1 CO$_2$ absorption into loaded aqueous MEA solutions: impact of 2 different model parameter correlations and thermodynamic models 3 on the absorption rate model predictions

4 Koteswara Rao Putta, Hallvard F. Svendsen, Hanna K. Knuutila[*]

5 Department of Chemical Engineering, Norwegian University of Science and Technology, N-6 7491 Trondheim, Norway

7 Abstract:

8 One-dimensional rate based model was used for assessing the impact of correlations and/or 9 models for VLE (thermodynamics), solubility (CO$_2$ henry's law constant), reaction rate kinetic 10 models and diffusivity of CO$_2$ in aqueous MEA solutions on the performance of absorber for lab-11 scale CO$_2$ capture. Experimental data from four different set-ups covering wide range of 12 condition was utilized for the assessment. Four different thermodynamic models and eight 13 different henry's constant correlations/models including the Aspen Plus V8.6 e-NRTL-RK 14 model was used in the study to evaluate the impact. Even though the individual models and 15 solubility were validated with independent experimental data, the use of different models gave 16 different predictions when used in the rate based simulation. It was seen that the impact of using 17 different henry's law constant correlations was observed to have very huge effect on model 18 predictions. Seven different reaction rate kinetic models were used to study impact on model 19 prediction accuracy and it was found that no single kinetic model able to predict the 20 experimental data from all the sources better than the base case kinetic model. Also it was seen 21 that transport property (CO$_2$ diffusivity in MEA) correlations could have large impact on the

[*] Corresponding author: hanna.knuutila@ntnu.no

22   accuracy of model predictions and correlations based on N_2O analogy were seem to be good

23   compared to the ones based on modified Stokes-Einstein correlation. As a special case,

24   frequently used kinetic models were used with thermodynamic model and transport properties

25   taken from Aspen Plus V8.6 and it was found that two kinetic models predict the experimental

26   data with acceptable accuracy.

1. Introduction

Due to world population growth and per capita income, there is continuous rise in energy demand. To meet the rising energy demand, energy sector relies heavily on fossil fuels (i.e., coal, petroleum, and natural gas) combustion for energy supply which contributes to greenhouse gas emissions. Global warming is an alarming issue right now and CO_2 is one of the key greenhouse gases. To limit the global temperature rise to 2 ^oC, capturing CO_2 from emitting sources is crucial. Among the current technologies available for post-combustion CO_2 capture, chemical absorption based on amine solvents appears to be the most mature technology and commercially feasible method. Post-combustion CO_2 capture with monoethanolamine (MEA) solvent has been considered as the base case in comparative studies for the development of new low energy intensive solvents. Though MEA has been studied extensively in the literature and considered as base case solvent, there are still gaps in thorough understanding of the complex phenomena (coupling between thermodynamics and diffusional processes in the gas and liquid phases in addition to complex chemical reactions in the liquid close to the interface) occurring and precise modelling of the process for industrial scale-up.

Two modelling approaches (equilibrium stage and rate based models) has been used for modelling the reactive absorption process. Equilibrium stage modelling concept fails for reactive absorption process using alkanolamines and rigorous rate based modelling, which takes into account the actual rates of mass and heat transfer and chemical reactions, is recommended (Kenig et al., 2003). The development of rigorous rate based process models helps to gain more knowledge about the effect of different process operating variables on the performance of the process. The main components of the process model are

(i)   Mass and energy balances for the phases (flow model);

53   (ii)   The gas-liquid interface model (accounts for the effect of chemical reactions);

54   (iii)   The thermodynamic model (describes phase and chemical equilibrium) and

55   (iv)   Auxiliary sub-models (for hydraulics, mass and heat transfer coefficients and

56   physical properties).

57   Process modelling and simulation plays key role in process design, analysis and development in

58   addition to in optimization of process. It is an integrated part of process development, and hence

59   it is essential to identify the strengths and weaknesses of such a model and user should always

60   remember that process simulators never perform better than the model upon which they are

61   based (Hessen et al., 2013). Thus the accuracy of the complete model largely depends on the

62   accuracy of sub-models used. The detailed information about accuracy, precision, assumptions

63   made during the development and the range of applicability of the sub-models is very crucial for

64   selecting the suitable property sub-model. All these sub-models used in the rigorous model were

65   developed from some form of experimental data and often the experimental data used in sub-

66   models development was taken from different sources with different magnitude of error. There is

67   great amount of information available on model parameters such as liquid density, viscosity,

68   reaction rate constants, mass and heat transfer coefficients, heat of absorption and solubility of

69   acid gases. Empirical correlations as function of temperature, pressure and composition were

70   used to represent some of these parameters while some were represented as constants (Kvamsdal

71   and Hillestad, 2012). In order to use simulation tools for technology qualification or verification

72   in process development, their performance must be documented by validating the results against

73   experimental data. Validation should be done on both the sub-model level (e.g. kinetic rate

74   models, thermodynamic models, hydraulic models, physical and transport property models) by

75   utilizing laboratory data (e.g. solution density, viscosity, VLE, kinetics, etc.) and by evaluating

76 the overall simulator performance using bench, pilot, demo and/or full scale data. Performance

77 evaluations should be performed at several scales or stages during the development phases (e.g.

78 bench, pilot, demo); and the effect of the scale should be investigated on each of these stages. If

79 there are any discrepancies or unexpected results compared to the previous scale stage, they

80 should be properly investigated and if possible quantified. In most of the cases, this indicated

81 that one or some of the sub-models need refinement. Therefore, the validation procedure must be

82 viewed as dynamic.

83 To gain in-depth knowledge about the design parameters, several studies on the sensitivity of

84 various operating and design parameters, model parameter correlations, physical properties and

85 reaction rate kinetic constants for CO_2 absorption using MEA has been performed. The objective

86 often is to find out with what mass transfer coefficient correlations, reaction rate kinetic

87 constants models and physical properties correlations are able to predict the pilot data. In Table

88 1, sensitivity studies made on CO_2 absorption using MEA are listed.

89 Table 1. Sensitivity studies for CO_2 absorption using MEA

Source	Parameters studied
(Abu-Zahra et al., 2007)	Solvent lean loading and temperature, percentage of CO_2 removal, solvent concentration, stripper pressure
(Mofarahi et al., 2008)	Solvent (type, concentration and circulation rate), reboiler and condenser duty and absorber and stripper columns stages
(Kvamsdal and Rochelle, 2008)	Liquid density, liquid heat capacity and mass transfer coefficients
(Khan et al., 2011)	Mass transfer coefficient correlations
(T�nnies et al., 2011)	Interfacial area, mass transfer coefficients, hold-up, Henry's law constant, heat of absorption, amine ion diffusivities, liquid density and viscosity
(Kvamsdal and Hillestad, 2012)	Liquid density, viscosity, heat capacity, heat of absorption, mass transfer coefficient (kg) and kinetic models

(Tan et al., 2012)	Viscosity, surface tension, CO_2 partial pressure, gas and liquid flow rates, absorbent concentration, liquid temperature,CO_2 loading, packing
(Razi et al., 2012)	Pressure drop correlations, gas and liquid mass transfer coefficients correlations, liquid hold-up correlations and interfacial area correlations
(Razi et al., 2013a)	Mass transfer coefficient correlations
(Razi et al., 2013b)	Kinetic models with corresponding thermodynamic model, mass transfer coefficient correlations
(Afkhamipour and Mofarahi, 2014)	Kinetic models in combination with mass transfer coefficient correlations
(Razi et al., 2014)	mass transfer coefficient and effective interfacial area correlations
(Morgan et al., 2015)	Liquid density, viscosity and surface tension

90

91 All the sensitivity studies listed above utilized pilot scale data for all these studies using rate-

92 based process models. As discussed above, rate based process model uses several sub-models for

93 kinetics, hydraulics, mass transfer coefficients and physical properties. Razi et al. (2012)

94 reviewed structured packings hydrodynamics and mass transfer correlations available in

95 literature and showed that uncertainty is large in applying the proposed pressure drop, gas and

96 liquid mass transfer coefficients, liquid hold-up and interfacial area correlations for large scale

97 packed column simulation. Kvamsdal and Hillestad (2012) couldn't see clear trend regarding

98 selection of model parameters and suggested that proper choice depends on conditions of the

99 specific case. From these studies, it was understood that absorber performance was highly

100 sensitivity to effective interfacial area, Henry's law constant, heat of absorption, kinetic

101 constants, surface tension and CO_2 loading. However, these studies gave qualitative knowledge

102 about the different process variables.

103 The main drawback of these sensitivity studies performed on pilot scale data is that the process

104 model used employed several parameters with large uncertainty and it is very difficult to assess

105   the impact of process parameters. Furthermore, the studies were not performed using the same

106   pilot scale experimental data. Hence, deeper understanding of the uncertainty associated with

107   using different correlations for same parameter in the simulation model is needed. This will also

108   help in selecting appropriate parameters sub-models. In order to see the sensitivity and assess the

109   effect of several parameters in a detailed manner, in this study lab-scale CO_2 data based on

110   equipment, where the interfacial area and mass transfer coefficients are known precisely, was

111   used. In this way we can eliminated some of the uncertain variables in the sensitivity study.

112

113   Llano-Restrepo and Araujo-Lopez (2015) reviewed 33 published rate-based absorber models

114   journal articles for simulation of CO_2 absorption using MEA and found that researchers had used

115   different models or correlations for the parameters needed in the absorber models. As shown by

116   Llano-Restrepo and Araujo-Lopez (2015), for the same process variable, researchers had used

117   different correlations. However, they didn't look into the effect of parameter estimation using

118   different methods/correlations on the process performance. In this work, we used different

119   thermodynamic models, correlations available for viscosity, diffusivities, henry's law constant

120   and reaction kinetics, published in literature. The objective is to compare the impact of various

121   parameter correlations on predicted performance of the process model. The selected correlations

122   are applied in detailed penetration theory based absorption model developed in our previous

123   work (Putta et al., 2016). The reasons for large variations in absorber performance are

124   investigated through the contributions of the individual correlations/models. No such comparison

125   was published in literature for lab-scale absorption data.

126

127   2.   Methodology and models/correlations

128   The experimental data used in this work was taken from three different experimental set-ups.

129   Lab-scale absorption data for CO_2 capture using MEA published in literature for wetted wall

130   column (WWC), laminar jet absorber (LAMJET) and string of discs column (SDC) were taken

131   from Luo et al. (2012, 2015), Aboudheir (2002), Aboudheir et al. (2003) and Puxty et al. (2010).

132   The lab-scale experimental data used in this study covers a wide range of conditions for

133   temperature (293-343 K), MEA concentration (0.5 – 9 M), CO_2 loading (0 - 0.5), CO_2 driving

134   force (0.16 –93 kPa) and gas side mass transfer resistance (with and without). The impact of

135   selecting different thermodynamic models, kinetic models, henry's law constant correlations,

136   correlations for diffusivity of CO_2 in MEA solution and viscosity correlations on the

137   performance of the CO_2 absorption model based on penetration theory is considered in this

138   study.

139   CO_2 absorption model based on penetration theory developed and validated with above

140   mentioned lab-scale data and presented in Putta et al. (2016), is considered as base case and used

141   for analysing the impact of different correlations/models considered in this study.

142   2.1 Thermodynamic models

143   Four different rigorous thermodynamic models were used to study the impact of thermodynamic

144   model selection. The extended UNIQUAC by Aronu et al. (2011), the un-symmetric electrolyte

145   NRTL property method (ENRTL-RK) of Aspen Plus V8.6 template (Aspen Technology, Inc.,

146   2015) ,the refined e-NRTL model of Hessen et al. (2010) and e-NRTL model were used in this

147   study. Aronu et al. (2011) used the new experimental VLE data (15-60 mass% MEA) and

148   physical CO_2 solubility data from the literature for fitting. used CO_2 partial pressures, binary

149   VLE, freezing point depression data and excess enthalpy data to regress of the refined e-NRTL

150   model interaction parameters.

151   Table 2. Different thermodynamic models used in this study

Model parameter	Reference for the model/correlation	Case Name
Thermodynamic models	(1) e-NRTL model: Putta et al. (2016)	TD1
	(2) extended-UNIQUAC model: Aronu et al. (2011)	TD2
	(3) refined e-NRTL model: Hessen et al. (2010)	TD3
	(4) e-NRTL-RK model: Aspen Technology, Inc. (2015)	TD4

152

153 2.2 Henry's law coefficient correlations or methods for CO_2 in MEA solution

154 In general, Henry's law coefficient of CO_2 in aqueous MEA solution has been calculated using

155 simple empirical correlations using N_2O analogy or rigorous thermodynamic models

156 (UNIQUAC or e-NRTL). Due to reactivity of acid gases with alkanolamine solutions, the direct

157 measurement of the physicochemical properties (free-gas solubility and the diffusivity of CO_2 in

158 amine solutions) is impossible. This has led to use of physicochemical properties data of similar

159 non-reacting gases to measure the properties of CO_2 ((Clarke, 1964; Hartono et al., 2014;

160 Bensetiti et al., 1999; Wang et al., 1992; Jiru et al., 2012; Lee et al., 2006; Li and Lai, 1995; Lee

161 et al., 2006; Li and Lee, 1996; Mandal et al., 2005, 2005, 2004, 2004; Monteiro and Svendsen,

162 2015; Samanta et al., 2007; Sema et al., 2012; Seo et al., 2011; Tsai et al., 2000; Versteeg and

163 Van Swaalj, 1988). Due to molecular similarities (structure and properties), the analogy with

164 N_2O is widely applied for estimation of CO_2 properties and has been referred to as the "N_2O

165 analogy". Clarke (1964) assumed that at constant temperature the ratios of CO_2 and N_2O

166 solubilities and diffusivities in water and in aqueous solutions of organic solvents are similar

167 within 5%. As per N_2O analogy, the equations for estimation of solubility/Henry's law constant

168 (=1/solubility) of CO_2 in aqueous amine solutions can be written as shown in equation (1):

169 $$He_{CO2\_amine} = \left(\frac{He_{CO2\_water}}{He_{N_2O\_water}} \right) He_{N_2O\_amine} \qquad (1)$$

170   N_2O solubility in aqueous MEA solutions was estimated using various empirical correlations

171   developed using experimental solubilities and using this solubility in N_2O analogy CO_2 henry's

172   law coefficient was estimated in amine solutions. As reported by Llano-Restrepo and Araujo-

173   Lopez (2015), no correlation or method stands out to be the most frequently used. Hence the

174   impact of these kinds of methods or correlations must be studied in detail. The correlations or

175   methods used in this study are listed in table 3.

176   Table 3. Henry's law constant calculation methods or correlations

Correlation source	Case name	Validity range			Remarks
		MEA (mass %)	CO_2 loading	T (°C)	
Hartono et al. (2014)	H1	0 - 100	0-0.5	25-100	Validated against different literature sources
Tsai et al. (2000)	H2	6.2 - 37 (1-6 M)	0	15-75	valid for unloaded solutions
Wang et al. (1992)	H3	100	0	20-85	Validated with data at 15 and 25 °C
		6.2 - 37 (1-6 M)	0	15-25	
Yaghi and Houache (2008)	H4	5 - 30	0	20-60	valid for unloaded solutions
Jiru et al. (2012)	H5	0-100	0	25-50	Validated with 18 and 30 mass% literature data in unloaded solutions
Aspen Technology,	H6	0-100	0-0.5	40-120	e-NRTL- RK model and validated P_{CO2} data for 18 and 30 mass%

Inc. (2015) (Aspen plus V8.6 template)					MEA solution
Aronu et al. (2010) extended- UNIQUAC model	H7	15-60	0-0.5	40-120	Validated with 30 mass% literature data in CO$_2$ loaded MEA solutions
Hessen et al. (2010) refined e-NRTL model	H8	15-60	0-0-5	40-120	validated with literature P$_{CO2}$ data for 30 mass% MEA solution
Putta et al. (2016) e-NRTL model	H9	15-60	0-0-5	40-120	validated with literature P$_{CO2}$ data for 30 mass% MEA solution

177

178   2.2 Transport property calculation methods or correlations

179   Two kinds of approaches, namely, N$_2$O analogy and modified Stokes-Einstein correlation, were

180   used for calculating the diffusivity of CO$_2$ in the liquid phase. Diffusivity correlations, based on

181   modified Stokes-Einstein relation, given by Versteeg and van Swaaij (1988) and Versteeg et al.

182   (1996) were more often used in literature. N$_2$O diffusivity correlations (developed using

183   experimental N$_2$O diffusivities) given by Ko et al. (2000), Jamal (2002) were also used in

184   literature. Recently Ying and Eimer (2012) developed new correlation for N$_2$O diffusivity. N$_2$O

185   analogy (equation (2)) and Modified Stokes-Einstein correlation (equation (3)) for estimation

186   CO$_2$ diffusivity in amine solutions are given as

187    $$D_{CO_2\_amine} = \left(\frac{D_{CO_2\_water}}{D_{N_2O\_water}} \right) D_{N_2O\_amine} \qquad\qquad (2)$$

188 $$D_{CO_2\_amine} = D_{CO_2\_water} \left(\frac{\mu_{amine}}{\mu_{water}} \right)^{-0.8} \hspace{2cm} (3)$$

189 Viscosity (μ) of the amine solution is used in the calculation of pressure drop and interfacial area

190 of the packing in addition to the calculation of diffusivities (Modified Stokes-Einstein

191 correlation, equation (3)). Different correlations have been developed based on experimental

192 solution viscosity data and these correlations have been used in simplified and also rate-based

193 simulation models. As mentioned earlier, the uncertainty in calculation of interfacial area is very

194 high, so it's difficult to assess the impact of different correlations. In this study the impact of

195 different viscosity estimation correlations on the performance is evaluated by using these

196 correlations in the calculation of diffusivities using equation (3). As per the review done by

197 Llano-Restrepo and Araujo-Lopez (2015), 66% of the works used Weiland et al. (1998)

198 correlation for the calculation of viscosity of the liquid phase. Recently Hartono et al. (2014) and

199 Morgan et al. (2015) proposed/updated the correlations for calculation of solution viscosity. All

200 these correlations were validated using CO_2 loaded MEA viscosity data. In this study, these

201 three correlations were used to study the effect of viscosity parameter estimation correlations.

202

203 Table 4. Overview of Correlations of N_2O diffusivity in amine solutions and/or solution viscosity correlations used

204 for CO_2 diffusivity calculation

Source of correlation	Case name	Temperature range [K]	Concentration range [mol/L]	CO_2 loading [mol/mol]	Remarks
N_2O analogy (equation (2))					
Ko et al. (2000)	DC1 (base case)	303-313	1 - 5	0	Valid for unloaded solutions up to 313 K.
Jamal (2002)	DC2	298-313	0 - 5	0	Valid only up to temperatures

					of 313 K. for unloaded solutions
Ying and Eimer (2012)	DC3	298-333	0 - 12	0	Valid for unloaded solutions
Modified Stokes-Einstein correlation (equation (3)) with different viscosity models					
Hartono et al. (2014)	DC4	298-353	0-pure MEA	0 – 0.5	-
Weiland et al. (1998)	DC5	298	1..6 – 6.5	0 - 0.5	Valid at 298 K
Morgan et al. (2015)	DC6	298-353	3.3 – 6.5	0 - 0.5	-

205

206   2.3 reaction rate kinetic models

207   In rate-based process modelling of a reactive absorption, kinetics plays a key role. For CO_2

208   absorption using aqueous MEA solutions, two different reaction mechanisms, namely,

209   Zwitterion mechanism and direct (termolecular) mechanism, were used to develop rate equation.

210   Detailed information about the reaction mechanisms is reviewed several researchers (Aboudheir

211   et al., 2003; Luo et al., 2012; Vaidya and Kenig, 2010, 2007; Versteeg et al., 1996), so it's not

212   presented here. We are interested in rate equations developed for CO_2-MEA system and their

213   validity and effect of their actual usage in simulation studies. It's observed that investigators in

214   CO_2 capture with aqueous MEA solutions, often use the kinetic models from the literature (for

215   example Hikita et al. (1977, 1979) and Versteeg et al. (1996) kinetic models (Kin1 and Kin2))

216   outside their validity range (in terms of temperature, amine concentrations and also CO_2

217   loading). Different kinds of rate expressions used in this study are listed below.

218   *Hikita et al. (1977, 1979) kinetic model:*

219   In CO_2 absorption into aqueous MEA solutions, two overall reactions were considered by Hikita

220   et al. (1977, 1979).

221     $CO_2 + 2MEA \leftrightarrow MEAH^+ + MEACOO^-$ (4)

222     $CO_2 + MEACOO^- + H_2O \leftrightarrow MEAH^+ + 2HCO_3^-$ (5)

223   In industrial absorption columns, due to short contact times between gas and liquid, the effect of

224   reaction (5) was neglected and reaction (4) occurs in two steps.

225     $CO_2 + MEA \leftrightarrow H^+ + MEACOO^-$ (6)

226     $H^+ + MEA \leftrightarrow MEAH^+$ (7)

227   Protonation reaction (7) was assumed to be instantaneous and reaction (6) was assumed second

228   order. The reaction rate equation was given as
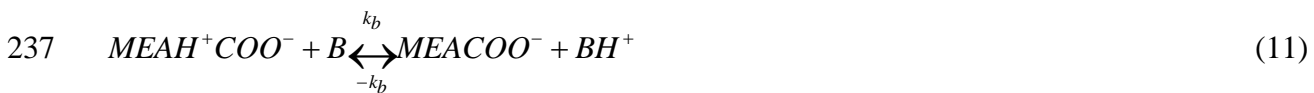
229     $R_{CO_2} = k_2[\text{MEA}][\text{CO}_2]$ (8)

230   Here k_2 is second order reaction rate constant and expressed as

231     $\log_e(k_2) = 10.99 - \dfrac{2152}{T}$ (9)

232   ***Versteeg et al. (1996) kinetic model:***

233   Versteeg et al. (1996) used zwitterion mechanism to evaluate CO_2 absorption into MEA. As per

234   zwitterion mechanism, the reaction between CO_2 and alkanolamine proceeds via the formation of

235   zwitterion followed by the deprotonation by a base.

236     $CO_2 + MEA \underset{-k_2}{\overset{k_2}{\longleftrightarrow}} MEAH^+COO^-$ (10)

237     $MEAH^+COO^- + B \underset{-k_b}{\overset{k_b}{\longleftrightarrow}} MEACOO^- + BH^+$ (11)

238   Versteeg et al. (1996) assumed for CO_2 reaction with aqueous MEA solution, the overall reaction

239   order as two based on zwitterion mechanism, i.e., zwitterion formation reaction (equation (10))

240   as the rate determining step.

241   The reaction rate is expressed as:

242    $R_{CO_2} = k_2[\text{MEA}][\text{CO}_2]$ (12)

243   Where k_2 is second order reaction rate constant and expressed as Arrhenius type of equation in

244   temperature

245    $k_2 = 4.4 x 10^8 \exp(-\dfrac{5400}{T})$ (13)

246   ***Aboudheir et al. (2003) kinetic model:***

247   Direct (termolecular) mechanism was used to determination reaction kinetic between CO_2 and

248   aqueous MEA solution. As per the termolecular mechanism, the bond formation and proton

249   transfer to the base take place simultaneously in a single step and the reaction order is three as

250   per this mechanism.

251    $CO_2 + MEA + B \leftrightarrow MEACOO^- + BH^+$ (14)

252   Here B represents bases present in the solution. Aboudheir et al. (2003) considered MEA and

253   H_2O as main bases participating in the reaction (14). The overall reaction rate is given as

254    $R_{CO_2} = \left(k_{MEA,c}[MEA] + k_{H_2O,c}[H_2O]\right)\left[[MEA][CO_2] - \dfrac{1}{K_{eq}}\left(MEACOO^-\right)\left(H_3O^+\right)\right]$ (15)

255   Where,

256    $k_{MEA,c} = 4.61 x 10^9 \exp(-\dfrac{4412}{T})$ (16)

257    $k_{H_2O,c} = 4.55 x 10^6 \exp(-\dfrac{3287}{T})$ (17)

258

259   ***Aspen Plus V8.6 kinetic model:***

260 The kinetic constants of reaction (18) were estimated from Hikita et al. (1977) and for reaction

261 (19) were calculated using the equilibrium constants of the reversible reactions (18) and (19)

262 and kinetic constants of reaction (18). The reactions considered in Aspen Plus are given in

263 equations (18) and (19).

264 $$CO_2 + MEA + H_2O \xrightarrow{k_{18}} MEACOO^- + H_3O^+ \tag{18}$$

265 $$MEACOO^- + H_3O^+ \xrightarrow{k_{19}} CO_2 + MEA + H_2O \tag{19}$$

266 The reaction rate is expressed in terms of activities as

267 $$R_{CO_2} = k \prod_i^N (\gamma_i x_i)^\nu \tag{20}$$

268 Where, γ, x, ν are activity coefficient, mole fraction and stoichiometric coefficient of component

269 'i' in the reaction respectively and N is number of components in the reaction.

270 For reaction (18) and (19) are the corresponding kinetic constants were given as (Aspen

271 Technology, Inc., 2015):

272 $$k_{18} = 3.02x10^{14} \exp(-\frac{4959.6}{T}) \tag{21}$$

273 $$k_{19} = 5.52x10^{23} \exp(-\frac{8312.2}{T}) \tag{22}$$

274 ***Luo et al. (2015) kinetic models:***

275 The chemical reactions considered by Luo et al. (2015) for describing the CO_2 absorption into

276 aqueous MEA system are written as:

277 Reaction (18) given above was considered for CO_2-H_2O-MEA. In addition to this reaction of

278 H_3O^+ with MEA is written as:

279 $$MEA + H_3O^+ \rightarrow MEAH^+ + H_2O \tag{23}$$

280 The overall reaction can be written by adding equations (18) and (23) as:

281 $$CO_2 + 2MEA \rightarrow MEACOO^- + MEAH^+ \tag{24}$$

282 Reaction rate equation considered by Luo et al. (2015) for estimation of reaction kinetics was

283 considered as:

284
$$R_{CO_2} = \left(k_{MEA,c}[MEA] + k_{H_2O,c}[H_2O]\right)\{[MEA][CO_2]\}$$
$$= \left(k_{MEA,a}\, g_{MEA}[MEA] + k_{H_2O,a}g_{H_2O}[H_2O]\right)\{g_{MEA}[MEA]g_{CO_2}[CO_2]\} \tag{25}$$

285 The kinetic constants for concentration based (with subscript 'c') and activity based (with

286 subscript 'a') models were given as:

287 $$k_{MEA,c} = 2.003x10^{10}\exp(-\frac{4742}{T}) \tag{26}$$

288 $$k_{H_2O,c} = 4.147x10^6\exp(-\frac{3110}{T}) \tag{27}$$

289 $$k_{MEA,a} = 1.844x10^{10}\exp(-\frac{4112}{T}) \tag{26}$$

290 $$k_{H_2O,a} = 2.064x10^5\exp(-\frac{1766}{T}) \tag{27}$$

291 ***Putta et al. (2016) kinetic models:***

292 Direct reaction mechanism was used in the development of kinetic models. The base

293 contributions of both MEA and H_2O were considered and the reactions were same as given in

294 equation (14). The reversibility of both reactions was also considered.

295 The reaction rates were given as:

296
$$r_{CO_2\_MEA} = k_{MEA,c}[MEA]^2[CO_2] - \left(\frac{k_{MEA,c}}{K_{eq,CO_2\_MEA,c}}\right)[MEAH^+][MEACOO^-]$$
$$= k_{MEA,a}\, g_{MEA}^2[MEA]^2 g_{CO_2}[CO_2] - \left(\frac{k_{MEA,a}}{K_{eq,CO_2\_MEA,a}}\right)g_{MEAH^+}[MEAH^+]g_{MEACOO^-}[MEACOO^-] \tag{28}$$

297
$$r_{CO_2\_H_2O} = k_{H_2O,c}\,[H_2O][MEA][CO_2] \left(\dfrac{k_{H_2O,c}}{K_{eq,CO_2\_H_2O,c}}\right)[H_3O^+][MEACOO^-]$$

$$= k_{H_2O,a}g_{H_2O}[H_2O]g_{MEA}[MEA]g_{CO_2}[CO_2] \left(\dfrac{k_{H_2O,a}}{K_{eq,CO_2\_H_2O,a}}\right)g_{H_3O^+}[H_3O^+]g_{MEACOO^-}[MEACOO^-]$$

298 　　　　(29)

299 The kinetic constants for concentration based and activity based models were given as:

300 $\quad k_{MEA,c} = 3.1732 \times 10^9 \exp(-\dfrac{4936.6}{T})$ （30）

301 $\quad k_{H_2O,c} = 1.0882 \times 10^8 \exp(-\dfrac{3900}{T})$ （31）

302 $\quad k_{MEA,a} = 4.5191 \times 10^{11} \exp(-\dfrac{5851.7}{T})$ （32）

303 $\quad k_{H_2O,a} = 2.1105 \times 10^6 \exp(-\dfrac{2382.4}{T})$ （33）

304 The validity range of above mentioned kinetic models is shown in table 5.

305

306 Table 5. Validity of kinetic models considered in this study

Source/ Kinetic model	Case name	Temperature range [K]	Concentration range [mol/L]	CO_2 loading [mole CO_2/mole MEA]	Remarks
Hikita et al. (1977, 1979)	Kin1	288-318	0.0152-0.177	0	Valid at low MEA concentrations and for unloaded solutions
Versteeg et al. (1996)	Kin2	278-313	0 - 4.8	0	Pseudo first order assumed and valid

					only up to temperatures of 313 K.
Aboudheir et al. (2003)	Kin3	293-333	3 - 9	0 - 0.5	Kent-Eisenberg thermodynamic model was used
Aspen Plus V8.6	Kin4	293-393	N. A	0 – 0.5	Estimated using Hikita et al. (1977) model
Luo et al. (2015)	Kin5	293-343	0.5 - 5	0 - 0.4	Pseudo first-order assumption
Putta et al. (2016)	Kin6	293-343	0.5 – 5 *c 0.5 – 9 *a	0 - 0.5	Concentration based model is valid up to 5 M MEA only

307   *c- Concentration based kinetic model, *a-activity based kinetic model

308

309   2.4 Using Aspen Plus thermodynamic model and properties

310   In research, often investigators use the published kinetic models in commercial software tool like

311   Aspen Plus, Hysys for parametric study, performance evaluation and investigation of optimal

312   process configurations as a part of process development. In order to see the impact of using

313   kinetic models available in literature with Aspen Plus thermodynamic model and properties,

314   frequently used kinetic models (Hikita et al. (1977, 1979), Versteeg et al. (1996), Aboudheir et

315   al. (2003)) and recently developed kinetic models (Putta et al. (2016) both activity and

316   concentration based) were used. In addition to these activity and concentration based kinetic

317   models given Aspen Plus V8.6 were also used to see model prediction ability of experimental

318   data.

319   3. Results and discussion

320   Above mentioned different models/correlations for estimation of model parameters in process

321   simulation were implemented into penetration theory based absorption model and the impact of

322   them on model predictions was calculated. In all the sub-studies, the impact of using different

323   methods and correlations was compared with base case. The methods and correlations used in

324   the base are given in table 6.

325

326   Table 6. Base case: parameter estimation models/correlations

Model parameter	Case name	Reference for the model/correlation
Thermodynamic method	TD1	e-NRTL model: Putta et al. (2016)
Kinetic model	Kin6	Penetration theory based kinetic model: Putta et al. (2016)
Henry's law constant of CO_2	H9	e-NRTL model: Putta et al. (2016)
Diffusivity of CO_2 in amine solutions	DC1	Ko et al. (2000) correlation based on N_2O analogy

327

328   In following sections, we will discuss the impact of these models/correlations on simulations

329   results in detail.

330   3.1   Impact of changing thermodynamic model

331   To study the impact of thermodynamic model on the performance of the absorber, only

332   thermodynamic model was changed and all other parameter correlations kept same as in the base

333   case.

334   Table 7. The impact of changing thermodynamic model on model predictions for different experimental source data

Thermody namic model	AARD (%)							
	Concentrations based kinetics simulation model				Activity based kinetics simulation model			
	Luo et al. (2012, 2015)		Puxty et al. (2010)	Aboudheir (2002)	Luo et al. (2012, 2015)		Puxty et al. (2010)	Aboudheir (2002)
	SDC	WWC	WWC	LAM.JET	SDC	WWC	WWC	LAM.JET
Base case (TD1)	**14.4**	**13.9**	**12.4**	**13.1**	**18.9**	**14.8**	**13.8**	**10.1**
TD2	14.5	13.9	17.9	14.1	19.1	14.2	19.4	9.2
TD3	32.0	25.9	32.6	30.9	26.4	20.9	28.6	17.8
TD4	35.3	12.8	37.1	13.5	27.7	12.2	27.6	13.8

335

336 From the table above, the degree of impact of the thermodynamic model depends on the type of

337 the simulation model used (concentrations or activity based) and experimental data conditions

338 used for. The base case thermodynamic model (Putta et al. (2016) e-NRTL model) (TD1), and

339 extended-UNIQUAC model by Aronu et al. (2011) (TD2) were developed (fitted) using the same

340 experimental VLE data but with different type of model (e-NRTL/extended UNIQUAC). The

341 extended UNIQUAC (Aronu et al. (2011)) (TD2) predicted same as the base case for Luo et al.

342 (2012, 2015) SDC and WWC data and Aboudheir (2002) laminar jet data. However, in case of

343 Puxty et al. (2010) WWC data, extended UNIQUAC (Aronu et al. (2011)) (TD2) predicted with

344 AARD of 6% higher than the base case in both activity and concentrations based models and

345 these deviations were found to be at loading 0.5. Hessen et al. (2010) refined e-NRTL model

346 (TD3) gives large deviations (AARDS: 12 -18 % more compared to base case) for data from all

347 the sources used in this study and the deviations decrease in activity based model (AARDS: 6.5 -

348 14.8 % more than the base case). Aspen Plus V8.6 (Aspen Technology, Inc. (2015)) e-NRTL-RK

349 model (TD4) improved model predictions than the base case for Luo et al. (2012, 2015) WWC

350   data in concentrations based simulation model and predicted with almost same accuracy (AARD)

351   as base case for Aboudheir (2002) laminar jet data. However, with the same Aspen Plus V8.6 e-

352   NRTL-RK model (TD4), the model predicted deviations (AARD) were more than 20% than the

353   base case for Luo et al. (2012, 2015) SDC and Puxty et al. (2010) WWC data in concentrations

354   based model and the deviations (AARD) were 9-14% more than the base case in activity based

355   model.

356   From the detailed analysis of the simulation results, it was found that the quality and type of

357   experimental data used for thermodynamic model development has more impact than the type of

358   model (UNIQUAC/e-NRTL). With Aspen Plus V8.6 e-NRTL-RK model (TD4), it was found

359   that the model deviations were lower at high CO_2 loadings (>0.15) in the activity based model.

360

361   3.2   Impact of changing Henry's law constant model/correlation

362   In order to find the impact of Henry's law constant model/correlation on the performance of the

363   absorber, only Henry's law constant estimation correlation/model was changed and all other

364   parameter correlations kept same as in the base case. In this part equilibrium concentrations

365   (VLE) and activity coefficients were determined same as in base case for all the cases in Table 8.

366   The correlations/models used in this work were listed in table 3. The AARDs of simulation

367   predictions by using different CO_2 Henry's law constant (in MEA) estimation correlations are

368   listed in table 8.

369

370   Table 8. The impact of changing CO_2 Henry's law constant estimation correlation on model predictions for different

371   experimental data

H_CO$_2$	AARD (%)	
(kPa/kmo	Concentrations based kinetics simulation model	Activity based kinetics simulation model

l-m^3)	Luo et al. (2012, 2015)		Puxty et al. (2010)	Aboudheir (2002)	Luo et al. (2012, 2015)		Puxty et al. (2010)	Aboudheir (2002)
	SDC	WWC	WWC	LAM.JET	SDC	WWC	WWC	LAM.JET
Base case (H9)	**14**	**13**	**12**	**13**	**19**	**15**	**14**	**10**
H1	12	15	15	16	16	15	15	12
H2	44	15	48	14	50	18	55	20
H3	123	42	225	69	129	40	235	71
H4	61	18	73	28	68	21	82	34
H5	64	22	83	30	72	25	93	36
H6	42	13	36	15	47	16	42	20
H7	14	14	12	14	19	14	13	10
H8	33	26	34	31	37	28	37	32

372

373 From the above table, it was seen that Henry's law constant estimation with Hartono et al. (2014)

374 empirical correlation (H1) and Aronu et al. (2010) extended-UNIQUAC model (H7) predicted

375 with almost same accuracy as base case (Puxty et al. (2010) e-NRTL model). Wang et al. (1992)

376 correlation (H3) found to give highest deviations when used in simulation model among all the

377 models and correlations used in this study. Wang et al. (1992) correlation (H3) was developed

378 for unloaded MEA solutions and at low temperatures (15°C -25°C).It was found from the

379 experimental Henry's law for CO_2, Wang et al. (1992) correlation (H3) gave under predictions

380 for temperatures above 323 K even for unloaded 1 M MEA solution and predicted CO_2 henry's

381 law constant was around 55-60% of experimental value at high loadings. This means that the

382 Wang et al. (1992) model (H3) is not valid at high temperatures and for loaded solutions. Tsai et

383 al. (2000) correlation (H2) always under predicts the experimental CO_2 Henry's law constant

384   even for unloaded MEA solutions and deviations were more at high loadings. When this

385   correlation (H2) was used in the model, the simulation predictions were found to have similar

386   deviations as base case for Luo et al. (2012, 2015) WWC data and Aboudheir (2002) laminar jet

387   absorber data whereas the deviations were about 3 – 4 times more than that of the base case for

388   Luo et al. (2012, 2015) SDC data and Puxty et al. (2010) WWC data in case of concentrations

389   based simulation model. Maximum deviations were seen at high loadings (0.4-0.5) and low

390   driving forces in case of for Luo et al. (2012, 2015) SDC data and Puxty et al. (2010) WWC

391   data. Hessen et al. (2010) refined e-NRTL model based CO_2 henry's law (H8) values when used

392   in the simulation, the predictions were found have AARDs about 26 – 37% for all the data from

393   all sources. Both Yaghi and Houache (2008) (H4) and Jiru et al. (2012) (H5) correlations were

394   found to give higher deviations (AARDs) for all the data than the base case. Also higher

395   deviations were seen for Luo et al. (2012, 2015) SDC data and Puxty et al. (2010) WWC data

396   than other sources data as clearly seen from Table 8. With Henry's law constant from Aspen plus

397   V8.6 (Aspen Technology, Inc. (2015)) (H6) , the predicted absorption rates found to have same

398   AARDs as in base case for Luo et al. (2012, 2015) WWC data and Aboudheir (2002) laminar jet

399   absorber data whereas the deviations were about 3 times more than that of the base case for Luo

400   et al. (2012, 2015) SDC data and Puxty et al. (2010) WWC data in case of concentrations based

401   simulation model. In the activity based model, for Aboudheir (2002) laminar jet absorber data

402   the AARD found to be 2 times the base case. With all Henry's law constant correlations/models

403   except Hartono et al. (2014) correlation (H1) and Aronu et al. (2010) extended-UNIQUAC

404   model (H7), the simulation was not able to represent the desorption which was found in base

405   case. This shows clearly that henry's law constant has huge impact on model performance. When

406   Henry's law constant is estimated using thermodynamic model, it is essential to fit the model

407   using physical solubility data of CO_2. The effect of using CO_2 solubility data in fitting can be

408   clearly seen with Hessen et al. (2010) refined e-NRTL model based CO_2 henry's law (H8)

409   (where CO_2 solubility is not used in the model fitting) and Aronu et al. (2010) extended-

410   UNIQUAC model (H7) (where solubility data is used).

411   3.3   Impact of changing reaction rate kinetic model

412   In order to find the impact of reaction rate kinetic models on the performance of the absorber,

413   only kinetic model was changed and all other parameter correlations kept same as in the base

414   case. In this study, the kinetic models that have been used in literature widely and also newly

415   proposed kinetic models (listed in table 5) were used to assess the degree of influence on the

416   simulation results. The AARDS of the predicted results by using the different kinetic models are

417   shown in table 9.

418

419   Table 9. The impact of changing reaction rate kinetic models on simulation predictions

Kinetic model	AARD (%)							
	Concentrations based kinetics simulation model				Activity based kinetics simulation model			
	Luo et al. (2012, 2015)		Puxty et al. (2010)	Aboudheir (2002)	Luo et al. (2012, 2015)		Puxty et al. (2010)	Aboudheir (2002)
	SDC	WWC	WWC	LAM.JET	SDC	WWC	WWC	LAM.JET
Base case (Kin6)	**14**	**13**	**12**	**13**	**19**	**15**	**14**	**10**
Kin1	18	22	41	25				
Kin2	19	20	42	22				
Kin3	16	22	33	30				

Kin4	22	25	264	30	28	42	51	38
Kin5	22	14	35	21	34	14	45	17

420

421 As can be seen from the above table, depending on the process conditions the errors in models

422 predictions can be very large. Hence when these models are used in the performance evaluation

423 of the pilot or industrial scale data, the interpretations can be very different from the actual

424 performance and can be worse if the simulations are used for scale up to an industrial scale. Both

425 Hikita et al. (1977, 1979) and Versteeg et al. (1996) kinetic models (Kin1 and Kin2) predict

426 experimental CO_2 absorption rates with almost same accuracy (AARD).Both kinetic models

427 (Kin1 and Kin2) were able to predict Luo et al. (2012, 2015) SDC and WWC data with AARDs

428 of 10% higher than the base case but Puxty et al. (2010) WWC data with AARD 3.5 times that

429 of base case and with of AARD almost 2 times the base case for Aboudheir (2002) laminar jet

430 absorber data. Aboudheir et al. (2003) kinetic model (Kin3) was developed using pure CO_2 in the

431 gas phase, i.e., without any gas phase resistance, with very small gas-liquid contact times (0.001-

432 0.015 s) and using simple Kent-Eisenberg thermodynamic model employing empirical

433 correlation for CO_2 solubility (Tsai et al., 2000). When this kinetic model (Kin3) is used for

434 systems with gas phase resistance (Luo et al. (2012, 2015) SDC and WWC) and long contact

435 times in combination with rigorous thermodynamic model (e-NRTL model: Putta et al. (2016)),

436 predicted simulation results have large error (almost double) even for the same data (Aboudheir

437 et al. (2003)) that was used in kinetic model (Kin3) development. This illustrates that extra error

438 can be introduced to the simulation predictions when certain kinetic model is used with different

439 VLE model.

440 Reaction kinetic models given in Aspen Plus V8.6 (Kin4) were used in this study but in the

441 combination of different thermodynamic model (TD1), both concentration based and activities

442 based kinetic model predictions gave large deviations (AARDS). In another case Luo et al.

443 (2015) kinetic models (Kin5) developed with pseudo-first order reaction assumption using Aronu

444 et al. (2010) extended-UNIQUAC thermodynamic model (TD2). As seen section 3.1, both base

445 case thermodynamic model (TD1) and Aronu et al. (2010) extended-UNIQUAC model (TD2)

446 were developed using same experimental data and gave almost same predictions as base case

447 except for CO_2 desorption cases. From the tables 7 and 9, it is seen that even though the

448 thermodynamic model is same, the error introduced by using the kinetic model based pseudo-

449 first order assumption (Kin5) is larger than with the kinetic model developed without pseudo-

450 first order assumption (Kin6). Large deviations were observed at high CO_2 loading (>

451 0.4mol/mol). Overall, it can be concluded that none of the kinetic models were able to predict

452 the experimental CO_2 absorption rates from all the apparatuses with same accuracy (AARD) as

453 the base case.

454 3.4   Impact of changing transport property correlations

455 In this section, the impact of different CO_2 diffusivity estimation correlations on model

456 predictions was studied by changing only the diffusivity correlations.

457 Table 10. The impact of changing CO_2 diffusivity correlations on simulation predictions

D_CO₂	AARD (%)							
	Concentrations based kinetics simulation model				Activity based kinetics simulation model			
in MEA model	Luo et al. (2012, 2015)		Puxty et al. (2010)	Aboudheir (2002)	Luo et al. (2012, 2015)		Puxty et al. (2010)	Aboudheir (2002)
	SDC	WWC	WWC	LAM.JET	SDC	WWC	WWC	LAM.JET
Base	14	14	12	13	19	15	14	10

case (DC1)								
DC2	27	12	22	12	31	13	27	12
DC3	13	15	12	16	17	16	13	13
DC4	16	23	26	36	17	24	25	35
DC5	14	22	23	33	17	23	23	31
DC6	14	22	23	32	17	23	23	31

458

459 It is observed that just by changing correlation for diffusivity of CO_2 in aqueous MEA solutions

460 from one correlation other correlation, the impact on the simulation predictions can vary

461 significantly depending on the amine concentration, CO_2 loading and temperatures as seen in

462 Table 10. Jamal (2002) correlation (DC2) predicts CO_2 diffusivity values higher than that of Ko

463 et al. (2000) correlation (DC1) and Versteeg et al. (1996) correlation based on modified Stokes-

464 Einstein correlation always predicts lower than the Ko et al. (2000) correlation (DC1).By using

465 Jamal (2002) correlation (DC2) instead of Ko et al. (2000) correlation (DC1), the change in the

466 AARDs of simulation results is found to be around 10-13% for Luo et al. (2012, 2015) SDC and

467 Puxty et al. (2010) WWC data and for Luo et al. (2012, 2015) WWC and Aboudheir (2002)

468 laminar jet absorber data, the difference in AARDs is insignificant (around 1-2 %). Ying and

469 Eimer (2012) correlation (DC3) predicted with same accuracy as the base case (DC1) (Maximum

470 difference in AARDs is 3%). In the Versteeg et al. (1996) correlation itself, depending on the

471 viscosity model used, the simulation predictions can also vary and it was seen that from changing

472 viscosity model from Hartono et al. (2014) correlation (DC4) to Weiland et al. (1998) correlation

473 (DC5), the AARDs decreased by 3-5 %. Morgan et al. (2015) (DC6) and Weiland et al. (1998)

474 (DC5) viscosity correlations gave predictions with same AARD (difference is less than 0.5%).

475 The difference in simulation predictions by employing different liquid viscosity correlations in

476   CO_2 diffusivity estimation found to be less significant (difference in AARDs is less than 5%)

477   compared to difference in simulation predictions due to CO_2 diffusivity calculation using N_2O

478   analogy and modified Stokes-Einstein correlation (Maximum difference in AARDs is 25%).

479   Overall, it can be concluded that care should be taken while selecting or changing correlation and

480   basis (N_2O analogy/ modified Stokes-Einstein correlation) for diffusivity of CO_2 in amine

481   solutions.

482

483   3.5   Impact of changing different combinations of parameter estimation models/correlations

484   In the literature, it has been seen that kinetic models of Hikita et al. (1977, 1979), Versteeg et al.

485   (1996) and Aboudheir et al. (2003) were implemented in Aspen Plus to study the absorber

486   performance and also evaluation of pilot scale experimental data. So, we studied impact of

487   combination of these reaction rate kinetic models with Aspen Plus properties on the absorber

488   performance. i.e., Thermodynamic model and physical and transport properties are taken from

489   Aspen Plus V8.6 e-NRTL-RK template (calculation of equilibrium concentrations, activity

490   coefficients and henry's law constant of CO_2 in MEA solutions and diffusivities, density and

491   viscosity). In addition to the literature kinetic models, the recently developed kinetic models by

492   Putta et al. (2016) were also tested.

493

494   Table 11. The impact of using different kinetic models in combination with Aspen Plus properties on absorber

495   predictions

Reaction rate kinetic model	Case name	AARD (%)		Puxty et al. (2010)	Aboudheir (2002)
		Luo et al. (2012, 2015)			
		SDC	WWC	WWC	LAM.JET

Hikita et al. (1977, 1979)	SP1	28	23	71	14
Versteeg et al. (1996)	SP2	31	22	79	14
Aboudheir et al. (2003)	SP3	17	19	16	12
Aspen Plus V8.6 Concentrations based	SP4	22	21	38	14
Aspen Plus V8.6 activities based	SP5	27	39	33	32
Putta et al. (2016) Concentrations based	SP6	23	16	33	11
Putta et al. (2016) activities based	SP7	18	16	23	7

496

497   From table 11, it can be seen that when Hikita et al. (1977, 1979) is used in combination with

498   thermodynamic model and other properties from Aspen Plus V8.6, except for Aboudheir (2002)

499   laminar jet absorber data, the simulation predictions have higher deviations than the base case

500   and for Puxty et al.(2010) WWC data the simulation predictions have AARD above 70%. When

501   compared the ability of the same kinetic model (Kin1) but in combination with Putta et al. (2016)

502   thermodynamic model and corresponding physical properties correlations (Table 9, Kin1), the

503   deviations (AARDs) were smaller for Luo et al. (2012, 2015) SDC and Puxty et al.(2010) WWC

504   data. There is no clear trend in model predictions with the change of thermodynamic and

505   property models. The prediction capacity is same for Luo et al. (2012, 2015) WWC data.

506   Furthermore, as shown in Table 11, the same trend was observed for Versteeg et al. (1996)

507   kinetic model (Kin2). In case of Aboudheir et al. (2003) kinetic model (Kin3), the predictions

508   are better with Aspen plus thermodynamic model and properties than with the ones used in base

509   case and the same trend was seen for Aspen Plus kinetic models (Kin4), i.e., for both

510   concentrations based and activity based kinetic models. Concentration based kinetic model by

511   Putta et al. (2016) gave deviations (AARDs) of 9% and 21% higher with Aspen Plus

512   thermodynamic model and properties than the base case (Table 9, Kin6) for Luo et al. (2012,

513   2015) SDC and Puxty et al.(2010) WWC data respectively. Luo et al. (2012, 2015) WWC data

514 was predicted with almost same accuracy as in the base case (difference in AARD is less than

515 5%). Putta et al. (2016) activity based model in combination with Aspen Plus thermodynamic

516 model and properties predicts experimental absorption rates from Luo et al. (2012, 2015) SDC

517 and WWC with same accuracy as the base case (Table 9, Kin6) and the deviations (AARD) are

518 10% higher than that of base case for Puxty et al.(2010) WWC data. Both kinetics models by

519 Putta et al. (2016) predicted data from Aboudheir (2002) laminar jet absorber with better

520 accuracy than the base case. Overall, it can be concluded that by using kinetic models along with

521 Aspen Plus thermodynamic model and properties, the simulation predictions can be improved for

522 some kinetic models whereas the predictions became worse for some kinetic models when

523 compared with predictions in combination with Putta et al. (2016) e-NRTL model and properties

524 mentioned in table 6.

525 All the parameters calculation model and correlations studied in the present study have varying

526 degree of impact on the rate based model predictions. Among all, CO_2 Henry's law constant

527 calculation correlations/models have highest impact on the predicted CO_2 absorption rates.

528 Kinetic models selection affects the simulation predictions more than thermodynamic model and

529 diffusivity correlations of CO_2 in amine solutions. Thermodynamic models selection has lower

530 impact on the predicted results than CO_2 diffusivity correlations selection.

531

532 4   Conclusions

533 In the present study, different thermodynamic models, CO_2 Henry's law constant correlations,

534 reactions rate kinetic models and CO_2 diffusivity correlations are applied to the rate based model.

535 The impact of using different models and correlations for the same property on the model

536 predictions is studied in detail. Experimental data from four different apparatuses with wide

537 range of process conditions is used to assess the impact of different models and correlations.

538 When the thermodynamic model is changed, it was seen that model prediction capacity can vary

539 greatly. The effect is more at high loadings and low CO_2 partial pressures. By keeping all other

540 parameters same as base case and when only changed the CO_2 Henry's law constant estimation

541 correlation/method, it was seen that the error in model predictions can be very large depending

542 on the correlation used. So the correlation prediction ability should be assessed or validated

543 before employing them in the simulations. From this study, we can clearly say that the one

544 should always be careful while using only kinetic model from published literature in the in-house

545 or commercial process simulators without taking all other parameters (physic-chemical and

546 thermodynamic properties) used in the kinetic model development as it can be seen that due to

547 many different reasons the predicted results can be very uncertain.

548 In this study of evaluating the different kinetic models prediction capacity, it was seen that most

549 of the kinetic models existing in the literature fail to represent the experimental CO_2 absorption

550 data from all the sources with same accuracy. In most of the cases, the models are able to predict

551 the experimental data from one source with good accuracy but fail to predict with same accuracy

552 from other sources. Also while evaluating the impact of CO_2 diffusivity correlations on the

553 model performance, it was seen that N_2O analogy gives better representation of the experimental

554 data compared to modified Stokes-Einstein correlation. From the present study, it is observed

555 that there are risks of introducing large errors to model predictions just by simply using different

556 property estimation correlation than the ones used initially in original model development. A

557 great caution is required while selecting the correct combination of property

558 methods/correlations. The following steps should be followed in order to evaluate the additional

559 errors in the model predictions is

560   (a) The deviation in that particular property value due to new correlation should be

561   quantified over the range of process conditions.

562   (b) Developer should quantify the error introduced to the predictions due to different

563   property correlation selection

564   (c) The model should be validated with experimental data

565   (d) Steps (a)-(c) should be followed for every property correlation changed.

566

References

Aboudheir, 2002. Kinetics, modeling, and simulation of carbon dioxide absorption into highly concentrated and loaded monoethanolamine solutions (Ph.D). University of Regina, Canada, Regina.

Aboudheir, A., Tontiwachwuthikul, P., Chakma, A., Idem, R., 2003. Kinetics of the reactive absorption of carbon dioxide in high CO2-loaded, concentrated aqueous monoethanolamine solutions. Chem. Eng. Sci. 58, 5195–5210. doi:10.1016/j.ces.2003.08.014

Abu-Zahra, M.R.M., Schneiders, L.H.J., Niederer, J.P.M., Feron, P.H.M., Versteeg, G.F., 2007. CO2 capture from power plants: Part I. A parametric study of the technical performance based on monoethanolamine. Int. J. Greenh. Gas Control, 8th International Conference on Greenhouse Gas Control Technologies GHGT-8 1, 37–46. doi:10.1016/S1750-5836(06)00007-7

Afkhamipour, M., Mofarahi, M., 2014. Sensitivity analysis of the rate-based CO2 absorber model using amine solutions (MEA, MDEA and AMP) in packed columns. Int. J. Greenh. Gas Control 25, 9–22. doi:10.1016/j.ijggc.2014.03.005

Aronu, U.E., Gondal, S., Hessen, E.T., Haug-Warberg, T., Hartono, A., Hoff, K.A., Svendsen, H.F., 2011. Solubility of CO2 in 15, 30, 45 and 60 mass% MEA from 40 to 120 °C and model representation using the extended UNIQUAC framework. Chem. Eng. Sci., Novel Gas Conversion Symposium- Lyon 2010, C1-C4 Catalytic Processes for the Production of Chemicals and Fuels 66, 6393–6406. doi:10.1016/j.ces.2011.08.042

Aronu, U.E., Svendsen, H.F., Hoff, K.A., 2010. Investigation of amine amino acid salts for carbon dioxide absorption. Int. J. Greenh. Gas Control 4, 771–775. doi:10.1016/j.ijggc.2010.04.003

Aspen Technology, Inc., 2015. Rate-based model of the CO2 capture process by MEA using Aspen Plus. Burlington (USA); 2015.

Bensetiti, Z., Iliuta, I., Larachi, F., Grandjean, B.P.A., 1999. Solubility of Nitrous Oxide in Amine Solutions. Ind. Eng. Chem. Res. 38, 328–332. doi:10.1021/ie980516f

Clarke, J.K.A., 1964. Kinetics of Absorption of Cardon Dioxide in Monoethanolamine Solutions at Short Contact Times. Ind. Eng. Chem. Fundam. 3, 239–245. doi:10.1021/i160011a012

Hartono, A., Mba, E.O., Svendsen, H.F., 2014. Physical Properties of Partially CO2 Loaded Aqueous Monoethanolamine (MEA). J. Chem. Eng. Data 59, 1808–1816. doi:10.1021/je401081e

Hessen, E.T., Bakhtiary-Davijany, H., Myhrvold, T., 2013. Process Modelling in Risk-based Qualification of Large-scale CO2 Absorption Processes. Energy Procedia, GHGT-11 37, 2802–2810. doi:10.1016/j.egypro.2013.06.165

Hessen, E.T., Haug-Warberg, T., Svendsen, H.F., 2010. The refined e-NRTL model applied to CO2–H2O–alkanolamine systems. Chem. Eng. Sci. 65, 3638–3648. doi:10.1016/j.ces.2010.03.010

Hikita, H., Asai, S., Ishikawa, H., Honda, M., 1977. The kinetics of reactions of carbon dioxide with monoethanolamine, diethanolamine and triethanolamine by a rapid mixing method. Chem. Eng. J., An International Journal of Research and Development 13, 7–12. doi:10.1016/0300-9467(77)80002-6

Hikita, H., Asai, S., Katsu, Y., Ikuno, S., 1979. Absorption of carbon dioxide into aqueous monoethanolamine solutions. AIChE J. 25, 793–800. doi:10.1002/aic.690250507

Jamal, A., 2002. Absorption and desorption of CO2 and CO in alkanolamine systems. (PhD Thesis). University of British Columbia, Vancouver, B.C.

Jiru, Y., Eimer, D.A., Wenjuan, Y., 2012. Measurements and Correlation of Physical Solubility of Carbon Dioxide in (Monoethanolamine + Water) by a Modified Technique. Ind. Eng. Chem. Res. 51, 6958–6966. doi:10.1021/ie3002588

Kenig, E. y., Kucka, L., Górak, A., 2003. Rigorous Modeling of Reactive Absorption Processes. Chem. Eng. Technol. 26, 631–646. doi:10.1002/ceat.200390096

Khan, F.M., Krishnamoorthi, V., Mahmud, T., 2011. Modelling reactive absorption of CO2 in packed columns for post-combustion carbon capture applications. Chem. Eng. Res. Des., Special Issue on Carbon Capture & Storage 89, 1600–1608. doi:10.1016/j.cherd.2010.09.020

Ko, J.-J., Tsai, T.-C., Lin, C.-Y., Wang, H.-M., Li, M.-H., 2000. Diffusivity of Nitrous Oxide in Aqueous Alkanolamine Solutions. J. Chem. Eng. Data 46, 160–165. doi:10.1021/je000138x

Kvamsdal, H.M., Hillestad, M., 2012. Selection of model parameter correlations in a rate-based CO2 absorber model aimed for process simulation. Int. J. Greenh. Gas Control 11, 11–20. doi:10.1016/j.ijggc.2012.07.013

Kvamsdal, H.M., Rochelle, G.T., 2008. Effects of the Temperature Bulge in CO2 Absorption from Flue Gas by Aqueous Monoethanolamine. Ind. Eng. Chem. Res. 47, 867–875. doi:10.1021/ie061651s

Lee, S., Song, H.-J., Maken, S., Shin, H.-C., Song, H.-C., Park, J.-W., 2006. Physical Solubility and Diffusivity of N2O and CO2 in Aqueous Sodium Glycinate Solutions. J. Chem. Eng. Data 51, 504–509. doi:10.1021/je0503913

Li, M.-H., Lai, M.-D., 1995. Solubility and Diffusivity of N2O and CO2 in (Monoethanolamine + N-Methyldiethanolamine + Water) and in (Monoethanolamine + 2-Amino-2-methyl-1-propanol + Water). J. Chem. Eng. Data 40, 486–492. doi:10.1021/je00018a029

Li, M.-H., Lee, W.-C., 1996. Solubility and Diffusivity of N2O and CO2 in (Diethanolamine + N-Methyldiethanolamine + Water) and in (Diethanolamine + 2-Amino-2-methyl-1-propanol + Water). J. Chem. Eng. Data 41, 551–556. doi:10.1021/je950224a

Llano-Restrepo, M., Araujo-Lopez, E., 2015. Modeling and simulation of packed-bed absorbers for post-combustion capture of carbon dioxide by reactive absorption in aqueous monoethanolamine solutions. Int. J. Greenh. Gas Control 42, 258–287. doi:10.1016/j.ijggc.2015.08.008

Luo, X., Hartono, A., Hussain, S., F. Svendsen, H., 2015. Mass transfer and kinetics of carbon dioxide absorption into loaded aqueous monoethanolamine solutions. Chem. Eng. Sci. 123, 57–69. doi:10.1016/j.ces.2014.10.013

Luo, X., Hartono, A., Svendsen, H.F., 2012. Comparative kinetics of carbon dioxide absorption in unloaded aqueous monoethanolamine solutions using wetted wall and string of discs columns. Chem. Eng. Sci. 82, 31–43. doi:10.1016/j.ces.2012.07.001

Mandal, B.P., Kundu, M., Bandyopadhyay, S.S., 2005. Physical Solubility and Diffusivity of N2O and CO2 into Aqueous Solutions of (2-Amino-2-methyl-1-propanol + Monoethanolamine) and (N-Methyldiethanolamine + Monoethanolamine). J. Chem. Eng. Data 50, 352–358. doi:10.1021/je049826x

Mandal, B.P., Kundu, M., Padhiyar, N.U., Bandyopadhyay, S.S., 2004. Physical Solubility and Diffusivity of N2O and CO2 into Aqueous Solutions of (2-Amino-2-methyl-1-propanol +

Diethanolamine) and (N-Methyldiethanolamine + Diethanolamine). J. Chem. Eng. Data 49, 264–270. doi:10.1021/je0301951

Mofarahi, M., Khojasteh, Y., Khaledi, H., Farahnak, A., 2008. Design of CO2 absorption plant for recovery of CO2 from flue gases of gas turbine. Energy 33, 1311–1319. doi:10.1016/j.energy.2008.02.013

Monteiro, J.G.M.-S., Svendsen, H.F., 2015. The N2O analogy in the CO2 capture context: Literature review and thermodynamic modelling considerations. Chem. Eng. Sci. 126, 455–470. doi:10.1016/j.ces.2014.12.026

Morgan, J.C., Bhattacharyya, D., Tong, C., Miller, D.C., 2015. Uncertainty quantification of property models: Methodology and its application to CO2-loaded aqueous MEA solutions. AIChE J. 61, 1822–1839. doi:10.1002/aic.14762

Putta, K.R., Pinto, D.D.D., Svendsen, H.F., Knuutila, H., 2016. CO2 absorption into loaded aqueous MEA solutions: Kinetics assessment using penetration theory. Int. J. Greenh. Gas Control submitted.

Puxty, G., Rowland, R., Attalla, M., 2010. Comparison of the rate of CO2 absorption into aqueous ammonia and monoethanolamine. Chem. Eng. Sci. 65, 915–922. doi:10.1016/j.ces.2009.09.042

Razi, N., Bolland, O., Svendsen, H., 2012. Review of design correlations for CO2 absorption into MEA using structured packings. Int. J. Greenh. Gas Control 9, 193–219. doi:10.1016/j.ijggc.2012.03.003

Razi, N., Svendsen, H.F., Bolland, O., 2014. Assessment of mass transfer correlations in rate-based modeling of a large-scale CO2 capture with MEA. Int. J. Greenh. Gas Control 26, 93–108. doi:10.1016/j.ijggc.2014.04.019

Razi, N., Svendsen, H.F., Bolland, O., 2013a. Validation of mass transfer correlations for CO2 absorption with MEA using pilot data. Int. J. Greenh. Gas Control 19, 478–491. doi:10.1016/j.ijggc.2013.10.006

Razi, N., Svendsen, H.F., Bolland, O., 2013b. The Impact of Design Correlations on Rate-based Modeling of a Large Scale CO2 Capture with MEA. Energy Procedia, GHGT-11 37, 1977–1986. doi:10.1016/j.egypro.2013.06.078

Samanta, A., Roy, S., Bandyopadhyay, S.S., 2007. Physical Solubility and Diffusivity of N2O and CO2 in Aqueous Solutions of Piperazine and (N-Methyldiethanolamine + Piperazine). J. Chem. Eng. Data 52, 1381–1385. doi:10.1021/je700083b

Sema, T., Edali, M., Naami, A., Idem, R., Tontiwachwuthikul, P., 2012. Solubility and Diffusivity of N2O in Aqueous 4-(Diethylamino)-2-butanol Solutions for Use in Postcombustion CO2 Capture. Ind. Eng. Chem. Res. 51, 925–930. doi:10.1021/ie200832c

Seo, J.-B., Jeon, S.-B., Lee, S.-S., Kim, J.-Y., Oh, K.-J., 2011. The physical solubilities and diffusivities of N2O and CO2 in aqueous ammonia solutions on the additions of AMP, glycerol and ethylene glycol. Korean J. Chem. Eng. 28, 1698–1705. doi:10.1007/s11814-011-0030-8

Snijder, E.D., te Riele, M.J.M., Versteeg, G.F., van Swaaij, W.P.M., 1993. Diffusion coefficients of several aqueous alkanolamine solutions. J. Chem. Eng. Data 38, 475–480. doi:10.1021/je00011a037

Tönnies, I., Mangalapally, H.P., Hasse, H., 2011. Sensitivity study for the rate-based simulation of the reactive absorption of CO2. Energy Procedia, 10th International Conference on Greenhouse Gas Control Technologies 4, 533–540. doi:10.1016/j.egypro.2011.01.085

703   Tan, L.S., Shariff, A.M., Lau, K.K., Bustam, M.A., 2012. Factors affecting CO2 absorption
704   efficiency in packed column: A review. J. Ind. Eng. Chem. 18, 1874–1883.
705   doi:10.1016/j.jiec.2012.05.013
706   Tsai, T.-C., Ko, J.-J., Wang, H.-M., Lin, C.-Y., Li, M.-H., 2000. Solubility of Nitrous Oxide in
707   Alkanolamine Aqueous Solutions. J. Chem. Eng. Data 45, 341–347.
708   doi:10.1021/je990253b
709   Vaidya, P.D., Kenig, E.Y., 2010. Termolecular Kinetic Model for CO2-Alkanolamine Reactions:
710   An Overview. Chem. Eng. Technol. 33, 1577–1581. doi:10.1002/ceat.201000050
711   Vaidya, P.D., Kenig, E.Y., 2007. CO2-Alkanolamine Reaction Kinetics: A Review of Recent
712   Studies. Chem. Eng. Technol. 30, 1467–1474. doi:10.1002/ceat.200700268
713   Versteeg, G.F., Van dijck, L.A.J., Van Swaaij, W.P.M., 1996. On the Kinetics Between Co2 and
714   Alkanolamines Both in Aqueous and Non-Aqueous Solutions. an Overview. Chem. Eng.
715   Commun. 144, 113–158. doi:10.1080/00986449608936450
716   Versteeg, G.F., van Swaaij, W.P.M., 1988. On the kinetics between CO2 and alkanolamines both
717   in aqueous and non-aqueous solutions—I. Primary and secondary amines. Chem. Eng.
718   Sci. 43, 573–585. doi:10.1016/0009-2509(88)87017-9
719   Versteeg, G.F., Van Swaalj, W., 1988. Solubility and diffusivity of acid gases (carbon dioxide,
720   nitrous oxide) in aqueous alkanolamine solutions. J. Chem. Eng. Data 33, 29–34.
721   doi:10.1021/je00051a011
722   Wang, Y.W., Xu, S., Otto, F.D., Mather, A.E., 1992. Solubility of N2O in alkanolamines and in
723   mixed solvents. Chem. Eng. J. 48, 31–40. doi:10.1016/0300-9467(92)85004-S
724   Weiland, R.H., Dingman, J.C., Cronin, D.B., Browning, G.J., 1998. Density and Viscosity of
725   Some Partially Carbonated Aqueous Alkanolamine Solutions and Their Blends. J. Chem.
726   Eng. Data 43, 378–382. doi:10.1021/je9702044
727   Yaghi, B., Houache, O., 2008. Solubility of Nitrous Oxide in Amine Aqueous Solutions. J. Eng.
728   Comput. Archit. 2.
729   Ying, J., Eimer, D.A., 2012. Measurements and Correlations of Diffusivities of Nitrous Oxide
730   and Carbon Dioxide in Monoethanolamine + Water by Laminar Liquid Jet. Ind. Eng.
731   Chem. Res. 51, 16517–16524. doi:10.1021/ie302745d
732