



# CO<sub>2</sub> solubility in amine based deep eutectic solvents: Review of literature data, experimental measurements for choline chloride plus 3-amino-1-propanol or 3-(methylamino)propylamine aqueous solutions and modeling with the modified Kent-Eisenberg model

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## ABSTRACT

The effect of water and choline chloride on the CO<sub>2</sub> absorption ability of amine based deep eutectic solvents is investigated. New experimental data are presented for four choline chloride – 3-amino-1-propanol (MPA) aqueous systems of various water contents and for an aqueous choline chloride – 3-(methylamino)propylamine (MAPA) system, which were modelled with the modified Kent-Eisenberg model. It was shown that, starting from an aqueous amine solution, the replacement of a small part of the amine by choline chloride does not significantly influence the moles of the absorbed CO<sub>2</sub> per mole of amine, but reduces the CO<sub>2</sub> solubility in the bulk, expressed as moles of CO<sub>2</sub> per kg of solvent. Furthermore, it was shown that if a small part of water is replaced by choline chloride, the CO<sub>2</sub> solubility in the bulk is not significantly altered. Moreover, the addition of water favors the chemical absorption, as the experimental results show increased absorbed moles of CO<sub>2</sub> per mole of amine. However, such phenomenon is not enough to compensate for the rather low CO<sub>2</sub> solubility in water and the overall absorption ability of the aqueous DES solution, expressed in moles of CO<sub>2</sub> per kg of solvent, decreases. The modified Kent-Eisenberg model satisfactorily correlates the experimental data showing deviations that range between 0.4–6.6 % in all cases. The model predictions for the speciation in the loaded solutions reveal that the unreacted amine content is very low at CO<sub>2</sub> partial pressures of the order of 1 kPa and that the increase of CO<sub>2</sub> solubility at higher partial pressures is attributed to the hydrolysis of the carbamate and the molecular CO<sub>2</sub> dissolution.

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>), a well-known greenhouse gas, is considered as the primary contributor to the rise of earth's surface temperature [1]. The combustion of fossil fuels in power plants is one of the major anthropogenic sources of CO<sub>2</sub> emissions [2], which are expected to increase drastically in the future, if no measures are taken, due to the increasing energy demands. Carbon capture and storage (CCS) is recognized as a viable near-term solution to reduce CO<sub>2</sub> emissions [3,4]. Among the available CCS technologies, chemical absorption/stripping using a 30 % wt. monoethanolamine (MEA) aqueous solution as a

solvent is considered the most viable and mature technology, due to its extensive use in the gas processing industry [5]. However, chemical CO<sub>2</sub> absorption using alkanolamines presents limitations such as significant solvent losses, due to amine volatility and degradation, and high energy demands for solvent regeneration. Furthermore, due to the volatile nature of amines, there are growing concerns regarding potential threats of such solvents to humans and to the environment [6].

CO<sub>2</sub> capture using ionic liquids (ILs) is considered as a promising alternative method to the conventional amine-based absorption. Due to their negligible volatility, ILs are often considered as environmentally benign solvents, while many of them present high CO<sub>2</sub> solubility [7].

**Abbreviations:** Am, Amine; AMP, 2-Amino-2-methyl-1-propanol; CCS, Carbon capture and storage; ChCl, Choline Chloride; DES, Deep eutectic solvents; EG, Ethylene glycol; HBA, Hydrogen bonding acceptor; HBD, Hydrogen bonding donor; ILs, Ionic liquids; MAPA, 3-(Methylamino)propylamine; MDEA, N-Methyldiethanolamine; MEA, Ethanolamine; RTIL, Room-temperature ionic liquids; S, Salt; TBAB, Tetrabutylammonium bromide; TEA, Triethanolamine; TEAC, Tetraethylammonium chloride; TMAC, Tetramethylammonium chloride; U, Urea.

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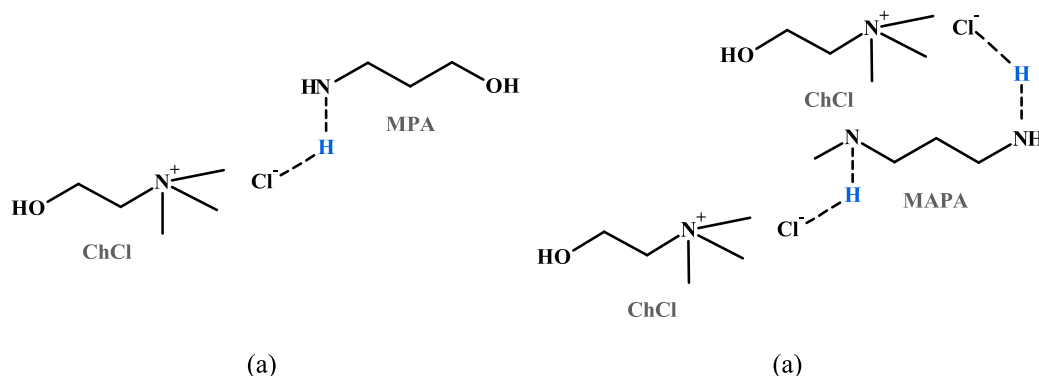


Fig. 1. Structure of investigated DES, a) ChCl/MPA and b) ChCl/MAPA.

Table 1

Literature studies investigating DES with amines.

Type of DES	References
Amine-based DES	Adeyemi et al. [26] Ali et al. [27] García-Argüelles et al. [28] Li et al. [29] Sarmad et al. [30] Shukla and Mikkola [31] Haider and Kumar [32]
Urea-based DES	Ali et al. [27] Jiang et al. [33] Leron et al. [34] Li et al. [35] Mirza et al. [36] Xie et al. [37]
Aqueous amine-based DES	Li et al. [29]
Aqueous urea-based DES	Hsu et al. [21] Ji et al. [38] Su et al. [20] Xie et al. [22]
Aqueous solutions containing DES + amine	Babaei & Haghtalab [39] Hsu et al. [21] Li et al. [29]

However, their high viscosity and complicated synthesis and purification are significant obstacles to their wide implementation as solvents for CO<sub>2</sub> capture [7,8].

Deep eutectic solvents (DES) are considered as a new class of ILs. They are formed by mixing a hydrogen bonding acceptor (HBA), such as substituted quaternary ammonium or phosphonium salts, and a hydrogen bonding donor (HBD), such as carboxylic acids, amides,

amines, alcohols, or metal halides. Recently, they have attracted intensive research effort due to many desirable solvent properties compared to conventional molecular solvents. Similarly to room-temperature ILs (RTIL), they present high thermal and chemical stability, high solvation capacity, negligible volatility, non-flammability, while they exist at a liquid state at a sufficient temperature range. However, unlike most RTIL, high purity DES can be easily prepared [9,10]. Furthermore, plenty of inexpensive organic salts, as well as plenty of cheap, biodegradable and non-toxic HBD are available, allowing the preparation of many novel solvent systems at a considerably lower cost compared to the production cost of RTIL [11]. Such new solvents have been studied for utilization in various fields such as drug solubilization [12], electrochemical processes [13,14], purification processes [15,16], organic [17] and material [18] synthesis.

The limitation of the high, in general, viscosity of ILs and DES can be overcome by mixing ILs or DES with common solvents such as water or ethylene glycol [15,19]. Except for viscosity, the presence of common solvents affects the corrosivity of the solvent and the CO<sub>2</sub> solubility [20–22]. In more detail, the dissolution of CO<sub>2</sub> into most ILs or DES is based on physical intermolecular interactions (physical absorption) and for this reason it is usually performed at relatively high pressures. To enhance the CO<sub>2</sub> uptake, or equivalently to obtain sufficient CO<sub>2</sub> solubility at relatively lower pressures, solvents capable for chemical CO<sub>2</sub> absorption are required and, in this direction, amine-based DES have been suggested for CO<sub>2</sub> capture applications. However non aqueous amine-based solvents are avoided due to their high corrosivity, and, for this reason, aqueous solutions are used instead. However, the reaction pathway and kinetics of CO<sub>2</sub> with amines is significantly altered by the existence of water. Consequently, the addition of water in such DES is crucial for reducing the viscosity and the corrosion behavior of the

Table 2

Literature review of CO<sub>2</sub> solubility in aqueous amine-based DES.

S-HBD	[S]/[HBD] mole ratio	% wt-H <sub>2</sub> O	CO <sub>2</sub> solubility [weight fraction]*	Temp. [K]	P <sub>CO2</sub>	Reference
ChCl-MEA	1:5	5	0.2644	303	atmospheric	Li et al. [29]
ChCl-MEA	1:5	10	0.3191	303	atmospheric	Li et al. [29]
ChCl-MEA	1:5	15	0.2718	303	atmospheric	Li et al. [29]
ChCl-MEA	1:5	20	0.2762	303	atmospheric	Li et al. [29]
ChCl-MEA	1:5	25	0.2667	303	atmospheric	Li et al. [29]
TEAC-MEA	1:5	5	0.2422	303	atmospheric	Li et al. [29]
TEAC-MEA	1:5	10	0.2835	303	atmospheric	Li et al. [29]
TEAC-MEA	1:5	15	0.2769	303	atmospheric	Li et al. [29]
TEAC-MEA	1:5	20	0.2733	303	atmospheric	Li et al. [29]
TEAC-MEA	1:5	25	0.2319	303	atmospheric	Li et al. [29]
TMAC-MEA	1:5	5	0.3383	303	atmospheric	Li et al. [29]
TMAC-MEA	1:5	10	0.3426	303	atmospheric	Li et al. [29]
TMAC-MEA	1:5	15	0.3368	303	atmospheric	Li et al. [29]
TMAC-MEA	1:5	20	0.3191	303	atmospheric	Li et al. [29]
TMAC-MEA	1:5	25	0.2910	303	atmospheric	Li et al. [29]

\*Data extracted from plots.

**Table 3**Literature review of CO<sub>2</sub> solubility in aqueous DES + Amine solutions.

S-HBD-Am	[S] + [HBD] + [Am]	% wt H <sub>2</sub> O	CO <sub>2</sub> solubility	P <sub>CO2</sub> [kPa]	Temp. [K]	Authors
TBAB-EG-AMP	19.01 + 10.99 + 30 %wt.	40	0.905–1.127 mol CO <sub>2</sub> /mol Amine	123–4994	313	Babaei & Haghtalab [39]
TBAB-EG-AMP	19.01 + 10.99 + 30 %wt.	40	0.809–1.113 mol CO <sub>2</sub> /mol Amine	155–5000	328	Babaei & Haghtalab [39]
TBAB-EG-AMP	19.01 + 10.99 + 30 %wt.	40	0.647–1.099 mol CO <sub>2</sub> /mol Amine	146–4968	343	Babaei & Haghtalab [39]
TBAB-EG-AMP	14.26 + 8.24 + 30 %wt.	47.5	0.922–1.144 mol CO <sub>2</sub> /mol Amine	110–5093	313	Babaei & Haghtalab [39]
TBAB-EG-AMP	14.26 + 8.24 + 30 %wt.	47.5	0.786–1.133 mol CO <sub>2</sub> /mol Amine	94–5268	328	Babaei & Haghtalab [39]
TBAB-EG-AMP	14.26 + 8.24 + 30 %wt.	47.5	0.612–1.116 mol CO <sub>2</sub> /mol Amine	95–5055	343	Babaei & Haghtalab [39]
TBAB-EG-AMP	9.51 + 5.49 + 30 %wt.	55	0.955–1.143 mol CO <sub>2</sub> /mol Amine	164–4746	313	Babaei & Haghtalab [39]
TBAB-EG-AMP	9.51 + 5.49 + 30 %wt.	55	0.880–1.132 mol CO <sub>2</sub> /mol Amine	167–4993	328	Babaei & Haghtalab [39]
TBAB-EG-AMP	9.51 + 5.49 + 30 %wt.	55	0.754–1.122 mol CO <sub>2</sub> /mol Amine	182–4950	343	Babaei & Haghtalab [39]
TBAB-EG-AMP	4.76 + 2.74 + 30 %wt.	62.5	0.951–1.160 mol CO <sub>2</sub> /mol Amine	117–5049	313	Babaei & Haghtalab [39]
TBAB-EG-AMP	4.76 + 2.74 + 30 %wt.	62.5	0.833–1.147 mol CO <sub>2</sub> /mol Amine	93–4905	328	Babaei & Haghtalab [39]
TBAB-EG-AMP	4.76 + 2.74 + 30 %wt.	62.5	0.762–1.137 mol CO <sub>2</sub> /mol Amine	168–4991	343	Babaei & Haghtalab [39]
(ChCl-U)-MEA	(50) + 15 % wt.	35	0.148–0.229 mol CO <sub>2</sub> /mol solute	75.2–818.5	313	Hsu et al. [21]
(ChCl-U)-MEA	(50) + 15 % wt.	35	0.099–0.181 mol CO <sub>2</sub> /mol solute	59.4–855.8	333	Hsu et al. [21]
(ChCl-U)-MEA	(50) + 15 % wt.	35	0.125–0.197 mol CO <sub>2</sub> /mol solute	66.1–804.1	353	Hsu et al. [21]
(ChCl-U)-MEA	(60) + 10 % wt.	30	0.110–0.202 mol CO <sub>2</sub> /mol solute	84.6–825.3	313	Hsu et al. [21]
(ChCl-U)-MEA	(60) + 10 % wt.	30	0.099–0.181 mol CO <sub>2</sub> /mol solute	66.1–834.9	333	Hsu et al. [21]
(ChCl-U)-MEA	(60) + 10 % wt.	30	0.097–0.171 mol CO <sub>2</sub> /mol solute	55.4–858.8	353	Hsu et al. [21]
(ChCl-U)-MEA	(70) + 5 % wt.	25	0.095–0.189 mol CO <sub>2</sub> /mol solute	50.2–813.3	313	Hsu et al. [21]
(ChCl-U)-MEA	(70) + 5 % wt.	25	0.086–0.171 mol CO <sub>2</sub> /mol solute	56.4–829.4	333	Hsu et al. [21]
(ChCl-U)-MEA	(70) + 5 % wt.	25	0.080–0.148 mol CO <sub>2</sub> /mol solute	86.1–808.6	353	Hsu et al. [21]
TEAC-MEA-TEA	1:5:0.5 mol ratio	10	*0.242 (weight fraction)	atmospheric	303	Li et al. [29]
ChCl-MEA-TEA	1:5:0.5 mol ratio	10	*0.253 (weight fraction)	atmospheric	303	Li et al. [29]
TEAC-MEA-MDEA	1:5:0.5 mol ratio	10	*0.254 (weight fraction)	atmospheric	303	Li et al. [29]
ChCl-MEA-MDEA	1:5:0.5 mol ratio	10	*0.260 (weight fraction)	atmospheric	303	Li et al. [29]
TMAC-MEA-TEA	1:5:0.5 mol ratio	10	*0.272 (weight fraction)	atmospheric	303	Li et al. [29]
TMAC-MEA-MDEA	1:5:0.5 mol ratio	10	*0.327 (weight fraction)	atmospheric	303	Li et al. [29]

\*Data extracted from plot.

**Table 4**

Chemicals used in this work and their purities (as provided by the supplier).

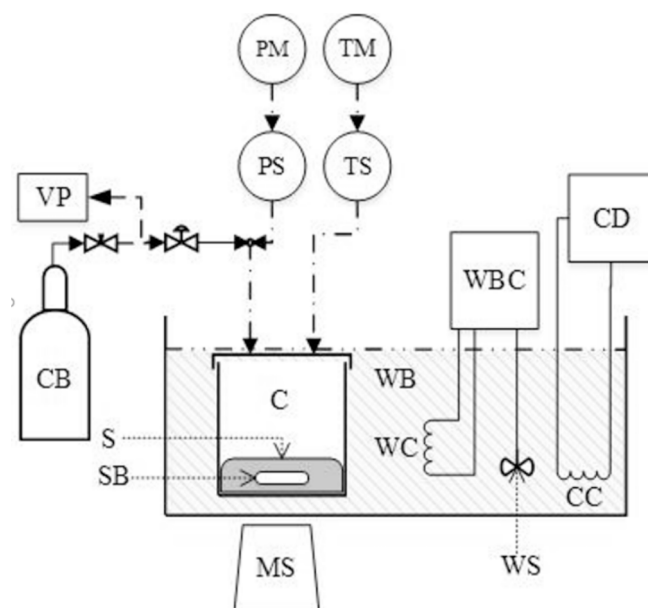
Product Name	Abbreviation	CAS-number	Purity <sup>a</sup>	Supplier
Carbon dioxide	CO <sub>2</sub>	124–38-9	0.999 (volume fraction)	Air Liquide
Choline chloride	ChCl	67–48-1	>0.98 <sup>b</sup> (mass fraction)	Sigma-Aldrich
3-(Methylamino)propylamine	MAPA	6291–84-5	>0.99 <sup>c</sup> (mass fraction)	Sigma-Aldrich
3-Amino-1-propanol	MPA	156–87-6	>0.99 <sup>c</sup> (mass fraction)	Aldrich
Water	H <sub>2</sub> O	7732–18-5	HPLC grade	Chem lab

<sup>a</sup>No further purification was conducted for the studied compounds. <sup>b</sup>According to the manufacturer, the water content of the choline chloride (estimated by Karl Fischer) is lower than 1% wt. <sup>c</sup>The water content in the studied amines was not reported by the manufacturers, and no separate determination of the water content was conducted.

solvent and has a severe effect on the CO<sub>2</sub> chemical absorption, which proceeds simultaneously with the physical dissolution.

The limited number of investigations on the CO<sub>2</sub> solubility in DES solutions conclude that the addition of water reduces the CO<sub>2</sub> solubility. In more detail, Su et al. observed that the CO<sub>2</sub> solubility in aqueous reline (ChCl–urea 1:2) solution decreases with increasing water content [20]. The same behavior was revealed from Henry's constant measurements for DES systems consisting of choline chloride (ChCl), as the salt, and ethylene glycol, glycerol, or malonic acid as the alternative HBDs [23]. Such results revealed that water acts as antisolvent, driving out the solute, i.e., the dissolved CO<sub>2</sub>, suggesting an alternative regeneration method.

Nevertheless, the reduction of CO<sub>2</sub> solubility with increasing water content is expected for systems that present physical CO<sub>2</sub> absorption, due to the very low solubility of CO<sub>2</sub> in water. However, as mentioned above, the existence of water in systems that present chemical CO<sub>2</sub> absorption alters the CO<sub>2</sub> – amine chemical reaction pathway. In this



**Fig. 2.** Experimental apparatus [25] for VLE measurements consisting of: equilibrium cell (C), solution (S), weighted CO<sub>2</sub> flask (CB), cooling coil (CC), cooling device (CD), magnetic stirrer (MS), pressure indicator (PM), pressure sensor (PS), stirring bar (SB), temperature indicator (TM), Pt-100 thermometer (TS), vacuum pump (VP), water bath (WB), temperature controller/heater (WBC), heating coil (WC), stirrer (WS).

direction, it is well known that more dilute aqueous amine solutions present higher CO<sub>2</sub> loadings (expressed as moles of CO<sub>2</sub> per mole of amine) [24,25]. Consequently, the addition of water in amine-based DES presents a dual effect, i.e., it reduces the molecular CO<sub>2</sub> solubility (physical absorption), as expected, but on the same time alters the chemical CO<sub>2</sub> absorption and, from this point of view, is an issue that requires further investigation.

**Table 5**

Compositions of the investigated aqueous solutions (the reported uncertainties encompass the uncertainty due to the purity, reported by the providers, and due to weighting).

DES	Amine to ChCl molar ratio	Choline chloride, % wt.	Amine, %wt.
ChCl + MPA, 15 % wt.	7.92	2.85 ± 0.06	12.15 ± 0.14
ChCl + MPA, 30 % wt.	7.92	5.68 ± 0.13	24.21 ± 0.33
ChCl + MPA, 50 % wt.	7.92	9.49 ± 0.25	40.42 ± 0.64
ChCl + MPA, 85 % wt.	7.92	16.13 ± 0.49	68.71 ± 1.38
ChCl + MAPA, 30 %wt.	8.06	4.92 ± 0.12	25.05 ± 0.34

**Table 6**

Parameters of Eq. (21).

Parameters	Relation
A	1
B	$[R_a R_b NH]_t + K_1$
C	$-K_4 - K_2[CO_2] + \frac{K_1 K_2 [CO_2]}{K_5}$
D	$-2K_2 K_3 [CO_2] - K_1 K_4 - K_1 K_2 [CO_2] - \frac{K_1 K_2 [CO_2]}{K_5} [R_a R_b NH]_t$
E	$-2K_1 K_2 K_3 [CO_2] - \frac{K_1 K_2 K_4 [CO_2]}{K_5} - \frac{K_1 K_2^2 [CO_2]^2}{K_5}$
F	$\frac{2K_1 K_2^2 K_3 [CO_2]^2}{K_5}$

However, upon addition of water a complex hydrogen bonding network is formed and the behaviour of DES stops resembling that of ionic liquids. Consequently, from another point of view, aqueous amine-based DES are not significantly different from aqueous amine solutions. In most cases, their difference is the existence of the hydrogen bonding acceptor (HBA), which is usually a substituted quaternary ammonium or phosphonium salt as presented in Fig. 1 for the two systems that are investigated in this study. However, the existence of the organic salt affects the hydrogen bonding behavior of both water and amine constituents, which may alter the CO<sub>2</sub> absorption (chemical or physical) ability of the solvent, revealing an issue which is not studied in literature.

Furthermore, amine volatility losses represent a significant drawback in conventional aqueous amine solvents used for CO<sub>2</sub> capture applications. They are mainly observed during the regeneration of the solvent, in which CO<sub>2</sub> is removed at elevated temperatures, and they increase with increasing vapor pressure of the solvent [3]. Since, as mentioned above, the addition of the salt ions introduces more strong

cross associating interactions (between salt ions and water or amine), molecules are more strongly bounded in the liquid, even in absence of the ions that are formed due to the dissolution of CO<sub>2</sub>, resulting in less vapor pressure. This is typical behavior of all salt (inorganic or organic salts, such as ionic liquids or DES) solutions. Consequently, the existence of the organic salt may positively influence the vapor pressure of the solvent, reducing its volatility and, in this way, helps to overcome the significant drawback of conventional aqueous amine solvents used for CO<sub>2</sub> capture applications.

However, although amine-based DES are promising for a potential greener and more energy efficient absorption/regeneration process, the relevant studies in the open literature are still scarce, as shown in Tables 1–3 and in Tables S1–S4 of the Supplementary information file, in which a thorough review of the literature studies containing CO<sub>2</sub> solubility data is presented. In more detail, in Table 1, an overview of the literature studies containing experimental data for the CO<sub>2</sub> solubility in amine and urea-based DES and aqueous systems with DES is presented. Most of such studies refer to non-aqueous systems for alkanolamine and urea-based DES, which are presented in Tables S1 and S2 of the Supplementary information file, respectively. Studies on aqueous solutions of DES are scarcer. Most of them refer to systems with urea, as presented in Table S3 of the Supplementary information file. The literature data for the solubility of CO<sub>2</sub> in aqueous amine (not urea) based DES are presented in Tables 2 and 3. It worth mentioning that only one study was found for aqueous solutions of amine-based DES, as shown in Table 2.

The thermodynamic modeling of CO<sub>2</sub> solubility in DES is not trivial. A rigorous approach requires accounting for the non-idealities of the liquid phase, especially due to the existence of ionic interactions, and, upon the existence of urea or amines, accounting for the chemical equilibrium due to the relevant reactions with CO<sub>2</sub>. Thus, the problem is usually simplified. Considering the simple case of non-amine (or urea) containing DES, in which CO<sub>2</sub> is dissolved due to physical intermolecular interactions, usually an equation of state is used [27,36] ignoring the ionic interactions in the liquid phase and effectively accounting for them with appropriate parameterization of the model. However, upon existence of a reacting component, such as an amine or urea, severe simplifications occur. Often, the chemical equilibrium is not accounted for, and Henry's constant approaches [20,35,40], or equations of state coupled with activity coefficient models for the liquid phase are used [22,32,37,38]. In other cases, the chemical equilibrium is accounted for, i.e., using the Kent-Eisenberg model, however, the non-idealities of the liquid phase are not explicitly accounted for and are lumped into effective values of model parameters [21,41]. Due to the severe complexity of the systems, in some cases purely empirical equations are used [39].

Aim of this work is to investigate the effect of water and choline chloride on the CO<sub>2</sub> absorption ability of amine based deep eutectic solvents. In this direction, new experimental data are presented for four

**Table 7**

Total pressure ( $P_{total}$ ), CO<sub>2</sub> partial pressure ( $P_{CO_2}$ ) and CO<sub>2</sub> solubility ( $\alpha_d$ , defined as moles of CO<sub>2</sub> per mole of DES (amine + choline chloride), value ± combined standard uncertainty) in aqueous 15 % wt. choline chloride (ChCl)-3-amino-1-propanol (MPA) (exact composition ChCl 2.85 ± 0.06 %wt. + MPA 12.15 ± 0.14 %wt.).

$P_{total}$ (kPa) <sup>b</sup>	Approximated $P_{CO_2}$ (kPa)	$\alpha_d$ (mol CO <sub>2</sub> / mol DES)	$P_{total}$ (kPa) <sup>b</sup>	$P_{CO_2}$ (kPa)	$\alpha_d$ (mol CO <sub>2</sub> / mol DES)
<sup>a</sup> 298.2 K			<sup>a</sup> 323.2 K		
521	518	0.96 ± 0.07	626	615	0.89 ± 0.07
725	722	1.03 ± 0.07	848	837	0.96 ± 0.07
1158	1155	1.08 ± 0.09	1334	1323	0.99 ± 0.09
1523	1520	1.13 ± 0.09	1750	1739	1.03 ± 0.09
<sup>a</sup> 313.2 K			<sup>a</sup> 333.2 K		
574	567	0.93 ± 0.07	670	652	0.86 ± 0.07
796	789	0.99 ± 0.07	893	875	0.94 ± 0.07
1267	1260	1.01 ± 0.09	1403	1385	0.96 ± 0.09
1667	1660	1.05 ± 0.09	1838	1820	1.00 ± 0.09

<sup>a</sup>Standard uncertainty in temperature  $u(T) = 0.10$  K.

<sup>b</sup>Standard uncertainty in total pressure  $u(p) = 0.005 \cdot P$ .

**Table 8**

Total pressure ( $P_{total}$ ), CO<sub>2</sub> partial pressure ( $P_{CO_2}$ ) and CO<sub>2</sub> solubility ( $\alpha_d$ , defined as moles of CO<sub>2</sub> per mole of DES (amine + choline chloride), value  $\pm$  combined standard uncertainty) in aqueous 30 % wt. choline chloride (ChCl)-3-amino-1-propanol (MPA) (exact composition ChCl  $5.68 \pm 0.13$  %wt. + MPA  $24.21 \pm 0.33$  %wt.).

$P_{total}$ (kPa) <sup>b</sup>	Approximated $P_{CO_2}$ (kPa)	$\alpha_d$ (mol CO <sub>2</sub> / mol DES)	$P_{total}$ (kPa) <sup>b</sup>	$P_{CO_2}$ (kPa)	$\alpha_d$ (mol CO <sub>2</sub> / mol DES)
<sup>a</sup> 298.15 K			<sup>a</sup> 323.15 K		
16	13	$0.56 \pm 0.03$	42	32	$0.55 \pm 0.03$
195	193	$0.78 \pm 0.04$	309	299	$0.72 \pm 0.04$
704	702	$0.90 \pm 0.04$	869	859	$0.82 \pm 0.05$
1153	1151	$0.95 \pm 0.05$	1374	1364	$0.87 \pm 0.05$
<sup>a</sup> 313.15 K			<sup>a</sup> 333.15 K		
27	20	$0.56 \pm 0.03$	59	41	$0.54 \pm 0.03$
258	252	$0.74 \pm 0.04$	363	346	$0.69 \pm 0.04$
805	799	$0.85 \pm 0.04$	950	933	$0.79 \pm 0.05$
1286	1280	$0.90 \pm 0.05$	1470	1453	$0.84 \pm 0.05$

<sup>a</sup>Standard uncertainty in temperature  $u(T) = 0.10$  K.

<sup>b</sup>Standard uncertainty in total pressure  $u(p) = 0.005 \bullet P$ .

choline chloride – 3-amino-1-propanol (MPA) aqueous systems with different water content. Furthermore, new experimental data are presented for an aqueous choline chloride – 3-(methyldamino)propylamine (MAPA) system and all the obtained experimental data are correlated with the modified Kent-Eisenberg model, which is one of the most popular approximate models for modeling the chemical absorption of CO<sub>2</sub> in aqueous amine systems.

## 2. Experimental

### 2.1. Materials

The materials used in this work are shown in Table 4. In all cases, they were used as received without further purification.

### 2.2. Experimental apparatus and procedure

The vapor–liquid equilibrium apparatus (Fig. 2), the experimental procedure and the validation of the experimental method are presented in previous studies [25,42–45]. They are briefly presented here. CO<sub>2</sub> solubility measurements in aqueous DES were conducted in a high-pressure stainless-steel equilibrium cell (with internal volume of  $152.2 \pm 1.6$  cm<sup>3</sup> at 25 °C), which is equipped with pressure transducer (WIKA A-10,  $\pm 0.5$  %) and a temperature sensor (Pt-100 thermometer,  $\pm 0.01$  K). To obtain isothermal conditions, the equilibrium cell is immersed into a water bath (Grant TC-120 with temperature stability of 0.1 K), equipped with a temperature controller and a water circulator. According to the experimental procedure, a measured (weighted with accuracy of 0.001 g) amount of the aqueous DES is introduced into the cell. Next, the cell is charged with a known (weighted, standard uncertainty  $\pm 0.005$  g) amount of pure CO<sub>2</sub> and is heated to the desired temperature

level. To ensure that solvent exists under its own vapor pressure, the equilibrium vessel is evacuated several times, before adding CO<sub>2</sub>. Equilibrium is confirmed once the pressure readings remain unchanged for at least one hour at constant temperature. During the experiment, the pressure and the temperature of the cell are recorded.

The CO<sub>2</sub> molar density,  $\rho_{CO_2}$ , (as obtained from NIST database [46]), the solvent density,  $\rho_{sol}$ , the total mass of the solvent,  $m_{sol}$ , added in the cell, the total moles of CO<sub>2</sub> loaded in the equilibrium cell,  $n_{CO_2}$ , the total moles of the DES added in the cell,  $n_{DES}$ , the volume of the cell  $V_T$  and the volume of the solvent  $V_{sol}$  are used to calculate the CO<sub>2</sub> solubility,  $\alpha_{CO_2}$ , expressed as moles of CO<sub>2</sub> absorbed into the liquid phase per mole of DES (choline chloride + amine),  $n_{DES}$ , as follows:

$$\alpha_{CO_2} = \frac{n_{CO_2} - n_{CO_2}^G}{n_{DES}}, \quad \delta \alpha_{CO_2} = \alpha_{CO_2} \left( \frac{\delta n_{CO_2} + \delta n_{CO_2}^G}{n_{CO_2} - n_{CO_2}^G} + \frac{\delta n_{DES}}{n_{DES}} \right) \quad (1)$$

$$n_{CO_2}^G \approx V_{vapor} \rho_{CO_2}, \quad \delta n_{CO_2}^G = n_{CO_2}^G \left( \frac{\delta V_{vapor}}{V_{vapor}} + \frac{\delta \rho_{CO_2}}{\rho_{CO_2}} \right) \quad (2)$$

$$V_{vapor} \approx V_T - V_{sol}, \quad \delta V_{vapor} = \delta V_T + \delta V_{sol} \quad (3)$$

$$V_{sol} = m_{sol} / \rho_{sol}, \quad \delta V_{solvent} = V_{sol} \left( \frac{\delta m_{sol}}{m_{sol}} + \frac{\delta \rho_{sol}}{\rho_{sol}} \right) \quad (4)$$

In Eqs. (1)–(4),  $n_{CO_2}^G$  denotes the moles of CO<sub>2</sub> in the vapor phase,  $V_{vapor}$  the volume of the vapor phase and  $\delta X$  the standard uncertainty of  $X$ .

According to such experimental procedure, the total pressure of the system is measured, while the CO<sub>2</sub> partial pressure is estimated through the subtraction of the solution's vapor pressure from the total pressure. In this study, we have used the approach suggested by Jou et al. [24],

**Table 9**

Total pressure ( $P_{total}$ ), CO<sub>2</sub> partial pressure ( $P_{CO_2}$ ) and CO<sub>2</sub> solubility ( $\alpha_d$ , defined as moles of CO<sub>2</sub> per mole of DES (amine + choline chloride), value  $\pm$  combined standard uncertainty) in aqueous 50 % wt. choline chloride (ChCl)-3-amino-1-propanol (MPA) (exact composition ChCl  $9.49 \pm 0.25$  %wt. + MPA  $40.42 \pm 0.64$  %wt.).

$P_{total}$ (kPa) <sup>b</sup>	Approximated $P_{CO_2}$ (kPa)	$\alpha_d$ (mol CO <sub>2</sub> / mol DES)	$P_{total}$ (kPa) <sup>b</sup>	$P_{CO_2}$ (kPa)	$\alpha_d$ (mol CO <sub>2</sub> / mol DES)
<sup>a</sup> 298.15 K			<sup>a</sup> 323.15 K		
68	66	$0.54 \pm 0.02$	139	130	$0.51 \pm 0.02$
471	469	$0.68 \pm 0.03$	663	654	$0.62 \pm 0.03$
944	942	$0.74 \pm 0.03$	1206	1197	$0.66 \pm 0.03$
1515	1513	$0.77 \pm 0.04$	1831	1822	$0.69 \pm 0.04$
<sup>a</sup> 313.15 K			<sup>a</sup> 333.15 K		
105	100	$0.53 \pm 0.02$	179	164	$0.50 \pm 0.02$
584	579	$0.64 \pm 0.03$	741	726	$0.60 \pm 0.03$
1099	1094	$0.69 \pm 0.03$	1309	1295	$0.64 \pm 0.03$
1704	1699	$0.72 \pm 0.04$	1958	1944	$0.67 \pm 0.04$

<sup>a</sup>Standard uncertainty in temperature  $u(T) = 0.10$  K.

<sup>b</sup>Standard uncertainty in total pressure  $u(p) = 0.005 \bullet P$ .



**Table 10**

Total pressure ( $P_{total}$ ),  $CO_2$  partial pressure ( $P_{CO_2}$ ) and  $CO_2$  solubility ( $\alpha_d$ , defined as moles of  $CO_2$  per mole of DES (amine + choline chloride), value  $\pm$  combined standard uncertainty) in aqueous 85 % wt. choline chloride (ChCl)-3-amino-1-propanol (MPA) (exact composition ChCl  $16.13 \pm 0.49$  %wt. + MPA  $68.71 \pm 1.38$  %wt.).

$P_{total}$ (kPa) <sup>b</sup>	Approximated $P_{CO_2}$ (kPa)	$\alpha_d$ (mol $CO_2$ / mol DES)	$P_{total}$ (kPa) <sup>b</sup>	$P_{CO_2}$ (kPa)	$\alpha_d$ (mol $CO_2$ / mol DES)
<sup>a</sup> 298.15 K			<sup>a</sup> 323.15 K		
154	153	$0.49 \pm 0.02$	174	170	$0.49 \pm 0.02$
691	690	$0.54 \pm 0.02$	754	750	$0.54 \pm 0.02$
1101	1100	$0.57 \pm 0.02$	1211	1207	$0.57 \pm 0.02$
<sup>a</sup> 313.15 K			<sup>a</sup> 333.15 K		
164	162	$0.49 \pm 0.02$	184	177	$0.49 \pm 0.02$
728	726	$0.54 \pm 0.02$	784	777	$0.54 \pm 0.02$
1166	1164	$0.57 \pm 0.02$	1258	1251	$0.57 \pm 0.02$

<sup>a</sup>Standard uncertainty in temperature  $u(T) = 0.10$  K.

<sup>b</sup>Standard uncertainty in total pressure  $u(p) = 0.005 \bullet P$ .

who calculated the solvent vapor pressure from Raoult's law knowing the compositions and the vapor pressures of pure compounds. Bearing in mind that the vapor pressure of the solvent is very low, such approximation results in insignificant corrections, especially at relatively high pressures (higher than 100 kPa) and is very common in similar pressure decay experimental studies [24,43,45,47]. The needed vapor pressures were obtained from Kim et al. [48] and the DIPPR database [49].

All the investigated aqueous solutions were prepared by mixing weighted amounts of choline chloride, amine and water (accuracy 0.001 g) in a volumetric flask (Din A) at 20 °C. In this way, the weight percent, the molarity and the density of the solution were estimated. Solution densities at 25, 40, 50 and 60 °C (temperature stability of 0.1 K, temperature sensor Pt-100 thermometer,  $\pm 0.01$  K) and atmospheric pressures were estimated in a similar way (see Table S5 of the Supplementary Information File), by knowing the volume change of the flask at each experimental temperature (estimated by measuring the mass of HPLC water needed to fill the flask at each temperature). The density of the solution loaded with  $CO_2$  was approximated equal to the density of the unloaded solution for applying Eq. (4). The compositions of the investigated aqueous solutions are presented in Table 5, from which it can be seen that in all cases DES with amine to choline chloride molar ratio around 8:1 were prepared. In Table 5, the overall DES (choline chloride + amine) content is mentioned in the first column, while the choline chloride and amine contents are also shown separately, e.g., the 15 % wt. choline chloride + MPA aqueous solution (see the first line of Table 5) contains 2.85 %wt. choline chloride and 12.15 %wt. MPA.

### 3. The modified Kent-Eisenberg model

According to Haji-Sulaiman et al. [50] for a carbamate forming ( $R_aR_bNH$ ) amine we can write the following chemical reactions:



where  $R_aR_bNH_2^+$  is the protonated form of the carbamate forming amine and  $R_aR_bNCOO^-$  is the carbamate anion. The relevant equilibrium constants are written as follows:

$$K_1 = \frac{[R_aR_bNH][H^+]}{[R_aR_bNH_2^+]} \quad (10)$$

$$K_2 = \frac{[HCO_3^-][H^+]}{[CO_2]} \quad (11)$$

$$K_3 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \quad (12)$$

$$K_4 = [OH^-][H^+] \quad (13)$$

$$K_5 = \frac{[R_aR_bNH][HCO_3^-]}{[R_aR_bNCOO^-]} \quad (14)$$

The molecular  $CO_2$  concentration in the liquid phase is given using the Henry's law, as follows:

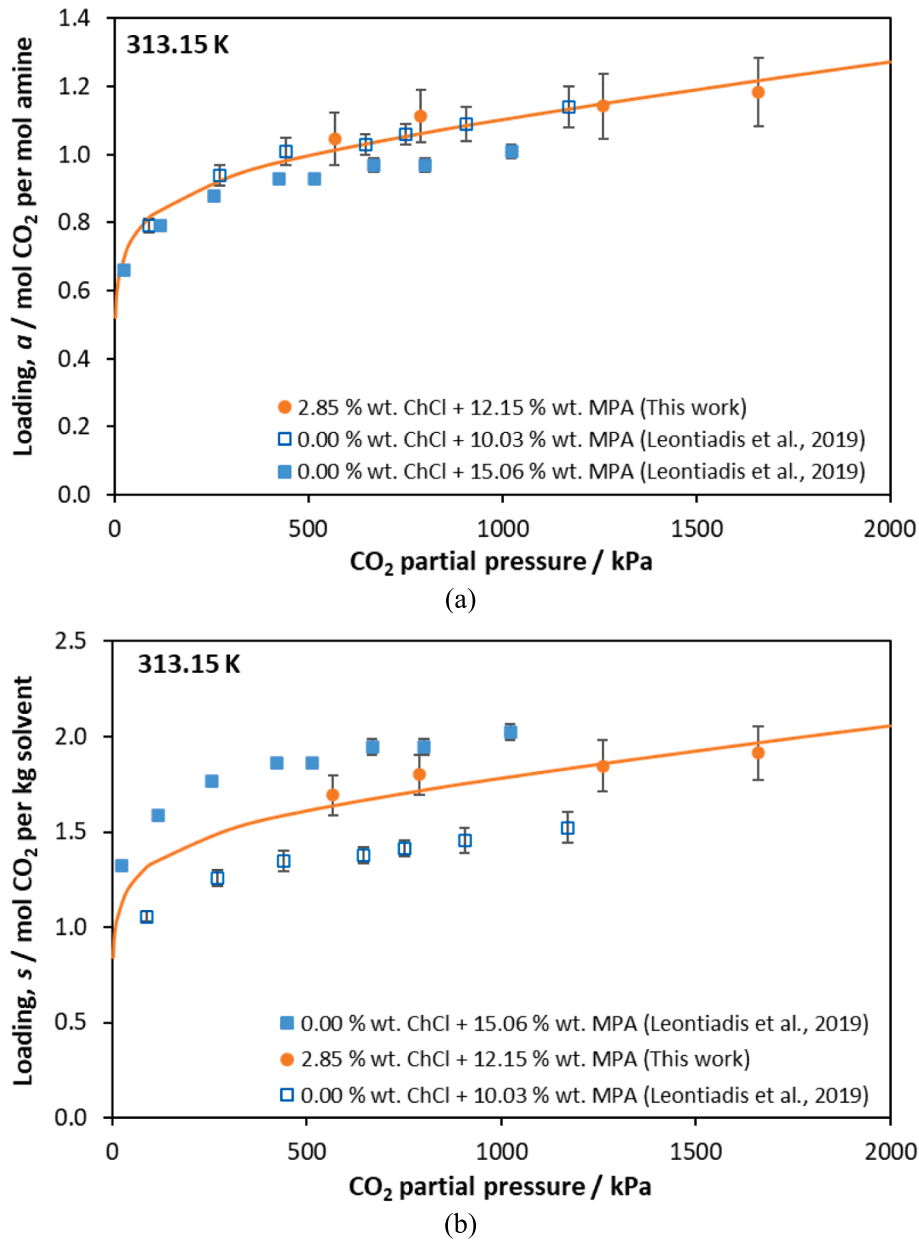
**Table 11**

Total pressure ( $P_{total}$ ),  $CO_2$  partial pressure ( $P_{CO_2}$ ) and  $CO_2$  solubility ( $\alpha_d$ , defined as moles of  $CO_2$  per mole of DES (amine + choline chloride), value  $\pm$  combined standard uncertainty) in aqueous 30 % wt. choline chloride (ChCl)-3-(Methylamino) propylamine (MAPA) (exact composition ChCl  $4.92 \pm 0.12$  %wt. + MAPA  $25.05 \pm 0.34$  %wt.).

$P_{total}$ (kPa) <sup>b</sup>	Approximated $P_{CO_2}$ (kPa)	$\alpha_d$ (mol $CO_2$ / mol DES)	$P_{total}$ (kPa) <sup>b</sup>	$P_{CO_2}$ (kPa)	$\alpha_d$ (mol $CO_2$ / mol DES)
<sup>a</sup> 298.15 K			<sup>a</sup> 323.15 K		
402	400	$1.32 \pm 0.05$	561	551	$1.22 \pm 0.05$
654	652	$1.40 \pm 0.06$	860	850	$1.27 \pm 0.06$
841	839	$1.43 \pm 0.06$	1065	1055	$1.31 \pm 0.06$
<sup>a</sup> 313.15 K			<sup>a</sup> 333.15 K		
495	489	$1.26 \pm 0.05$	631	614	$1.18 \pm 0.05$
778	772	$1.32 \pm 0.06$	929	912	$1.24 \pm 0.06$
974	968	$1.35 \pm 0.06$	1158	1141	$1.26 \pm 0.06$

<sup>a</sup>Standard uncertainty in temperature  $u(T) = 0.10$  K.

<sup>b</sup>Standard uncertainty in total pressure  $u(p) = 0.005 \bullet P$ .



**Fig. 3.** Solubility of CO<sub>2</sub> in 15 % wt. choline chloride + MPA (circles), MPA 10 % wt. (open squares) and MPA 15 % wt. (solid squares) [25] aqueous solutions expressed as (a) moles of CO<sub>2</sub> per mole of amine and (b) moles of CO<sub>2</sub> per kg of solvent. Experimental data (symbols) and modified Kent-Eisenberg correlations (line) for the solubility in the choline chloride + MPA aqueous solution.

$$P_{\text{CO}_2} = H_{\text{CO}_2}[\text{CO}_2] \quad (15)$$

where  $P_{\text{CO}_2}$  and  $H_{\text{CO}_2}$  are the vapor phase CO<sub>2</sub> partial pressure and the Henry's constant, respectively.

To set up the problem, we can write two independent mass balance and one charge balance equations as follows [50]:

*Amine mass balance*

$$[R_a R_b \text{NH}]_t = [R_a R_b \text{NH}] + [R_a R_b \text{NH}_2^+] + [R_a R_b \text{NCOO}^-] \quad (16)$$

*CO<sub>2</sub> balance:*

$$\alpha_{\text{CO}_2} [R_a R_b \text{NH}]_t = [R_a R_b \text{NCOO}^-] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2] \quad (17)$$

*Charge balance:*

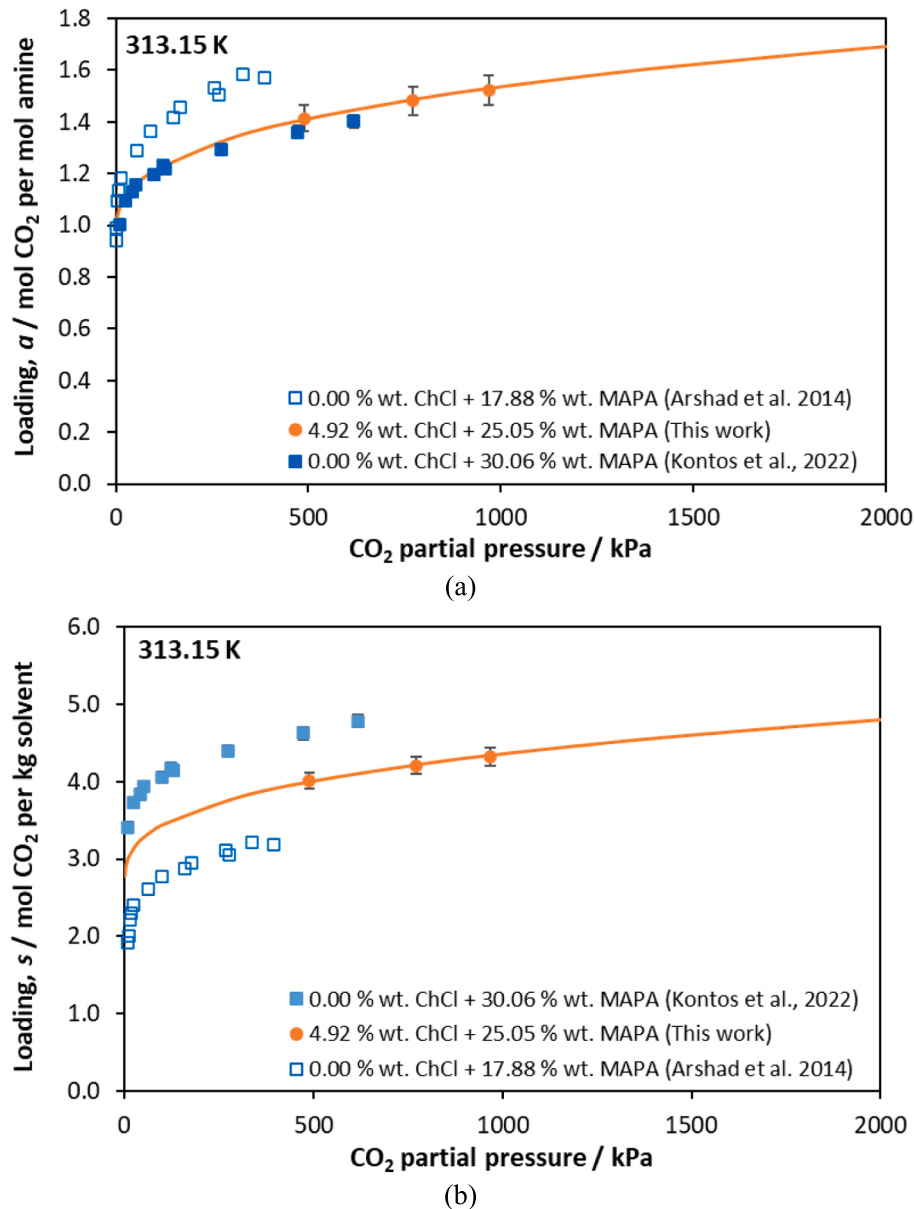
$$[\text{H}^+] + [R_a R_b \text{NH}_2^+] = [R_a R_b \text{NCOO}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (18)$$

where  $[R_a R_b \text{NH}]_t$  is the total concentration of the amine in the mixture and  $\alpha_{\text{CO}_2}$  is the carbon dioxide loading (expressed as moles of CO<sub>2</sub> per mole of amine). After some algebra, Eqs. (10)–(18) reduce to the following system of two equations with two unknowns,  $[\text{H}^+]$  and  $[R_a R_b \text{NH}_2^+]$ :

$$[R_a R_b \text{NH}]_t = \left( 1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2 [\text{CO}_2]}{K_5 [\text{H}^+]^2} \right) [R_a R_b \text{NH}_2^+] \quad (19)$$

$$[R_a R_b \text{NH}_2^+] \left( 1 - \frac{K_1 K_2 [\text{CO}_2]}{K_5 [\text{H}^+]^2} \right) = \frac{K_4}{[\text{H}^+]} + \frac{K_2 [\text{CO}_2]}{[\text{H}^+]} + \frac{2K_2 K_3 [\text{CO}_2]}{[\text{H}^+]^2} - [\text{H}^+] \quad (20)$$

The following polynomial equation is obtained, after some algebra:



**Fig. 4.** Solubility of CO<sub>2</sub> in choline chloride + MAPA 30 % wt. (circles), MAPA 18 % wt. (open squares) [47] and MAPA 30 % wt. (solid squares) [44] aqueous solutions. Experimental data (symbols) and modified Kent-Eisenberg correlations (line) for the solubility in the choline chloride + MAPA aqueous solution.

$$A[H^+]^5 + B[H^+]^4 + C[H^+]^3 + D[H^+]^2 + E[H^+] + F = 0 \quad (21)$$

where parameters  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $E$  and  $F$  are presented in Table 6.

Only the root with physical meaning, i.e.,  $pH \in [7, 12]$ , is kept from Eq. (21) [50]. Then, the CO<sub>2</sub> loading is calculated through the following relation:

$$\alpha_{CO_2} = \frac{\left( [CO_2] + \frac{K_2[CO_2]}{[H^+]} + \frac{K_2K_3[CO_2]}{[H^+]^2} + [RRNCOO^-] \right)}{[R_aR_bNH]_t} \quad (22)$$

where:

$$[RRNCOO^-] = \frac{K_1K_2[CO_2][R_aR_bNH]_t}{(K_5[H^+]^2 + K_1K_5[H^+] + K_1K_2[CO_2])} \quad (23)$$

In all cases, the following empirical relation is used to describe the temperature dependence of the equilibrium constants,  $K_i$ , and the

Henry's law constant [51]:

$$\ln K_i = \frac{A_i}{T} + B_i \ln T + C_i T + D_i \quad (24)$$

## 4. Results and discussion

### 4.1. Experimental results

In all cases, aqueous solutions of ChCl + MPA and ChCl + MAPA, as presented in Table 5, were studied at 298, 313, 323 and 333 K and the obtained experimental data are presented in Tables 7–11, expressed as moles of absorbed CO<sub>2</sub> per mole of DES (ChCl + amine). The same experimental data, expressed as moles of CO<sub>2</sub> per mole of amine or as moles of CO<sub>2</sub> per kg of solvent are presented in Tables S6–S10 of the Supplementary information file. The uncertainties, which are presented in the experimental solubility values of Tables 7–11, denote the combined standard uncertainty, which was calculated through propagation



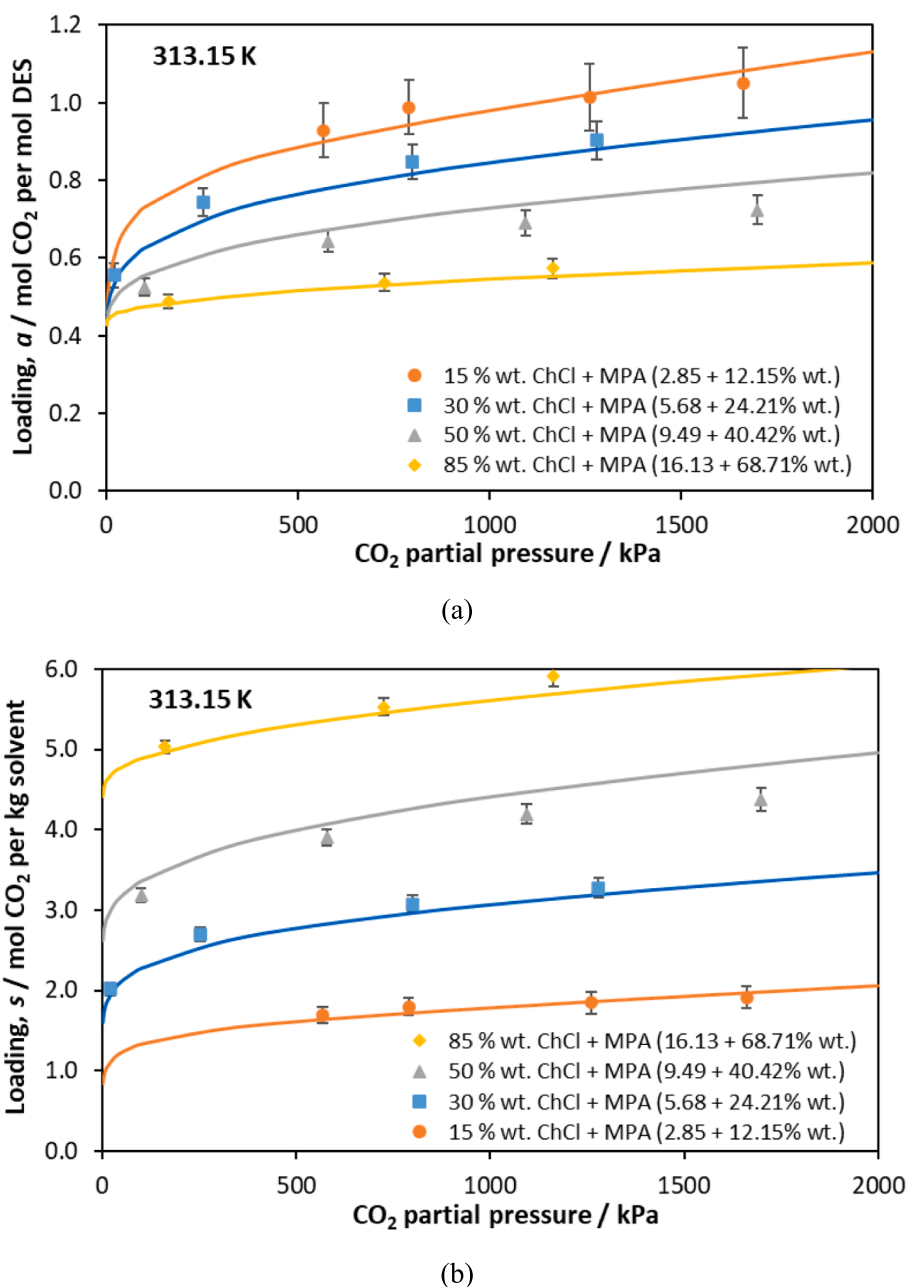


Fig. 5. Solubility of CO<sub>2</sub> in choline chloride + MPA solutions expressed as (a) moles of CO<sub>2</sub> per mole of DES (ChCl + MPA) and (b) moles of CO<sub>2</sub> per kg of solvent.

of errors, considering the uncertainties of all used values for the solubility calculation (uncertainty in the weights of the added materials, the total volume of the cell, the estimated densities etc, see Eq. (1)). Representative results are shown in Figs. 3–6.

#### 4.1.1. Effect of choline chloride

In Figs. 3 and 4 the experimental results of this study are compared with literature data for aqueous solutions of MPA and MAPA, respectively. To facilitate such comparison, in Figs. 3a and 4a, the experimental solubility (CO<sub>2</sub> loading) values are presented in moles of CO<sub>2</sub> per mole of amine (MPA or MAPA). In more detail, in Fig. 3a the experimental data for the ChCl + MPA 15 % wt. DES solution are compared with the data of Leontiadis et al. [25] for 10 and 15 % wt. aqueous MPA solutions. It is shown that the CO<sub>2</sub> solubility in the aqueous 15 % wt. DES solution, expressed as moles of CO<sub>2</sub> per mole of amine, is higher than that of the 15 % wt. aqueous MPA solution and similar to that of the 10 % wt. aqueous MPA solution. Furthermore, in Fig. 4a, the experimental

data for the ChCl + MAPA 30 % wt. DES solution are compared with the data of Kontos et al. [44] and Arshad et al. [47] for a 30 % wt. and a 18 % wt. MAPA aqueous solution, respectively. As shown, the CO<sub>2</sub> solubility in the 30 % wt. DES solution, expressed as moles of CO<sub>2</sub> per mole of amine, is similar to that of the 30 % wt. MAPA solution. From such observations it is concluded that the DES aqueous solutions present similar or marginally higher CO<sub>2</sub> solubility than the corresponding pure amine aqueous solutions, revealing that the addition of choline chloride did not considerably alter (but one can claim a marginal increase at least for ChCl + MPA) the CO<sub>2</sub> solubility, expressed in moles of CO<sub>2</sub> per mole of amine, which in both cases is mainly attributed to chemical absorption.

Two main factors should be taken into consideration for explaining such observations: the effect of the ChCl salt on the basicity of the solution and the new sites for physical interactions with CO<sub>2</sub> that are introduced upon the addition of the salt. Since the choline cation (Ch<sup>+</sup>) acts as weak acid, which can remove OH<sup>−</sup> from the solution forming its

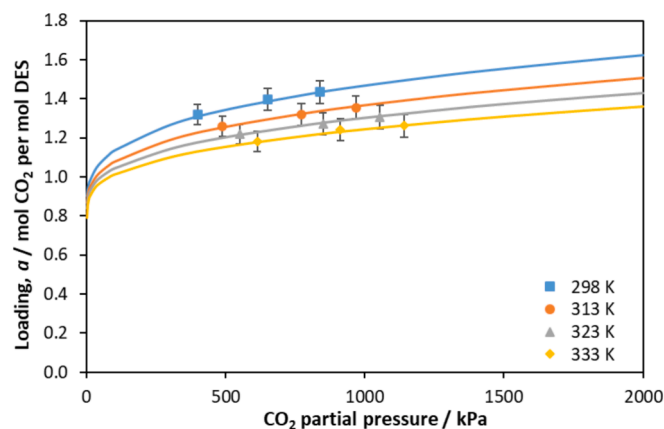


Fig. 6. Solubility of CO<sub>2</sub> in choline chloride + MAPA solutions (4.92 wt. ChCl + 25.05 wt. MAPA) expressed as moles of CO<sub>2</sub> per mole of DES (ChCl + MAPA).

conjugated base ChOH, it tends to decrease the basicity of the solution and, consequently, tends to decrease the chemical absorption of the acid gas (CO<sub>2</sub>). On the contrary, the addition of the salt introduces new available sites for favorable intramolecular interactions with CO<sub>2</sub>, such as the alcoholic –OH group, that tend to increase the physical CO<sub>2</sub> solubility [52]. The net effect of all these factors is described by the observation mentioned above, i.e., the addition of choline chloride did not considerably alter, but one can claim a marginal increase at least for ChCl + MPA, the CO<sub>2</sub> solubility expressed as moles of CO<sub>2</sub> per mole of amine.

However, in industrial practice, the evaluation of solvent performance is usually based on comparisons of solubility expressed as moles of CO<sub>2</sub> per kg of solvent (the aqueous solution on this case). In this direction, such aqueous DES solutions can be considered as solutions obtained from neat amine aqueous solutions by replacing an amount of amine with ChCl. For example, the 2.85 % wt. ChCl + 12.15 % wt. MPA aqueous solution can be obtained from a 15 % wt. neat MPA solution by replacing 2.85 % wt. of amine by equal mass of choline chloride. As shown in Fig. 3b, the CO<sub>2</sub> solubility of the 2.85 % wt. ChCl + 12.15 % wt. aqueous MPA solution, expressed in moles of CO<sub>2</sub> per kg of solvent, is lower than that of the 15 % neat MPA solution. Similarly, as shown in Fig. 4b, the CO<sub>2</sub> solubility of the 4.92 % wt. ChCl + 25.05 % wt. MAPA, expressed in moles of CO<sub>2</sub> per kg of solvent, is lower than that of the 30 % neat MAPA solution. Consequently, it can be concluded that replacing an amount of amine with equal mass of ChCl decreases the CO<sub>2</sub> solubility in the bulk (solubility expressed as moles of CO<sub>2</sub> per kg of solvent).

#### 4.1.2. Replacing water with choline chloride

However, such aqueous DES solutions can be evaluated from another point of view: they can be considered as solutions obtained from neat amine aqueous solutions by replacing an amount of water with ChCl. Fig. 3b reveals that the CO<sub>2</sub> solubility in the bulk (solubility expressed as moles of CO<sub>2</sub> per kg of solvent) of the 2.85 % wt. ChCl + 12.15 % wt. MPA aqueous solution is lower than that of the 15 % neat MPA solution and higher than that of the 10 % neat MPA solution, as it would be expected for a neat MPA 12 % aqueous solution. Also, Fig. 4b reveals that the CO<sub>2</sub> solubility in the bulk (solubility expressed as moles of CO<sub>2</sub> per kg of solvent) of the 4.92 % wt. ChCl + 25.05 % wt. MAPA aqueous solution is lower than the that of the 30 % neat MAPA solution and higher than that of the 18 % neat MAPA solution, as it would be expected for a neat MAPA 25 % aqueous solution. Such results reveal the possibility of replacing an amount of water with choline chloride, i.e., to use for example a 3 % ChCl + 12 % MPA aqueous solution instead of a 12 % MPA solution, without significantly altering the CO<sub>2</sub> solubility in the bulk (solubility expressed as moles of CO<sub>2</sub> per kg of solvent). Such addition is expected to reduce the vapor pressure of the solvent and, since choline chloride is non-toxic, the new solvent is not expected to be more environmentally hazardous.

#### 4.1.3. Effect of water

The effect of water on the CO<sub>2</sub> solubility is revealed in Fig. 5. From Fig. 5a it is concluded that the CO<sub>2</sub> solubility, expressed as moles of CO<sub>2</sub> per mole of DES (ChCl + MPA), increases with the addition of water. Such behavior is similar to the behavior of most amine solutions, which are capable of higher CO<sub>2</sub> absorption per mole of amine, as the amine solution becomes more dilute [25]. In more detail, the addition of water in primary and secondary amine aqueous solutions favors the hydrolysis of the carbamate, which results in the formation of more HCO<sub>3</sub><sup>−</sup> and free amine, according to reaction (9). The produced free amine molecules can be protonated through reaction (5) and, thus, the H<sup>+</sup> concentration tends to decrease. Such consumption of H<sup>+</sup>, as well increase of water concentration, favors the consumption of more CO<sub>2</sub> through reaction (6).

However, also similarly to the pure amine aqueous solutions, the increased chemical CO<sub>2</sub> absorption per mole of amine is not enough to compensate for the decrease of CO<sub>2</sub> absorption ability due to the addition of water, which presents rather low CO<sub>2</sub> solubility. Thus, as presented in Fig. 5b, if the overall CO<sub>2</sub> solubility in the aqueous DES solution is expressed as moles of CO<sub>2</sub> per kg of solvent, the opposite behavior is observed, i.e., it decreases with the addition of water, similarly to the non-amine containing DES [23]. Furthermore, as expected, the CO<sub>2</sub> solubility in all cases decreases with increasing temperature, as shown in Tables 7–11 and as illustrated in Fig. 6 for the

Table 12

Parameters of Eq. (24) for the investigated aqueous solutions.

Parameter (T in K)	Units	A	B	C	D	Regression range (K)	Reference
$K_{1MPA}$	mol/kg	−6168.01	0	0	−3.4131	298–333	[45]
$K_{5MPA}$	mol/kg	−3097.68	0	0	6.6946	298–333	[45]
$K_{1MAPA}$	mol/kg	−6164.85	0	0	−4.1080	313–383	[44]
$K_{5MAPA}$	mol/kg	−3534.70	0	0	7.4398	313–383	[44]
$K_2$	mol/kg	−12092.10	−36.7816	0	235.482	273–498	[54]
$K_3$	mol/kg	−12431.70	−35.4819	0	220.067	273–498	[54]
$K_4$	mol <sup>2</sup> /kg <sup>2</sup>	−13445.90	−22.4773	0	140.932	273–498	[54]
$^aH_{CO_2}$ (MPA DES)	atm kg/mol	−543.54 • w − 1719.6	0	0	9.3000	298–333	This work
$H_{CO_2}$ (MAPA DES)	atm kg/mol	−2012.97	0	0	10.330	298–333	This work

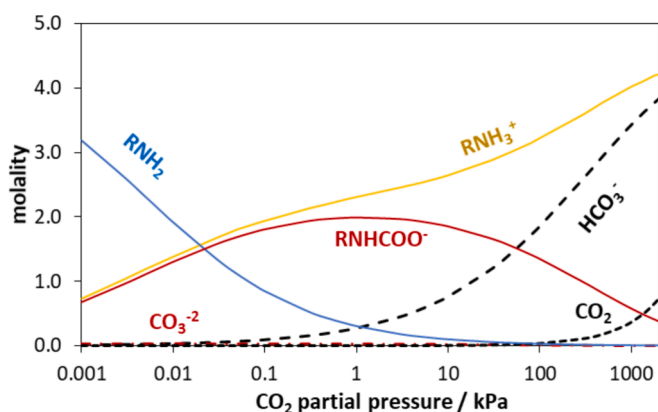
<sup>a</sup>w is the DES weight fraction (0.15, 0.30, 0.50 or 0.85).

**Table 13**

Percentage average absolute deviations (%AAD) of models' predictions from the experimental data of this study.

System	%AAD <sup>a</sup>
ChCl + MAPA, 30 %wt.	0.44
ChCl + MPA, 15 %wt.	2.45
ChCl + MPA, 30 %wt.	4.10
ChCl + MPA, 50 %wt.	6.60
ChCl + MPA, 85 %wt.	4.00

<sup>a</sup> %AAD =  $100 \cdot |a_{exp} - a_{calc}| / a_{exp}$ , where  $a_{exp}$  and  $a_{calc}$  stand for the experimental and calculated CO<sub>2</sub> loading (expressed as moles of CO<sub>2</sub> per mole of amine), respectively.



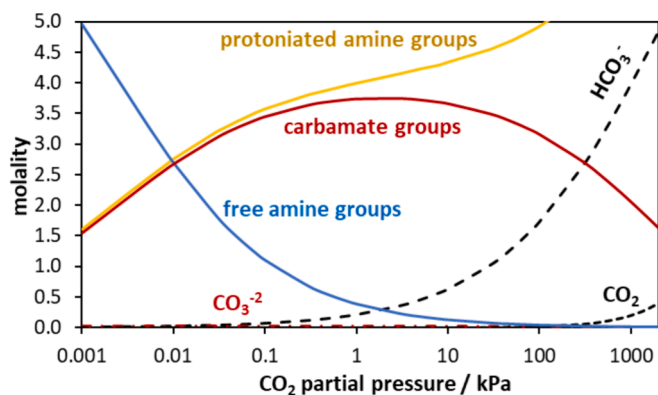
**Fig. 7.** Model predictions for the liquid phase content of a CO<sub>2</sub> loaded ChCl + MPA 30 % wt. aqueous solution at 313.15 K.

ChCl + MAPA aqueous solution.

#### 4.2. Modelling results

Amines react with CO<sub>2</sub> in presence of water, but primary and secondary amines present a different reaction mechanism than tertiary amines. In more detail, non-sterically hindered primary and secondary amines react according to reactions (5)–(9), forming carbamates. According to such reaction mechanism, the stoichiometric limit of the chemical CO<sub>2</sub> absorption is 0.5 mol of CO<sub>2</sub> per mole of amine. However, such limit may be exceeded due to significant carbamate hydrolysis, particularly at high pressures [53].

The reaction mechanism should be known before applying the Kent-



**Fig. 8.** Model predictions for the liquid phase content of a CO<sub>2</sub> loaded ChCl + MAPA 30 % wt. aqueous solution at 313.15 K.

Eisenberg model. Thus, in this study we have adopted the modeling approach of our previous investigations [44,45] and both MPA and MAPA were considered as carbamate forming amines, which react with CO<sub>2</sub> according to reactions (5)–(9). Furthermore, similarly to Kontos et al. [44], MAPA, which is a diamine consisting of one primary and one secondary amine group, was modeled assuming independent and equal reactivity for each amine group, i.e., that the reactivity of each group does not depend on the potential reaction of the other one. Such approximation resembles the Flory's principle of independent reactivity, often considered in polymerizations, which assumes that the reactivity of a characteristic group is independent of the chain length, and it is as a very good approximation for species with higher than 3–5 carbon atoms [44]. Consequently, MAPA was also modeled using Eqs. (10)–(23), but, using such approximation, all the concentrations of amine species shown in such equations denote moles of amine groups and not moles of molecules. Thus, the calculated loading from Eq. (22) should be appropriately transformed to be compared with the experimental data (for example, it should be multiplied by two to be transformed to moles of CO<sub>2</sub> per mole of amine molecules).

In this study, literature parameters were used for the estimation of  $K_1$  through  $K_5$  from Eq. (24). In more detail, the corresponding MAPA and MPA parameters for  $K_1$  and  $K_5$  were adopted from Kontos et al. [44,45]. Furthermore, the parameters for  $K_2$  through  $K_4$  were adopted from Edwards et al. [54]. In this way, only the corresponding parameters of Eq. (24) for Henry's constant were adjusted to the experimental data of this study. In more detail, every aqueous solution considered in this study has a different choline chloride composition, which is expected to influence the physical absorption of CO<sub>2</sub>. Thus, a different Henry's constant was considered for each solution. However, it was found that for choline chloride-MPA aqueous solutions, a linear relation of the A parameter of Eq. (24) with the DES weight fraction and a constant value of D parameter were enough for a satisfactory correlation of all solutions with different DES content. All the used parameters and their sources are presented in Table 12.

Using the parameters of Table 12, the model was applied to correlate the experimental data of this study. The average absolute deviations of model correlations from the experimental data are shown in Table 13. Deviations that range between 0.5 and 6.6 % were obtained in all cases. Representative calculations are illustrated in Figs. 3–6, from which it is observed that the model successfully describes the experimental data.

Besides the calculation of the CO<sub>2</sub> solubility, the model can be applied to predict the concentration of all species in the loaded aqueous solution. Representative predictions are presented in Figs. 7 and 8 for two aqueous solutions investigated in this study, namely the ChCl + MPA 30 %wt. and the ChCl + MAPA 30 %wt. (see Table 5), at 313 K. It is revealed that the free amine concentration becomes very low at relative low CO<sub>2</sub> partial pressures, i.e., at 1 kPa of CO<sub>2</sub> partial pressure, only the 6.6 % and 2.2 % of the initial amine moles remain free (unreacted) for the MPA and MAPA, respectively, while such figures become 2.2 % and 0.7 % for 10 kPa of CO<sub>2</sub> partial pressure. Also, the carbamate concentration presents a maximum around 1 and 3 kPa, for MPA and MAPA, respectively. Such observations reveal that the increase of CO<sub>2</sub> solubility at CO<sub>2</sub> partial pressures higher than around 1–10 kPa is mainly attributed to substantial carbamate hydrolysis. As mentioned in section 4.1.3, the hydrolysis of the carbamate results in the formation of more HCO<sub>3</sub><sup>-</sup> and free amine, according to reaction (9). The produced free amine molecules can be protonated through reaction (5) and, thus, the H<sup>+</sup> concentration tends to decrease. Such consumption of H<sup>+</sup> favors the reaction of more CO<sub>2</sub> through reaction (6). Finally, as shown by the CO<sub>2</sub> concentration line presented in Figs. 7 and 8, at CO<sub>2</sub> partial pressures higher than around 100 kPa, there is a non-negligible contribution to the total CO<sub>2</sub> solubility from molecular CO<sub>2</sub> dissolution.

## 5. Conclusions

The solubility of CO<sub>2</sub> in aqueous solutions of amine-based DES, consisting of choline chloride + MPA and choline chloride + MAPA, was experimentally investigated. It is concluded that such solutions present similar or marginally higher CO<sub>2</sub> solubility, expressed as moles of CO<sub>2</sub> per mole of amine, than the corresponding pure amine aqueous solutions, revealing that the addition of choline chloride does not significantly influence the CO<sub>2</sub> absorption behavior, which in both cases is mainly attributed to chemical absorption. Furthermore, an increase in the water content results in an increase of the absorbed CO<sub>2</sub> moles per mole of amine. However, such increase of the chemical absorption is not enough to compensate for the decrease in CO<sub>2</sub> absorption ability due to the addition of water, which presents rather low CO<sub>2</sub> solubility. Consequently, the overall CO<sub>2</sub> solubility, expressed in moles of CO<sub>2</sub> per kg of solvent, decreases with addition of water, similarly to the non-amine containing DES investigated in literature. Finally, it was shown that, starting from an aqueous amine solution, if a small part of water is replaced by choline chloride, the CO<sub>2</sub> solubility in the bulk (solubility expressed as moles of CO<sub>2</sub> per kg of solvent) is not significantly altered. However, such addition is expected to reduce the vapor pressure of the solvent and, since choline chloride is non-toxic, the new solvent is not expected to be more environmentally hazardous.

The experimental CO<sub>2</sub> solubility data were used to parameterize the modified Kent-Eisenberg model, which in turn was applied to predict the speciation in CO<sub>2</sub> loaded solutions. The model predictions reveal that the free amine content (unreacted amine) is very low already from relatively low CO<sub>2</sub> partial pressures of the order of 1 kPa. Consequently, the increase of CO<sub>2</sub> solubility at higher CO<sub>2</sub> partial pressures is mainly attributed to the hydrolysis of the carbamate and, at CO<sub>2</sub> partial pressures higher than 100 kPa, to a non-negligible contribution from molecular CO<sub>2</sub> dissolution.

Nevertheless, the study investigates a major aspect for selecting an aqueous DES solution as potential solvent for CO<sub>2</sub> capture, such as the thermodynamic CO<sub>2</sub> solubility, which reveals the overall absorption ability of the solvent system. Nevertheless, several other aspects such as the absorption and desorption kinetics, the regeneration performance, the cyclic capacity, the viscosity of the solvent, the volatility losses, the thermal and oxidative degradation behavior, as well as economic aspects, such as the regeneration cost, need to be studied.

## CRedit authorship contribution statement

**Giannis Kontos:** Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Maria Anna Soldatou:** Investigation. **Ioannis Tsivintzelis:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Methodology, Formal analysis, Conceptualization.

## Declaration of competing interest

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

## Data availability

All data are presented in the article

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## Appendix A. Supplementary data

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