Monoalkylcarbonate Formation in the System Monoethanolamine–Water–Carbon Dioxide

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Abstract

In a recent study, we have shown by NMR spectroscopy that monoalkylcarbonates are formed in substantial amounts in aqueous solutions of the tertiary alkanolamine methyldiethanolamine (MDEA) upon loading with carbon dioxide (CO₂). These species had been overlooked by most authors previously. In the present work, this study was extended to the primary alkanolamine monoethanolamine (MEA). Also here monoalkylcarbonates were found, but only at CO₂ loadings above 0.5 mol CO₂ per mol MEA. Both the amine and its carbamate form monoalkylcarbonates. The concentration of the monoalkylcarbonates was determined with ¹³C NMR spectroscopy in a wide range of CO₂ loadings, MEA concentrations, and temperatures. Based on this comprehensive data the chemical equilibrium constants of the formation of the monoalkylcarbonates were determined.

Keywords: Reactive absorption of CO₂, Chemical equilibrium constants, ¹³C NMR spectroscopy, Monoethanolamine, Monoalkylcarbonate

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1. Introduction

Recently, we identified and quantified monoalkylcarbonates in aqueous solutions of the tertiary alkanolamine methyldiethanolamine (MDEA) loaded with carbon dioxide (CO_2) at temperatures between 293–333 K [1]. At those temperatures, about 10 mol % of the absorbed CO_2 are bound in monoalkylcarbonates at all CO_2 loadings. Unlike tertiary alkanolamines, primary and secondary alkanolamines form carbamates with CO_2 . Yamada et al. [2] have shown that despite the formation of carbamates, monoalkylcarbonates can also be found in CO_2 loaded aqueous solutions of 2-(ethylamino)ethanol, a secondary alkanolamine. Hence there was reason to believe that monoalkylcarbonates are formed also in CO_2 loaded aqueous solutions of primary alkanolamines like monoethanolamine (MEA). Very recently, Cieslarova et al. [3] came to the same conclusion and looked for monoalkylcarbonates in the system $\text{MEA-H}_2\text{O-NaHCO}_3$ with ^{13}C NMR spectroscopy. They found a peak at high ^{13}C chemical shifts, which they assigned to the monoalkylcarbonate of MEA. Moreover, Cieslarova et al. [3] assumed that ^{13}C NMR peaks in the system $\text{MEA-H}_2\text{O-CO}_2$, which were assigned by Jakobsen et al. [4] to impurities, are in fact monoalkylcarbonates of MEA and of the carbamate of MEA. However, Cieslarova et al. [3] neither conducted a thorough peak identification nor a structure elucidation and did not discuss the presence of 1,3-Oxazolidin-2-one (named here as oxazolidone).

It is worthwhile discussing the presence of oxazolidone as its formation was stated by several authors [5–8]. It is assumed that this species plays an important role in the degradation of MEA. For example, Talzi and Ig-

nashin [5] analyzed aqueous solutions of MEA taken from various stages of an industrial gas treatment facility and identified species, which they stated to be reaction products of the conversion of oxazolidone. Under laboratory conditions, the formation of oxazolidone in the system MEA–H₂O–CO₂ is assumed to take up to eight weeks and occurs at temperatures between 373–423 K [7]. In the presence of additional species like carbonyl sulfide (COS) or Fe₂⁺ ions, the formation of oxazolidone is reported to be faster and to occur at moderate temperatures [5, 8]. In freshly prepared solutions, at moderate temperatures, in the absence of additional species, the formation of oxazolidone is normally not observed in the system MEA–H₂O–CO₂ [5]. Even though these conditions were fulfilled in the study of Böttinger et al. [6], these authors assumed that some unknown peaks in their ¹³C NMR spectra were caused by oxazolidone.

In this work, the composition of the liquid phase in CO₂ loaded aqueous solutions of MEA was investigated by NMR spectroscopy with a special focus on the thorough elucidation of all species existent in the liquid phase. By means of two-dimensional NMR techniques, the presence of the monoalkylcarbonate of monoethanolamine (2-ammonioethyl carbonate) and the monoalkylcarbonate of the carbamate of monoethanolamine (2-(carboxylatoamino)ethyl carbonate) was proven. It was furthermore shown that the NMR peaks, which were assigned by Böttinger et al. [6] to oxazolidone, result from the monoalkylcarbonate of MEA. The experimental results show that at CO₂ loadings above 0.5 mol/mol about 10 mol % of the CO₂ is bound in monoalkylcarbonates. To enable the correct description of the composition of the liquid phase even at high CO₂ loadings, an exist-

ing thermodynamic model of the system MEA–H₂O–CO₂ was extended so that it includes the formation of the monoalkylcarbonate of MEA and of the monoalkylcarbonate of the carbamate of MEA.

Experiments were carried out to determine the chemical equilibrium constants of the formation of the monoalkylcarbonates. The chemical equilibria constants of the other reactions were taken from Wagner et al. [9]. The strong thermodynamic nonidealities in the liquid phase was accounted for using an extended version of Pitzer’s model as described by Wagner et al. [9]. The new model is able to predict the formation of monoalkylcarbonates and thus of all species present in the system MEA–H₂O–CO₂ in the temperature range 293–313 K. Moreover, this study shows that no oxazolidone is formed at moderate temperatures, and in the absence of additional substances, when CO₂ loaded aqueous solution of MEA are stored only for a short time.

2. Reaction System

Figure 1 shows an exemplary ¹³C NMR spectrum of the liquid phase of an aqueous solution of MEA at high CO₂ loading ($\alpha_{\text{CO}_2} = 0.894$ mol/mol) and moderate temperature ($T = 293$ K). By employing two-dimensional NMR techniques, all peaks were assigned to species and the molecular structure of all species was elucidated. Details on the two-dimensional NMR studies are presented in the Supplementary Material. An overview of the species found in the solution including the notation of their groups is given in Figure 2. For brevity, the carbamate of MEA is abbreviated as MEA₁, the monoalkylcarbonate of MEA is abbreviated as MEA₂, and the monoalkylcarbonate of the carbamate of MEA is abbreviated as MEA₃.

The following reactions (I)-(V) are commonly considered to describe the chemical equilibrium in the system MEA-H₂O-CO₂ [9]:

The formation of the monoalkylcarbonates MEA₂ and MEA₃ is described here by additional reactions (VI)-(VII)

Reactions (VI) and (VII) are analogous to those used in our previous work on the formation of the monoalkylcarbonates of MDEA [1]. In principle, not only MEA⁺ but also the unprotonated MEA should be able to form monoalkylcarbonates. However, at low CO₂ loadings where only MEA is present in the solution, we found no monoalkylcarbonates. We assume, that at low CO₂ loadings the formation of monoalkylcarbonates from MEA is prevented by the much stronger formation of carbamates. Therefore, the formation of monoalkylcarbonates of the unprotonated MEA is neglected here.

3. Experimental

3.1. Chemicals

Table 1 gives information on the used chemicals, the suppliers and the purities. All chemicals were used without further purification. Water was deionized and purified with a water purification system (Milli-Q Reference A+ System, Merck Millipore).

Table 1: Provenance and purity of the pure components.

chemical name	source	initial fraction purity	purification method	final fraction purity	analysis method
MEA ^a	Sigma-Aldrich	≥ 0.99 g/g	none	≥ 0.99 g/g	stated by supplier
OXA ^b	Sigma-Aldrich	≥ 0.998 g/g	none	≥ 0.998 g/g	stated by supplier
D ₂ O ^c	Sigma-Aldrich	≥ 0.999 mol/mol	none	≥ 0.999 mol/mol	stated by supplier
CO ₂	Air Liquide	≥ 0.99995 mol/mol	none	≥ 0.99995 mol/mol	stated by supplier
methanol	Merck	≥ 0.998 g/g	none	≥ 0.998 g/g	stated by supplier
H ₂ O	SWK ^d	n.a.	ion-exchange and filtration	> 0.99999 g/g	conductometry

^a MEA = monoethanolamine (IUPAC: 2-aminoethanol)

^b OXA = oxazolidone (IUPAC: 1,3-oxazolidin-2-one)

^c D₂O = deuterium oxide

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3.2. Experimental Procedure

In this work, two different procedures were used to prepare samples of MEA–H₂O–CO₂. In the first procedure, an aqueous solution of MEA was prepared gravimetrically using a laboratory balance (PR2003 Comparator, Mettler Toledo, estimated standard uncertainty of the mass fraction of MEA: $u(w_{\text{MEA}}^0) = 0.00002$ g/g), and then loaded inside a valved NMR sample tube with CO₂ at room temperature. Details on this procedure are described in the previous work of our group [1].

The second procedure was first developed in our group to prepare samples for the investigation of the solubility of CO₂ in aqueous solution of amines [10]. This procedure was used here to prepare large quantities of CO₂

loaded aqueous solution of MEA that were not only used for the studies presented in this paper but also for the determination of other physico-chemical properties. An aqueous solution of MEA was prepared under vacuum in a glass cylinder. The composition was determined gravimetrically with the same laboratory balance and the same standard uncertainty as mentioned above. The aqueous solution of MEA was then transferred into an evacuated pressure resistant stainless steel container, and charged with CO₂. To attain equilibrium, the container was rotated for about 4–5 h and finally stored for about 24 h. The container with the equilibrated CO₂ loaded aqueous solution of MEA was then connected to a valved NMR sample tube which was pressurized with nitrogen at 1.2 bar. The container was then pressurized with nitrogen and the CO₂ loaded aqueous solution of MEA was transferred through a riser in the container into the valved NMR sample tube. The pressurization of the sample tube prevented flashing of the solution during the filling process. More details on the second procedure is given in the Supplementary Material.

After a valved NMR sample tube filled with a CO₂ loaded aqueous solution of MEA had been prepared, it was placed in an oven and was equilibrated for 4 hours at a certain temperature (estimated standard uncertainty of the temperature T : $u(T) = 1$ K). Then, the NMR sample tube was placed inside the NMR spectrometer. The temperature of the sample tube was controlled using the nitrogen gas flow provided by the NMR spectrometer. The temperature inside the sample was determined from the reading of the temperature control of the NMR spectrometer using a calibration curve that was determined in calibration experiments with methanol as described by Ammann

et al. [11]. The estimated standard uncertainty of the temperature of the sample is $u(T) = 0.5$ K.

3.3. NMR Spectroscopy and Data Analysis

Like in our previous study [1], the composition of the liquid phase was determined with quantitative ^{13}C NMR spectroscopy. The NMR settings and the evaluation are presented here again as certain changes were made for the system MEA–H₂O–CO₂. In this work, two 400 MHz NMR spectrometer of Bruker (magnet: Ascend 400, console: Avance 3 HD 400) were used. Each NMR spectrometer was equipped with a probe, both from Bruker: one with cryogenically cooled electronics (Probe 1: CryoProbe Prodigy), the other with standard electronics (Probe 2: Double Resonance Broad Band Probe).

All quantitative measurements were carried out with a ^{13}C inverse gated pulse sequence: 30°, 60°, or 90° flip angle, 60 s relaxation delay, and 64–2048 scans based on experience from previous work on similar systems [1]. For a 90° flip angle, the pulse repetition time should be $5 \times T_1$ to ensure quantitative measurements [12]. The carbon atom of the carbamate group of MEA₁ has the longest T_1 -relaxation time ($T_1 = 6$ s) such that this requirement is easily fulfilled. The post-processing was carried out manually. The peak areas, A_i , were determined by direct integration. The full set of acquisition and processing parameters are listed in the Supplementary Material.

The results were expressed as molar ratios, ζ_i , of the amount of species i , n_i , related to the sum of the amount of all carbon-containing species:

$$\zeta_i = \frac{n_i}{\sum_{i=1}^{N_C} n_i} \quad (1)$$

where N_C is the number of all carbon-containing species. Furthermore, from the evaluation of the ^{13}C NMR spectra information on the CO_2 loading of the aqueous solution of MEA was obtained. The CO_2 loading, α_{CO_2} , was defined as the overall amount of absorbed CO_2 , $\tilde{n}_{\text{CO}_2}$, related to the overall amount of MEA, $\tilde{n}_{\text{MEA}}$, in the liquid phase:

$$\alpha_{\text{CO}_2} = \frac{\tilde{n}_{\text{CO}_2}}{\tilde{n}_{\text{MEA}}} \quad (2)$$

According to the Reactions (I)–(VII), α_{CO_2} was calculated from the true amounts of substance as follows:

$$\alpha_{\text{CO}_2} = \frac{n_{\text{CO}_2} + n_{\text{HCO}_3^-} + n_{\text{CO}_3^{2-}} + n_{\text{MEA}_1} + n_{\text{MEA}_2} + 2 \cdot n_{\text{MEA}_3}}{n_{\text{MEA}} + n_{\text{MEA}^+} + n_{\text{MEA}_1} + n_{\text{MEA}_2} + n_{\text{MEA}_3}} \quad (3)$$

The molar ratio, ζ_i , and the CO_2 loading, α_{CO_2} , were determined directly from the areas, A_i , under the peaks that correspond to the species i as described below. Figure 1 shows an example for a ^{13}C NMR spectrum of an aqueous solution of MEA at high CO_2 loading ($\alpha_{\text{CO}_2} = 0.894$ mol/mol) and moderate temperature ($T = 293$ K). By employing two-dimensional NMR techniques, the peaks were assigned to the different species. Details

on the two-dimensional NMR techniques are presented in the Supplementary Material. The notation scheme of the groups of the MEA species is depicted in Figure 2. A two-digit notation scheme is used here. The first digit indicates the position and type of the group within a molecule. The second digit represents the species: 0 for MEA and MEA^+ , 1 for MEA_1 , 2 for MEA_2 , and 3 for MEA_3 . Protonated and unprotonated species cannot be distinguished in the NMR spectra. Like in our previous work [1], an index “x” is used, which represents the number of fast exchanging protons per molecule. In this work, only peaks were evaluated that do not overlap with other peaks.

Because of the chosen NMR sequence, the peak areas, A_i , are directly proportional to the number of nuclei that cause the peak. Furthermore, it is shown that the proportionality factors are the same for all carbon nuclei [1]. Therefore, the observed values, ζ_i^{obs} and $\alpha_{\text{CO}_2}^{\text{obs}}$, were obtained directly from the peak areas:

$$\zeta_i^{\text{obs}} = \frac{A_i}{\sum_{i=1}^{N_C} A_i} \quad (4)$$

$$\alpha_{\text{CO}_2}^{\text{obs}} = \frac{A_{\text{CO}_2} + A_{\text{H}_x\text{CO}_3} + A_{\text{MEA}_1} + A_{\text{MEA}_2} + 2 \cdot A_{\text{MEA}_3}}{A_{\text{MEA}_x} + A_{\text{MEA}_1} + A_{\text{MEA}_2} + A_{\text{MEA}_3}} \quad (5)$$

When more than one non-overlapping peak of a species was evaluable, the mean of the corresponding peak areas was used.

Mole fractions, x_i^{obs} , were calculated from:

$$x_i^{\text{obs}} = \frac{A_i}{(A_{\text{MEA}_{\text{H}_x}} + A_{\text{MEA}_1} + A_{\text{MEA}_2} + A_{\text{MEA}_3}) \left(X_{\text{H}_2\text{O,MEA}}^{(\text{n}),0,\text{obs}} + 1 \right) + A_{\text{CO}_2}} \quad (6)$$

where $X_{\text{H}_2\text{O,MEA}}^{(\text{n}),0,\text{obs}}$ is the molar loading of MEA with water in the unloaded stock solution which is available from the gravimetric preparation of the samples.

The relative standard uncertainty of the CO_2 loading is estimated to be about $u_r(\alpha_{\text{CO}_2}) = 0.05$ with a minimal standard uncertainty of $u(\alpha_{\text{CO}_2}) = 0.03$ mol/mol. The relative standard uncertainty of the mole fractions is estimated to be about $u_r(x_i) = 0.05$ except for mole fractions below 0.001 mol/mol where it is about $u_r(x_i) = 0.1$. These numbers are adopted from our previous study on a similar system that was evaluated with the same methods and for which a detailed investigation of the uncertainty was carried out [1].

4. Modeling and Parameter Estimation

The chemical equilibrium of the reaction j (with $j = \text{I}, \dots, \text{VII}$) is described here in the same way like in the model of the previous work [1]. Molality based activities normalized similar to Henry's law for all solutes (including MEA) and a mole fraction based activity normalized according to Raoult's law for water were used:

$$K_{a,j}(T) = \prod_i^N a_i^{\nu_{i,j}} \quad (7)$$

$$\text{with } a_{\text{H}_2\text{O}} = x_{\text{H}_2\text{O}} \cdot \gamma_{\text{H}_2\text{O}}$$

$$\text{and } a_i = \frac{m_i}{m^0} \gamma_i^{\text{m}*} \text{ for all } i \neq \text{H}_2\text{O}.$$

$\nu_{i,j}$ is the stoichiometric factor of species i for reaction j . The dependence of the chemical potential on pressure is neglected so that the chemical equilibrium constant, $K_{a,j}$, is only a function of temperature. The temperature dependence of the chemical equilibrium constants is described by empirical correlations. For Reactions (I)–(V) these correlations were taken from Wagner et al. [9]. The activity coefficients, $\gamma_i^{\text{m}*}$, of all species but water are described using an extended form of Pitzer’s equation [13, 14]. Where available, the interaction parameters were taken from Wagner et al. [9]. The parameters describing the interaction of the new species MEA₂ and MEA₃ with all other species were set to zero. Thus, the activity coefficients of these two species are described by the contribution from the Debye–Hückel–term (empirically modified by Pitzer [13, 14]) only. The activity coefficient, $\gamma_{\text{H}_2\text{O}}$, of water is calculated from the Gibbs–Duhem equation.

Using Eq. (7), the molar ratio, ζ_i^{model} , was calculated as a function of the $K_{a,j}$ for a given CO₂ loading, $\alpha_{\text{CO}_2}^{\text{obs}}$, and mass fraction, $w_{\text{MEA}}^{0,\text{obs}}$, of the aqueous stock solution of MEA. The chemical equilibrium constants for Reactions (VI) and (VII) were determined by solving the minimization problem using the sum of squared errors as objective function:

$$\begin{aligned}
K_{a,j}(T_l) &= \arg \min_{K_{a,j} \in \mathbb{R}^+} \sum_{k=1}^{M_l} \sum_{i=1}^2 \left(\zeta_{i,k}^{\text{obs}} - \zeta_i^{\text{model}} \left(K_{a,j}(T_l), \alpha_{\text{CO}_2,k}^{\text{obs}}, w_{\text{MEA},k}^{0,\text{obs}} \right) \right)^2 \\
i &= \{1 \text{ for MEA}_2, 2 \text{ for MEA}_3\} \\
k &= 1 \dots M_l
\end{aligned} \tag{8}$$

where M_l is the total number of observations carried out at the temperature T_l . The optimization problem was solved in MATLAB using a trust-region algorithm embedded in the MATLAB solver lsqnonlin. ζ_i^{model} was calculated using a Newton–Raphson algorithm.

5. Results and Discussion

5.1. Experimental

In ^{13}C NMR spectra of the system MEA–H₂O–CO₂, the NMR peaks of the monoalkylcarbonate of MEA (MEA₂) can be easily misinterpreted as oxazolidone because of similar ^{13}C NMR shifts. As a consequence, Böttinger et al. [6] reported ^{13}C NMR peaks as oxazolidone. In the present work, however, these peaks were unambiguously assigned to MEA₂. We proofed that MEA₂ is formed instead of oxazolidone by comparing the ^1H - ^{13}C Heteronuclear Multiple Bond Correlation (HMBC) NMR spectrum of a CO₂ loaded aqueous solution of MEA with the HMBC NMR spectrum of oxazolidone dissolved in D₂O. In HMBC NMR spectra, multiple bond ^1H - ^{13}C correlations are observed allowing the assignment of protons with a two to three bonds distance from a carbon atom. Because of the different chemical structure of the linear MEA₂ and the circular oxazolidone, the carbon atom of the car-

bonate group of MEA_2 only correlates with the protons of one CH_2 group, whereas the carbon atom of the carbonyl group of oxazolidone correlates with both CH_2 groups. The HMBC NMR spectra and more details on the structure elucidation of all species are given in the Supplementary Material.

The composition of aqueous solutions containing 0.3 g/g of MEA at 293 K is presented in Figure 3 as a function of the CO_2 loading. Both the experimental data of this work and of Böttinger et al. [6] are plotted. The results from the model developed in the present work are shown as well. The corresponding numerical values are listed in Table 2. The numerical values of the molar ratio, ζ_i , are listed in Table S2 in the Supplementary Material.

The data of this work agree well with the data of Böttinger et al. [6], which were obtained also by NMR spectroscopy, but with a significantly different method. Only at CO_2 loadings above 0.8 mol/mol minor deviations are observed for the experimental results of MEA_x . Consistent with the finding that oxazolidone was a misinterpretation of MEA_2 , the mole fractions of oxazolidone published by Böttinger et al. [6] are in good agreement with the mole fractions of the MEA_2 measured in the present work. Because of the technical advances in NMR spectroscopy, the limit of quantification of the NMR spectrometer used in the present work is lower than the limit of quantification of the NMR spectrometer of Böttinger et al. [6]. For this reason, no experimental data of Böttinger et al. [6] are available for MEA_3 . Furthermore, molecular CO_2 could be quantified in the present work also for CO_2 loadings at which Böttinger et al. [6] could not get such data.

The experimental results (cf. Figure 3) show that at CO_2 loadings below 0.5 mol/mol the absorbed CO_2 is completely bound in MEA_1 . At CO_2

Table 2: Experimental values of mole fraction x_i at temperature T , mass fraction w_{MEA}^0 of MEA in the unloaded aqueous stock solution, and CO_2 loading α_{CO_2} with standard uncertainty $u(\alpha_{\text{CO}_2})$ for the liquid phase of the system MEA- H_2O - CO_2 in chemical equilibrium.^a

T K	w_{MEA}^0 g/g	α_{CO_2} mol/mol	$u(\alpha_{\text{CO}_2})$ mol/mol	x_{CO_2} mol/mol	$x_{\text{H}_x\text{CO}_3}$ mol/mol	x_{MEA_x} mol/mol	x_{MEA_1} mol/mol	x_{MEA_2} mol/mol	x_{MEA_3} mol/mol
293.15	0.150	0.24	0.03	—	—	0.0377	0.0117	—	—
		0.48	0.03	—	0.0030	0.0286	0.0208	—	—
		0.50	0.03	—	0.0036	0.0285	0.0210	—	—
	0.146	0.50	0.03	—	0.0036	0.0278	0.0203	—	—
		0.50	0.03	—	0.0036	0.0277	0.0204	—	—
		0.52	0.03	—	0.0041	0.0274	0.0206	—	—
	0.153	0.65	0.03	—	0.0168	0.0346	0.0153	0.0002	0.0003
		0.66	0.03	—	0.0167	0.0342	0.0156	0.0002	0.0004
	0.150	0.69	0.03	—	0.0185	0.0342	0.0145	0.0005	0.0003
		0.69	0.03	—	0.0186	0.0342	0.0146	0.0004	0.0003
		0.99	0.05	0.0024	0.0409	0.0442	0.0038	0.0013	0.0001
	0.300	0.06	0.03	—	—	0.1060	0.0062	—	—
	0.301	0.08	0.03	—	—	0.1037	0.0089	—	—
		0.11	0.03	—	—	0.1005	0.0121	—	—
	0.300	0.26	0.03	—	—	0.1005	0.0122	—	—
		0.32	0.03	—	0.0008	0.0833	0.0288	—	—
	0.301	0.32	0.03	—	—	0.0767	0.0359	—	—
		0.32	0.03	—	—	0.0763	0.0363	—	—
	0.300	0.33	0.03	—	0.0013	0.0766	0.0360	—	—
		0.45	0.03	—	0.0031	0.0649	0.0474	—	—
	0.301	0.56	0.03	—	0.0151	0.0655	0.0454	0.0006	0.0007
		0.60	0.03	—	0.0250	0.0710	0.0396	0.0011	0.0010
	0.300	0.60	0.03	—	0.0248	0.0705	0.0398	0.0011	0.0012
		0.62	0.03	—	0.0252	0.0691	0.0412	0.0012	0.0011
		0.64	0.03	—	0.0324	0.0743	0.0352	0.0016	0.0012
		0.70	0.03	—	0.0424	0.0776	0.0314	0.0019	0.0012
		0.83	0.04	0.0014	0.0644	0.0863	0.0204	0.0036	0.0015
298.15	0.150	0.88	0.04	0.0021	0.0727	0.0900	0.0166	0.0040	0.0012
		0.89	0.04	0.0029	0.0756	0.0917	0.0144	0.0044	0.0013
		0.69	0.03	—	0.0190	0.0346	0.0141	0.0005	0.0002
		0.74	0.04	—	0.0235	0.0365	0.0119	0.0007	0.0003
		0.90	0.05	0.0012	0.0355	0.0416	0.0065	0.0011	0.0002
	0.300	0.17	0.03	—	0.0006	0.0933	0.0188	—	—
		0.26	0.03	—	0.0007	0.0832	0.0289	—	—
		0.31	0.03	—	0.0010	0.0780	0.0340	—	—
		0.45	0.03	—	0.0028	0.0644	0.0475	—	0.0001
		0.51	0.03	—	0.0067	0.0617	0.0498	0.0002	0.0003
	0.311	0.69	0.03	—	0.0392	0.0758	0.0328	0.0019	0.0015
		0.66	0.03	—	0.0188	0.0355	0.0137	0.0003	—
		0.83	0.04	—	0.0327	0.0412	0.0072	0.0011	—
		0.90	0.05	0.0033	0.0352	0.0433	0.0047	0.0012	—
		0.30	0.03	—	—	0.0823	0.0354	—	—
313.15	0.300	0.44	0.03	—	0.0025	0.0652	0.0469	—	—
	0.275	0.49	0.03	—	0.0047	0.0564	0.0443	—	—
	0.311	0.53	0.03	—	0.0126	0.0683	0.0494	—	—
	0.275	0.68	0.03	—	0.0355	0.0684	0.0295	0.0018	0.0011
	0.300	0.69	0.03	—	0.0381	0.0747	0.0343	0.0018	0.0014
		0.70	0.03	—	0.0444	0.0789	0.0305	0.0018	0.0008

^a Standard uncertainties: $u(T) = 0.5$ K, $u(w_{\text{MEA}}^0) = 0.00002$ g/g. Relative standard uncertainties: $u_r(x_i) = 0.1$ for $x_i < 0.001$ mol/mol, $u_r(x_i) = 0.05$ for $x_i > 0.001$ mol/mol.

loadings above 0.5 mol/mol CO_2 is also bound in H_xCO_3 (bicarbonate and carbonate) and the amount of MEA_1 decreases with increasing CO_2 loading. At the same time, MEA_2 and MEA_3 are formed. The amount of MEA_2 continuously increases with increasing CO_2 loading while the amount of MEA_3 reaches a maximum at a CO_2 loading of about 0.8 mol/mol.

5.2. Chemical Equilibrium Constants of the Monoalkylcarbonate Formation

The chemical equilibrium constants for the Reactions (VI) and (VII), which were determined by solving the minimization problem given in Eq. (8) for the different data sets, are listed in Table 3. The standard uncertainties $u(K_{a,j})$ reported in Table 3 are the 95% confidence intervals obtained from the parameter estimation procedure. The chemical equilibrium constants for the formation of MEA_2 (Reaction (VI)) are similar to the chemical equilibrium constants for the formation of the monoalkylcarbonate of MDEAH^+ [1]. It can be concluded that the reactivity of the hydroxyethyl group in forming alkylcarbonates is not significantly affected by the substitutes of the nitrogen atom.

Table 3: Chemical equilibrium constants $K_{a,j}$ (on the molality scale) of the formation of MEA_2 (Reaction (VI)) and of MEA_3 (Reaction (VII)) with standard uncertainties $u(K_{a,j})$ at temperature T .^a

T / K	$1000 \cdot K_{a,\text{VI}}$	$1000 \cdot u(K_{a,\text{VI}})$	$1000 \cdot K_{a,\text{VII}}$	$1000 \cdot u(K_{a,\text{VII}})$
293.15	70.6	4.1	1.15	0.14
298.15	70.4	5.0	1.26	0.18
313.15	68.9	9.9	0.73	0.24
average	70.0		1.05	

^a standard uncertainty: $u(T) = 0.5 \text{ K}$.

The chemical equilibrium constants in Table 3 show no significant tem-

perature dependence. Also for the formation of the monoalkylcarbonates of MDEA no temperature dependence of the chemical equilibrium constants was observed [1].

5.3. Simulation Results

The upper bound of the range of the CO_2 loading that is relevant for typical applications of aqueous MEA solutions in industrial gas absorption processes is $\alpha_{\text{CO}_2} = 0.5 \dots 0.6$ mol/mol [15]. Up to this CO_2 loading, the experimental results of all species are in very good agreement with the simulation results as depicted in Figure 3. Minor deviations between the experimental results and model prediction of MEA_x and of MEA_1 are observed for CO_2 loadings above 0.8 mol/mol. At those CO_2 loadings, MEA_2 , MEA_3 and CO_2 are still well described. These results can be compared to those of the model of Wagner et al. [9], which does not account for the formation of MEA_2 and MEA_3 . For the species that are accounted for in both models, the present model gives an improved description of the experimental data, as shown in the Supplementary Material.

The significance of the monoalkylcarbonates of MDEA was illustrated in the previous work by showing the distribution of the overall amount of absorbed CO_2 to the different species [1]. This plot was also generated for the system studied here and is shown in Figure 4. It gives the results for an aqueous solution containing 0.3 g/g of MEA at 293 K and can, hence, be compared directly to the corresponding plot for MDEA from our previous study [1]. In contrast to MDEA, where at all CO_2 loadings about 10 mol % CO_2 is bound as monoalkylcarbonates, the amount of monoalkylcarbonates is negligible for MEA at CO_2 loadings below 0.5 mol/mol. Only at CO_2

loadings above 0.5 mol/mol the combined amount of CO_2 that is bound in MEA_2 and MEA_3 is about 10 mol % and thus comparable to that observed in the system with MDEA.

In our previous work [1], the model of Ermatchkov and Maurer [16], which describes the vapor-liquid equilibrium of the system $\text{MDEA-H}_2\text{O-CO}_2$, was extended to account for the presence of the monoalkylcarbonates. The extension of the model of Ermatchkov and Maurer [16] was found to be important regarding the composition of the liquid phase, but only minor regarding the overall gas solubility. The findings for the system that was studied in the present work are similar. The present model is an extension of the model of Wagner et al. [9] for describing the vapor-liquid equilibrium of the system $\text{MEA-H}_2\text{O-CO}_2$. Figure 5 depicts the partial pressure of CO_2 , p_{CO_2} , and the total pressure, p , as a function of the CO_2 loading, α_{CO_2} , at 313 K for both models along with experimental data of Wagner et al. [9]. It can be seen that accounting for the monoalkylcarbonates in the model has only minor effect on the predicted partial pressure of CO_2 , p_{CO_2} , and the total pressure p . The reason for this is that neither the predicted activity of CO_2 nor that of H_2O is significantly changed by introducing the formation of the monoalkylcarbonates. Therefore, the extended Henry’s law for CO_2 and the extended Raoult’s law for H_2O yield almost the same partial pressure of CO_2 , p_{CO_2} , and the same total pressure, p .

6. Conclusion

In this work, the equilibrium composition of the liquid phase of the system $\text{MEA-H}_2\text{O-CO}_2$ was investigated. By using two-dimensional NMR spec-

troscopy, it is proven that the monoalkylcarbonate of monoethanolamine (2-ammonioethyl carbonate, abbreviated here as MEA₂) and the monoalkylcarbonate of the carbamate of monoethanolamine (2-(carboxylatoamino)ethyl carbonate, abbreviated here as MEA₃) are present in the liquid phase. At the same time, it is shown that no oxazolidone is present and that previous reports on that species result from a misinterpretation of signals from MEA₂ [6]. Based on the new experimental data, a thermodynamic consistent model of the chemical equilibrium in the studied complex electrolyte solutions was developed. It is an extension of the model of Wagner et al. [9]. The extended model describes the composition in the complete CO₂ loading range for the reported experimental conditions (293 – 313 K) very well.

The study shows that about 10 mol % of the absorbed CO₂ is bound in monoalkylcarbonates at CO₂ loadings above 0.5 mol/mol. However, at CO₂ loadings below 0.5 mol/mol – i.e. the CO₂ loading range relevant for technical applications – almost no CO₂ is bound in monoalkylcarbonates. This finding can be explained by the concurrent formation of carbamates at CO₂ loadings below 0.5 mol/mol.

However, monoalkylcarbonates could be important in the recovery and regeneration of MEA solutions. They could also play a role in the degradation of MEA. In the literature, oxazolinode has repeatedly been discussed as an intermediate in degradation routes [5, 7, 8]. It is shown here that MEA₂ can be misinterpreted easily as oxazolidone, so that those degradation routes might have to be reevaluated. Based on the results from the present study, the amount of monoalkylcarbonates in mixtures of MEA, water and CO₂ can now be assessed.

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Appendix A. Supplementary Material

Supplementary Material associated with this article can be found, in the online version, at ...

The Supplementary Material includes: Structure Elucidation by 2D NMR Spectroscopy, Experimental Procedure, NMR Acquisition and Processing Parameters, Simulation Results from the Model of Wagner et al., Numerical Results.

Nomenclature

Abbreviations

H_x	sum of a molecule with different amount of fast exchanging protons (e.g. $MEA H_x$ as the sum of MEA and $MEA H^+$)
MDEA	methyldiethanolamine
MEA	monoethanolamine
$MEA H^+$	protonated form of monoethanolamine
MEA_1	carbamate of monoethanolamine
MEA_2	monoalkylcarbonate of monoethanolamine
MEA_3	monoalkylcarbonate of the carbamate of monoethanolamine
NMR	nuclear magnetic resonance

Symbols and Indices

A_i	peak area under a peak in a ^{13}C NMR spectrum corresponding to the component i
a_i	activity of component i
$K_{a,j}$	chemical equilibrium constant of reaction j
m^0	reference molality: 1 mole solute per 1 kg of water
m_i	molality of component i in pure water
M_l	total number of observations carried out at temperature T_l
N	number of species
N_C	number of carbon-containing species
n_i	true amount of component i
$\tilde{n}_i$	overall amount of component i
T	temperature
w_{MEA}^0	mass fraction of MEA in the unloaded aqueous stock solution
$X_{\text{H}_2\text{O,MEA}}^{(n),0}$	molar loading of water in MEA in the unloaded aqueous stock solution
x_i	mole fraction of component i
α_{CO_2}	CO_2 loading
$\gamma_{\text{H}_2\text{O}}$	mole fraction based activity coefficient of water
$\gamma_i^{\text{m}*}$	molality based activity coefficient of component i
$\delta^{13\text{C}}$	chemical shift of the ^{13}C NMR spectrum in ppm
ζ_i	molar ratio of component i related to the sum of the amount of all carbon-containing species
$\nu_{i,j}$	stoichiometric factor of component i for the reaction j
model	index for a calculated value
obs	index for an observed value

References

- [1] R. Behrens, E. von Harbou, W. R. Thiel, W. Böttinger, T. Ingram, G. Sieder, H. Hasse, *Ind. Eng. Chem. Res.* 56 (2017) 9006–9015. doi:10.1021/acs.iecr.7b01937.
- [2] H. Yamada, Y. Matsuzaki, K. Goto, *Ind. Eng. Chem. Res.* 53 (2014) 1617–1623. doi:10.1021/ie4034889.
- [3] Z. Cieslarova, V. B. dos Santos, C. L. do Lago, *International Journal of Greenhouse Gas Control* 76 (2018) 142–149. doi:10.1016/j.ijggc.2018.07.005.
- [4] J. P. Jakobsen, J. Krane, H. F. Svendsen, *Ind. Eng. Chem. Res.* 44 (2005) 9894–9903. doi:10.1021/ie048813+.
- [5] V. P. Talzi, S. V. Ignashin, *Russian Journal of Applied Chemistry* 75 (2002) 80–85. doi:10.1023/A:1015573008284.
- [6] W. Böttinger, M. Maiwald, H. Hasse, *Fluid Phase Equilibria* 263 (2008) 131–143. doi:10.1016/j.fluid.2007.09.017.
- [7] J. Davis, G. Rochelle, *Energy Procedia* 1 (2009) 327–333. doi:10.1016/j.egypro.2009.01.045.
- [8] A. F. Ciftja, A. Hartono, A. Grimstvedt, H. F. Svendsen, *Energy Procedia* 23 (2012) 111–118. doi:10.1016/j.egypro.2012.06.064.
- [9] M. Wagner, I. von Harbou, J. Kim, I. Ermatchkova, G. Maurer, H. Hasse, *J. Chem. Eng. Data* 58 (2013) 883–895. doi:10.1021/je301030z.

- [10] V. Ermatchkov, A. Pérez-Salado Kamps, G. Maurer, *Ind. Eng. Chem. Res.* 45 (2006) 6081–6091. doi:10.1021/ie0604270.
- [11] C. Ammann, P. Meier, A. Merbach, *Journal of Magnetic Resonance* (1969) 46 (1982) 319–321. doi:10.1016/0022-2364(82)90147-0.
- [12] P. T. Callaghan, *Principles of Nuclear Magnetic Resonance Microscopy*, Clarendon Press, Oxford, 1993.
- [13] K. S. Pitzer, *J. Phys. Chem.* 77 (1973) 268–277. doi:10.1021/j100621a026.
- [14] K. S. Pitzer, *Activity Coefficients in Electrolyte Solutions*, CRC Press, Boca Raton, FL, 1991.
- [15] A. L. Kohl, R. Nielsen, *Gas Purification*, Gulf Pub., Houston, Tex., 1997.
- [16] V. Ermatchkov, G. Maurer, *Fluid Phase Equilibria* 302 (2011) 338–346. doi:10.1016/j.fluid.2010.06.001.

Figure 1: ^{13}C NMR spectrum of MEA- D_2O - CO_2 , for $w_{\text{MEA}}^0 = 0.3$ g/g, $\alpha_{\text{CO}_2} = 0.894$ mol/mol, $T = 293$ K. Notation of the peaks according to Figure 2. The peak H_xCO_3 results from H_2CO_3 , HCO_3^- , and CO_3^{2-} .

Figure 2: Chemical structure of MEA, MEA H^+ , carbamate of MEA (MEA $_1$), 2-ammonioethyl carbonate (MEA $_2$), and 2-(carboxylatoamino)ethyl carbonate (MEA $_3$) with notation of the groups used in the present work.

Figure 3: Composition of the liquid phase of the system MEA-H₂O-CO₂ in chemical equilibrium, for $w_{\text{MEA}}^0 = 0.3$ g/g, $T = 293$ K. Open symbols: experimental data from the present work. Filled symbols: experimental data from Böttinger et al. [6]. Lines: model from the present work.

Figure 4: Distribution of the overall CO_2 to the different species calculated with the model from the present work, for $w_{\text{MEA}}^0 = 0.3 \text{ g/g}$, $T = 293 \text{ K}$.

Figure 5: Results from the model from the present work (solid lines) and that of Wagner et al. [9] (dashed lines) for the total pressure (thick lines) and the partial pressure of CO_2 (thin lines) above CO_2 loaded aqueous solution of MEA, for $w_{\text{MEA}}^0 = 0.3 \text{ g/g}$, $T = 313 \text{ K}$. Symbols are experimental data from Wagner et al. [9] $\triangle$: partial pressure p_{CO_2} , $\blacktriangle$: total pressure p .

Graphical Abstract