CO$_2$ solubility in aqueous solutions of blended amines: Experimental data for mixtures with MDEA, AMP and MPA and modeling with the modified Kent-Eisenberg model

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ABSTRACT

Recently, a vast quantity of new amine-based solvent systems, alternative to aqueous ethanolamine solutions, have been suggested for CO$_2$ capture applications. In numerous cases amine blends are used, since a careful selection of the amine ratio may effectively alter the absorption capacity, the absorption kinetics and the regeneration efficiency. In this direction accurate experimental data are needed for screening applications, but most importantly for parameterizing and evaluating theoretical models used in design applications. In this work, new experimental data are presented for the CO$_2$ solubility in aqueous solutions of amine blends containing *N*-methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP) and 3-amino-1-propanol (MPA) at 298, 313, 323 and 333 K and pressures up to approximately 800 kPa. The modified Kent-Eisenberg model, parameterized using experimental data solely for single amine solutions, is subsequently applied to predict the CO$_2$ absorption in blended amine solutions. Satisfactory model predictions are observed. The average absolute deviations from the experimental data of this study range between 2 and 5%.

1. Introduction

Chemical absorption using aqueous amine solutions is a mature process for CO$_2$ capture applications. Recently, significant research effort has been conducted to find new solvent systems, alternative to the currently used aqueous ethanolamine (MEA) solutions, that facilitate economically viable processes for CO$_2$ capture applications. In this direction, various single amine or blended amine solutions have been suggested.

Amines' performance in CO$_2$ capture applications is mainly affected by the reaction mechanism. More specifically, the presence of a carbamate as a reaction product is the key factor, which affects the CO$_2$ absorption capacity, the absorption rate, the regeneration performance [1] and the corrosion behavior [2,3]. Primary amines, such as ethanolamine (MEA) and 3-amino-1-propanol (MPA), and secondary amines, such as diethanolamine (DEA), rapidly react with CO$_2$ through the carbamate reaction [4,5]. On the other hand, tertiary amines, such as *N*-methyldiethanolamine (MDEA), do not form carbamates and therefore react slowly with CO$_2$ through the neutralization reaction. Moreover,

sterically hindered alkanolamines, such as 2-amino-2-methyl-1-propanol (AMP), form unstable carbamates [6].
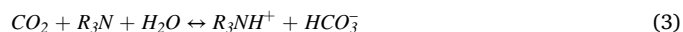
Thus, the most common categorization of amines is their distinction according to their reaction mechanism and the stoichiometrically imposed maximum CO$_2$ loading. Unhindered primary and secondary amines react with CO$_2$ according to the zwitterion mechanism, resulting in a stable carbamate formation, through the following overall reaction:

$$2R_aR_bNH + CO_2 \leftrightarrow R_aR_bNH_2^+ + R_aR_bNCOO^- \qquad (1)$$
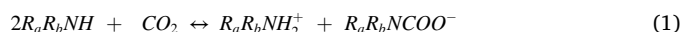
In hindered primary and secondary amines, the resulting carbamate is unstable and the bicarbonate ion is the main product [6]:

$$R_aR_bNH + CO_2 + H_2O \leftrightarrow R_aR_bNH_2^+ + HCO_3^- \qquad (2)$$

Finally, tertiary amines react with CO$_2$ in presence of water, in 1:1 mole ratio, as shown below [7,8]:

$$CO_2 + R_3N + H_2O \leftrightarrow R_3NH^+ + HCO_3^- \qquad (3)$$

According to the above overall reactions, the maximum, due to

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stoichiometric restrictions, CO_2 loading of tertiary and sterically hindered amines is equal to 1 mole of CO_2 per mole of amine, while that for the unhindered primary and secondary amines is 0.5 mole of CO_2 per mole of amine. However, the CO_2 loading may exceed such limits due to significant CO_2 physical absorption and due to significant carbamate hydrolysis, particularly at high pressures [9].

Usually, unhindered primary and secondary amines are selected because they present fast kinetics, while hindered or tertiary amines are selected due to their high loading capacity. For example, at 313 K and around 100 kPa of CO_2 partial pressure, aqueous 2 M MDEA (which is a tertiary amine) and AMP (which is sterically hindered amine) solutions present a loading of 0.80 and 0.97 mole of CO_2 per mole of amine, respectively [10,11], which is significantly higher than the 0.64 mole of CO_2 per mole of amine presented by the 5 M MEA (which is a primary amine) solutions [12]. The heat released by the CO_2 reaction with MDEA and AMP, at 313 K, is 60.9 kJ/mol CO_2 [13] and 80.91 kJ/mol CO_2 [14], respectively, much lower than that of the reaction with MEA (85.6 kJ/mol CO_2) [13]. Assuming that the desorption of CO_2 in the stripper results due to an inverse reaction of CO_2 absorption by the amine solution, the heat of absorption is considered approximately equal to the heat of CO_2 desorption. Thus, in general, lower heat of absorption results in lower regeneration energy. Therefore, the use of MDEA or AMP as alternatives to MEA presents lower regeneration energy in the stripping process [15]. Moreover, in comparison to MEA, other amines, such as MDEA and AMP, have been found to be less corrosive on carbon steel [2, 3]. However, despite such important characteristics, the reaction rate constant of CO_2 with AMP, $k_{AMP} = 810.4 \ m^3/kmol\cdot s$ [16], and MDEA, $k_{MDEA} = 3.5 \ m^3/kmol\cdot s$ [17], at 298 K is much lower than that of MEA, $k_{MEA} = 3630 \ m^3/kmol\cdot s$ [18].

Another way to categorize the suggested amines is their distinction as absorption activators and regeneration promoters, based on their performance in the overall process [19]. The former ones exhibit fast reaction kinetics, while the latter amines allow for high regenerability, since they desorb high amounts of CO_2 in the regeneration temperature.

Since it is difficult to find a single amine that will incorporate high absorption capacity, high absorption rate, high regenerabilty, low energy demands and low corrosive behavior, the use of blended amine solutions has attracted significant research interest, because they maximize the desirable characteristics of the constituent amines, such as high absorption capacity, high absorption rate, low heat duty and low corrosive behavior [20,21].

To improve the CO_2 performance of amine solutions, many investigators have worked on blending a primary amine with a tertiary or sterically hindered amine. A few of these works are introduced here. In more detail, the absorption rate for a 4 M AMP/1 M MEA aqueous solution was found to be significantly higher than that of 5 M AMP solution [22]. Moreover, an experimental study of MEA-MDEA blends, with constant total amine concentration of 10% wt., showed that by replacing 3% wt. MEA with 3% wt. MDEA the CO_2 absorption capacity remains close to that of the 10% wt. MEA, while the regeneration efficiency increases [23]. Also, an aqueous solution containing 12% wt. AMP and 18% wt. MEA showed 51.2% higher CO_2 loading than the 30% wt. MEA solution and a higher reaction rate than the respective pure AMP aqueous solution [24]. The regeneration energy for a 5% wt. DEA / 25% wt. AMP (3.03 GJ/ton CO_2) [25] was found much lower than that of the 30% wt. MEA (3.7 GJ/ton CO_2) [26]. Finally, in another study, it has been found that blends of 5 M MEA-AMP and 5 M MEA-MDEA present lower corrosion rate than 5 M MEA at 80 °C [27].

Consequently, the use of aqueous solutions of blended amines presents a very important advantage, i.e., it allows the fine tuning of the solvent properties, since by altering the concentration of the amine constituents, one can effectively change the absorption capacity and kinetics, as well as the regeneration efficiency and the corrosion behavior. Although solutions of blended amines, such as MPA-MDEA, MPA-AMP or AMP-MDEA can be potential solvents for CO_2 removal,

experimental data for the CO_2 solubility in MPA-based amine systems have not been reported yet, while there are only few data for the AMP-MDEA aqueous solutions. An extensive literature survey on the CO_2 solubility in blended amine solutions containing AMP or MDEA is summarized in Tables 1-3.

The thermodynamic modeling of such CO_2 containing aqueous solutions of blended amines require to simultaneously account for both the chemical and the physical equilibrium. The latter requires to account for all intermolecular interactions, including ionic interactions among the various ions existing in the CO_2 loaded solutions and, thus, an electrolyte thermodynamic model is needed. However, such approach presents significant complexity and usually several simplifications are performed. In this direction, in many cases the chemical interactions are not explicitly accounted for and are indirectly considered using a pseudo-chemical reaction approach through the hydrogen bonding term of the relevant thermodynamic equations of state [56–58].

Nevertheless, it was observed that many relatively simpler empirical approaches result in very satisfactory correlations for the solubility of CO_2 and other acid gasses in aqueous amine solutions [59]. The most important of such approaches is the Kent-Eisenberg model [60], which requires the knowledge of the equilibrium constants for all reactions taking place when CO_2 or other acid gasses are dissolved in the aqueous amine solution. Usually, the literature values for the equilibrium constants of common reactions, such as the reactions of acid gasses with water, are used, while the equilibrium constants for the carbamate hydrolysis or the amine ionization reaction are considered as adjustable parameters. According to Jou et al. [61], the effective values of such adjustable parameters absorb all non-idealities of the model and, usually, very satisfactory correlations are obtained, which rendered the model very popular in modeling the CO_2 solubility in aqueous alkanolamine solutions. Consequently, several modifications and modeling

Table 1

Literature studies reporting CO_2 solubility in aqueous solutions of blended amines containing AMP. Blends of two amines.

A + B	[A] + [B]	Temperature [K]	Reference
AMP + AEEA	5 + 15, 10 + 15 wt.%	303, 313, 323	[28]
AMP + DEA	5 + 25, 10 + 20 wt.%	313, 373	[29]
AMP + DEA	12 + 18, 18 + 12, 24 + 6 wt.%	313, 333, 353	[30]
AMP + DEA	10 + 20, 20 + 10 wt.%	313, 333, 353	[31]
AMP + DETA	1 + 2, 1.5 + 1.5, 2 + 1, 2.5 + 0.5 kmol/m³	313	[32]
AMP + HMDA	10 + 20, 15 + 15, 20 + 10, 25 + 5 wt.%	303, 313, 323, 333	[33]
AMP + MDEA	1.278 + 1.266 mol/kg	313	[34]
AMP + MEA	6 + 24, 12 + 18, 18 + 12, 24 + 6 wt.%	313, 333, 353, 373	[35]
AMP + MEA	10 + 20, 20 + 10, 25 + 5 wt.%	313, 333, 353	[31]
AMP + NH₃	20 + 1, 20 + 3, 20 + 5, 20 + 7 wt.%	313, 373	[36]
AMP + PZ	3 + 1.5 M	313, 333, 353, 373, 393	[37]
AMP + PZ	32 + 8, 35 + 5, 38 + 2 wt. %	303, 313, 323	[38]
AMP + PZ	42 + 8, 45 + 5, 48 + 2 wt. %	318, 328	[38]
AMP + PZ	32 + 8, 35 + 5, 38 + 2 wt. %	303, 313, 323	[39]
AMP + PZ	22 + 8, 25 + 5, 28 + 2 wt. %	298, 308, 318, 328	[40]
AMP + PZ	2.3 + 5, 4 + 2 m	373, 383, 393, 403, 413, 423, 433	[41]
AMP + PZ	20 + 10, 25 + 5 wt.%	313, 333, 373, 393	[42]
AMP + PZ	2 + 0.5, 2 + 1, 2 + 1.5, 3 + 0.5, 3 + 1, 3 + 1.5 kmol/m³	313, 333, 353	[43]

Table 2
Literature studies reporting CO_2 solubility in aqueous solutions of blended amines containing AMP. Blends of three amines.

A + B + C	[A] + [B] + [C]	Temperature [K]	Reference
AMP + MDEA + DEA	4 + 32.5 + 12.5, 6 + 32.5 + 12.5, 10 + 32.5 + 12.5 wt.%	313, 343, 393	[44]
AMP + MDEA + DETA	2 + 1 + 1.5, 1.5 + 1.5 + 1.5, 1 + 2 + 1.5 kmol/m³	313	[45]
AMP + PZ + MEA	2.5 + 0.5 + 1.5, 2 + 1 + 1.5, 1.5 + 1.5 + 1.5 kmol/m³	313	[46]

Table 3
Literature studies reporting CO_2 solubility in aqueous solutions of blended amines containing MDEA. Blends of two amines.

A + B	[A] + [B]	Temperature [K]	Reference
MDEA + AEEA	5 + 15, 10 + 15 wt.%	303, 313, 323	[28]
MDEA + AEEA	5.11+0.26, 4.88+0.49, 4.77+0.60 mol/kg	313, 328, 343, 358	[47]
MDEA + DEA	32.5 + 12.5 wt.%	313, 343, 393	[44]
MDEA + DEA	18 + 12, 6 + 24 wt.%	313, 333, 353, 373	[48]
MDEA + DEA	3.4 + 0.8, 2.1 + 2.1 M	343, 373, 393, 413, 433, 453	[49]
MDEA + DEA	15 + 10, 10 + 20, 35 + 10 wt.%	313	[29]
MDEA + DEA	20 + 10 wt.%	313, 393	[29]
MDEA + DEA	1.5 + 0.5 M	303, 313, 323	[50]
MDEA + DEA	0.5 + 1.5, 1 + 1 M	303	[50]
MDEA + DEA	25 + 25, 30 + 20 wt.%,	362, 412,	[55]
MDEA + MEA	2 + 2 M	313, 353	[51]
MDEA + MEA	3.4 + 0.8, 2.1 + 2.1 M	343, 373, 393, 413, 433, 453	[49]
MDEA + MEA	10 + 20, 20 + 10, 27 + 3, 28.5 + 1.5 wt.%	298, 313, 353, 393	[52]
MDEA + MEA	10 + 20 wt.%	333, 373, 423	[52]
MDEA + MEA	12 + 18, 24 + 6 wt.%	313, 333, 353, 373	[53]
MDEA + PZ	4.28 + 0.103, 4.28 + 0.308, 4.28 + 0.696, 3.46 + 0.103, 3.46 + 0.154, 3.46 + 0.206, 1.72 + 0.103, 1.72 + 0.154, 1.72 + 0.206 M		[54]

routes appeared in literature, which were recently reviewed [62].

In this work, we present new experimental data for the CO_2 solubility in aqueous solutions of amine blends containing MDEA, MPA and AMP. Furthermore, we present all the needed equations for applying the modified Kent-Eisenberg model to mixtures of a) one carbamate forming and one non-carbamate forming amine, and b) two non-carbamate forming amines. Finally, we evaluate the predicting ability of the model against the new experimental data of this study for blended amine solutions using parameters solely adjusted to single amine solutions' data. The experimental and modeling results of this study are of interest in designing carbon capture processes based on the CO_2 absorption from flue gasses in liquid amine solvents.

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

All the investigated alkanolamine solutions were prepared by mixing weighted amounts of alkanolamines and water (accuracy 0.001 g) in a 150 or a 250 mL (Din A) volumetric flasks 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 were estimated in a similar manner, by knowing the volume change of the flask at each temperature (estimated using HPLC water).

The experimental set up (Fig. 1) and its validation, as well as the detailed experimental procedure are presented in our previous studies [10,11,57,63]. They are briefly presented here. Vapor-liquid equilibrium (VLE) measurements in aqueous solutions of blended amines were performed using a high-pressure stainless-steel equilibrium cell (with internal volume of 152.2 ± 1.6 cm³ at 25 °C), which is equipped with pressure transducer (WIKA A-10, −1 to 24 bar, ±0.5%) and a Pt-100 thermometer (±0.01 K), tested at 20–60 °C against a Systemteknik S 1220 with resolution of 0.001 °C and accuracy of ±0.002 °C, equipped with a Pt-100 thermometer which was calibrated against NPL, UK, class 1. The equilibrium cell is placed into a water bath (model, Grant TC-120), equipped with a temperature controller (temperature stability of 0.1 K) and a water circulator. After the establishment of thermal stability, a measured (weighted with accuracy of 0.001 g) amount (approximately 20 g) of the solvent is added in the equilibrium cell. Before starting the experimental run, the equilibrium cell and all the lines are evacuated, so the solvent exists under its own vapor pressure. Next, the cell is filled with a known (weighted, maximum error ±0.005 g) amount of pure CO_2. Equilibrium is confirmed once the pressure remains stable for at least one hour at constant temperature. Pressure and temperature readings are recorded during all the experimental time.

Knowing the CO_2 density, obtained from the NIST data base [64], the solvent density, the total mass of the solvent and the total mass of CO_2 loaded in the equilibrium cell, the volume of the cell, as well as the pressure and the temperature of the system, the absorbed amount of CO_2 is calculated through the mass balance equations [11]. According to this experimental procedure, the total pressure of the system is measured. The partial pressure of CO_2 is estimated through the subtraction of the vapor pressure of the solution from the total pressure. In this study, having in mind that the total amines' mole fraction is around 0.04 or lower in all cases, we have used the approach suggested by Jou et al. [12], who calculated the solvent vapor pressure from Raoult's law knowing the compositions and the vapor pressures of pure compounds.

Such approximation is used very often in similar pressure decay experimental studies [11,12,57,65] and results in small corrections, especially at relatively high pressures (higher than 100 kPa), due to the very low vapor pressure of the investigated solutions. Using such procedure, the aqueous solutions of blended amines that are presented in Table 5 were investigated at 298, 313, 323 and 333 K.

3. The modified Kent-Eisenberg model for blended amine solutions

In this study, the modified Kent-Eisenberg model was used to predict the CO_2 solubility in the investigated aqueous solutions of blended amines. Contrary to the original model, equations are not solved iteratively, but a polynomial equation is set for estimating the concentration of hydrogen cations, as presented by Haji-Sulaiman et al. [50]. The equations for such modified Kent-Eisenberg model that refer to single amine solutions are reported in may studies [50,62]. However, the

Table 4
Chemicals used in this work.

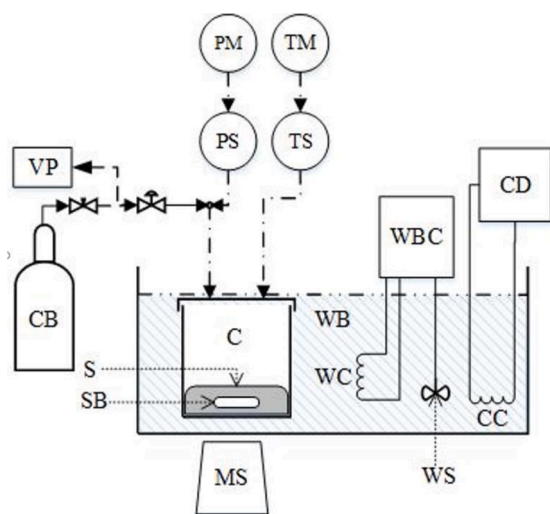| Product Name	Abbreviation	CAS-number	Purity	Supplier
Carbon dioxide	CO₂	124–38–9	99.9% (vol.)	Air Liquide
N-methyldiethanolamine	MDEA	105–59–9	99.0% (mole fraction)	Aldrich
2-Amino-2-methyl-1-propanol	AMP	124–68–5	99.0% (mole fraction)	Aldrich
3-Amino-1-propanol	MPA	156–87–6	99.0% (mole fraction)	Aldrich
Water	H₂O	7732–18–5	HPLC grade	Chem lab

Fig. 1. Experimental apparatus [10] for VLE measurements consisting of: equilibrium cell (C), solution (S) weighted CO_2 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).

Table 5
Amine content (±0.02 wt.%) of the investigated aqueous solutions.

A + B amines	[A] + [B] amine content	[A] + [B] amine concentration
AMP + MPA	9.43 + 7.53 wt.%	1.05 + 1.00 M
AMP + MDEA	8.87 + 11.90 wt.%	1.00 + 1.00 M
MPA + MDEA	7.46 + 11.83 wt.%	1.00 + 1.00 M
MPA + MDEA	4.84 + 7.69 wt.%	0.65 + 0.65 M

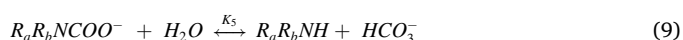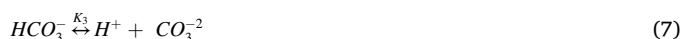relevant equations for systems containing more than one amines are not always reported.

According to Suleman et al. [62], who recently reviewed the use of the Kent-Eisenberg model in modeling the CO_2 solubility in amine solutions, there are three possible ways of modeling systems with blended amines. According to the first and most approximate one, the single amine models are solved independently, and the resulting CO_2 solubilities are summed up to estimate the solubility in the blended amine solution. According to the second, but still very approximate one, the polynomial equations that are used for calculating the hydrogen cation concentration of the single amine models are summed up and then the loading is calculated through a combined equation. However, both approaches are not rigorous and add unnecessary empiricism to the model. Only the third approach is rigorous and does not add unnecessary empiricism to the model. According to this, the mass and charge balances for the multicomponent mixture are set, resulting in rigorous equations for calculation of all species' concentrations. Using such model, the non-ideality of the vapor phase is often neglected and the Henry's law is used to calculate the molecular CO_2 solubility. Also, in most studies, recently reviewed [62], the activities of the liquid phase

compounds are assumed equal to unity, which results in a severe simplification, but to considerably less complexity of the model. However, studies using activity coefficients from more rigorous thermodynamic approaches coupled with the Kent-Eisenberg model are also found in literature [66].

In this study, we adopt the third route that is reported by Suleman et al. [62] and activities equal to unity for setting up the equations of the model and the relevant procedure is described in the next sections for mixtures of two non-carbamate forming amines (i.e., AMP-MDEA blends), and mixtures of one carbamate forming and one non-carbamate forming amine (i.e., AMP-MPA or MDEA-MPA blends).

3.1. Mixtures of one non-carbamate forming and one carbamate forming amine

According to Tzirakis et al. [63] in a mixture of one carbamate forming (R_aR_bNH) and one non-carbamate forming (R_cR_dNH) amine we can write the following chemical reactions:

$$R_aR_bNH_2^+ \xleftrightarrow{K_{11}} R_aR_bNH + H^+ \tag{4}$$

$$R_cR_dNH_2^+ \xleftrightarrow{K_{12}} R_cR_dNH + H^+ \tag{5}$$

$$H_2O + CO_2 \xleftrightarrow{K_2} H^+ + HCO_3^- \tag{6}$$

$$HCO_3^- \xleftrightarrow{K_3} H^+ + CO_3^{-2} \tag{7}$$

$$H_2O \xleftrightarrow{K_4} H^+ + OH^- \tag{8}$$

$$R_aR_bNCOO^- + H_2O \xleftrightarrow{K_5} R_aR_bNH + HCO_3^- \tag{9}$$

where $R_aR_bNH_2^+$ and $R_cR_dNH_2^+$ are the protonated forms of the carbamate and the non-carbamate forming amine, respectively, and $R_aR_bNCOO^-$ is the carbamate anion. The relevant equilibrium constants are written as follows:

$$K_{11} = \frac{[R_aR_bNH][H^+]}{[R_aR_bNH_2^+]} \tag{10}$$

$$K_{12} = \frac{[R_cR_dNH][H^+]}{[R_cR_dNH_2^+]} \tag{11}$$

$$K_2 = \frac{[HCO_3^-][H^+]}{[CO_2]} \tag{12}$$

$$K_3 = \frac{[CO_3^{-2}][H^+]}{[HCO_3^-]} \tag{13}$$

$$K_4 = [OH^-][H^+] \tag{14}$$

$$K_5 = \frac{[R_aR_bNH][HCO_3^-]}{[R_aR_bNCOO^-]} \tag{15}$$

The molecular CO_2 concentration in the liquid phase is given through a Henry's law relation, as follows:

$$P_{CO_2} = H_{CO_2}[CO_2] \tag{16}$$

where P_{CO2} and H_{CO2} are the CO_2 partial pressure in the vapor phase and the Henry's constant, respectively.

To set up the problem, we can write three independent mass balance and one charge balance equations as follows:

Amine mass balances

$$[R_aR_bNH]_t = [R_aR_bNH] + [R_aR_bNH_2^+] + [R_aR_bNCOO^-] \tag{17}$$

$$[R_cR_dNH]_t = [R_cR_dNH] + [R_cR_dNH_2^+] \tag{18}$$

$$[Amine]_t = [R_aR_bNH]_t + [R_cR_dNH]_t \tag{19}$$

CO_2 *balance:*

$$\alpha_{CO_2}[Amine]_t = [R_aR_bNCOO^-] + [HCO_3^-] + [CO_3^{-2}] + [CO_2] \tag{20}$$

Charge balance:

$$[H^+] + [R_aR_bNH_2^+] + [R_cR_dNH_2^+] = [R_aR_bNCOO^-] + [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] \tag{21}$$

where α_{CO_2} is the carbon dioxide loading (expressed as mole of CO_2 per mole of amines in the system) and $[Amine]_t$ is the total concentration of amines in the mixture. After some algebra, Eqs. (10)-(21) reduce to the following system of three equations with three unknowns, $[H^+]$, $[R_aR_bNH_2^+]$ and $[R_cR_dNH_2^+]$:

$$[R_aR_bNH]_t = \left(1 + \frac{K_{11}}{[H^+]} + \frac{K_{11}K_2[CO_2]}{K_5[H^+]^2}\right)[R_aR_bNH_2^+] \tag{22}$$

$$[R_cR_dNH]_t = \left(1 + \frac{K_{12}}{[H^+]}\right)[R_cR_dNH_2^+] \tag{23}$$

$$[R_aR_bNH_2^+]\left(1 - \frac{K_{11}K_2[CO_2]}{K_5[H^+]^2}\right) + [R_cR_dNH_2^+]$$
$$= \frac{K_4}{[H^+]} + \frac{K_2[CO_2]}{[H^+]} + \frac{2K_2K_3[CO_2]}{[H^+]^2} - [H^+] \tag{24}$$

The following polynomial equation is obtained, after some algebra:

$$A[H^+]^6 + B[H^+]^5 + C[H^+]^4 + D[H^+]^3 + E[H^+]^2 + F[H^+] + G = 0 \tag{25}$$

where parameters *A, B, C, D, E, F and G* are shown in Table 6.

Only the root with physical meaning, i.e., $pH \in [7, 12]$, is kept from Eq. (25) [50]. Then, the CO_2 loading is calculated through the following relation:

$$\alpha_{CO_2} = \frac{\left([CO_2] + \frac{K_2[CO_2]}{[H^+]} + \frac{K_2K_3[CO_2]}{[H^+]^2} + [RRNCOO^-]\right)}{[Amine]_t} \tag{26}$$

where:

$$[RRNCOO^-] = \frac{K_{11}K_2[CO_2][R_aR_bNH]_t}{\left(K_5[H^+]^2 + K_{11}K_5[H^+] + K_{11}K_2[CO_2]\right)} \tag{27}$$

The above equations are sufficient for mixtures of one carbamate forming and one non-carbamate forming amine.

3.2. Mixtures of two non-carbamate forming amines

Here we extend the above formalism to a mixture of two non-carbamate forming amines. In that case, reaction (9) and Eq. (15) are omitted. Consequently, $[RRNCOO^-]$ is omitted from Eqs. (17), (20) and (21), while the system of Eqs. (22) – (24) takes the following form:

$$[R_aR_bNH]_t = \left(1 + \frac{K_{11}}{[H^+]}\right)[R_aR_bNH_2^+] \tag{28}$$

$$[R_cR_dNH]_t = \left(1 + \frac{K_{12}}{[H^+]}\right)[R_cR_dNH_2^+] \tag{29}$$

$$[R_aR_bNH_2^+] + [R_cR_dNH_2^+] = \frac{K_4}{[H^+]} + \frac{K_2[CO_2]}{[H^+]} + \frac{2K_2K_3[CO_2]}{[H^+]^2} - [H^+] \tag{30}$$

Thus, the following polynomial equation is obtained:

$$A[H^+]^5 + B[H^+]^4 + C[H^+]^3 + D[H^+]^2 + E[H^+] + F = 0 \tag{31}$$

where parameters *A, B, C, D, E* and *F* are shown in Table 7.

As in the previous case, only the root with physical meaning, i.e., $pH \in [7, 12]$, is kept from Eq. (31) [50]. The CO_2 loading is calculated through the following equation:

$$\alpha_{CO_2} = \frac{\left([CO_2] + \frac{K_2[CO_2]}{[H^+]} + \frac{K_2K_3[CO_2]}{[H^+]^2}\right)}{[Amine]_t} \tag{32}$$

In all cases, the temperature dependence of the equilibrium constants, K_i, and the Henry's law constant, H_{CO_2}, is given through the following empirical relation [62]:

$$\ln K_i = \frac{A_i}{T} + B_i \ln T + C_i T + D_i \tag{33}$$

4. Results and discussion

4.1. Experimental results

In all cases, aqueous solutions of blended amines, with amine content as presented in Table 5, were studied at 298, 313, 323 and 333 K. The obtained experimental data are presented in Tables 8-11, respectively. The uncertainties that are presented in the experimental loading values of Tables 8-11 denote the maximum error, calculated through propagation of errors, considering the uncertainties of all used data for loading calculation (uncertainty in the weights of the materials added in the

Table 6
Parameters of Eq. (25).

Parameters	Relation
A	$-K_5$
B	$-K_5[R_aR_bNH]_t - K_5[R_cR_dNH]_t - K_{11}K_5 - K_{12}K_5$
C	$-K_{12}K_5[R_aR_bNH]_t - K_{11}K_5[R_cR_dNH]_t + K_4K_5 + K_2K_5[CO_2] - K_{11}K_2[CO_2] - K_{11}K_{12}K_5$
D	$K_{11}K_2[R_aR_bNH]_t[CO_2] - K_{11}K_2[R_cR_dNH]_t[CO_2] + 2K_2K_3K_5[CO_2] + K_{11}K_4K_5 + K_{11}K_2K_5[CO_2] - K_{11}K_{12}K_2[CO_2] + K_{12}K_4K_5 + K_{12}K_2K_5[CO_2]$
E	$K_{11}K_{12}K_2[R_aR_bNH]_t[CO_2] + 2K_{11}K_2K_3[CO_2] + K_{11}K_2K_4[CO_2] + K_{11}K_2^2[CO_2]^2 + 2K_{12}K_2K_3K_5[CO_2] + K_{11}K_{12}K_4K_5 + K_{11}K_{12}K_2K_5[CO_2]$
F	$2K_{11}K_2^2K_3[CO_2]^2 + K_{11}K_{12}K_2K_4[CO_2] + K_{11}K_{12}K_2^2[CO_2]^2 + 2K_{11}K_{12}K_2K_3K_5[CO_2]$
G	$2K_{11}K_{12}K_2^2K_3[CO_2]^2$

Table 7
Parameters of Eq. (31).

Parameters	Relation
A	1
B	$K_{11} + K_{12} + [R_aR_bNH]_t + [R_cR_dNH]_t$
C	$K_{11}K_{12} - K_2[CO_2] - K_4 + K_{12}[R_aR_bNH]_t + K_{11}[R_cR_dNH]_t$
D	$-K_4(K_{11} + K_{12}) - K_2(K_{11} + K_{12})[CO_2] - 2K_2K_3[CO_2]$
E	$-K_{11}K_{12}K_4 - K_{11}K_{12}K_2[CO_2] - 2K_2K_3(K_{11} + K_{12})[CO_2]$
F	$-2K_{11}K_{12}K_2K_3[CO_2]$

Table 8

CO$_2$ solubility in aqueous AMP + MPA (9.43 + 7.53%wt., 1.05 + 1.00 M) solutions at 298–333 K[a].

P_{total} (kPa)[b]	P_{CO_2} (kPa)	α_{CO_2} (mol CO$_2$/ mol amine)	P_{total} (kPa)[b]	P_{CO_2} (kPa)	α_{CO_2} (mol CO$_2$/ mol amine)
298.1 K			323.1 K		
18	15	0.73 ± 0.04	48	37	0.70 ± 0.04
31	28	0.80 ± 0.05	73	62	0.76 ± 0.05
118	115	0.92 ± 0.05	182	171	0.86 ± 0.05
279	276	1.00 ± 0.05	357	346	0.94 ± 0.05
681	678	1.05 ± 0.06	796	785	0.98 ± 0.06
313.1 K			333.1 K		
31	24	0.72 ± 0.04	68	50	0.69 ± 0.04
53	46	0.78 ± 0.05	99	81	0.74 ± 0.05
154	147	0.89 ± 0.05	216	198	0.83 ± 0.05
323	317	0.96 ± 0.05	396	378	0.91 ± 0.05
751	745	1.01 ± 0.06	847	829	0.96 ± 0.06

[a] *Standard uncertainty in temperature u(T) = 0.20 K.*
[b] *Standard uncertainty in total pressure u(p) = 0.005•P.*

Table 9

CO$_2$ solubility in aqueous AMP + MDEA (8.87 + 11.90%wt., 1.00 + 1.00 M) solutions at 298–333 K[a].

P_{total}(kPa)[b]	P_{CO_2} (kPa)	α_{CO_2} (mol CO$_2$/ mol Amine)	P_{total} (kPa)[b]	P_{CO_2} (kPa)	α_{CO_2} (mol CO$_2$/ mol Amine)
298.1 K			323.1 K		
17	14	0.76 ± 0.05	51	40	0.73 ± 0.05
27	24	0.84 ± 0.05	73	62	0.80 ± 0.05
89	86	0.96 ± 0.05	158	147	0.88 ± 0.05
273	270	1.04 ± 0.05	345	334	0.98 ± 0.05
695	692	1.06 ± 0.06	801	790	1.00 ± 0.06
313.1 K			333.1 K		
33	26	0.75 ± 0.05	79	61	0.70 ± 0.05
50	43	0.82 ± 0.05	106	88	0.76 ± 0.05
128	122	0.91 ± 0.05	199	181	0.84 ± 0.05
313	307	1.01 ± 0.05	391	373	0.94 ± 0.05
759	753	1.02 ± 0.06	850	832	0.98 ± 0.06

[a] *Standard uncertainty in temperature u(T) = 0.20 K.*
[b] *Standard uncertainty in total pressure u(p) = 0.005•P.*

Table 10

CO$_2$ solubility in aqueous MPA + MDEA (4.84 + 7.69%wt., 0.65 + 0.65 M) solutions at 298–333 K[a].

P_{total} (kPa)[b]	P_{CO_2} (kPa)	α_{CO_2} (mol CO$_2$/ mol Amine)	P_{total} (kPa)[b]	P_{CO_2} (kPa)	α_{CO_2} (mol CO$_2$/ mol Amine)
298.1 K			323.1 K		
103	100	0.93 ± 0.03	166	155	0.85 ± 0.03
302	299	1.00 ± 0.04	377	366	0.92 ± 0.04
461	458	1.03 ± 0.04	548	537	0.96 ± 0.04
612	609	1.11 ± 0.05	716	705	1.03 ± 0.05
792	789	1.20 ± 0.05	913	902	1.12 ± 0.05
1173	1170	1.21 ± 0.06	1338	1327	1.12 ± 0.06
313.1 K			333.1 K		
131	124	0.90 ± 0.03	199	180	0.82 ± 0.03
339	332	0.96 ± 0.04	414	395	0.89 ± 0.04
515	508	0.98 ± 0.04	587	568	0.93 ± 0.04
674	667	1.06 ± 0.05	764	745	1.00 ± 0.05
864	857	1.15 ± 0.05	969	950	1.09 ± 0.05
1280	1273	1.14 ± 0.06	1413	1394	1.08 ± 0.06

[a] *Standard uncertainty in temperature u(T) = 0.20 K.*
[b] *Standard uncertainty in total pressure u(p) = 0.005•P.*

Table 11

CO$_2$ solubility in aqueous MPA + MDEA (7.46 + 11.83%wt., 1.00 + 1.00 M) solutions at 298–333 K[a].

P_{total} (kPa)[b]	P_{CO_2} (kPa)	α_{CO_2} (mol CO$_2$/ mol Amine)	P_{total} (kPa)[b]	P_{CO_2} (kPa)	α_{CO_2} (mol CO$_2$/ mol Amine)
298.1 K			323.1 K		
73	70	0.85 ± 0.04	152	141	0.78 ± 0.04
186	183	0.93 ± 0.04	280	269	0.85 ± 0.04
222	219	0.96 ± 0.04	322	311	0.88 ± 0.04
324	321	0.98 ± 0.04	431	420	0.90 ± 0.04
337	334	1.00 ± 0.04	446	435	0.92 ± 0.04
488	485	1.02 ± 0.05	608	597	0.94 ± 0.05
567	564	1.03 ± 0.05	697	686	0.95 ± 0.05
703	700	1.06 ± 0.05	838	827	0.98 ± 0.05
874	871	1.08 ± 0.05	1029	1018	1.00 ± 0.05
313.1 K			333.1 K		
115	108	0.81 ± 0.04	197	179	0.74 ± 0.04
239	232	0.89 ± 0.04	332	314	0.81 ± 0.04
280	273	0.91 ± 0.04	375	357	0.84 ± 0.04
390	384	0.93 ± 0.04	484	466	0.86 ± 0.04
399	393	0.95 ± 0.04	503	485	0.88 ± 0.04
560	554	0.97 ± 0.04	664	646	0.91 ± 0.05
647	641	0.97 ± 0.05	754	736	0.91 ± 0.05
783	777	1.01 ± 0.05	900	882	0.95 ± 0.05
972	966	1.02 ± 0.05	1096	1078	0.97 ± 0.05

[a] *Standard uncertainty in temperature u(T) = 0.20 K.*
[b] *Standard uncertainty in total pressure u(p) = 0.005•P.*

equilibrium cell, volume of the cell, densities etc.).

Representative data of this study are illustrated in Figs. 2-5. For all investigated mixtures, the obtained experimental CO$_2$ loading values for the blended amines solutions were compared with the relevant neat amine solutions that were reported in our previous studies [10,11]. It was revealed that in all cases, the CO$_2$ loading values that were measured for the blended amine systems fall within the experimental values of the neat amine solutions, as illustrated in Fig. 2 for the AMP+MPA system. Thus, in all cases, not pronounced synergistic effect of the blended amines was revealed.

As it is presented in Tables 1-3 of the introduction section, there are only few similar literature experimental data and only for the AMP + MDEA system. Such data are compared with the data of this study in Fig. 3, from which a rather satisfactory agreement is observed at higher pressures, but small deviations are observed at relatively lower pressures.

4.2. Modeling results

As mentioned in the introduction section, MDEA is a tertiary amine and, thus, it is modeled as a non-carbamate forming amine. AMP is a sterically hindered amine, which results in an unstable carbamate, and, consequently, it is usually modelled as a non-carbamate forming amine. On the other hand, MPA is a primary amine and, thus, it is modeled as a carbamate forming amine. Consequently, considering the mixtures of this study, the AMP + MPA and the MDEA + MPA were modeled using the relevant equations of Section 3.1 for mixtures of one carbamate forming and one non-carbamate forming amine, while the AMP + MDEA
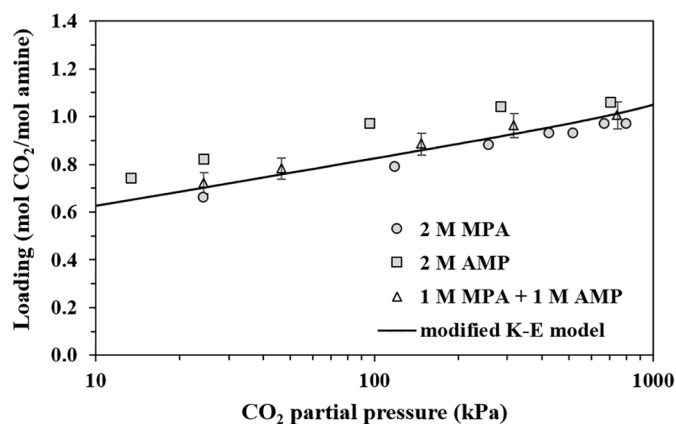
Fig. 2. CO_2 solubility in aqueous amine solutions at 313 K. Experimental data (points) for AMP+MPA (1 + 1 M, this work), AMP 2 M [11] and MPA 2 M [10] and modified Kent-Eisenberg model (line).
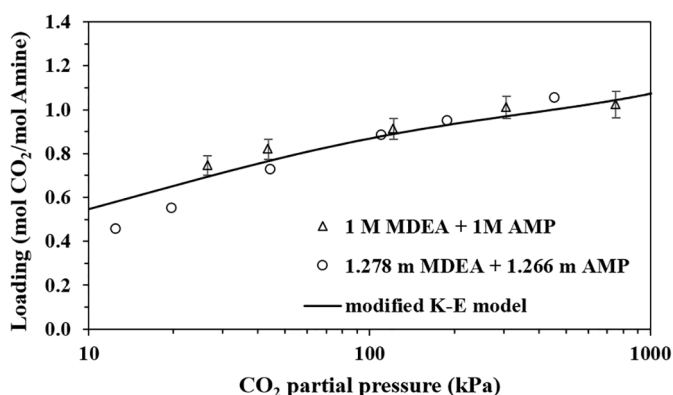

Fig. 3. CO_2 solubility in aqueous AMP + MDEA at 313 K. Experimental data (points) for AMP+MDEA 1 + 1 M form this work and for 1.266 + 1.278 m from Silkenbäumer et al. [34] and modified Kent-Eisenberg model (line).
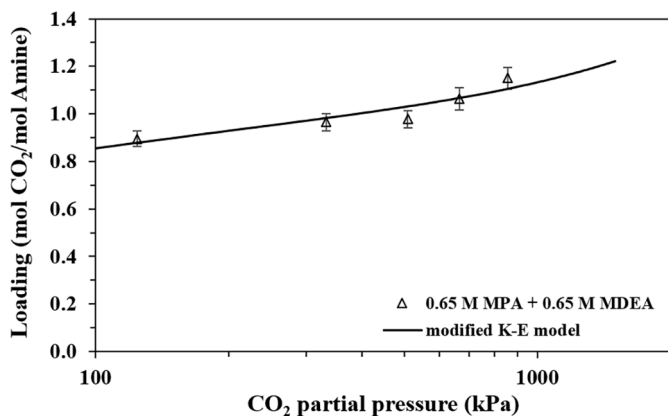

Fig. 4. CO_2 solubility in aqueous MDEA + MPA (0.65 + 0.65 M) solutions at 313 K. Experimental data (points) form this work and modified Kent-Eisenberg model (line).

mixtures were modeled using the equations of Section 3.2 for mixtures of two non-carbamate forming amines.

In this work, in order to evaluate the predicting ability of the model, no parameter was adjusted to experimental data of this study. We have used the literature values of the parameters of Eqs. (33) for K_2 to K_4 and H_{CO_2}. Also, for all amines we have adopted the values of parameters of Eqs. (33) form the respective pure amine solutions. In more detail, the

AMP parameters from Kontos et al. [11] were used. Also, MDEA and MPA parameters were adjusted by minimizing the average absolute deviation (AAD) of model calculations from the experimental data of the respective neat amine solutions presented by Leontiadis et al. [10]. In this way, the AAD of model calculations from the used data [10] is 2.65% and 1.58% for MDEA and MPA, respectively. All the used parameters, for modeling the investigated systems, are listed in Table 12.

Using the parameters of Table 12, form which none was adjusted to the data of this study, the model was applied to predict the experimental data of this work. The average absolute deviations of model predictions form the experimental data are presented in Table 13, from which it is observed that deviations that range between 2 and 5% were obtained in all cases. Some representative calculations are illustrated in Figs. 2-5, from which it is observed that the model predictions fall within the uncertainty of the experimental data in most cases.

Since, acceptable model predictions were obtained, the model was applied to predict the speciation in the CO_2 loaded blended amine aqueous solutions. Representative results for 313 K are illustrated in Figs. 6-8 for the mixture compositions of the experimental data.

In more detail, Figs. 6 and 7 show the speciation in the two studied mixtures that contain one carbamate forming (MPA) with one non-carbamate forming (AMP or MDEA) amine. It is revealed that in both cases the free MPA is very low and significantly lower than the free AMP or MDEA, even at very low CO_2 partial pressures. This observation shows that MPA shows a higher reactivity than the two non-carbamate forming amines. Furthermore, Fig. 8, which presents results for the mixture of the two non-carbamate forming amines (AMP and MDEA), reveals that AMP shows higher reactivity than MDEA, since the free AMP is lower than the free MDEA in all the investigated pressure range. A comparison of all plots of Figs. 6-8 reveals that more than 90% of the initial MPA has reacted at CO_2 partial pressures higher than 1 kPa, while the AMP reaches such limit at CO_2 partial pressures around 20 kPa and MDEA at CO_2 partial pressures around 200 kPa, revealing the differences in the reactivity of those amines.

Finally, since in all cases free amine concentration becomes very low at CO_2 partial pressures higher than approximately 100–200 kPa the overall CO_2 solubility mainly increases through the dissolution of molecular CO_2, as shown by the respective curves in Figs. 6-8, and the carbamate hydrolysis, in the case of MPA, as shown by the $MPACOO^-$ curve in Figs. 6-7.

5. Conclusions

In this work, the solubility of CO_2 in aqueous solutions of blended amines containing MPA, AMP and MDEA was experimentally measured, at 298, 313, 323 and 333 K, using a pressure decay method. The available literature experimental data for such systems are extremely rare, but the limited existing ones present a satisfactory agreement with the new data of the study. The comparison of the measured data for blended amine solutions with that of the neat amine solutions revealed that the data for amine mixtures always fall within the corresponding ones for pure amines and, thus, no significant synergistic effect of the blended amines can be concluded.

Since the use of blended amine solutions has been suggested from many researchers, such data are useful for evaluating the predicting ability of theoretical models. In this direction, the modified Kent-Eisenberg model was applied to predict the CO_2 loading values, without adjusting any parameter to the experimental data for blended amines, but using the parameters previously obtained from the respective pure amine solutions. It was observed that the modified Kent Eisenberg model predictions presents a satisfactory agreement with the experimental data of this study with average absolute deviations between 2 and 5%. Subsequently the model was applied to predict the composition of the CO_2-solvent liquid phase. It was revealed that, at 313 K, more than 90% of the initial MPA has reacted at CO_2 partial pressures higher than 1 kPa, while the AMP reaches such limit at CO_2 partial

Table 12

Parameters of Eqs. (33) for the investigated aqueous solutions.

Parameter (T in K)	Units	A	B	C	D	Regression range (K)	Reference
$K_{1\ AMP}$	mol/kg	−5936.63	0	0	−3.1347	298 - 383	[11]
$K_{1\ MDEA}$	mol/kg	−5366.71	0	0	−3.1469	298 - 333	This work
$K_{1\ MPA}$	mol/kg	−6168.01	0	0	−3.4131	298 - 333	This work
$K_{5\ MPA}$	mol/kg	−3097.68	0	0	6.6946	298 - 333	This work
K_2	mol/kg	−12,092.10	−36.7816	0	235.482	273–498	[67]
K_3	mol/kg	−12,431.70	−35.4819	0	220.067	273–498	[67]
K_4	mol^2/kg^2	−13,445.90	−22.4773	0	140.932	273–498	[67]
H_{CO_2}	atm mol/kg	−6789.04	−11.4519	−0.010454	94.4914	273–498	[67]

Table 13

Percentage average absolute deviations (%AAD) of model predictions form the experimental data of this study.

System	%AAD
AMP + MPA (1 + 1 M)	2.82
AMP + MDEA (1 + 1 M)	4.99
MPA + MDEA (0.65+0.65 M)	2.57
MPA + MDEA (1 + 1 M)	2.37
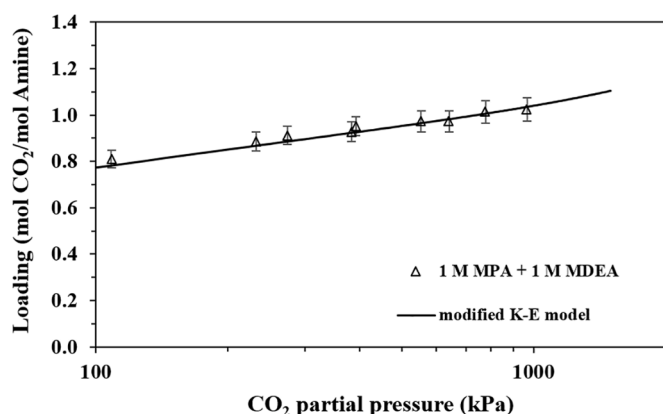
Fig. 5. CO$_2$ solubility in aqueous MDEA + MPA (1 + 1 M) solutions at 313 K. Experimental data (points) form this work and modified Kent-Eisenberg model (line).
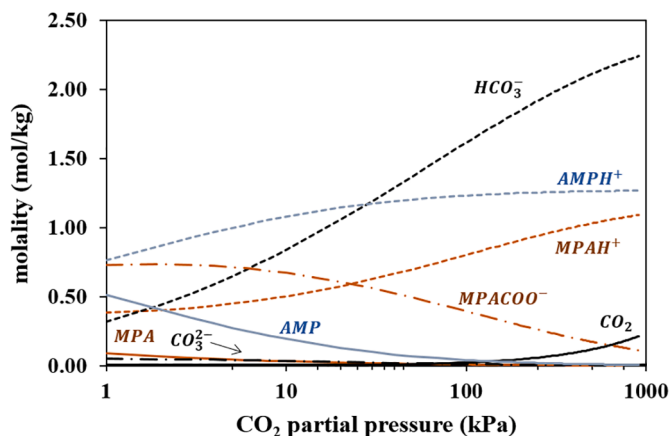
Fig. 6. Liquid-phase speciation in CO$_2$ loaded aqueous MPA + AMP (1 + 1 M) solution at 313 K calculated using the modified Kent-Eisenberg model.
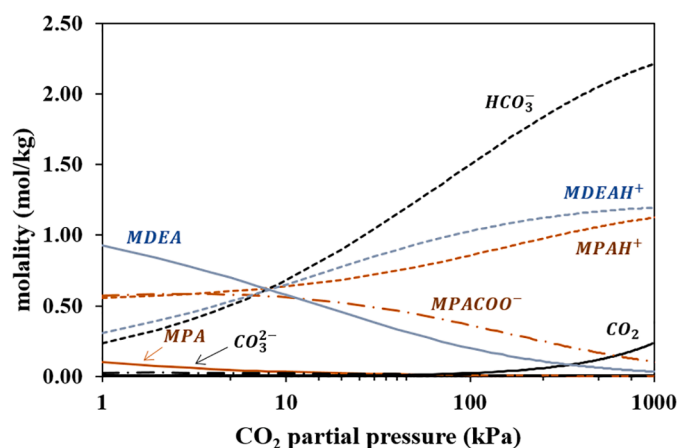
Fig. 7. Liquid-phase speciation in CO$_2$ loaded aqueous MPA + MDEA (1 + 1 M) solution at 313 K calculated using the modified Kent-Eisenberg model.
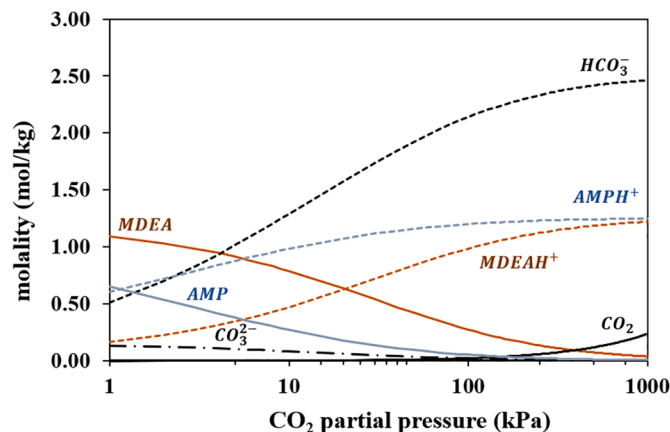
Fig. 8. Liquid-phase speciation in CO$_2$ loaded aqueous MDEA + AMP (1 + 1 M) solution at 313 K calculated using the modified Kent-Eisenberg model.

pressures around 20 kPa and MDEA at CO$_2$ partial pressures around 200 kPa, revealing the differences in the reactivity of those amines.

The very low complexity of the Kent-Eisenberg model, compared to thermodynamic models usually applied to such systems, renders it a rather satisfactory choice if the prediction of the CO$_2$ loading in various pressure and temperature conditions is needed.

CRediT authorship contribution statement

Giannis Kontos: Investigation, Software, Visualization, Validation,

Writing – original draft, Writing – review & editing. **Konstantinos Leontiadis:** Investigation. **Ioannis Tsivintzelis:** Conceptualization, Methodology, Supervision, Validation, Software, Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Data availability

All data are presented in the manuscript

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