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1 **A new reactive absorption model using extents of reaction and activities.**

2 **II. Application to CO₂ absorption into aqueous MDEA solutions**

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11 Keywords

12 Gas-liquid absorption, Kinetic model, Non ideality, MDEA solution, CO₂ absorption

13 Abstract

14 Absorption into basic aqueous solutions is widely used for CO₂ separation from raw natural gas or
15 from flue gases. This study implements a general steady-state model for reactive gas-liquid
16 absorption. This work expands upon a first case study where the model was applied with the
17 stagnant film theory (Whitman, 1923) to alkaline salts-water-CO₂ systems. This second case study
18 uses the resulting Arrhenius expression to examine published CO₂ absorption and desorption flux
19 data in MDEA-water-CO₂ system. Arrhenius parameters are optimised for the reaction CO₂ + MDEA +
20 H₂O ↔ HCO₃⁻ + MDEAH⁺ with $\ln k \text{ (m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}) = 16.69 - 6385/T \text{ (K)}$. Results emphasise the role of
21 CO₂ physical solubility representation in reactive absorption model overall performance. Global
22 modelling is needed: kinetic parameters should be used together with all underlying parameters with
23 which they were obtained. The relevance of activity-based modelling is shown, especially at high CO₂
24 absorption/desorption driving force.

25

26 Nomenclature

27	A	Logarithm of Arrhenius pre-exponential factor
28	c_i	Molar concentration of species i (mol.m^{-3})
29	$c_{1,0}$	Concentration of absorbed gas at gas-liquid interface (mol.m^{-3})
30	$c_{\text{abs,tot}}$	Total absorptive species concentration (mol.m^{-3})
31	C_i	Normalised concentration of species i (-)
32	E_A	Activation energy (J.mol^{-1})
33	E'	Flux density (-)
34	f_{obj}	Optimisation objective function (-)
35	H_1	Henry's constant of absorbed gas at infinite dilution (Pa)
36	j_i	Flux of species i through liquid film ($\text{mol.m}^{-2}.\text{s}^{-1}$)
37	k_j	Reaction j kinetic constant
38	K_j	Reaction j equilibrium constant
39	$k_{L,1}$	Liquid-side mass transfer coefficient regarding the absorbed gas (m.s^{-1})
40	n_c	Number of solute constituents in liquid phase
41	$n_{R,\text{kin}}$	Number of finite-rate reactions in the reaction mechanism
42	$n_{R,\text{eq}}$	Number of reactions at equilibrium in the reaction mechanism
43	P	Pressure (Pa)
44	Re	Reynolds number
45	r_j	Reaction rate of reaction j ($\text{mol.m}^{-3}.\text{s}^{-1}$)
46	Sc	Schmidt number
47	Sh	Sherwood number
48	T	Temperature (K)
49	<i>Constants</i>	
50	R	Ideal gas constant ($\text{J.mol}^{-1}.\text{K}^{-1}$)
51	<i>Greek letters</i>	
52	α	CO_2 loading in solution (mol.mol MDEA^{-1})
53	γ_i	Activity coefficient of species i (-)
54	μ_s	Solution viscosity (Pa.s)
55	ξ_j	Extent of reaction j (-)
56	ρ_s	Solution density (kg.m^{-3})
57	ω_i	Mass fraction of species i (-)
58	$\omega_{\text{MDEA,app}}$	Apparent mass fraction of MDEA (equivalent MDEA mass fraction of a given solution at zero CO_2 loading)
59		
60	<i>Subscripts and superscripts</i>	
61	app	Apparent (=in equivalent unloaded solution)
62	calc	Calculated
63	eq	At equilibrium
64	exp	Experimental
65	0	At interface
66	1	Absorbed gas
67	$\sim c$	Molar concentration-based symmetric thermodynamic convention

68 **1. Introduction**

69 Chemical absorption of CO₂ into basic solutions has been in use since the 1930s for its separation
70 from raw natural gas or from flue gases (Bottoms 1931). Solvent screening and design are at the
71 heart of the research effort to increase both CO₂ absorption rate and capacity, and to decrease
72 solvent regeneration duty (e.g., aqueous amine blends). Kinetic parameters are typically obtained
73 from absorption or desorption flux measurements in laboratory gas-liquid contactors of known mass
74 transfer coefficient and interfacial area.

75 Experiments should be carried out as close to industrial conditions as possible (amine content, CO₂
76 partial pressure and loading, temperature). Yet, most kinetic studies deal with absorption
77 experiments into unloaded basic solutions. Only one irreversible reaction is considered between
78 absorbed gas and amine (e.g., (Pohorecki et Moniuk 1988), (Pani, et al. 1997), (Derks, et al. 2006)).
79 Moreover, rate expressions are based on molarities. However, when CO₂ is absorbed, bicarbonate,
80 carbonate and carbamate ions are formed. This increases ionic strength, and solution non ideality as
81 well. Therefore, absorption models based on activities rather than molarities should lead to more
82 relevant process simulation.

83 CO₂ reaction with hydroxide ion HO⁻ takes place in all aqueous systems with CO₂. In amine-based
84 solutions, its rate cannot always be disregarded compared to that of CO₂ reaction with the amine
85 species. Furthermore, through molecular simulation, (Rozanska, Wimmer et de Meyer 2021) show
86 that CO₂ kinetics in aqueous tertiary amine solutions can be written as a function of CO₂ and HO⁻
87 concentrations only. For pilot effective mass transfer area measurement by CO₂ absorption into
88 NaOH solutions, (Sheng, et al. 2019) obtain large deviations in estimated area based on five literature
89 kinetic constants. They additionally conclude that inconsistencies between kinetic and physical
90 parameter sources should be avoided. The need for global modelling is emphasised.

91 For these reasons, part I of the present work focused on CO₂ absorption kinetics into alkaline salts
92 solutions (Delgado, et al. 2023). It introduced a reactive absorption model where equilibrium
93 relations, Nernst-Planck diffusion fluxes and reaction rates are written based on activities. This model
94 can be applied in any chemical system and to validate any reaction mechanism. For steady-state
95 mass transfer representations, local fluxes are related by stoichiometric constraints through extents
96 of reactions and ensure mass conservation. This significantly reduces the number of differential
97 equations to solve. This model with the stagnant film theory (Whitman, 1923) was then applied to
98 alkaline salts-water-CO₂ systems for validation. Arrhenius parameters of the direct kinetic constant of
99 reaction $\text{CO}_2 + \text{HO}^- \leftrightarrow \text{HCO}_3^-$ were obtained in the 298-338 K temperature range. Resulting values
100 were coherent with previous works.

101 Following this first case study, the purpose of this article is to apply the developed general reactive
102 absorption model to CO₂ absorption and desorption in aqueous N-methyldiethanolamine (MDEA)
103 solutions. Both CO₂ reactions with MDEA and with hydroxide ion are considered, so that their
104 individual contribution to absorption can be quantified. Most available literature datasets are
105 included, covering broad experimental condition ranges (see Table 1). The last column indicates the
106 number of available CO₂ absorption and/or desorption flux measurements.

107

108 **Table 1** Summary of lab-scale CO₂ absorption studies in aqueous MDEA solutions

Ref, apparatus	$\omega_{\text{MDEA,app}}$	α (mol.mol MDEA ⁻¹)	T (K)	P _{CO₂} (kPa)	n _{data}
(Rinker, Sami et Sandall 1995), SC	0.1-0.3	0	293-342	72-100	21
(Pani, et al. 1997), LC	0.1-0.52	0	295-344	100-196	34
(Cadours 1998), LC	0.25-0.5	0.02-0.85	312-383	2.3-1757	114
(Ko et Li 2000), WWC	0.12-0.29	0.01-0.03	303-313	37-98	12
(Pacheco et Kaganoi 2000), WWC	0.35-0.5	0.03-0.32	298-373	67-748	9
(Benamor et Aroua 2007), LC	0.12-0.46	0-0.17	293-323	9.1-59	99
(Camacho, et al. 2009), LC	0.009-0.38	0	288-313	88-95	42
(Qian et Guo 2009), WWC	0.1-0.3	0.01-0.04	300-313	94-98	12
(Kierzkowska-Pawlak et Chacuk 2010), LC	0.1-0.2	0	293-333	26-108	30
(Hamborg et Versteeg 2012), LC	0.23	0-0.8	298-333	1.7-136	21
(Costa, et al. 2019), MC	0.12-0.35	0	298	14	3

HSC: "Hemispherical Contactor", LC: "Lewis Cell", MC: "Membrane Contactor", SC: "Spherical Wetted-Wall Contactor", WWC: "Wetted-Wall Column"

109

110 Firstly, a data coherence analysis over available absorption and desorption flux measurements is
 111 carried out (section 2). It consists in a graphical analysis of flux density E' (see eq. 1) as a function of
 112 temperature and CO₂ loading. Outlier points are identified and filtered out. Over the consolidated
 113 dataset, the model is then applied to CO₂ absorption and desorption in aqueous MDEA solutions with
 114 a complete reaction mechanism considering four reversible reactions (two finite rate reactions and
 115 two acid-base equilibria). This third section aims at fitting the parameters of an Arrhenius-type
 116 expression for the direct kinetic constant of reaction $\text{CO}_2 + \text{MDEA} + \text{H}_2\text{O} \leftrightarrow \text{MDEAH}^+ + \text{HCO}_3^-$.
 117 Optimisation is carried out in both concentration- and activity-based modelling frameworks. Kinetic
 118 parameters of CO₂ reaction with hydroxide ion from (Delgado, et al. 2023) are reused here. An
 119 overall average absolute deviation (AAD) of calculated to experimental fluxes of 12% was obtained in
 120 (Delgado, et al. 2023), with slightly better performance than (Gondal, Svendsen et Knuutila 2016).

121

122 **2. Data coherence analysis**

123 Flux density E' of an absorption or desorption experiment is defined in eq. (1).

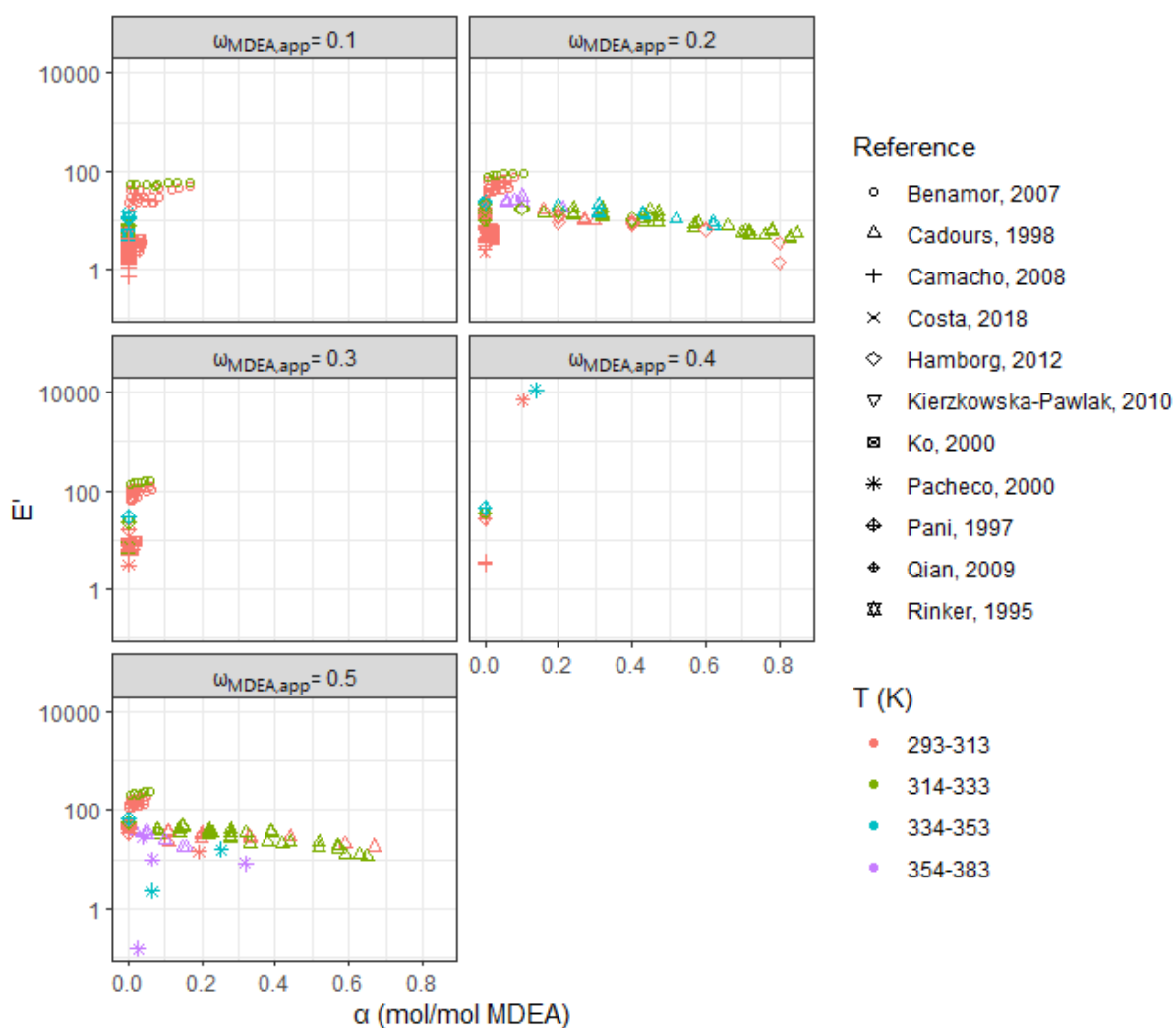
$$E' = \frac{j_{\text{CO}_2,\text{exp}}}{\frac{k_{\text{L,CO}_2}}{H_{\text{CO}_2,\text{app}}} (p_{\text{CO}_2,0} - p_{\text{CO}_2,\text{eq}})} \quad (1)$$

124 Where, for a given data point, flux density E' is a normalised flux considering proximity to
 125 equilibrium. $j_{\text{CO}_2,\text{exp}}$, the algebraic experimental CO₂ absorption (>0) or desorption (<0) flux, $k_{\text{L,CO}_2}$, the
 126 liquid-side CO₂ mass transfer coefficient, and $p_{\text{CO}_2,0}$, the CO₂ partial pressure at gas-liquid interface
 127 are provided by literature sources. $H_{\text{CO}_2,\text{app}}$, the apparent Henry's constant of CO₂, is calculated with
 128 the correlation by (Vinel et Bouallou 2004), and $p_{\text{CO}_2,\text{eq}}$, the equilibrium CO₂ partial pressure, is

129 calculated as a function of experimental conditions with the thermodynamic model described in the
 130 Supplementary Material.

131 This variable can be read as a comparison of chemical absorption or desorption flux $j_{CO_2,exp}$ to a
 132 physical absorption flux in an equivalent non-reactive system $\frac{k_{L,CO_2}}{H_{CO_2,app}}(p_{CO_2,0} - p_{CO_2,eq})$. Moreover,
 133 flux density is always positive. Therefore, CO₂ absorption and desorption data can be represented
 134 and compared on one diagram.

135 E' is plotted as a function of CO₂ loading and at different MDEA concentration levels in Figure 1.
 136 Datasets are sorted according to five rounded apparent MDEA mass fraction. Colours reflect four
 137 different temperature intervals.



138
 139 **Figure 1** Graphical coherence analysis of available CO₂ absorption and desorption flux data in
 140 aqueous MDEA solutions as a function of CO₂ loading and apparent MDEA mass fraction $\omega_{MDEA,app}$

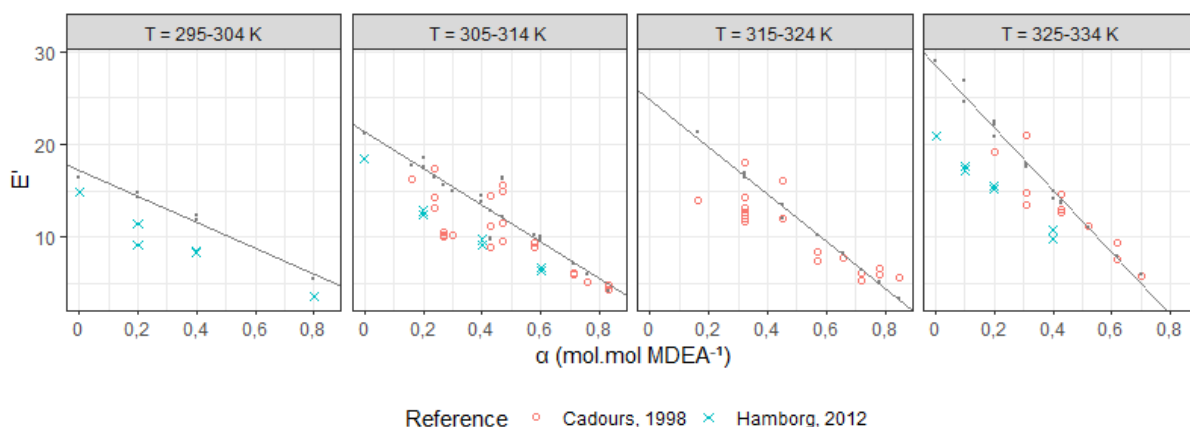
141 Figure 1 shows a decreasing trend of flux density with increasing CO₂ loading at 0.2 and 0.5 MDEA
 142 mass fractions. Data are mostly available in unloaded solutions, where flux density spans a wide

143 interval. This can stem from variability between data sources and visualising all temperatures in the
144 same plot. The choice of thermodynamic representation could also play a role in this result.

145 Outlier points are mainly from two references. On the one hand, flux density of (Benamor et Aroua
146 2007) data is systematically above that of other data sources in unloaded solutions and remains
147 constant or increases slightly with increasing CO₂ loading. This behaviour is incompatible with other
148 data sources. Therefore, absorption flux measurements by (Benamor et Aroua 2007) are not selected
149 in the following section.

150 On the other hand, outlier points from (Pacheco et Kaganoi 2000) data at 0.4 MDEA mass fraction
151 have flux densities close to 1.10⁴ whereas flux densities from other sources are not over 1.10². At 0.5
152 MDEA mass fraction, another of their points stands out with a flux density around 0.1 at low CO₂
153 loading whereas it is not below 1 in other sources. Three more points stand out from the trend
154 outlined by the data from (Cadours 1998) and (Hamborg et Versteeg 2012) with a higher flux density
155 of around 10 that remains constant regardless of temperature or CO₂ loading. Considering outliers
156 represent more than half of the data from (Pacheco et Kaganoi 2000), their absorption flux
157 measurements are not selected either in section 3.

158 Figure 2 focuses on calculated flux density from (Cadours 1998) and (Hamborg et Versteeg 2012)
159 data as a function of CO₂ loading at $\omega_{\text{MDEA,app}} = 0.23\text{-}0.25$. Activity-based model trend is also
160 represented with the kinetic parameters determined in section 3. Flux density tends to decrease with
161 growing CO₂ loading, as in Figure 1. However, data from (Hamborg et Versteeg 2012) systematically
162 display lower densities than the trend of (Cadours 1998). Selected data sources for CO₂-loaded
163 solutions appear incompatible. Both were kept in section 3 because of missing discrimination
164 method, such as a third data source with CO₂-loaded solutions.



165

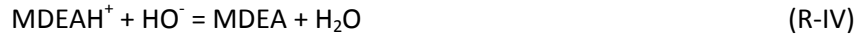
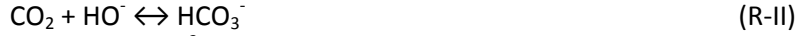
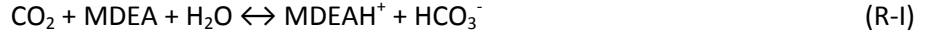
166 **Figure 2** (Cadours 1998) and (Hamborg et Versteeg 2012) data flux density as a function of CO₂
167 loading at $\omega_{\text{MDEA,app}} = 0.23\text{-}0.25$. Grey dots and lines: activity-based model flux density and trend.

168

169 **3. Application to MDEA-water-CO₂ system**

170 The mass transfer modelling framework is described in part I of the present work (Delgado, et al.
 171 2023). Therefore, only MDEA-specific parameters are specified in the following section (see
 172 Supplementary Material section 1 and (Delgado, et al. 2023) for modelling framework description).

173 In this system, six species are considered: CO_2 , HCO_3^- , CO_3^{2-} , MDEA, MDEAH^+ and HO^- ($n_c=6$). The
 174 mechanism consists in four reversible reactions ($n_R=4$):



175

176 Reactions R-I and R-II are reversible and with finite rate ($n_{R,\text{kin}}=2$). As in most studies, a direct CO_2
 177 reaction with MDEA is considered according to the mechanism proposed by (Donaldson et Nguyen
 178 1980).

$$r_I = r_{(\text{CO}_2, \text{MDEA})} = \tilde{k}_{(\text{CO}_2, \text{MDEA})}^c \left(\tilde{Y}_{\text{CO}_2} \tilde{Y}_{\text{MDEA}} c_{\text{CO}_2} c_{\text{MDEA}} - \frac{\tilde{Y}_{(\text{MDEAH}^+)} c_{(\text{MDEAH}^+)} \tilde{Y}_{(\text{HCO}_3^-)} c_{(\text{HCO}_3^-)}}{\tilde{K}_{(\text{CO}_2, \text{MDEA})}^c} \right) \quad (2)$$

$$r_{II} = r_{(\text{CO}_2, \text{HO}^-)} = \tilde{k}_{(\text{CO}_2, \text{HO}^-)}^c \left(\tilde{Y}_{\text{CO}_2} \tilde{Y}_{(\text{HO}^-)} c_{\text{CO}_2} c_{(\text{HO}^-)} - \frac{\tilde{Y}_{(\text{HCO}_3^-)} c_{(\text{HCO}_3^-)}}{\tilde{K}_{(\text{CO}_2, \text{HO}^-)}^c} \right) \quad (3)$$

179 Where $\tilde{k}_{(\text{CO}_2, \text{MDEA})}^c$ and $\tilde{k}_{(\text{CO}_2, \text{HO}^-)}^c$ ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) are the forward kinetic constants of reactions R-I and
 180 R-II, and $\tilde{K}_{(\text{CO}_2, \text{MDEA})}^c$ (dimensionless) and $\tilde{K}_{(\text{CO}_2, \text{HO}^-)}^c$ ($\text{m}^3 \cdot \text{mol}^{-1}$) are their equilibrium constants.
 181 $\tilde{k}_{(\text{CO}_2, \text{MDEA})}^c$ is the constant to determine. \tilde{c} refers to the molar concentration-based symmetric
 182 thermodynamic convention (see eq. SM24 and following in Supplementary Material).

183 In addition, acid-base equilibria between HCO_3^- and CO_3^{2-} (reaction R-III) and MDEAH^+ and MDEA
 184 (reaction R-IV) are considered ($n_{R,\text{eq}}=2$). Equilibrium constant parameters of reactions R-II and R-III
 185 are taken from (Kamps, Balaban, et al. 2001). (Kamps et Maurer, 1996) provides equilibrium constant
 186 parameters of reactions R-I and R-IV.

187 New correlations have been developed for density and viscosity of both CO_2 -unloaded and -loaded
 188 solutions. CO_2 and MDEA liquid phase diffusion coefficients are calculated using modified Stokes-
 189 Einstein relations (Versteeg et Van Swaaij, Solubility and diffusivity of acid gases (carbon dioxide,
 190 nitrous oxide) in aqueous alkanolamine solutions 1988). All ionic species are assumed to have the
 191 same diffusivity as MDEA (see Supplementary Material section 1 for detailed correlations). As stated
 192 in part I of the present work, the necessary data to implement a distinction in ionic diffusivities is not
 193 available. Ionic diffusivities are primarily measured at infinite dilution. However, they are expected to
 194 depend on the composition of the solution, but these effects have not been measured in ionic
 195 systems. The current assumption is a result of the lack of data. Moreover, this effect is expected to
 196 be small compared to the uncertainty of CO_2 absorption and desorption flux measurements and of
 197 relevant physico-chemical parameters like viscosity.

198 As a base case, the mass transfer model is tested with no deviation from ideality. This modelling
 199 framework is denoted “concentration-based model”. N₂O physical solubility in aqueous MDEA
 200 solutions is calculated with the correlation of (Vinel et Bouallou 2004). CO₂ Henry’s constant is
 201 calculated with the so-called CO₂-N₂O analogy. Since the physical solubility correlation only considers
 202 unloaded solutions, this base case is applied to low-loading flux data ($\alpha \leq 0.05$ mol.mol MDEA⁻¹).

203 Secondly, the activity-based model is implemented. Equilibria and solution non-ideality are
 204 represented with one thermodynamic model, described in the Supplementary Material. Thus, all
 205 selected datapoints in CO₂-unloaded and -loaded solutions are considered. Several hundred CO₂
 206 absorption and desorption flux measurements are available in the literature, from a variety of gas-
 207 liquid contactors over broad ranges of operating conditions (293-383 K, 0.009-0.52 apparent MDEA
 208 mass fraction, 0-0.85 mol.mol MDEA⁻¹ CO₂ loading and 0.2-1757 kPa CO₂ partial pressure).

209 The pre-exponential factor A and the temperature of activation E_A/R of reaction R-I direct kinetic
 210 constant are fitted. The Arrhenius equation is shown in eq. (4) and the objective function is specified
 211 in eq. (5).

$$\ln k_{(\text{CO}_2, \text{MDEA})} = A - \frac{E_A}{RT} \quad (4)$$

$$f_{\text{obj}} = \sum_{i \text{ points}} \frac{1}{2} \left(\left(\frac{j_i^{\text{calc}} - j_i^{\text{exp}}}{j_i^{\text{exp}} + s\varepsilon} \right)^2 + \left(\frac{j_i^{\text{calc}} - j_i^{\text{exp}}}{j_i^{\text{calc}} + s\varepsilon} \right)^2 \right) \quad (5)$$

212 Where j is the CO₂ absorption flux and ε is a constant set to 1.10^{-4} to mitigate error value for very
 213 small absorption fluxes. Because both absorption and desorption fluxes are available in this system, a
 214 factor s represents the experimental flux sign (s=1 if $j_i^{\text{exp}} > 0$, -1 otherwise). As indicated in (Delgado,
 215 et al. 2023), the two terms give this objective function a symmetric behaviour regarding flux
 216 underestimation and overestimation. Optimisation function fminsearch in Matlab R2013a is used to
 217 adjust Arrhenius parameters of the kinetic constant. This function implements the simplex algorithm
 218 by (Lagarias, et al. 1998).

219 Model application to selected flux measurements aims at optimising Arrhenius parameters of the
 220 direct kinetic constant of reaction R-I to minimise f_{obj} . Arrhenius parameters obtained in (Delgado, et
 221 al. 2023) are used for the direct kinetic constant of reaction R-II.

222

223 Table 2 and Figure 3 compare adjusted Arrhenius parameters in each modelling approach to previous
224 studies. The concentration-based model leads to similar Arrhenius parameters to (Littel, Van Swaaij
225 et Versteeg 1990), (Rangwala, et al. 1992), (Pani, et al. 1997), (Kierzkowska-Pawlak et Chacuk 2010)
226 and (Jamal, Meisen et Lim 2006). On the other hand, the activity-based model leads to higher values
227 for A and E_a/R compared to Arrhenius parameters of previous studies. For instance, the resulting
228 kinetic constant is 1.8 times higher than that of (Jamal, Meisen et Lim 2006) over the entire
229 temperature interval. The higher activity-based model kinetic constant can be caused by a product of
230 CO_2 and MDEA activity coefficients lower than one. It can also stem from the different representation
231 of equilibria, with lower calculated absorption/desorption driving force in the activity-based model
232 compared to the concentration-based model. As will be seen in Figure 7 and Figure 8, driving force is
233 indeed lower according to the activity-based model. Among the listed studies, the activity-based
234 model in the present work is the only modelling framework considering system deviation from
235 ideality through the liquid film. Only in (Cadours 1998) and (Hamborg et Versteeg 2012) is CO_2
236 loading factored in CO_2 Henry's constant, by an ionic-strength-dependent correction factor or an
237 experimental assessment with the $\text{N}_2\text{O}-\text{CO}_2$ analogy (see Table 2).

238

239 **Table 2** Resulting Arrhenius parameters for the direct kinetic constant of reaction R-I and comparison to previous studies

Reference	A	E _A /R (K)	T (K)	Transfert model	Non-ideality representation	Reactions
Activity-based model	16.69	6385	293-383	Film	Deshmukh-Mather	I-IV
Concentration-based model	13.60	5567	293-383	Film	Ideal solution	I-IV
(Versteeg et van Swaaij 1988)	11.69	5103	293-333	Penetration	Ideal solution	I, II, V
(Tomcej et Otto 1989)	11.99	5134	298-348	Film (pfo)	Ideal solution	I, II, V
(Littel, Van Swaaij et Versteeg 1990)	14.11	5771	293-333	Penetration	Ideal solution	I, II
(Rangwala, et al. 1992)	13.96	5770	298-333	Film (pfo)	Ideal solution	I
(Rinker, Sami et Sandall 1995)	10.28	4579	293-343	Penetration	Ideal solution	I-IV, VI
(Pani, et al. 1997)	13.06	5461	296-343	Film	Ideal solution	I
(Cadours 1998)	12.60	5333	296-343	Film	H _{CO2} = f(I)	I
(Ko et Li 2000)	12.90	5400	303-313	Film	Ideal solution	I, II
(Jamal, Meisen et Lim 2006)	14.51	5798	303-353	Penetration	Ideal solution	I-IV, VI
(Camacho, et al. 2009)	15.49	6244	288-313	Film	Ideal solution	I,II
(Qian et Guo 2009)	12.28	5190	300-313	Penetration	Ideal solution	I-VI
(Kierzkowska-Pawlak et Chacuk 2010)	14.54	5913	293-333	Film	Ideal solution	I
(Hamborg et Versteeg 2012)	9.72	4504	298-333	Penetration	Ideal solution*	I-IV, VI

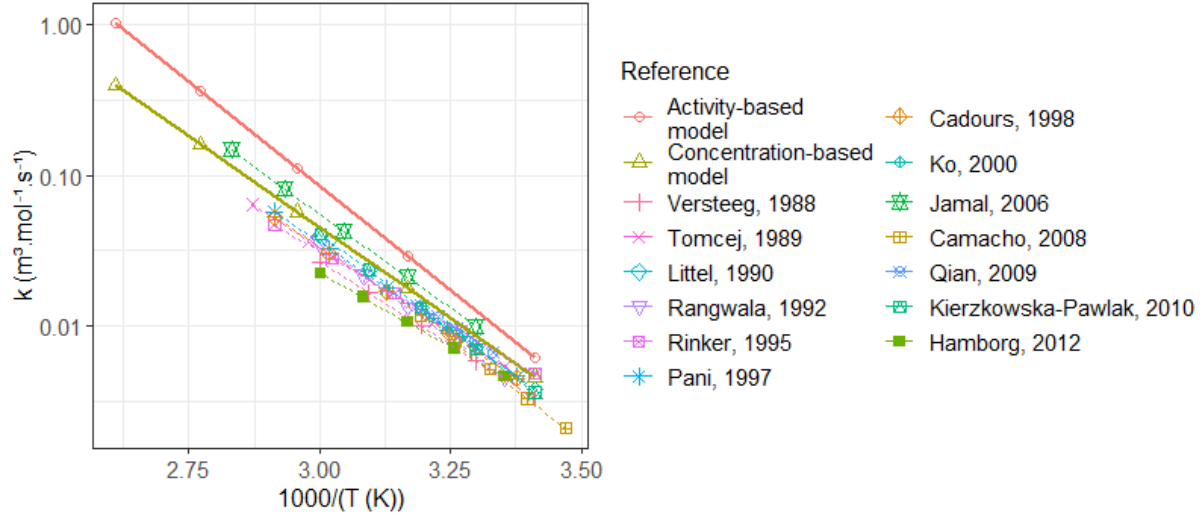
pfo: "pseudo-first order", H_{CO2}: CO₂ Henry's constant, I: ionic strength

* (Hamborg et Versteeg 2012) experimentally assess H_{N2O} in CO₂-loaded solution and use the N₂O-CO₂ analogy to calculate H_{CO2}

Reactions: (V) CO₂ + H₂O ↔ HCO₃⁻ + H⁺, (VI) 2H₂O = HO⁻ + H₃O⁺

240

241



242

243 **Figure 3** Arrhenius plots obtained in concentration-based and activity-based modelling frameworks
 244 and in previous studies for the direct kinetic constant of reaction R-I

245 Model performance criteria are presented in Table 3, including average absolute deviation (AAD, eq.
 246 (6)) and bias (eq. (7)).

$$\text{AAD} = \frac{1}{n_{\text{data}}} \sum_{i \text{ data}} \left| \frac{j_i^{\text{calc}} - j_i^{\text{exp}}}{j_i^{\text{exp}}} \right| \times 100 \quad (6)$$

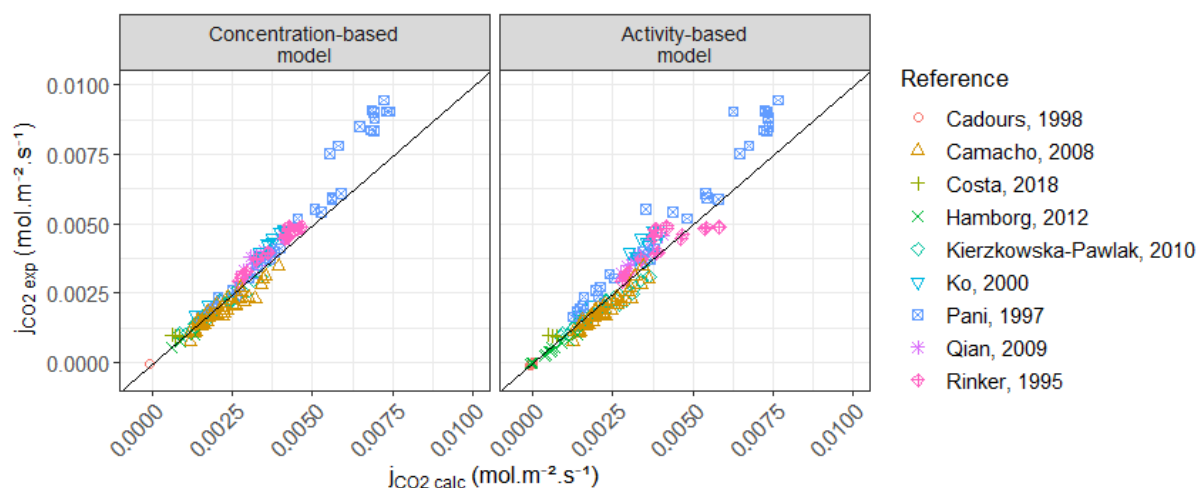
$$\text{bias} = \frac{1}{n_{\text{data}}} \sum_{i \text{ data}} \frac{j_i^{\text{calc}} - j_i^{\text{exp}}}{j_i^{\text{exp}}} \times 100 \quad (7)$$

247 **Table 3** Mass-transfer modelling performance for MDEA-water-CO₂ system

(%)	Model	Concentration-based ($\alpha \leq 0.05$)		Activity-based (all selected data)	
Reference		AAD	Bias	AAD	Bias
(Rinker, Sami et Sandall 1995)		9	-9	11	-5
(Pani, et al. 1997)		11	-10	17	-17
(Cadours 1998)		29	29	17	0.8
(Ko et Li 2000)		15	-15	17	-17
(Camacho, et al. 2009)		17	16	20	20
(Qian et Guo 2009)		11	-11	13	-13
(Kierzkowska-Pawlak et Chacuk 2010)		6	2	10	9
(Hamborg et Versteeg 2012)		20	20	42	42
(Costa, et al. 2019)		24	-24	35	-35
Overall	$\alpha \leq 0.05$	12	-0.6	16	-0.2
	All selected data	-	-	18	3

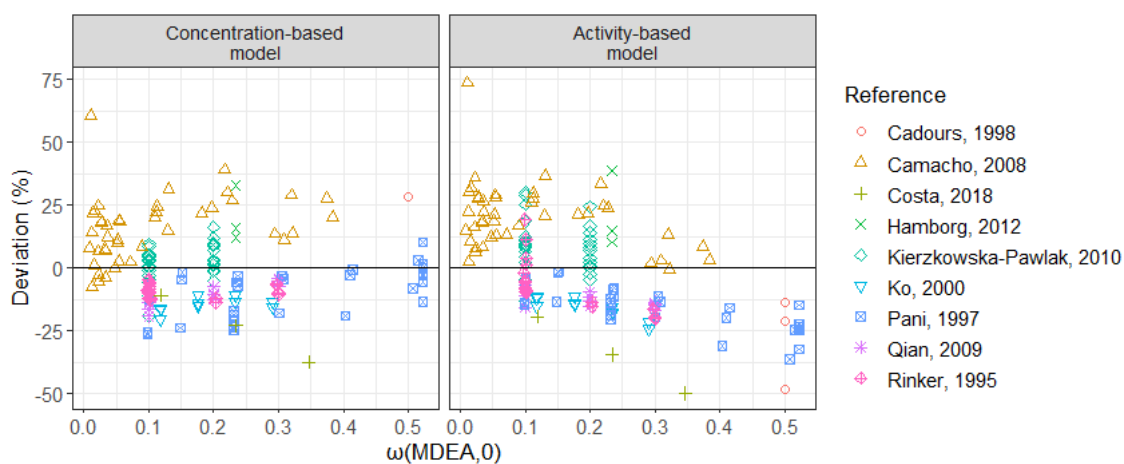
248

249 Parity and deviation plots are shown in Figure 4, Figure 5 and Figure 6.



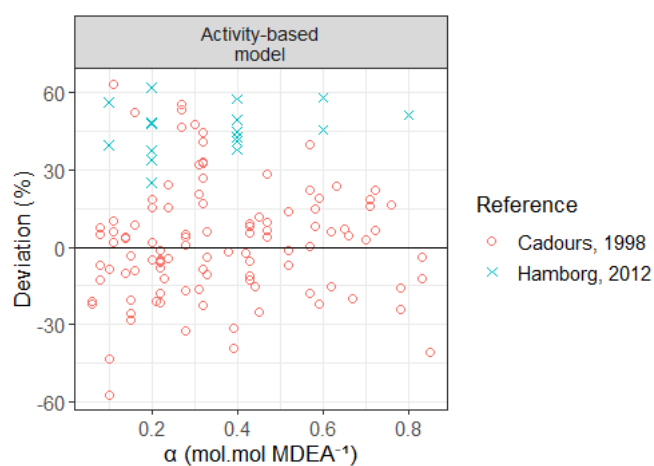
250

251 **Figure 4** Reactive absorption model parity plot for MDEA-water-CO₂ system. Concentration-based
 252 model: $\alpha \leq 0.05$, activity-based model: all selected data.



253

254 **Figure 5** Reactive absorption model deviations for MDEA solutions at low CO₂ loading ($\alpha \leq 0.05$)



255

256 **Figure 6** Reactive activity-based absorption model deviations for MDEA solutions at high CO₂ loading
 257 ($\alpha > 0.05$)

258 Both approaches give reliable representation of selected data at low CO₂ loading (AAD 12% vs. 16%).
 259 Figure 5 shows (Camacho, et al. 2009) data is better represented by activity-based model when
 260 amine mass fraction increases, whereas (Pani, et al. 1997) data is increasingly underestimated with
 261 this model. The concentration-based model results in slightly better performance at low CO₂ loading,
 262 but the activity-based model considers non-ideality with a unique thermodynamic model: (1) in
 263 diffusion via Nernst-Planck equation, (2) in kinetics via activity-based rates of reactions and (3) in
 264 equilibria as part of the selected thermodynamic representation. Moreover, the use of CO₂ solubility
 265 correlations based on N₂O-CO₂ analogy is avoided. This is a major advantage for model generality.

266 The main area for improvement of the activity-based model concerns the thermodynamic
 267 representation of the system, specifically that of CO₂ physical solubility in solution. Indeed, Henry's
 268 constant in solution is calculated based on CO₂ Henry's constant in pure water (see Supplementary
 269 Material). It might be beneficial to consider amine concentration as well instead of simply correcting
 270 Henry's constant in pure water by the CO₂ activity coefficient factor. (Zhang et Chen 2011) achieve
 271 this by introducing a mixing rule for CO₂ Henry's constant normalised by solute activity coefficient at
 272 infinite dilution in each component of the solvent.

273 At high CO₂ loading (see Figure 6), (Cadours 1998) data is well represented by the activity-based
 274 model. Absorption and desorption flux measurements by (Hamborg et Versteeg 2012) are
 275 systematically overestimated by the activity-based model (bias=AAD=42%). This is coherent with
 276 previous observations of the incompatibility of the two datasets in the data coherence analysis (see
 277 Figure 2). Optimisation currently favours (Cadours 1998) data representation because of the
 278 difference in data point numbers between the two sources (114 vs. 21).

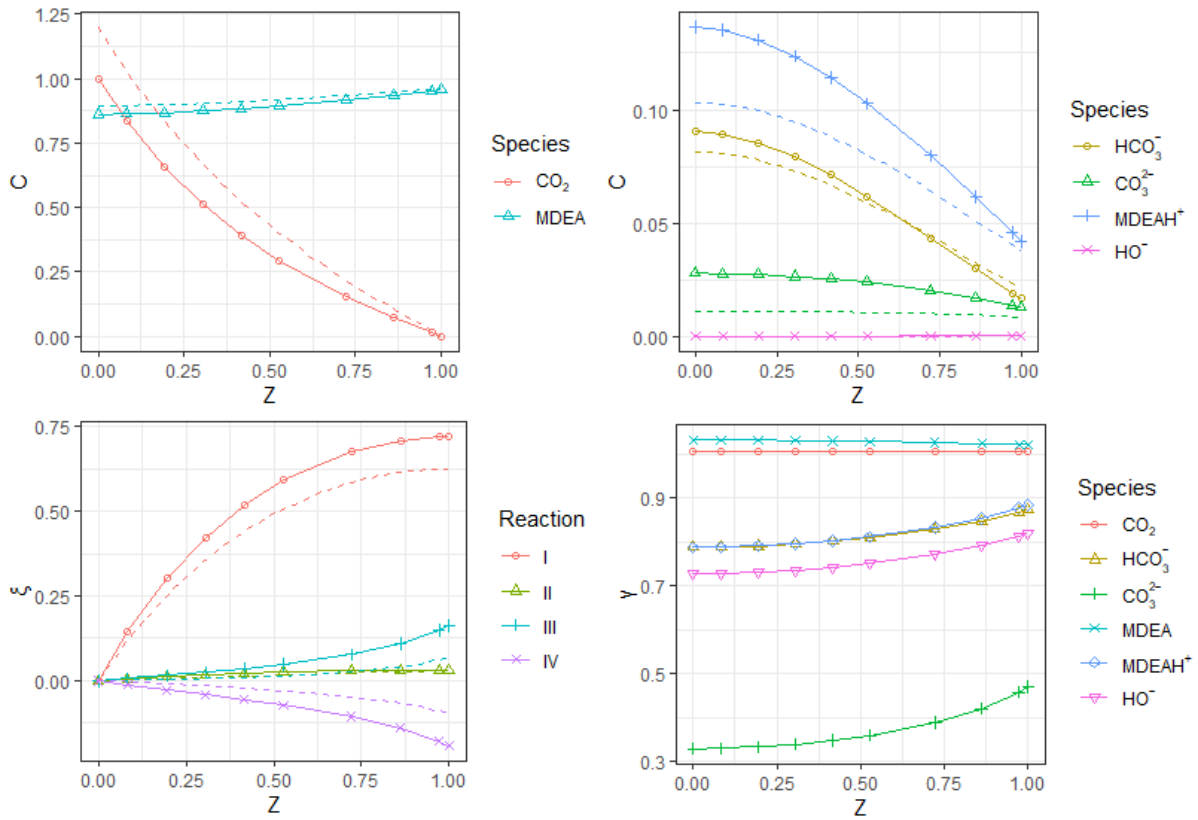
279 Activity-based model results at specific conditions are then examined (Figure 7 to Figure 10,
 280 conditions listed in Table 4). The four selected points cover the examined data experimental
 281 conditions (MDEA concentration, temperature, CO₂ partial pressure and loading, absorption and
 282 desorption experiments). For each point, normalised concentration, extent of reaction and activity
 283 coefficient profiles obtained with the activity-based model are plotted. In unloaded solutions,
 284 concentration-based model normalised concentration and extent of reaction profiles are also plotted
 285 in dashed lines. As a reminder, CO₂ concentration is normalised by $c_{1,0}$, its interfacial concentration,
 286 while all other concentrations are normalised by $c_{\text{abs,tot}} = C_{\text{MDEA,app}}$.

287 **Table 4** Conditions of selected points for concentration, extent of reaction and activity coefficient
 288 profile simulation

Figure	Reference	$\omega_{\text{MDEA,app}}$	α	T (K)	P_{CO_2} (kPa)	$k_{L,1}$ (m.s ⁻¹)	$c_{1,0}$ (mol.m ⁻³)*
Figure 7	(Qian et Guo 2009)	0.10	0.03	300	94.6	$5.38 \cdot 10^{-5}$	24.3
Figure 8	(Pani, et al. 1997)	0.51	0	318	104.9	$5.43 \cdot 10^{-6}$	6.3
Figure 9	(Cadours 1998)	0.50	0.28	332	70.1	$9.44 \cdot 10^{-6}$	5.1
Figure 10	(Hamborg et Versteeg 2012)	0.23	0.10	333	22.6	$1.84 \cdot 10^{-5}$	2.7

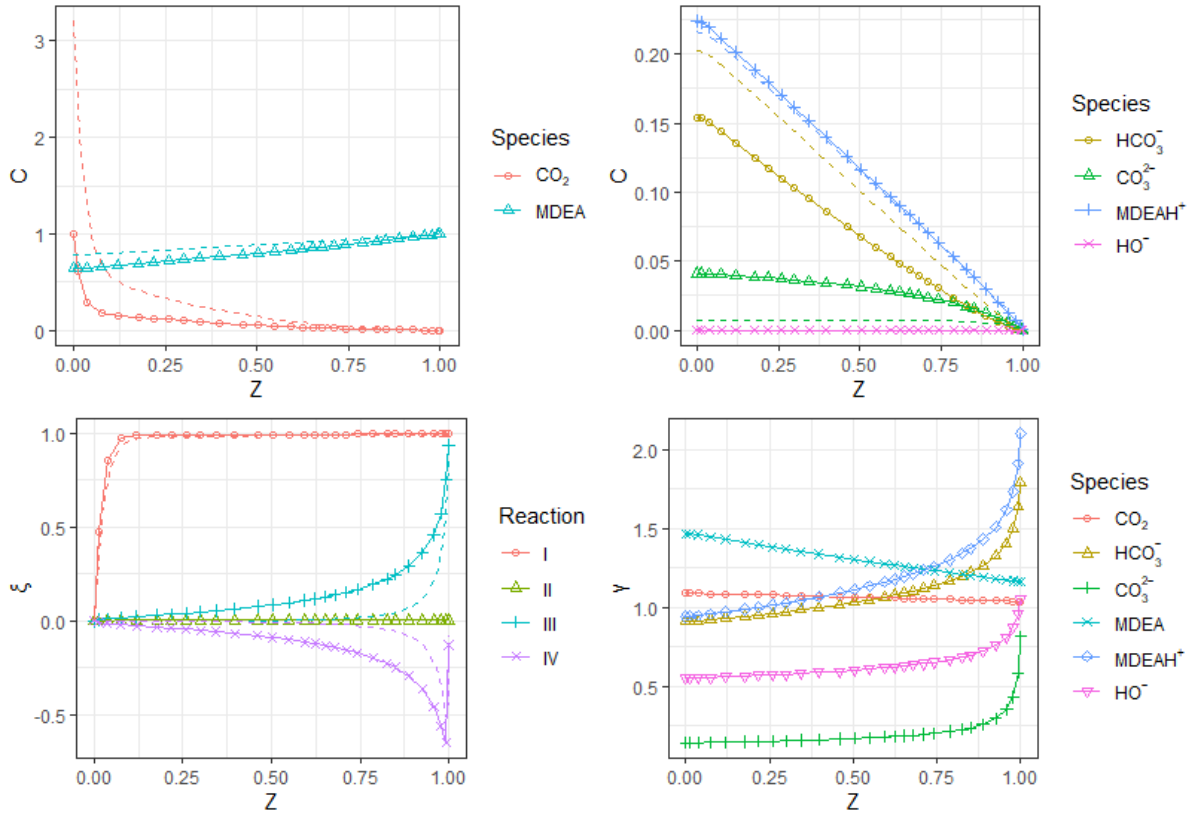
*Calculated variable (see (Delgado, et al. 2023)), in the activity-based model framework.

289



290

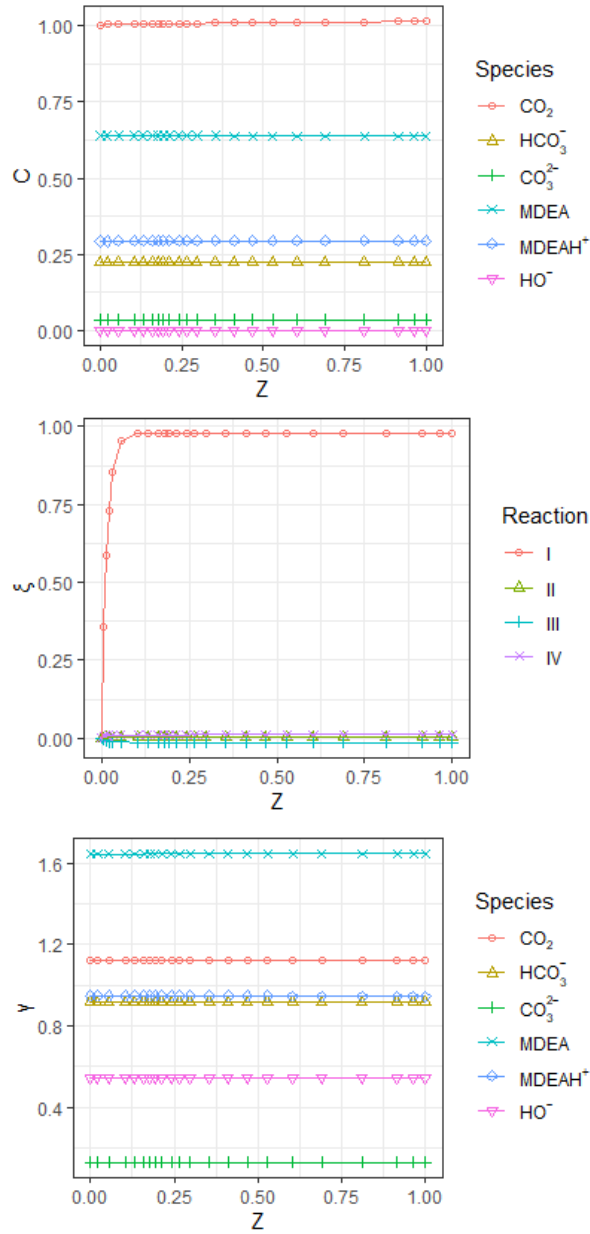
291 **Figure 7** Simulated CO₂ absorption in aqueous MDEA solution at $\omega_{\text{MDEA,app}} = 0.10$ and $\alpha = 0.03$
 292 mol/mol MDEA, 300 K and $P_{\text{CO}_2} = 94.6$ kPa measured by (Qian et Guo 2009). C: normalised
 293 concentration, ξ : extent of reaction, γ : activity coefficient. Solid line & symbol: activity-based model,
 294 dashed line: concentration-based model (C and ξ).



295

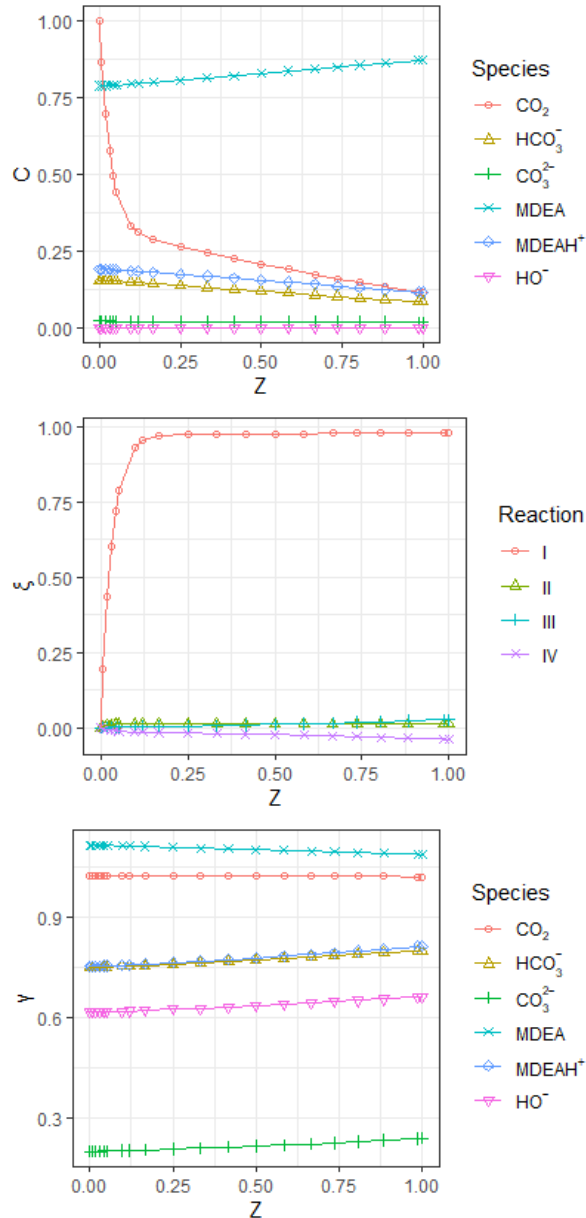
296 **Figure 8** Simulated CO₂ absorption in aqueous MDEA solution at $\omega_{\text{MDEA,app}} = 0.51$ and $\alpha = 0$ mol/mol
 297 MDEA, 318 K and $P_{\text{CO}_2} = 104.9$ kPa measured by (Pani, et al. 1997). C: normalised concentration, ξ :
 298 extent of reaction, γ : activity coefficient. Solid line & symbol: activity-based model, dashed line:
 299 concentration-based model (C and ξ).

300 For selected points at low CO₂ loading, concentration and extent of reaction profiles calculated with
 301 non-ideality consideration (solid lines and symbols in Figure 7 and Figure 8) or with ideal solution
 302 hypothesis (dashed lines in Figure 7 and Figure 8) display similar trends. In both cases, estimated CO₂
 303 concentration at interface is higher in concentration-based model than in activity-based model.
 304 However, the difference is way higher at $\omega_{\text{MDEA,app}} = 0.51$ (Figure 8: +221%) than at $\omega_{\text{MDEA,app}} = 0.10$
 305 (Figure 7: +20%). This is linked to the thermodynamic representation of CO₂ physical solubility
 306 discussed previously. Moreover, activity coefficients differ from unity in activity-based model and
 307 significantly vary through the film, which is another difference factor with concentration-based
 308 model.



309

310 **Figure 9** Simulated CO₂ desorption from aqueous MDEA solution by the activity-based model at
 311 $\omega_{\text{MDEA,app}} = 0.5$ and $\alpha = 0.28$ mol/mol MDEA, 332 K and $P_{\text{CO}_2} = 70.1$ kPa measured by (Cadours 1998).
 312 C: normalised concentration, ξ : extent of reaction, γ : activity coefficient.



313

314 **Figure 10** Simulated CO₂ absorption in aqueous MDEA solution by the activity-based model at
 315 $\omega_{\text{MDEA,app}} = 0.23$ and $\alpha = 0.1$ mol/mol MDEA, 333 K and $P_{\text{CO}_2} = 22.6$ kPa measured by (Hamborg et
 316 Versteeg 2012). C: normalised concentration, ξ : extent of reaction, γ : activity coefficient.

317 From all four extent of reaction plots, the reaction between CO₂ and HO⁻ ion (R-II) appears to have no
 318 influence ($\xi_{\text{II}} \approx 0$). HO⁻ concentration is negligible, especially close to the interface.

319 Extents of acid-base reactions (R-III and R-IV) are significant in initially unloaded solutions. However,
 320 contrary to alkaline salts systems studied in (Delgado, et al. 2023), CO₃²⁻ conversion through the film
 321 remains marginal. HCO₃⁻ and MDEAH⁺ are the main reaction products, even at low CO₂ loadings
 322 where pH is highest.

323 The apparition of activity coefficient gradients seems much more influenced by
 324 absorption/desorption driving force than by CO₂ loading, MDEA composition or temperature. In

325 Figure 7 and Figure 8, absorption into initially unloaded solutions at $\omega_{\text{MDEA,app}} = 0.10$ and 0.51 and $T =$
326 300 and 332 K, with CO_2 driving forces of around 100 kPa (94.6 and 104.9 kPa) shows the highest
327 activity coefficient gradients (especially MDEAH^+ and CO_3^{2-} activity coefficients). Additionally, at these
328 conditions, an important drop in MDEA concentration at the interface takes place (respectively 0.10
329 and 0.51 of total MDEA mass fractions). Therefore, the “pseudo-first order absorption regime”
330 assumption cannot apply.

331 On the other hand, profiles calculated in already loaded solutions (Figure 9 and Figure 10), with CO_2
332 driving forces below 20 kPa, either in the positive or negative, don't display any significant activity
333 coefficient gradient. However, activity coefficients appreciably differ from unity. Although CO_3^{2-} is
334 never a main product of CO_2 absorption or desorption, CO_3^{2-} activity coefficient is always lower than
335 0.5 .

336 **4. Conclusion**

337 The current two-part study implements a steady-state reactive absorption model applied to the
338 stagnant film theory and focusing on solution non-ideality representation in equilibrium relations,
339 Nernst-Planck diffusion fluxes and reaction rates. This approach is more complete than literature
340 models where activity coefficients are assumed constant, and most often equal to unity. Extents of
341 reactions, a new feature for reactive absorption models, reduces the number of differential problem
342 variables while maintaining a general formulation. This formulation with Nernst-Planck equation for
343 molecular diffusion and activity-based rate expressions consists in a system of $n_C + n_{R,kin}$ first-order
344 ordinary differential equations, whereas writing local balances per species leads to a system of n_C
345 second-order differential equations. The relation between fluxes and extents of reactions is dictated
346 by stoichiometric constraints.

347 In (Delgado, et al. 2023), this model was first applied to alkaline salts-water- CO_2 systems and the CO_2
348 absorption flux data from the literature. In part II presented here, CO_2 absorption into aqueous
349 MDEA solutions was studied. Firstly, a graphical data coherence analysis was carried out by plotting a
350 flux density variable against CO_2 loading. Outliers from (Benamor et Aroua 2007) and (Pacheco et
351 Kaganoi 2000) were then filtered out.

352 Then, using the selected data, Arrhenius parameters of the reaction between MDEA and CO_2 were
353 optimised in both concentration- and activity-based models. Results emphasise the role of CO_2
354 physical solubility representation in reactive absorption model overall performance. N_2O - CO_2 analogy
355 and activity-coefficient-corrected CO_2 Henry's constant in pure water lead to incompatible
356 estimations of CO_2 interfacial concentration at high MDEA concentrations. This supports the need for
357 global modelling: kinetic parameters should be used with all underlying parameters with which they
358 were obtained. This is especially true when designing industrial columns.

359 For aqueous MDEA solutions, N_2O - CO_2 analogy is not proven theoretically. Having access to direct
360 measurements of molecular CO_2 concentration in aqueous MDEA solutions would be beneficial to
361 kinetic modelling. Such measurements exist for reactive systems, such as CO_2 in aqueous
362 diethanolamine solutions (Diab, et al. 2012). In their absence, molecular simulation could provide
363 estimates. Results of the present study suggest that amine concentration should be considered as
364 well as water in CO_2 Henry's constant calculation at infinite dilution.

365 Lastly, simulated profiles through the liquid film indicate the relevance of the developed
366 representation, especially considering the high deviation from ideality of the system and the
367 apparition of activity coefficient gradients through the film at high absorption driving force. This
368 implies kinetic parameters obtained at high absorption driving force with a simplified approach
369 disregarding this effect could be incompatible with low absorption driving force experimental
370 absorption/desorption flux data, and vice versa. This could be a factor impeding laboratory-scale
371 data comparisons obtained at different absorption driving force conditions.

372

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377

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