. Hartono et al. [22] do not mention experimental details and present experimental data as a figure illustration. Kim et al. [18] used a semi-batch absorption apparatus operated at a pressure slightly higher than the atmospheric one and using a CO₂ – N₂ gas stream to load the liquid solvent. Chang et al. [53] used a vapor – liquid equilibrium apparatus, which was verified against data for MEA. The composition of the vapor phase was measured by gas chromatography, while the CO₂ concentration of the liquid phase was measured using the BaCl₂ and an acid titration method. The existence of such differences in the literature data was an additional reason for performing experiments using two experimental techniques. The two data series of this work, obtained using different experimental methods, are

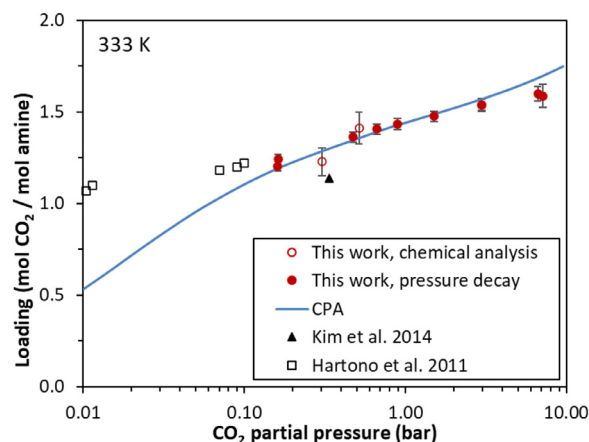


Fig. 2. Solubility of CO₂ in aqueous DETA solutions at 333 K. Experimental data (points) [18,22] and CPA correlations (line).

Table 6
Loading of 30.0 ± 0.1 %wt. aqueous TETA solutions with pressure decay method.

Temperature ^a , T/K	CO ₂ Partial Pressure ^b , P/kPa	Loading, α / mol CO ₂ per mol amine
313.15	41.9	1.87 ± 0.04
	58.9	1.93 ± 0.04
	154.9	2.01 ± 0.04
	246.9	2.07 ± 0.05
	435.0	2.13 ± 0.05
333.15	698.0	2.18 ± 0.05
	87.95	1.82 ± 0.04
	112.0	1.87 ± 0.04
	225.0	1.93 ± 0.04
	330.0	1.99 ± 0.05
	541.1	2.03 ± 0.05
	817.2	2.09 ± 0.05

^a Standard uncertainty in temperature $u(T) = 0.10$ K

^b Standard uncertainty in total pressure $u(p) = 0.005 \cdot P$.

in good agreement with each other, while they are in reasonable agreement with the data of Hartono et al. [22], despite the differences in the investigated pressure range.

3.2. TETA results

The experimental results for the TETA aqueous mixtures are presented in Table 6. Only limited literature experimental data exist for the CO₂ capacity of TETA aqueous mixtures, as shown in Table 6 and in Figs. 3 and 4. As presented in the Figures and similarly to the data for DETA systems, the experimental data of this work present higher loading values than those reported by Kim et al. [18], but are in reasonable agreement with the data presented by Schäffer et al. [17].

4. Correlation with the CPA equation of state

4.1. The CPA EoS

The experimental data were used for estimation of parameters needed in the CPA equation of state (EoS). CPA comprises two contributions, a physical and association one, as follows:

$$Z = Z^{\text{phys}} + Z^{\text{assoc}} \quad (1)$$

The first term is adopted from the Soave-Redlich-Kwong (SRK) EoS, while the second one is adopted from the perturbation theory and is identical to the respective term of the SAFT type models [54]. Consequently, the model in terms of pressure is written as follows [47,55]:

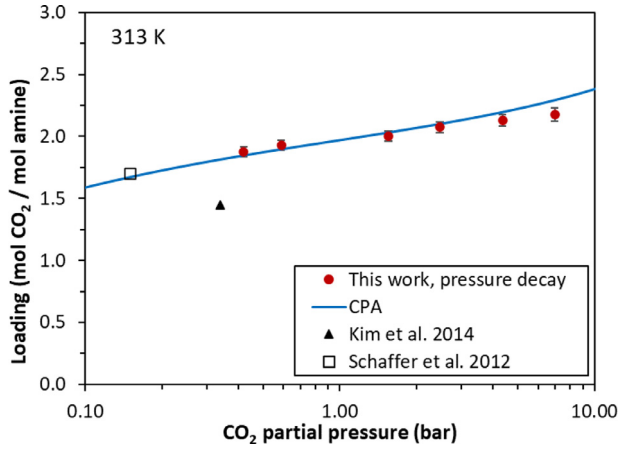


Fig. 3. Solubility of CO₂ in aqueous TETA solutions at 313 K. Experimental data (points) [17,18] and CPA correlations (line).

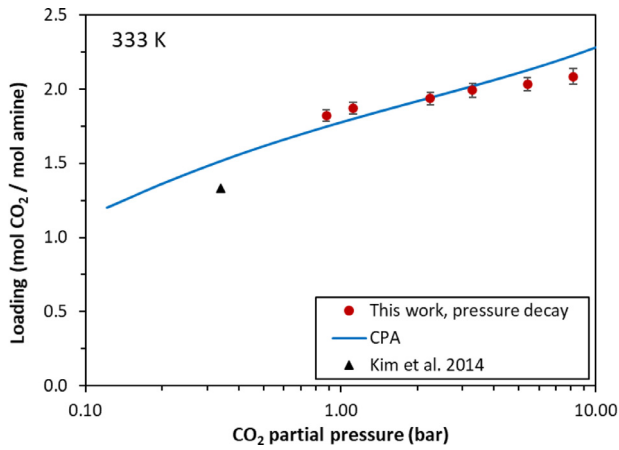


Fig. 4. Solubility of CO₂ in aqueous TETA solutions at 333 K. Experimental data (points) [18] and CPA correlations (line).

$$P = \frac{R \cdot T}{V_m - b} - \frac{a(T)}{V_m \cdot (V_m + b)} - \frac{1}{2} \frac{R \cdot T}{V_m} \left(1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \cdot \sum_{A_i} (1 - X_{A_i}) \quad (2)$$

The energy parameter, $a_i(T)$, is given by a Soave – type temperature dependency, while the co-volume parameter, b , is temperature independent [56].

$$a_i(T) = a_{0,i} \left[1 + c_{1,i} \cdot \left(1 - \sqrt{T_r} \right) \right]^2 \quad (3)$$

where T_r is the reduced temperature and $c_{1,i}$ is an SRK parameter.

X_{A_i} represents the fraction of sites A of molecule i that are not bonded with other active sites, while x_i is the mole fraction of component i . X_{A_i} is related to the association strength between two sites belonging to two different molecules, e.g. site A on molecule i and site B on molecule j , and is determined from [56] as:

$$X_{A_i} = \frac{1}{1 + \rho \cdot \sum_j x_j \sum_{B_j} (X_{B_j} \cdot \Delta^{A_i B_j})} \quad (4)$$

where the association strength $\Delta^{A_i B_j}$ is given by the following relation:

$$\Delta^{A_i B_j} = g(V_m) \left[\exp \left(\frac{\epsilon^{A_i B_j}}{R \cdot T} \right) - 1 \right] b_{ij} \cdot \beta^{A_i B_j} \quad (5)$$

In the previous expression for the association strength, $\Delta^{A_i B_j}$, the parameters $\epsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are called the association energy and the association volume, respectively, while $b_{ij} = \frac{b_i + b_j}{2}$ and the radial distribution

function, $g(V_m)$ is given from a simplified expression as a function of the co-volume, b , parameter and the molar volume, V_m [55]:

$$g(V_m) = \left[1 - \frac{1.9 \cdot b}{4 \cdot V_m} \right]^{-1} \quad (6)$$

The association energy, $\epsilon^{A_i B_j}$, and association volume, $\beta^{A_i B_j}$, parameters are only used for associating components, and together with the three additional parameters of the SRK term (a_0 , b , c_1), they comprise the five pure compound parameters of the model [56]. They are usually obtained by fitting the predictions of the model to pure fluid vapor pressure and liquid density data. For inert (not self-associating) components, e.g., hydrocarbons, only the three parameters of the SRK term are required, which can be obtained either from vapor pressures and liquid densities or calculated in the conventional manner using critical data and the acentric factor [56].

When CPA is used for mixtures, the conventional mixing and combining rules are employed in the physical term (SRK) for the energy and co-volume parameters [56]:

$$a(T) = \sum_i \sum_j x_i \cdot x_j \cdot a_{ij}(T) \quad (7)$$

$$a_{ij}(T) = \sqrt{a_i(T) \cdot a_j(T)} \cdot (1 - k_{ij}) \quad (8)$$

$$b = \sum_i x_i \cdot b_i \quad (9)$$

where, k_{ij} is the binary interaction parameter. For mixtures containing two self-associating compounds, e.g., amines and water, combining rules for the association energy ($\epsilon^{A_i B_j}$) and the association volume ($\beta^{A_i B_j}$) are required. The standard Combining Rule (CR-1) was used in this work [57]:

$$\epsilon^{A_i B_j} = \frac{\epsilon^{A_i B_i} + \epsilon^{A_j B_j}}{2}, \beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \cdot \beta^{A_j B_j}} \quad (10)$$

For mixtures presenting cross association interactions between one self-associating and one non self-associating compound, the modified CR-1 combining rule is used [57].

$$\epsilon^{A_i B_j} = \frac{\epsilon^{A_i B_i} + \epsilon^{A_j B_j}}{2}, \beta^{A_i B_j} = \text{adjustable} \quad (11)$$

4.2. The pseudo-chemical reaction approach

As in our previous study [45], we use the pseudo-chemical reaction approach for modeling CO₂ - amine interactions, i.e., to account for chemical interactions as very strong specific interactions. This is an approximation often used in equation of state models and arises from their inability to account for chemical interactions [42–46].

Consequently, amine groups (both primary and secondary) are modeled assuming one proton donor and one proton acceptor sites that can form hydrogen bonds (2B association scheme) and one chemical site that can only interact with CO₂.

Furthermore, CO₂ is modeled assuming one site that can only cross associate with water [58] and additional chemical sites that can only associate with amine groups [45]. Two such chemical sites are active in cases of primary or secondary amines, as in this study. In this way, one CO₂ molecule can simultaneously interact with two amine groups and the stoichiometric limit of 0.5 CO₂ moles per mole of amine groups, which occurs if the carbamate formation is the dominant reaction, is confirmed. Moreover, as described by Leontiadis et al. [45], in cases of tertiary or sterically hindered amines, one CO₂ chemical site is active. In this way, one CO₂ molecule can interact only with one amine group and the stoichiometric limit of 1 CO₂ mole per mole of amine groups is also confirmed. An illustration of such pseudo-chemical interactions is shown in Figure 5.

Table 7
Pure fluid parameters used in this study.

	Critical Temperature (K)	a_0 (L ² ·bar·mol ⁻²)	B (L·mol ⁻¹)	c_1	ϵ^{AiBi} (bar·L·mol ⁻¹)	β^{AiBi}	Association scheme	Reference
CO ₂	304.2	3.5079	0.0272	0.7602	-	-	-	[58]
H ₂ O	647.3	1.2277	0.0145	0.6736	166.55	0.0692	4C	[58]
DETA	676.0	25.0245	0.1012	1.0622	86.64	0.0229	3 × 2B	This study
TETA	733.2	27.9225	0.1002	1.1049	86.64	0.0229	4 × 2B	This study

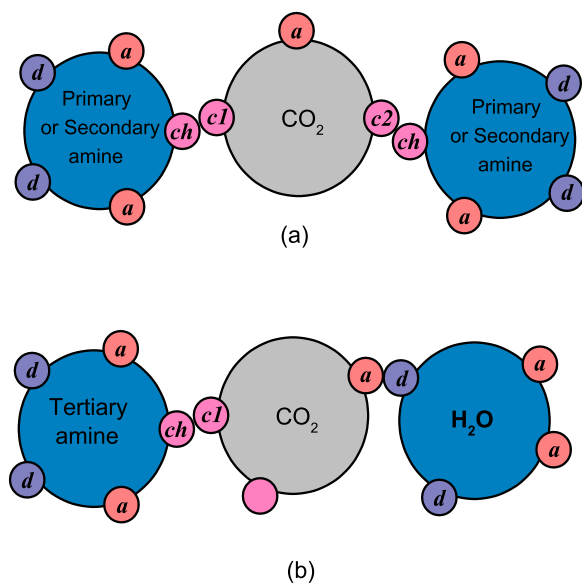


Fig. 5. The pseudo-chemical interactions for primary or secondary amines (a) and tertiary or sterically hindered amines (b). The association sites are presented, i.e. sites for chemical interactions (*ch*, *c1*, *c2*), as well as proton donor (*d*) and proton acceptor sites (*a*) capable for hydrogen bonding.

4.3. Modeling results

Pure fluid parameters for CO₂ and water were adopted from Tsvintzelis et al. [58], while those for the investigated amines were estimated by adjusting the predictions of the model to vapor pressure and liquid density experimental data. In more detail, the pure fluid parameters for DETA were obtained using the experimental vapor pressures of Bouzina et al. [59] and the normal boiling point reported by NIST [50], while the liquid densities were obtained using the experimental data of Hartono et al. [20]. The pure fluid parameters of TETA were obtained using the experimental vapor pressures of Efimova et al. [60], while the liquid densities were obtained using the experimental data of Rouleau and Thompson [61]. Since, as mentioned in the previous section, primary and secondary amine groups are modeled assuming one proton donor and one proton acceptor sites that can form hydrogen bonds, the 3 × 2B and the 4 × 2B association schemes were used for DETA and TETA, respectively, as defined by Huang and Radosz [62]. In this way, it was possible to keep constant the association parameters, ϵ^{AiBi} and β^{AiBi} , of both amines. Consequently, DETA and TETA pure fluid parameters were simultaneously regressed, by keeping the same values for association parameters of both compounds. The percentage absolute average deviations of model calculations from the experimental vapor pressures are 1.2% and 4.1% for DETA and TETA, respectively, while the corresponding values for the liquid densities are 0.8% and 1.7%, respectively.

All pure fluid parameters are presented in Table 7, while results for the amines' vapor pressures are illustrated in Fig. 6.

All the used binary parameters are presented in Table 8. Binary parameters for CO₂ - water were adopted from Tsvintzelis et al. [58],

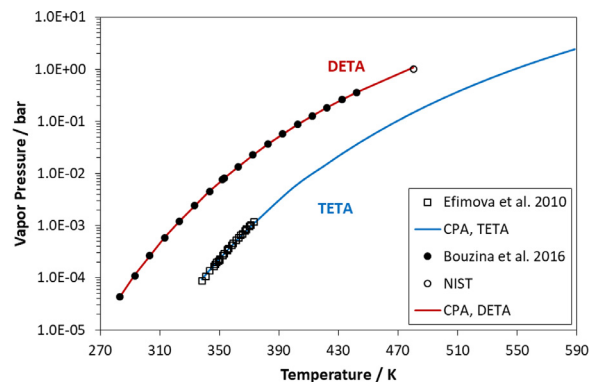


Fig. 6. DETA and TETA vapor pressures. Experimental data (points, [59,60]) and CPA correlations (lines).

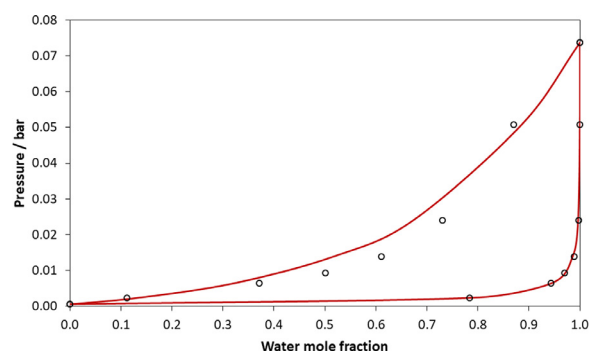


Fig. 7. DETA -water VLE behavior. Experimental data (points, [59]) and CPA correlations (lines).

who suggested modeling CO₂ with one association site that is capable to cross associate with water and used the experimental value for the cross association energy of this specific interaction.

The binary interaction parameter for DETA-water sub-binary mixture was estimated using the experimental vapor-liquid equilibrium data of Bouzina et al. [59]. Some characteristic calculations for the VLE of this system are presented in Fig. 7. The obtained k_{ij} value is rather high and reflects the inaccuracy of the combining rule for estimating the cross-association parameters, since such combining rules present limited physical meaning. For this reason, it was suggested to use experimental values (e.g. from calorimetry or spectroscopy) or theoretical (e.g. from ab-initio calculations), at least for the cross-association energy [58]. However, such data are scarce and not available for the investigated systems. Due to the lack of experimental data for the TETA-water system, the binary parameter was adopted from the DETA-water mixture.

The binary parameters for amine - CO₂ sub-binary systems were calculated by adjusting the model predictions to the experimental data of this study. In both systems (DETA - CO₂ and TETA - CO₂), a temperature independent binary interaction parameter (k_{ij}) was used, which shows rather high values, mainly in order to compensate the approximation of

Table 8
Binary parameters used in this study

	k_{ij}	ϵ_{cross} (bar·L·mol ⁻¹)	β_{cross}	ϵ_{cross} (bar·L·mol ⁻¹)	β_{cross}
CO ₂ - water	0.11406 ^a	Exp. 142.0 ^b	mCR1: 0.0162 ^a	-	-
DETA - water	-0.4	CR-1	CR-1	-	-
TETA - water	-0.4 ^b	CR-1	CR-1	-	-
CO ₂ - DETA	0.423	318.9	0.0023	318.9	0.0023
CO ₂ - TETA	0.423	318.9	0.0013	318.9	0.0013

^a CO₂-H₂O (Tsivintzelis et al. [58])

^b Adopted from DETA-water

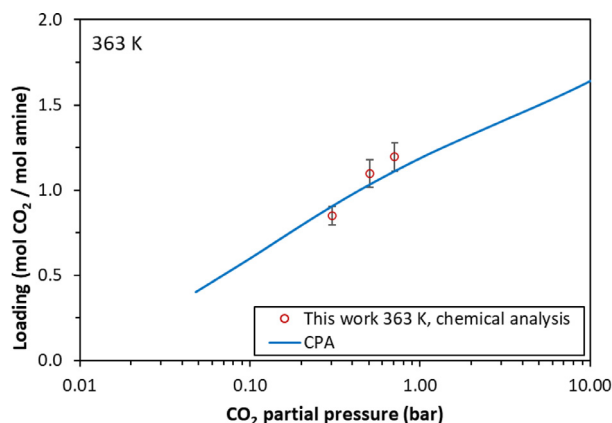


Fig. 8. Solubility of CO₂ in aqueous DETA solutions at 363 K. Experimental data (points, this work) and CPA correlations (line).

the pseudo-chemical reaction approach. The two chemical sites of primary and secondary amine groups, in general, are not considered identical and, consequently, two different sets of cross-association parameters are needed, i.e. one for each interaction with CO₂ [45]. However, as shown in Table 8, in order to minimize the number of adjustable parameters for the investigated mixtures, the association parameters for both the CO₂-amine chemical interactions were kept constant. Also the same association energy value was used for both amine systems. In this way, using three binary adjustable parameters, the CPA equation of state rather satisfactorily describes the experimental data of this study as shown in Figs. 1–4 and 8. It is worth mentioning that Wang et al. [14], using the same approach with the Peng-Robinson CPA model, implemented seven adjustable parameters for the CO₂ – MEA and five for the CO₂ – MDEA binary systems, while Leontiadis et al. [45] used four binary parameters for CO₂ - MDEA.

Consequently, using the binary parameters of Table 8, the CPA equation of state rather satisfactorily describes the experimental data of this study.

5. Conclusions

In this work, diethylenetriamine and triethylenetetramine aqueous solutions were experimentally investigated in terms of CO₂ absorption capacity using a pressure decay method, while the former system was also studied using a chemical analysis technique. In this way, new experimental data were obtained that shed light in the VLE behavior of such systems, considering also the scarce and contradictory existing literature data.

Subsequently, the CPA equation of state, coupled with the pseudo-chemical reaction approach, was parameterized using also the experimental data of this work and satisfactory correlations were obtained using three adjustable parameters that were optimized in the multicomponent systems' data. mmc1.pdf

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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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ctta.2021.100017.

References

- [1] M. Bui, C.S. Adjiman, A. Bardow, E.J. Anthony, A. Boston, S. Brown, P.S. Fennell, S. Fuss, A. Galindo, L.A. Hackett, J.P. Hallett, H.J. Herzog, G. Jackson, J. Kemper, S. Krevor, G.C. Maitland, M. Matuszewski, I.S. Metcalfe, C. Petit, G. Puxty, J. Reimer, D.M. Reiner, E.S. Rubin, S.A. Scott, N. Shah, B. Smit, J.P.M. Trusler, P. Webley, J. Wilcox, N. Mac Dowell, Carbon capture and storage (CCS): The way forward, *Energy Environ. Sci.* 11 (2018) 1062–1176, doi:10.1039/c7ee02342a.
- [2] T.N. Borhani, M. Wang, Role of solvents in CO₂ capture processes: The review of selection and design methods, *Renew. Sustain. Energy Rev.* 114 (2019) 109299, doi:10.1016/j.rser.2019.109299.
- [3] J. Zhang, Study on CO₂ Capture Using Thermomorphic Biphasic Solvents with Energy-Efficient Regeneration, TU Dortmund, 2013 PhD Thesis.
- [4] A. Hartono, E.F. da Silva, H.F. Svendsen, Kinetics of carbon dioxide absorption in aqueous solution of diethylenetriamine (DETA), *Chem. Eng. Sci.* 64 (2009) 3205–3213, doi:10.1016/j.ces.2009.04.018.
- [5] A. Hartono, E.F. da Silva, H. Grasdalen, H.F. Svendsen, Qualitative Determination of Species in DETA-H₂O-CO₂ System Using ¹³C NMR Spectra, *Ind. Eng. Chem. Res.* 46 (2007) 249–254, doi:10.1021/ie0603868.
- [6] A.I. Papadopoulos, F. Tzirakis, I. Tsivintzelis, P. Seferlis, Phase-change solvents and processes for post-combustion CO₂ capture: a detailed review, *Ind. Eng. Chem. Res.* 58 (2019) 5088–5111, doi:10.1021/acs.iecr.8b06279.
- [7] Q. Ye, X. Wang, Y. Lu, Screening and evaluation of novel biphasic solvents for energy efficient post-combustion CO₂ capture, *Int. J. Greenh. Gas Control* 39 (2015) 205–214, doi:10.1016/j.ijggc.2015.05.025.
- [8] Q. Ye, L. Zhu, X. Wang, Y. Lu, On the mechanisms of CO₂ absorption and desorption with phase transitional solvents, *Int. J. Greenh. Gas Control* 56 (2017) 278–288, doi:10.1016/j.ijggc.2016.11.027.
- [9] X. Zhou, F. Liu, B. Lv, Z. Zhou, G. Jing, Evaluation of the novel biphasic solvents for CO₂ capture: performance and mechanism, *Int. J. Greenhouse Gas Control* 60 (2017) 120–128, doi:10.1016/j.ijggc.2017.03.013.
- [10] L. Wang, S. An, S. Yu, S. Zhang, Y. Zhang, M. Li, Q. Li, Mass transfer characteristics of CO₂ absorption into a phase-change solvent in a wetted-wall column, *Int. J. Greenh. Gas Control* 64 (2017) 276–283, doi:10.1016/j.ijggc.2017.08.001.
- [11] W. Luo, D. Guo, J. Zheng, S. Gao, J. Chen, CO₂ absorption using biphasic solvent: blends of diethylenetriamine, sulfolane, and water, *Int. J. Greenh. Gas Control* 53 (2016) 141–148, doi:10.1016/j.ijggc.2016.07.036.
- [12] S. Sartori, F. Leder, 1980, Process and amine-solvent absorbent for removing acidic gases from gaseous mixtures, US4240923A. <https://patents.google.com/patent/US4240923A/en>
- [13] K.M. Sarker, Theoretical effect of concentration, circulation rate, stages, pressure and temperature of single amine and amine mixture solvents on gas sweetening performance, *Egypt. J. Pet.* 25 (2016) 343–354, doi:10.1016/j.ejpe.2015.08.004.
- [14] L. Wang, S. Yu, Q. Li, Y. Zhang, S. An, S. Zhang, Performance of sulfolane/DETA Hybrids for CO₂ absorption: phase splitting behavior, *Kinet. Thermodyn. Appl. Energy* 228 (2018) 568–576.

- [15] S. Zhang, Y. Shen, P. Shao, J. Chen, L. Wang, Kinetics, thermodynamics, and mechanism of a novel biphasic solvent for CO₂ Capture from flue gas, *Environ. Sci. Technol.* 52 (6) (2018) 3660–3668, doi:10.1021/acs.est.7b05936.
- [16] Y. Shen, C. Jiang, S. Zhang, J. Chen, L. Wang, J. Chen, Biphasic solvent for CO₂ capture: amine property-performance and heat duty relationship, *Appl. Energy* 230 (2018) 726–733, doi:10.1016/j.apenergy.2018.09.005.
- [17] A. Schäffer, G. Brechtel, G. Scheffknecht, Comparative study on differently concentrated aqueous solutions of MEA and TETA for CO₂ capture from flue gases, *Fuel* 101 (2012) 148–153, doi:10.1016/j.fuel.2011.06.037.
- [18] Y. Kim, S.J. Moon, Y.I. Yoon, S.K. Jeong, K.T. Park, S.T. Bae, S.C. Nam, Heat of absorption and absorption capacity of CO₂ in aqueous solutions of amine containing multiple amino groups, *Sep. Purif. Technol.* 122 (2014) 112–118, doi:10.1016/j.seppur.2013.10.030.
- [19] U.A. Maheswari, K. Palanivelu, Alkyl amine and vegetable oil mixture—a viable candidate for CO₂ capture and utilization, *Environ. Sci. Pollut. Res.* 24 (2016) 5733–5745, doi:10.1007/s11356-016-8306-5.
- [20] A. Hartono, H.F. Svendsen, Density, viscosity, and excess properties of aqueous solution of diethylenetriamine (DETA), *J. Chem. Thermodyn.* 41 (2009) 973–979, doi:10.1016/j.jct.2008.11.012.
- [21] A. Hartono, H.F. Svendsen, Kinetics reaction of primary and secondary amine group in aqueous solution of diethylenetriamine (DETA) with carbon dioxide, *Energy Proced.* 1 (2009) 853–859, doi:10.1016/j.egypro.2009.01.113.
- [22] A. Hartono, K.A. Hoff, T. Mejdell, H.F. Svendsen, Solubility of carbon dioxide in aqueous 2.5 M of diethylenetriamine (DETA) solution, *Energy Proced.* 4 (2011) 179–186, doi:10.1016/j.egypro.2011.01.039.
- [23] I. Eide-Haugmo, H. Lepaumier, A. Einbu, K. Vernstad, E. Falck, Chemical stability and biodegradability of new solvents for CO₂ capture, *Energy Proced.* 4 (2011) 1631–1636, doi:10.1016/j.egypro.2011.02.034.
- [24] C.F. Martín, M.B. Sweatman, S. Brandani, X. Fan, Wet impregnation of a commercial low cost silica using DETA for a fast post-combustion CO₂ capture process, *Appl. Energy* 183 (2016) 1705–1721, doi:10.1016/j.apenergy.2016.09.081.
- [25] J. Lee, Y.K. Hong, J.K. You, Phase separation characteristics in biphasic solvents based on mutually miscible amines for energy efficient CO₂ capture, *Korean J. Chem. Eng.* 34 (2017) 1840–1845, doi:10.1007/s11814-017-0067-4.
- [26] C. Nwaoha, C. Saiwan, T. Supap, R. Idem, P. Tontiwachwuthikul, W. Rongwong, M.J. Al-Marri, A. Benamor, Carbon dioxide (CO₂) capture performance of aqueous tri-solvent blends containing 2-amino-2-methyl-1-propanol (AMP) and methyldiethanolamine (MDEA) promoted by diethylenetriamine (DETA), *Int. J. Greenh. Gas Control* 53 (2016) 292–304, doi:10.1016/j.jggc.2016.08.012.
- [27] Q. Ye, X. Wang, Y. Lu, Experimental investigation and thermodynamic modeling of phase transition and equilibria in a biphasic solvent system for CO₂ capture, *Ind. Eng. Chem. Res.* 57 (29) (2018) 9627–9640, doi:10.1021/acs.iecr.8b00990.
- [28] F. Liu, G. Jing, X. Zhou, B. Lv, Z. Zhou, Performance and mechanisms of triethylene tetramine (TETA) and 2-amino-2-methyl-1-propanol (AMP) in aqueous and non-aqueous solutions for CO₂ capture, *ACS Sustain. Chem. Eng.* 6 (1) (2017) 1352–1361, doi:10.1021/acssuschemeng.7b03717.
- [29] Y. Li, C. Liu, R. Parnas, Y. Liu, B. Liang, H. Lu, The CO₂ absorption and desorption performance of the triethylenetetramine + N,N-diethylethanolamine + H₂O system, *Chin. J. Chem. Eng.* 26 (2018) 2351–2360, doi:10.1016/j.cjche.2018.04.014.
- [30] L. Wang, S. Liu, R. Wang, Q. Li, S. Zhang, Regulating phase separation behavior of a DEEA–TETA biphasic solvent using sulfolane for energy-saving CO₂ capture, *Environ. Sci. Technol.* 53 (21) (2019) 12873–12881, doi:10.1021/acs.est.9b02787.
- [31] J. Ye, C. Jiang, J. Chen, Y. Shen, S. Zhang, L. Wang, J. Chen, Novel biphasic solvent with tunable phase separation for CO₂ capture: role of water content in mechanism, kinetics, and energy penalty, *Environ. Sci. Technol.* 53 (2019) 4470–4479, doi:10.1021/acs.est.9b00040.
- [32] Y. Shen, H. Chen, L. Wang, S. Zhang, C. Jiang, J. Ye, L. Wang, J. Chen, Two-stage interaction performance of CO₂ absorption into biphasic solvents: Mechanism analysis, quantum calculation and energy consumption, *Appl. Energy* 260 (2020) 114343, doi:10.1016/j.apenergy.2019.114343.
- [33] S. Zheng, M. Tao, Q. Liu, L. Ning, Y. He, Y. Shi, Capturing CO₂ into the precipitate of a phase-changing solvent after absorption, *Environ. Sci. Technol.* 48 (2014) 8905–8910, doi:10.1021/es501554h.
- [34] M. Tao, J. Gao, W. Zhang, Y. Li, Y. He, Y. Shi, Novel Phase-changing non-aqueous Solution for CO₂ capture with high capacity, thermostability, and regeneration efficiency, *Ind. Eng. Chem. Res.* 57 (28) (2018) 9305–9312, doi:10.1021/acs.iecr.8b01775.
- [35] X. Zhou, X. Xu, X. Chen, G. Yu, Novel ionic liquids phase change solvents for CO₂ capture, *Int. J. Greenh. Gas Control* 98 (2020) 103068, doi:10.1016/j.jggc.2020.103068.
- [36] P. Ramezani, S. Mazinani, R.S. Di Felice, B. Van der Bruggen, Experimental and correlation study of corrosion rate, absorption rate and CO₂ loading capacity in five blend solutions as new absorbents for CO₂ capture, *J. Nat. Gas Sci. Eng.* 45 (2017) 599–608, doi:10.1016/j.jngse.2017.06.028.
- [37] R.L. Kent, B. Eisenberg, Better data for amine treating, *Hydrocarb. Proc.* 55 (2) (1976) 87–90.
- [38] F.Y. Jou, A.E. Mather, F.D. Otto, Solubility of H₂S and CO₂ in aqueous methyldiethanolamine solutions, *Ind. Eng. Chem. Proc. Des. Dev.* 21 (1982) 539–544, doi:10.1021/i200019a001.
- [39] H. Suleman, A.S. Maulud, P.L. Fosbøl, Q. Nasir, R. Nasir, M.Z. Shahid, M. Nawaz, M. Abunowara, A review of semi-empirical equilibrium models for CO₂-alkanolamine-H₂O solutions and their mixtures at high pressure, *J. Environ. Chem. Eng.* 9 (2021) 104713, doi:10.1016/j.jece.2020.104713.
- [40] M. Uyan, G. Sieder, T. Ingram, C. Held, Predicting CO₂ solubility in aqueous N-methyldiethanolamine solutions with ePC-SAFT, *Fluid Phase Equil.* 393 (2015) 91–100, doi:10.1016/j.fluid.2015.02.026.
- [41] A. Wängler, G. Sieder, T. Ingram, M. Heiling, C. Held, Prediction of CO₂ and H₂S solubility and enthalpy of absorption in reacting N-methyldiethanolamine/water systems with ePC-SAFT, *Fluid Phase Equil.* 461 (2018) 15–27, doi:10.1016/j.fluid.2017.12.033.
- [42] J. Rodriguez, N.M. Dowell, F. Llovel, C.S. Adjiman, G. Jackson, A. Galindo, Modeling the fluid phase behavior of aqueous mixtures of multifunctional alkanolamines and carbon dioxide using transferable parameters with the SAFT-VR approach, *Mol. Phys.* (2012) 1325–1348, doi:10.1080/00268976.2012.665504.
- [43] A. Chremos, E. Forte, V. Papaioannou, A. Galindo, G. Jackson, C.S. Adjiman, Modeling the phase and chemical equilibria of aqueous solutions of alkanolamines and carbon dioxide using the SAFT- γ SW group contribution approach, *Fluid Phase Equilib.* 407 (2016) 280–297, doi:10.1016/j.fluid.2015.07.052.
- [44] A.I. Papadopoulos, F.A. Perdomo, F. Tzirakis, G. Shavaliava, I. Tsvintzelis, P. Kazepidis, E. Nessi, S. Papadokonstantakis, P. Seferlis, A. Galindo, G. Jackson, C.S. Adjiman, Molecular engineering of sustainable phase-change solvents: from digital design to scaling-up for CO₂ capture, *Chem. Eng. J.* (2020) 127624, doi:10.1016/j.cej.2020.127624.
- [45] K. Leontiadis, E. Tzimpilis, D. Aslanidou, I. Tsvintzelis, Solubility of CO₂ in 3-amino-1-propanol and in N-methyldiethanolamine aqueous solutions: experimental investigation and correlation using the CPA equation of state, *Fluid Phase Equil.* 500 (2019) 112254, doi:10.1016/j.fluid.2019.112254.
- [46] T. Wang, E. El Ahmar, C. Coquelet, G.M. Kontogeorgis, Improvement of the PR-CPA equation of state for modeling of acid gases solubilities in aqueous alkanolamine solutions, *Fluid Phase Equil.* 471 (2018) 74–82.
- [47] G.M. Kontogeorgis, E.C. Voutsas, I.V. Yakoumis, D.P. Tassios, An equation of state for associating fluids, *Ind. Eng. Chem. Res.* 35 (1996) 4310–4318, doi:10.1021/ie9600203.
- [48] G.M. Kontogeorgis, M.L. Michelsen, G.K. Folas, S. Derawi, N. Von Solms, E.H. Stenby, Ten Years with the CPA (Cubic-Plus-Association) equation of state. Part 2. Cross-associating and multicomponent systems, *Ind. Eng. Chem. Res.* 45 (2006) 4869–4878, doi:10.1021/ie051306n.
- [49] F. Tzirakis, I. Tsvintzelis, A.I. Papadopoulos, P. Seferlis, Experimental measurement and assessment of equilibrium behavior for phase change solvents used in CO₂ capture, *Chem. Eng. Sci.* 199 (2019) 20–27, doi:10.1016/j.ces.2018.12.045.
- [50] National Institute of Standards and Technology (NIST), Isothermal properties for carbon dioxide. <http://webbook.nist.gov/chemistry/>. (Accessed in May 2021).
- [51] M.W. Arshad, H.F. Svendsen, P.L. Fosbøl, N. Von Solms, K. Thomsen, Equilibrium total pressure and CO₂ solubility in binary and ternary aqueous solutions of 2-(Diethylamino)ethanol (DEEA) and 3-(Methylamino)propylamine (MAPA), *J. Chem. Eng. Data* 59 (2014) 764–774, doi:10.1021/je400886w.
- [52] F.Y. Jou, A.E. Mather, F.D. Otto, The solubility of CO₂ in a 30 mass percent monoethanolamine solution, *Can. J. Chem. Eng.* 73 (1995) 140–147, doi:10.1002/cjce.5450730116.
- [53] Y.-C. Chang, R. Leron, M.-H. Li, Equilibrium solubility of carbon dioxide in aqueous solutions of (diethylenetriamine + piperazine), *J. Chem. Thermodyn.* 64 (2013) 106–113, doi:10.1016/j.jct.2013.05.005.
- [54] G.M. Kontogeorgis, G.K. Folas, *Thermodynamic models for industrial applications. From Classical and Advanced mixing rules to association theories*, Wiley, 2010.
- [55] G.M. Kontogeorgis, I.V. Yakoumis, H. Meijer, H. Hendriks, T. Moorwood, Multicomponent phase equilibrium calculations for water-methanol-alkane mixtures, *Fluid Phase Equil.* 158–160 (1999) 201–209, doi:10.1016/S0378-3812(99)00060-6.
- [56] G.M. Kontogeorgis, G.K. Folas, N. Muro-Suñé, F. Roca Leon, M.L. Michelsen, Solvation phenomena in association theories with applications to oil & gas and chemical industries, *Oil Gas Sci. Technol. Rev. IFP* 63 (2008) 305–319, doi:10.2516/ogst.2008025.
- [57] G.K. Folas, G.M. Kontogeorgis, M.L. Michelsen, E.H. Stenby, Application of the cubic-plus-association (CPA) equation of state to complex mixtures with aromatic hydrocarbons, *Ind. Eng. Chem. Res.* 45 (2006) 1527–1538, doi:10.1021/ie050976q.
- [58] I. Tsvintzelis, G.M. Kontogeorgis, M.L. Michelsen, E.H. Stenby, Modeling phase equilibria for acid gas mixtures using the CPA equation of state. Part II: Binary mixtures with CO₂, *Fluid Phase Equil.* 306 (2011) 38–56, doi:10.1016/j.fluid.2011.02.006.
- [59] Z. Bouzina, F. Dergal, I. Mokbel, A. Negadi, J. Saab, J. Jose, L. Negadi, Liquid-vapor equilibria of pure and aqueous solutions of diethylenetriamine or dipropylenetriamine, *Fluid Phase Equil.* 414 (2016) 164–169, doi:10.1016/j.fluid.2016.01.022.
- [60] A.A. Efimova, V.N. Emel'yanenko, S.P. Verevkin, Y. Chernyak, Vapour pressure and enthalpy of vaporization of aliphatic poly-amines, *J. Chem. Thermodyn.* 42 (2010) 330–336, doi:10.1016/j.jct.2009.09.003.
- [61] D.J. Rouleau, R.A. Thompson, Densities and refractive indices of aqueous solutions, *J. Chem. Eng. Data* 7 (1962) 356–357, doi:10.1021/je60014a010.
- [62] H.S. Huang, M. Radosz, Equation of state for small, large, polydisperse, and associating molecules, *Ind. Eng. Chem. Res.* 29 (1990) 22-84-2294, doi:10.1021/ie00107a014.