

# **CO<sub>2</sub> absorption into loaded aqueous MEA solutions: impact of different model parameter correlations and thermodynamic models on the absorption rate model predictions**

Koteswara Rao Putta, Hallvard F. Svendsen, Hanna K. Knuutila\*

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

Abstract:

A two-dimensional discretized rate-based model was used for assessing the impact of correlations and/or models for VLE (thermodynamics), solubility (CO<sub>2</sub> Henry's law constant), reaction rate kinetic models and diffusivity of CO<sub>2</sub> in aqueous MEA solutions on the absorber model predictions for CO<sub>2</sub> capture. Experimental data from four different set-ups covering a wide range of conditions were utilized for the assessment. Four different thermodynamic models and eight different Henry's constant correlations/models including the Aspen Plus V8.6 e-NRTL-RK model was used in the study. Even though the individual sub-models, e.g. solubility, physical properties, were validated with independent experimental data, the use of a random selection of these models will give different predictions when used in a rate-based simulation. It was seen that using different Henry's law constant correlations had a huge effect on model predictions. Seven different reaction rate kinetic models were used and it was found that no single kinetic model was able to predict the experimental data from all the sources better than the chosen base case kinetic model. It was also seen that transport property (CO<sub>2</sub> diffusivity in MEA) correlations could have a large impact on the outcome of model predictions and correlations based on the N<sub>2</sub>O analogy were better than the

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\* Corresponding author: [hanna.knuutila@ntnu.no](mailto:hanna.knuutila@ntnu.no)

ones based on a modified Stokes-Einstein correlation. As a special case, frequently used kinetic models were used with the thermodynamic model and transport properties taken from Aspen Plus V8.6. It was found that two of the kinetic models predicted the experimental data with acceptable accuracy.

*Keywords: Thermodynamic models; reaction rate kinetic models; rate-based model; penetration theory; Henry's law constant; lab-scale experimental data*

## 1 Introduction

Due to growth in both world population and per capita income, there is a continuous rise in energy demand. To meet the rising energy demand the energy sector still relies heavily on fossil fuels (i.e., coal, petroleum, and natural gas) for energy supply resulting in large contributions to greenhouse gas emissions. Global warming is an alarming issue and CO<sub>2</sub> is one of the key greenhouse gasses. To limit the global temperature rise to 2 °C, capturing CO<sub>2</sub> from emitting sources is crucial [1]. Among the current technologies available for post-combustion CO<sub>2</sub> capture, chemical absorption based on amine solvents appears to be the most mature technology and commercially feasible method [2]. Post-combustion CO<sub>2</sub> 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 the understanding of the complex phenomena (the coupling between thermodynamics and the diffusional processes in the gas and liquid phases in addition to the complex chemical reactions in the liquid close to the interface) occurring and for precise modelling of the process for industrial scale-up [3].

Two modeling approaches (equilibrium stage and rate-based models) have been used for modeling the reactive absorption process. Equilibrium stage modeling concepts often fail for reactive absorption processes using alkanolamines and rigorous rate-based modeling, which takes into account the actual rates of mass and heat transfer and chemical reactions, is recommended [4]. 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 CO<sub>2</sub> capture rate-based process model are [5–7]

- (i) Mass and energy balances for the phases (flow model): An overall flow model including separate equations for mass and energy transfer in both the liquid and gas-phase. This yields the backbone of the model and defines mass and energy transfer continuously throughout the defined mass transfer section (the packing) in the column.
- (ii) The gas-liquid interface model (accounts for the effect of chemical reactions): This sub-model accounts for the effects of the chemical reactions and the molecular transport of species for calculating the interfacial mass transfer rates.
- (iii) The thermodynamic model (describes phase and chemical equilibrium): The thermodynamic framework of the reactive equilibrium models is based on two types of equilibrium, the dissociation and reaction equilibrium of the species in the bulk liquid solution, and the vapor liquid equilibrium of the molecular species. The model consists of equilibrium relationships for each reaction involved, mass balances of the amine or amines, total elemental balances, as well as total and local electro-neutrality. The equilibrium relationship for the components can be modelled by using either rigorous theories accounting for the activities of the components in the liquid-phase, or more simplified approximations that lump non-idealities into a few parameters for example, Kent-Eisenberg model.
- (iv) Auxiliary sub-models (for hydraulics, mass, and heat transfer coefficients and physical properties).

Process modeling and simulation plays a key role in process design, analysis and development in addition to in optimization of the process. It is an integral part of any process development, and hence it is essential to identify the strengths and weaknesses of such a model [8]. The user should always remember that process simulators never perform better than the model upon which they

are based [8,9]. Thus, the accuracy of the complete model largely depends on the accuracy of the sub-models used. Detailed information about data accuracy, precision and assumptions made during the development and the range of applicability of the sub-models is very crucial for selecting the suitable property sub-models. All sub-models used in rigorous models are developed based on some form of experimental data and often the experimental data used are taken from different sources with different magnitudes of error [10]. There is a great amount of information available on sub-models such as liquid density, viscosity, reaction rate constants, mass and heat transfer coefficients, the heat of absorption and solubility of acid gasses. Empirical correlations as a function of temperature, pressure, and composition have been used to represent some of these properties while some were represented as constants [11]. In order to use simulation tools for technology qualification or verification during process development, their performance must be documented by validation against experimental data. Validation should be done on both the sub-model level (e.g. kinetic rate models, thermodynamic models, hydraulic models, physical and transport property models) by utilizing laboratory data (e.g. solution density, viscosity, VLE, kinetics, etc.) and by evaluating the overall simulator performance using bench, pilot, demo and/or full scale data [12–18]. Performance evaluations should be performed at several scales or stages during the development phases (e.g. bench, pilot, demo); and the effect of scale should be investigated in each of these stages. If there are any discrepancies or unexpected results compared to the previous scale stage, they should be properly investigated and if possible quantified. In most cases, this may indicate that one or some of the sub-models need refinement. Therefore, the validation procedure must be viewed as dynamic [8].

To gain in-depth knowledge about the importance of property sub-models, several studies on the sensitivity of various operating and design parameters, model parameter correlations, physical

properties and reaction rate kinetic constants for CO<sub>2</sub> absorption using MEA have been performed. The objective was often to find out which mass transfer coefficient correlations, reaction rate kinetic constants models and physical properties correlations would be able to predict pilot plant data. In Table 1, sensitivity studies made on CO<sub>2</sub> absorption using MEA are listed.

Table 1. Sensitivity studies for CO<sub>2</sub> absorption using MEA

Source	Parameters studied	Simulation tool used
Abu-Zahra et al. [19]	Solvent lean loading and temperature, percentage of CO <sub>2</sub> removal, solvent concentration, stripper pressure	Aspen Plus
Mofarahi et al. [20]	Solvent (type, concentration and circulation rate), reboiler and condenser duty and absorber and stripper columns stages	Hysys
Kvamsdal and Rochelle [21]	Liquid density, liquid heat capacity and mass transfer coefficients	gPROMS
Khan et al. [22]	Mass transfer coefficient correlations	Microsoft Excel
Tönnies et al. [23]	Interfacial area, mass transfer coefficients, hold-up, Henry's law constant, heat of absorption, amine ion diffusivities, liquid density and viscosity	Aspen Plus
Kvamsdal and Hillestad [11]	Liquid density, viscosity, heat capacity, heat of absorption, mass transfer coefficient (kg) and kinetic models	MATLAB
Tan et al. [24]	Viscosity, surface tension, CO <sub>2</sub> partial pressure, gas and liquid flow rates, absorbent concentration, liquid temperature, CO <sub>2</sub> loading, packing	-
Razi et al. [25]	Pressure drop correlations, gas and liquid mass transfer coefficients correlations, liquid hold-up correlations and interfacial area correlations	MATLAB
Razi et al. [26]	Mass transfer coefficient correlations	Aspen Plus

Razi et al. [27]	Kinetic models with corresponding thermodynamic model, mass transfer coefficient correlations	Aspen Plus
Afkhamipour and Mofarahi [28]	Kinetic models in combination with mass transfer coefficient correlations	MATLAB
Razi et al. [29]	mass transfer coefficient and effective interfacial area correlations	Aspen Plus
Morgan et al. [30]	Liquid density, viscosity and surface tension	Aspen Plus

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All the sensitivity studies listed above, utilized pilot scale data and rate-based process models. As discussed above, rate-based process models use several sub-models for kinetics, hydraulics, mass transfer coefficients and physical properties. Razi et al. [25] reviewed structured packing hydrodynamics and mass transfer correlations available in literature and showed that the uncertainty is large when applying various proposed pressure drop, gas and liquid mass transfer coefficient, liquid hold-up and interfacial area correlations for large scale packed column simulation. Kvamsdal and Hillestad [11] couldn't see clear trends regarding the selection of model parameters and suggested that a proper choice will depend on the conditions of the specific case. This is of course an unfortunate situation. From these studies giving qualitative knowledge about the different process variables, it was found that that absorber performance predictions are highly sensitivity to the effective interfacial area, Henry's law constant, the heat of absorption, kinetic constants, surface tension and CO<sub>2</sub> loading. The effect of these parameters are very similar. For example, Kvamsdal et al. [31] studied the effect of kinetic constant models on the prediction rich loading in the absorber. They found that depending on the kinetic constant model, the rich loading and prediction of CO<sub>2</sub> removal rates were up to 20% off. Similarly, the existing models for effective mass transfer are can predict effective area values up to 50% off compared to measured values for 30wt% MEA and 0.3M NaOH [32].

The main drawback of these sensitivity studies performed on pilot scale data is that the process model used employed several parameters with large uncertainty and it is difficult to distinguish between the impacts of the different parameters. Furthermore, the studies were not performed using data from the same pilot scale. The parameter with possibly the largest associated uncertainty in pilot plant data is the active area and is influenced by maldistribution. In the present study, we use lab-scale CO<sub>2</sub> absorption data based on equipment where the interfacial area is known and where the gas side mass transfer coefficient can be determined from other experiments. In this way, we can eliminate some of the most uncertain variables in the sensitivity study.

Llano-Restrepo and Araujo-Lopez [10] reviewed 33 published rate-based absorber model journal articles for simulation of CO<sub>2</sub> absorption using MEA and found that researchers had used a variety of models or correlations for the parameters needed in the absorber models. However, they did not study the effect of using the different methods and correlations on the process performance. In this work, we have used different thermodynamic models, different correlations available for viscosity, diffusivities, Henry's law constant and reaction kinetics published in the literature. The objective is to compare the impact of the various parameter correlations on the predicted performance of the process model. The selected correlations are applied in a discretized penetration theory based absorption model developed in previous work [33]. The reasons for large variations in absorber performance are investigated through the contributions of the individual correlations/models. No such comparison has, to the authors knowledge, been published in the literature for lab-scale absorption data.

## 2 Methodology and models/correlations



The experimental data used in this work were taken from three different experimental set-ups. Lab-scale absorption data for CO<sub>2</sub> capture using MEA published in literature for a wetted wall column (WWC), laminar jet absorber (LAMJET) and string of discs column (SDC) were taken from literature [3,34–37]. The lab-scale experimental data used in this study covers a wide range of conditions for temperature (293-343 K), MEA concentration (0.5 – 9 M), CO<sub>2</sub> loading (0 - 0.5), CO<sub>2</sub> driving force (0.16 – 93 kPa) and gas-side mass transfer resistance (with and without). The impact of selecting different thermodynamic models, kinetic models, Henry's law constant correlations, correlations for diffusivity of CO<sub>2</sub> in MEA solution and liquid viscosity on the performance of the CO<sub>2</sub> absorption model were evaluated in this study.

The CO<sub>2</sub> absorption model based on penetration theory developed and validated with the above mentioned lab-scale data and presented in Putta et al. [33], is considered as the base case and used for analyzing the impact of the different correlations/models considered in this study. The CO<sub>2</sub> absorption model equations are given in equations (1) and (2). The numerical method and solution methodology were not discussed here as it is mentioned in Putta et al. [33]. This model utilizes of course a certain set of underlying thermodynamic, thermal, transport and physical property models and kinetic parameters fitting was done in this context. For ease of reference, the main equations are also given here.

The average mass transfer flux is calculated from the difference between the concentration profile at time equal to the contact time ( $\tau$ ) for the laboratory equipment used and the initial flat profile:

$$N_{CO_2} = \frac{1}{\tau} \int_{x=0}^{x=\delta} (C_{CO_2}^x - C_{CO_2}^{bulk}) * dx \quad (1)$$

The component and thermal transport in the reaction film is modeled by

$$\frac{\partial [C_i]}{\partial t} = D_i^{Solution} \frac{\partial^2 [C_i]}{\partial x^2} \pm r_i \quad (2)$$

$$\frac{\partial T}{\partial t} = \alpha_{sol} \frac{\partial^2 T}{\partial x^2} + \sum \left( \frac{\Delta H_j}{\rho_{Solution} C_{P_{Solution}}} \right) * \Gamma_j \quad (3)$$

Here  $i = \text{CO}_2, \text{MEA}, \text{MEA}^+, \text{MEACOO}^-, \text{H}_2\text{O}, \text{HCO}_3^-, \text{OH}^-$  and  $\text{CO}_3^{2-}$ .

With initial conditions

$$[C_i]_{t=0, x \geq 0} = [C_i]_0 \quad \text{and} \quad T_{t=0, x \geq 0} = T_0 \quad (4)$$

and boundary condition at end of film ( $t > 0, x = \infty$ ):

$$\left. \frac{\partial C_i}{\partial x} \right|_{t>0, x=\infty} = 0 \quad \text{and} \quad \left. \frac{\partial T}{\partial x} \right|_{t>0, x=\infty} = 0 \quad (5)$$

Boundary conditions at gas liquid interface ( $t > 0, x = 0$ ):

$$\left. \frac{\partial [C_i]}{\partial x} \right|_{x=0} = 0 \quad (6)$$

Where 'i' is the non-transferring component (=  $\text{MEA}^+, \text{MEACOO}^-, \text{HCO}_3^-, \text{OH}^-$  and  $\text{CO}_3^{2-}$ )

$$k_g \left( P_{i, g, bulk} - P_{i, g, interface} \right) = -D_i^{liquid} \left. \frac{\partial [C_i]}{\partial x} \right|_{x=0} \quad (7)$$

Where 'i' the transferring component (=  $\text{CO}_2, \text{MEA}$  and  $\text{H}_2\text{O}$ )

$$\lambda \frac{\partial T}{\partial x} = h(T|_{x=0} - T_g) + MW_{CO_2} C_{p, CO_2} (T|_{x=0} - T_g) N_{CO_2} + h_{H_2O}^{vap} N_{H_2O} + h_{MEA}^{vap} N_{MEA} \quad (8)$$

Equilibrium prevails at the interface modeled by a Henry's law coefficient for  $\text{CO}_2$  and by the equilibrium pressure for water and MEA according to the thermodynamic model used.

$$H_{CO_2}^{Solution} = \frac{P_{CO_2, g, i}}{[CO_2]_{l, i}} = \gamma_{CO_2} H_{CO_2-H_2O}^{\infty} \quad (9)$$

The absolute average relative flux deviation (AARD) is calculated by:

$$AARD = \frac{1}{n} \sum_i^n \left| \frac{N_{CO_2, exp} - N_{CO_2, model}}{N_{CO_2, exp}} \right| * 100 \quad (10)$$

This implies that the results reported in this paper show how sensitive the calculated mass transfer rates are to variations in the various property models and do not say anything about the quality of the property models themselves.

## 2.1 Thermodynamic models

Four different rigorous thermodynamic models were tested in this work. The extended UNIQUAC by Aronu et al. [38], the un-symmetric electrolyte NRTL property method (eNRTL-RK) of Aspen Plus V8.6 template [39], the refined e-NRTL model of Hessen et al. [40] and the e-NRTL model from Putta et al. [33] were used in this study. The models are fitted to somewhat different data, and small differences in the models might lead larger differences in modelling of kinetics. When the thermodynamic model is changed, it changes the equilibrium concentrations and CO<sub>2</sub> driving force (as Henry's law constant changes). For example the physical solubility of CO<sub>2</sub> is small and unless the model is fitted to the physical CO<sub>2</sub> solubility data, the ability of the model to represent the CO<sub>2</sub> solubility and thus the model the Henry's law constant can vary a lot. In the equilibrium based process modelling this is irrelevant, but for kinetics studies the ability of the model to predict Henry's law constant becomes very important.

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. [33]	TD1
	(2) extended-UNIQUAC model: Aronu et al. [38]	TD2
	(3) refined e-NRTL model: Hessen et al. [40]	TD3
	(4) e-NRTL-RK model: Aspen Plus V8.6 [39]	TD4

## 2.2 Henry's law coefficient correlations or models for CO<sub>2</sub> in MEA solution

In general, Henry's law coefficient for CO<sub>2</sub> in aqueous MEA solution has been calculated from either empirical correlations based on the N<sub>2</sub>O analogy or fitted to experimental data, e.g. PCO<sub>2</sub> as a function of loading, in rigorous thermodynamic models (UNIQUAC or e-NRTL). Due to the reactivity of acid gases with amine solutions, a direct measurement of the free-gas solubility and the diffusivity of CO<sub>2</sub> is impossible. This has led to use similarity principles based on non-reacting gases to infer the properties of CO<sub>2</sub> [41–56]. Due to molecular similarities (structure and properties), the analogy with N<sub>2</sub>O is widely applied for estimation of CO<sub>2</sub> properties and has been referred to as the “N<sub>2</sub>O analogy”. Clarke [41] assumed that at constant temperature the ratios of CO<sub>2</sub> and N<sub>2</sub>O solubilities and diffusivities in water and in aqueous solutions of organic solvents are similar within 5%. As per the N<sub>2</sub>O analogy, the equations for estimating solubility or Henry's law constant of molecular CO<sub>2</sub> in aqueous amine solutions is given as shown in equation (11):

$$He_{CO_2\_amine} = \left( \frac{He_{CO_2\_water}}{He_{N_2O\_water}} \right) He_{N_2O\_amine} \quad (11)$$

The N<sub>2</sub>O solubility in aqueous MEA solutions was modeled using various empirical correlations developed based on experimental data for N<sub>2</sub>O solubilities in water and amine solutions. Using these correlations and the solubility of CO<sub>2</sub> in water in the N<sub>2</sub>O analogy, the CO<sub>2</sub> Henry's law coefficient can be estimated in amine solutions. Henry's law constant estimated using both empirical correlations based on N<sub>2</sub>O analogy [3,11,34,36,57–67] and rigorous thermodynamic models [4,26,27,29,68–85] are used in literature for process modelling and for mass transfer data analysis. As reported by Llano-Restrepo and Araujo-Lopez [10] and Monteiro and Svendsen [51], no correlation or method stands out to be the most frequently used. Hence, the impact of

these kinds of methods or correlations must be studied in detail. The correlations or methods used in this study are listed in table 3.

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

Correlation source	Case name	Validity range			Remarks
		MEA (mass %)	CO <sub>2</sub> loading	T (°C)	
Hartono et al. [42]	H1	0 - 100	0-0.5	25-100	Validated against different literature sources
Tsai et al. [55]	H2	6.2 - 37 (1-6 M)	0	15-75	valid for unloaded solutions
Wang et al. [44]	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 [86]	H4	5 - 30	0	20-60	valid for unloaded solutions
Ying et al. [45]	H5	0-100	0	25-50	Validated with 18 and 30 mass% literature data in unloaded solutions
Aspen Technology, Inc. [39]	H6	0-100	0-0.5	40-120	e-NRTL- RK model and validated P <sub>CO2</sub> data for 18 and 30 mass% MEA solution
Aronu et al. [38] extended-UNIQUAC model	H7	15-60	0-0.5	40-120	Validated with 30 mass% literature data in CO <sub>2</sub> loaded MEA solutions

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Hessen et al. [40] refined e- NRTL model	H8	15-60	0-0.5	40-120	validated with literature $P_{CO_2}$ data for 30 mass% MEA solution
Putta et al. [33] e-NRTL model	H9	15-60	0-0.5	40-120	Validated with 15 and 30 mass% literature data in $CO_2$ loaded MEA solutions

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### 2.3 Transport property calculation methods or correlations

Two kinds of approaches, namely the  $N_2O$  analogy and the modified Stokes-Einstein correlation are commonly used for calculating the diffusivity of  $CO_2$  in the liquid phase. Diffusivity correlations based on a modified Stokes-Einstein relation as given by Versteeg and van Swaaij [87] and Versteeg et al. [88] are the most often used in literature.  $N_2O$  analogy diffusivity correlations (developed using experimental  $N_2O$  diffusivities) given by Ko et al. [89] and Jamal [90] were also used in the literature. Recently, Ying and Eimer [91] developed a new correlation for  $N_2O$  diffusivity. The  $N_2O$  analogy (equation (12)) and modified Stokes-Einstein correlation (equation (13)) for estimating  $CO_2$  diffusivity in amine solutions are given as:

$$D_{CO_2\_amine} = \left( \frac{D_{CO_2\_water}}{D_{N_2O\_water}} \right) D_{N_2O\_amine} \quad (12)$$

$$D_{CO_2\_amine} = D_{CO_2\_water} \left( \frac{\mu_{amine}}{\mu_{water}} \right)^{-0.8} \quad (13)$$

Viscosity ( $\mu$ ) of the amine solution is used in the calculation of pressure drop and interfacial area of the packing in addition to the calculation of diffusivities (modified Stokes-Einstein correlation, equation (13)). Different correlations have been developed based on experimental solution viscosity data and these correlations have been used in simplified and rate-based simulation

models. As mentioned earlier, the uncertainty in the calculation of interfacial area is very high, so it is difficult to assess the impact of different correlations. In this study, the impact of different viscosity estimation correlations on the performance is evaluated by using these correlations in equation (13). According to Llano-Restrepo and Araujo-Lopez [10], 66% of the studies they reviewed used the Weiland et al. [92] correlation for the calculation of viscosity of the liquid phase. Recently, Hartono et al. [42] and Morgan et al. [30] presented updated or new correlations for calculation of solution viscosity. All these three correlations were validated using CO<sub>2</sub> loaded MEA viscosity data. In this study, these three correlations were used to study the effect of viscosity parameter estimation correlations.

Table 4. Overview of Correlations of N<sub>2</sub>O diffusivity in amine solutions and/or solution viscosity correlations used for CO<sub>2</sub> diffusivity calculation

Source of correlation	Case name	Temperature range [K]	Concentration range [mol/L]	CO <sub>2</sub> loading [mol/mol]	Remarks
<b>N<sub>2</sub>O analogy (equation (12))</b>					
Ko et al. [89]	DC1 (base case)	303-313	1 - 5	0	Valid for unloaded solutions up to 313 K.
Jamal [90]	DC2	298-313	0 - 5	0	Valid only up to temperatures of 313 K. for unloaded solutions
Ying and Eimer [91]	DC3	298-333	0 - 12	0	Valid for unloaded solutions
<b>Modified Stokes-Einstein correlation (equation (13)) with different viscosity models</b>					
Hartono et al. [42]	DC4	298-353	0-pure MEA	0 – 0.5	-

Weiland et al. [92]	DC5	298	1.6 – 6.5	0 - 0.5	Valid at 298 K
Morgan et al. [30]	DC6	298-353	3.3 – 6.5	0 - 0.5	-

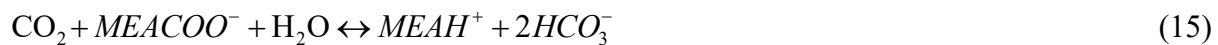
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## 2.4 Reaction kinetic models

In rate-based process modeling of reactive absorption, kinetics play a key role. For CO<sub>2</sub> absorption using aqueous MEA solutions, two different reaction mechanisms, namely the zwitterion mechanism and the direct (termolecular) mechanism were used in the literature to develop rate equations. Detailed information about the reaction mechanisms is reviewed by several researchers [34,36,88,93,94], and is not presented here. We are interested in the effect of their actual usage in simulation studies. It is observed that investigators in CO<sub>2</sub> capture with aqueous MEA solutions often use the kinetic models from the literature (for example the Hikita et al. [95,96] and Versteeg et al. [88] kinetic models (here called Kin1 and Kin2)) outside their validity range in terms of temperature, amine concentrations and also CO<sub>2</sub> loading. The rate expressions used in this study are listed below.

### **Hikita et al. [95,96] kinetic model (Kin 1):**

For CO<sub>2</sub> absorption into aqueous MEA solutions, two overall reactions were considered by Hikita et al. [95,96]:



In industrial absorption columns, due to short contact times between gas and liquid, the effect of reaction (15) was neglected and reaction (14) was assumed to occur in two steps.







The protonation reaction (17) was assumed instantaneous and reaction (16) was assumed second order. The reaction rate equation was given as:

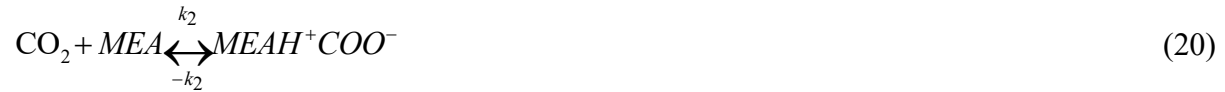
$$R_{CO_2} = k_2[MEA][CO_2] \quad (18)$$

Here  $k_2$  is the second order reaction rate constant and expressed as

$$\log_{10}(k_2) = 10.99 - \frac{2152}{T} \quad (19)$$

### Versteeg et al. [88] kinetic model (Kin 2):

Versteeg et al. [88] used the zwitterion mechanism to evaluate CO<sub>2</sub> absorption into MEA. According to this mechanism, the reaction between CO<sub>2</sub> and alkanolamine proceeds via the formation of a zwitterion followed by the deprotonation by a base.



Versteeg et al. [88] assumed the overall reaction order as two based on zwitterion mechanism, i.e., zwitterion formation reaction (equation (20)) as the rate determining step.

The reaction rate is expressed as:

$$R_{CO_2} = k_2[MEA][CO_2] \quad (22)$$

Here  $k_2$  is the second order reaction rate constant and expressed as an Arrhenius type equation in temperature

$$k_2 = 4.4 \times 10^8 \exp\left(-\frac{5400}{T}\right) \quad (23)$$

### Aboudheir et al. [34] kinetic model (Kin 3):

The direct (termolecular) mechanism was used to model the reaction kinetics between CO<sub>2</sub> and aqueous MEA. According to the termolecular mechanism, the bond formation and proton transfer to the base take place simultaneously in a single step and the reaction order is three as per this mechanism.



Here B represents bases present in the solution. Aboudheir et al. [34] considered both MEA and H<sub>2</sub>O as main bases participating in reaction (24) and the reaction order with respect to MEA can vary between one and two depending on the base effect of water. The overall reaction rate is given as

$$R_{CO_2} = (k_{MEA,c} [MEA] + k_{H_2O,c} [H_2O]) [MEA] [CO_2] - \frac{1}{K_{eq}} [MEACOO^-] [H_3O^+] \quad (25)$$

Where,

$$k_{MEA,c} = 4.61 \times 10^9 \exp\left(-\frac{4412}{T}\right) \quad (26)$$

$$k_{H_2O,c} = 4.55 \times 10^6 \exp\left(-\frac{3287}{T}\right) \quad (27)$$

#### ***Aspen Plus V8.6 kinetic model (Kin 4):***

The reactions considered in Aspen Plus are given in equations (28) and (29). The kinetic constants of reaction (28) were estimated from Hikita et al. [95] and for reaction (29) were calculated using the equilibrium constants of the reversible reactions (28) and (29) and the kinetic constants of reaction (28).





The reaction rate is expressed in terms of activities as

$$R_{CO_2} = k \prod_i^N (\gamma_i x_i)^\nu \quad (30)$$

Where,  $\gamma, x, \nu$  are activity coefficient, mole fraction and stoichiometric coefficient of component 'i' in the reaction respectively and N is the number of components in the reaction.

For reaction (28) and (29) the corresponding kinetic constants were given as [39]:

$$k_{28} = 3.02 \times 10^{14} \exp\left(-\frac{4959.6}{T}\right) \quad (31)$$

$$k_{29} = 5.52 \times 10^{23} \exp\left(-\frac{8312.2}{T}\right) \quad (32)$$

#### **Luo et al. [37] kinetic model (Kin 5):**

The chemical reactions considered by Luo et al. [37] for describing the CO<sub>2</sub> absorption into aqueous MEA system are given as:

Reaction (18) given above was considered for CO<sub>2</sub>-H<sub>2</sub>O-MEA.

In addition, the reaction between H<sub>3</sub>O<sup>+</sup> and MEA is written as:



The overall reaction can be written by adding equations (28) and (33) as:



The forward reaction rate equation considered by Luo et al. [37] was based on the termolecular(direct) mechanism and written as:

$$\begin{aligned} R_{CO_2} &= (k_{MEA,c} [MEA] + k_{H_2O,c} [H_2O]) \{ [MEA] [CO_2] \} \\ &= (k_{MEA,a} g_{MEA} [MEA] + k_{H_2O,a} g_{H_2O} [H_2O]) \{ g_{MEA} [MEA] g_{CO_2} [CO_2] \} \end{aligned} \quad (35)$$

The kinetic constants for concentration based (with subscript ‘c’) and activity based (with subscript ‘a’) models were given as:

$$k_{MEA,c} = 2.003 \times 10^{10} \exp\left(-\frac{4742}{T}\right) \quad (36)$$

$$k_{H_2O,c} = 4.147 \times 10^6 \exp\left(-\frac{3110}{T}\right) \quad (37)$$

$$k_{MEA,a} = 1.844 \times 10^{10} \exp\left(-\frac{4112}{T}\right) \quad (38)$$

$$k_{H_2O,a} = 2.064 \times 10^5 \exp\left(-\frac{1766}{T}\right) \quad (39)$$

#### Putta et al. [33] kinetic model (Kin 6):

The direct reaction mechanism was used in the development of this kinetic model. The base contributions of both MEA and H<sub>2</sub>O were considered and the reactions were same as given in equation (24). The reversibility of both reactions was also considered.

The reaction rates were given as:

$$\begin{aligned} r_{CO_2\_MEA} &= k_{MEA,c} [MEA] [CO_2] \frac{\frac{\partial}{\partial t} MEAH^+ - \frac{\partial}{\partial t} MEACOO^-}{K_{eq,CO_2\_MEA,c}} \\ &= k_{MEA,a} g_{MEA}^2 [MEA] g_{CO_2} [CO_2] \frac{\frac{\partial}{\partial t} MEAH^+ - \frac{\partial}{\partial t} MEACOO^-}{K_{eq,CO_2\_MEA,a}} \end{aligned} \quad (40)$$

$$\begin{aligned} r_{CO_2\_H_2O} &= k_{H_2O,c} [H_2O] [MEA] [CO_2] \frac{\frac{\partial}{\partial t} H_3O^+ - \frac{\partial}{\partial t} MEACOO^-}{K_{eq,CO_2\_H_2O,c}} \\ &= k_{H_2O,a} g_{H_2O} [H_2O] g_{MEA} [MEA] g_{CO_2} [CO_2] \frac{\frac{\partial}{\partial t} H_3O^+ - \frac{\partial}{\partial t} MEACOO^-}{K_{eq,CO_2\_H_2O,a}} \end{aligned} \quad (41)$$

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

$$k_{MEA,c} = 3.1732 \times 10^9 \exp\left(-\frac{4936.6}{T}\right) \quad (42)$$

$$k_{H_2O,c} = 1.0882 \times 10^8 \exp\left(-\frac{3900}{T}\right) \quad (43)$$

$$k_{MEA,a} = 4.5191 \times 10^{11} \exp\left(-\frac{5851.7}{T}\right) \quad (44)$$

$$k_{H_2O,a} = 2.1105 \times 10^6 \exp\left(-\frac{2382.4}{T}\right) \quad (45)$$

The validity ranges for the above-mentioned kinetic models are shown in table 5.

Table 5. Validity of kinetic models considered in this study

Source/ Kinetic model	Case name	Temperature range [K]	Concentration range [mol/L]	CO <sub>2</sub> loading [mole CO <sub>2</sub> / mole MEA]	Remarks
Hikita et al. [95,96]	Kin1	288-318	0.0152-0.177	0	Valid at low MEA concentrations and for unloaded solutions
Versteeg et al. [88]	Kin2	278-313	0 - 4.8	0	Pseudo first order assumed and valid only up to temperatures of 313 K.
Aboudheir et al. [34]	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. [95] model
Luo et al. [37]	Kin5	293-343	0.5 - 5	0 - 0.4	Pseudo first-order assumption
Putta et al. [33]	Kin6		0.5 – 5 <sup>*c</sup>		Concentration based model is valid up to 5 M MEA only
		293-343	0.5 – 9 <sup>*a</sup>	0 - 0.5	

<sup>\*c</sup>- Concentration based kinetic model, <sup>\*a</sup>-activity based kinetic model

## 2.5 Using the Aspen Plus thermodynamic model and properties

In research, often investigators use published kinetic models in commercial software tools like Aspen Plus or Hysys for parametric studies, performance evaluations and investigation of optimal process configurations as a part of process development. In order to see the impact of using kinetic models available in the literature with the Aspen Plus thermodynamic model and properties, frequently used kinetic models [34,88,95,96] and recently developed kinetic models (Putta et al. [33] both concentration and activity based models) were used. In addition to these, the activity and concentration based kinetic models given in Aspen Plus V8.6 were also used.

## 3 Results and discussion

The above-mentioned different models and correlations for estimation of model parameters in process simulation were implemented into a penetration theory based absorption model and the impact of them on model predictions were calculated. In all the sub-studies, the impact of using

different methods and correlations was compared with a base case. The methods and correlations used in the base are given in table 6.

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. [33]
Kinetic model	Kin6	Penetration theory based kinetic model: Putta et al. [33]
Henry's law constant of CO <sub>2</sub>	H9	e-NRTL model: Putta et al. [33]
Diffusivity of CO <sub>2</sub> in amine solutions	DC1	Ko et al. [89] correlation based on N <sub>2</sub> O analogy

In the following sections, we will discuss the impact of changing these models and correlations on simulations results in detail.

### 3.1 Impact of changing thermodynamic model

In Table 7 the results from changing the thermodynamic model are given. When changing the thermodynamic model also the Henry's law model used in the kinetic model was changed to the one used in the corresponding thermodynamic model. All other parameter correlations were kept the same as in the base case.

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

		AARD (%)						
Thermodynamic model	Concentration based kinetics simulation model				Activity based kinetics simulation model			
	Luo et al. [36,37]	Puxty et al. [35]	Aboudheir [3]	LAM.JET	Luo et al. [36,37]	Puxty et al. [35]	Aboudheir [3]	LAM.JET
	SDC	WWC	WWC	LAM.JET	SDC	WWC	WWC	LAM.JET

<b>Base case</b>	<b>14.4</b>	<b>13.9</b>	<b>12.4</b>	<b>13.1</b>	<b>18.9</b>	<b>14.8</b>	<b>13.8</b>	<b>10.1</b>
<b>(TD1)</b>								
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

From the table above it is seen that the degree of impact of the thermodynamic model depends on the type of the simulation model used (concentration or activity based) and experimental database used. The base case thermodynamic model (Putta et al. [33] e-NRTL model) (TD1), and extended-UNIQUAC model by Aronu et al. [38] (TD2) were developed (fitted) using the same experimental VLE data but with a different type of model (e-NRTL and extended UNIQUAC). The extended UNIQUAC (Aronu et al. [38] TD2) gave the same mass transfer rate prediction accuracy as the base case for the Luo et al. [36,37] SDC and WWC data and the Aboudheir [3] laminar jet data. However, in the case of the Puxty et al. [35] WWC data, the extended UNIQUAC (Aronu et al. [38] TD2) predicted with an AARD of 6% higher than the base case for the both activity and concentration based models. Most of these deviations were found to be at loading 0.5. Using the Hessen et al. [40] refined e-NRTL model (TD3) gives large deviations (AARD: 12 -18 % more than the base case) for data from all sources used in this study. The deviations decrease when using the activity-based model (AARD: 6.5 -14.8 % more than the base case). Using the Aspen Plus V8.6 [39] e-NRTL-RK model (TD4) improved model predictions compared to the base case for the Luo et al. [36,37] WWC data for both concentration and activity based simulations and predicted with almost the same accuracy (AARD) as base case for Aboudheir [3] laminar jet data. However, with the same Aspen Plus V8.6 e-NRTL-RK model (TD4), the model predicted deviations (AARD) were more than 20% than the base case for Luo et al. [36,37] SDC and Puxty



et al. [35] WWC data in concentrations based model and the deviations (AARD) were 9-14% more than the base case in activity based model.

When the thermodynamic model is changed, it changes the equilibrium concentrations and CO<sub>2</sub> driving force (as Henry's law constant changes). Hence, it will affect both the reaction rates and the concentration profiles obtained from the model, which in turn will affect the CO<sub>2</sub> flux estimations.

From the detailed analysis of the simulation results, it was found that the quality and type of experimental data used for thermodynamic model development has more impact than the type of model (UNIQUAC versus e-NRTL). Both models TD1 and TD2 were fitted to molecular CO<sub>2</sub> solubility data whereas TD3 was not. Hence, both models TD1 and TD2 give reasonable values of free CO<sub>2</sub> in the solution whereas the model TD3 does not necessarily do that. This will affect significantly the liquid phase free CO<sub>2</sub> values and thus the reaction rates. This could be the reason for the large deviations seen for TD3 with concentration-based kinetics and that the deviations become smaller with activity-based kinetics, which include the activity coefficients. With the Aspen Plus V8.6 e-NRTL-RK model (TD4), it was found that the model deviations were lower at high CO<sub>2</sub> loadings (>0.15) in the activity based model.

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

In order to find the impact of the Henry's law constant on the performance of the absorber, only the Henry's law constant correlation or model was changed and all other parameter correlations were kept same as in the base case. In this part, the equilibrium concentrations (VLE) and activity coefficients were determined in the same way as in the base case for all cases in Table 8. The Henry's law correlations or models used in this work are listed in table 3. The AARDs of the

simulation predictions by using the different CO<sub>2</sub> Henry's law constant correlations are listed in table 8. When the Henry's law constant correlation is changed, the CO<sub>2</sub> transferred into the liquid phase changes and hence the corresponding free CO<sub>2</sub> concentration and reaction rates.

Table 8. The impact of changing CO<sub>2</sub> Henry's law constant estimation correlation on model predictions for different experimental data

		AARD (%)							
H <sub>2</sub> O		Concentrations based kinetics simulation model				Activity based kinetics simulation model			
(kPa/km ol-m <sup>3</sup> )		Puxty et al. [36,37]		Aboudheir [35]	Puxty et al. [36,37]		Aboudheir [35]	LAM.JET [3]	
		SDC	WWC	WWC	LAM.JET	SDC	WWC	WWC	LAM.JET
<b>Base</b>									
<b>case</b>		<b>14</b>	<b>13</b>	<b>12</b>	<b>13</b>	<b>19</b>	<b>15</b>	<b>14</b>	<b>10</b>
<b>(H9)</b>									
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

From the above table, it is seen that the Henry's law constant estimations with the Hartono et al.[42] empirical correlation (H1) and the Aronu et al. [38] extended-UNIQUAC model (H7) gave predictions with almost the same accuracy as the base case (Putta et al. [33] e-NRTL model). The

Wang et al. [44] correlation (H3) was found to give the highest deviations when used in the simulation model. The Wang et al. [44] correlation (H3) was developed for unloaded MEA solutions and only for low temperatures (15°C -25°C). It was found when comparing with experimental Henry's law data for CO<sub>2</sub> that the Wang et al. [44] correlation (H3) under-predicts the Henry's law constant for temperatures above 323 K even for unloaded 1 M MEA solution. The predicted CO<sub>2</sub> Henry's law constant was around 55-60% of the experimental value at high loadings. This means that the Wang et al. [44] model (H3) is not valid at high temperatures and for loaded solutions. The Tsai et al. [55] correlation (H2) always under-predicts the experimental CO<sub>2</sub> Henry's law constant even for unloaded MEA solutions and deviations become larger at high loadings. When this correlation, (H2), was used in the model, the simulation predictions were found to give similar AARD as the base case for the Luo et al. [36,37] WWC data and Aboudheir [3] laminar jet absorber data. However, the deviations were about 3 – 4 times higher than those of the base case for the Luo et al. [36,37] SDC data and the Puxty et al. [35] WWC data when using a concentrations based simulation model. The maximum deviations were seen at high loadings (0.4-0.5) and low driving forces. The Hessen et al. [40] refined e-NRTL model based CO<sub>2</sub> Henry's law (H8) was used in the simulations and the predictions were found have AARDs about 26 – 37% for all the data from all sources. This supports the arguments in the discussion on changing thermodynamic model. Both the Yaghi and Houache [86] (H4) and Ying et al. [45] (H5) correlations were found to give higher deviations (AARDs) for all the data than the base case. Also, for these models, higher deviations were seen for the Luo et al. [36,37] SDC data and the Puxty et al. [35] WWC data than for the other data sources. With the Henry's law constant from Aspen plus V8.6 [39] (H6) , the predicted absorption rates were found to have same AARDs as in base case for the Luo et al. [36,37] WWC and Aboudheir [3] laminar jet absorber data. However,

the deviations were about 3 times higher than for the base case for the Luo et al. [36,37] SDC and Puxty et al. [35] WWC data for the concentrations based simulation model. In the activity-based model, for the Aboudheir [3] laminar jet absorber data, the AARD was found to be 2 times the base case value. With all Henry's law constant correlations/models except the Hartono et al. [42] correlation (H1) and the Aronu et al. [38] extended-UNIQUAC model (H7), the simulations were not able to represent the desorption which was found in the base case. This shows clearly that Henry's law constant has a very strong impact on model performance. When Henry's law constant is estimated using thermodynamic model, it is essential to fit the model using physical solubility data of CO<sub>2</sub>. The effect of using CO<sub>2</sub> solubility data in fitting can be clearly seen with Hessen et al. [40] refined e-NRTL model based CO<sub>2</sub> Henry's law (H8) (where CO<sub>2</sub> solubility is not used in the model fitting) and the Aronu et al. [38] extended-UNIQUAC model (H7) (where solubility data are used).

### 3.3 Impact of changing reaction kinetic model

In order to find the impact of the reaction rate kinetic model on the predicted performance of the absorber, only the kinetic model was changed and all other parameter correlations kept the same as in the base case. In this study, kinetic models that are widely used in literature and also newly proposed kinetic models (listed in table 5), were used to assess the degree of influence on the simulation results. The AARDs of the predicted results by using the different kinetic models are shown in table 9.

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

		AARD (%)							
		Concentrations based kinetics simulation model				Activity based kinetics simulation model			
Kinetic model		Luo et al. [36,37]		Puxty et al. [35]	Aboudheir [3]	Luo et al. [36,37]		Puxty et al. [35]	Aboudheir [3]
		SDC	WWC	WWC	LAM.JET	SDC	WWC	WWC	LAM.JET
<b>Base</b>									
<b>case</b>		<b>14</b>	<b>13</b>	<b>12</b>	<b>13</b>	<b>19</b>	<b>15</b>	<b>14</b>	<b>10</b>
<b>(Kin6)</b>									
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

As can be seen from the above table, depending on the process conditions, the errors in model predictions can be very large. Hence, when these models are used in performance evaluations of pilot or industrial scale data, the interpretations can be very different from the actual performance and design simulations used for scale up to industrial scale. Both the Hikita et al. [95,96] and Versteeg et al. [86] kinetic models (Kin1 and Kin2) predict experimental CO<sub>2</sub> absorption rates with almost the same accuracy (AARD). Both these models (Kin1 and Kin2) were able to predict the Luo et al. [36,37] SDC and WWC data with AARDs only 10% higher than the base case. However, with the Puxty et al. [35] WWC data the AARD was 3.5 times than the base case and almost 2 times higher than the base case for the Aboudheir [3] laminar jet absorber data. The Aboudheir et al. [34] kinetic model (Kin3) was developed using pure CO<sub>2</sub> in the gas phase, i.e.,

without any gas phase resistance, with very small gas-liquid contact times (0.001-0.015 s) and using a simple Kent-Eisenberg thermodynamic model employing an empirical correlation for CO<sub>2</sub> solubility [55]. When this kinetic model (Kin3) is used for systems with gas phase resistance, as in Luo et al. [36,37] SDC and WWC, and with long contact times in combination with a rigorous thermodynamic model (e-NRTL model: Putta et al. [33]), the predicted simulation results show large errors (almost double) even for the same data that were used in the kinetic model (Kin3) development [34]. This illustrates how extra errors can be introduced to the simulation predictions when a certain kinetic model is used along with a different VLE model.

The reaction kinetic models given in Aspen Plus V8.6 (Kin4) were used in this study but in combination with a different thermodynamic model (TD1). Both the concentration and activity based kinetic model predictions gave large deviations (AARDs). In another case, the Luo et al. [37] kinetic model (Kin5) developed with the pseudo-first order reaction assumption using the Aronu et al. [38] extended-UNIQUAC thermodynamic model (TD2) was used. As seen in section 3.1 table 7, both the base case thermodynamic model (TD1) and the Aronu et al. [38] extended-UNIQUAC model (TD2) were developed using the same experimental data and gave almost the same predictions as the base case except for the CO<sub>2</sub> desorption cases. From the tables 7 and 9, it is seen that even though the thermodynamic model is the same, the error introduced by using a kinetic model based on the pseudo-first order assumption (Kin5) is larger than with a kinetic model developed without the pseudo-first order assumption (Kin6). Large deviations were observed at high CO<sub>2</sub> loading (> 0.4mol/mol). Overall, it can be concluded that none of the kinetic models were able to predict the experimental CO<sub>2</sub> absorption rates from all the apparatuses with same accuracy (AARD) as the base case. It can also be speculated if these differences in the performance

are related to kinetic constant fitting procedures. It might be that some of the fitting procedures have reached only local instead of global minimum. Furthermore, all the models except the base case has been fitted to data from only one experimental setup. Thus, any issues for example at measurement at high loading or uncertainties related to the amount of CO<sub>2</sub> absorbed, will not influence the fitting but will influence the predictions during validation with data from other equipment. It could be concluded that to develop a good kinetic models, data from several equipment and global optimization should be used.

### 3.4 Impact of changing transport property correlations

In this section, the impact of different CO<sub>2</sub> diffusivity estimation correlations on model predictions was studied by changing only the diffusivity correlations.

Table 10. The impact of changing CO<sub>2</sub> diffusivity correlations on simulation predictions

		AARD (%)							
D_CO <sub>2</sub> in MEA model	Concentrations based kinetics simulation model				Activity based kinetics simulation model				
	Luo et al. [36,37]		Puxty et al. [35]	Aboudheir [3]	Luo et al. [36,37]		Puxty et al. [35]	Aboudheir [3]	
	SDC	WWC	WWC	LAM.JET	SDC	WWC	WWC	LAM.JET	
<b>Base case</b>	<b>14</b>	<b>14</b>	<b>12</b>	<b>13</b>	<b>19</b>	<b>15</b>	<b>14</b>	<b>10</b>	
<b>(DC1)</b>									
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	

It is observed that just by changing correlation for diffusivity of CO<sub>2</sub> in aqueous MEA solutions from one to another correlation, the impact on the simulation predictions can vary significantly depending on the amine concentration, CO<sub>2</sub> loading, and temperatures as seen in Table 10. The Jamal [90] correlation (DC2) predicts CO<sub>2</sub> diffusivity values higher than that of Ko et al. [89] (DC1). The Versteeg et al. [86] correlation based on a modified Stokes-Einstein correlation always predicts lower diffusivities than the Ko et al. [89] correlation (DC1). By using the Jamal [90] correlation (DC2) instead of the Ko et al. [89] correlation (DC1), the change in the AARDs of simulation results was found to be around 10-13% for the Luo et al. [36,37] SDC and Puxty et al. [35] WWC data. For the Luo et al. [36,37] WWC and Aboudheir [3] laminar jet absorber data, the difference in AARDs is insignificant (around 1-2 %). The Ying and Eimer [91] correlation (DC3) predicted with the same accuracy as the base case (DC1) (maximum difference in AARDs is 3%). In the Versteeg et al. [86] correlation itself, depending on the viscosity model used, the simulation predictions can also vary and it was seen that from changing viscosity model from the Hartono et al. [42] correlation (DC4) to the Weiland et al. [92] correlation (DC5), the AARDs decreased by 3-5 %. The Morgan et al. [30] (DC6) and Weiland et al. [92] (DC5) viscosity correlations gave predictions with the same AARD ( the difference is less than 0.5%). The difference in simulation predictions by employing different liquid viscosity correlations in CO<sub>2</sub> diffusivity estimation was found to be less significant (difference in AARDs is less than 5%) compared to the difference in simulation predictions due to CO<sub>2</sub> diffusivity calculation using either the N<sub>2</sub>O analogy or a modified Stokes-Einstein correlation (maximum difference in AARDs is 25%). Overall, it can be concluded that care should be taken when selecting or changing correlation and basis (N<sub>2</sub>O analogy versus modified Stokes-Einstein correlation) for diffusivity of CO<sub>2</sub> in amine solutions.



### 3.5 Impact of using different combinations of parameter estimation models/correlations

In the literature, it has been seen that the kinetic models of Hikita et al. [95,96], Versteeg et al. [86] and [34] were implemented in Aspen Plus to study the absorber performance and also to evaluate pilot scale experimental data. Thus, we studied the impact of the combination of these reaction kinetic models with Aspen Plus properties on the absorber performance. This was done by taking the thermodynamic model and physical and transport properties from the Aspen Plus V8.6 e-NRTL-RK template (calculation of equilibrium concentrations, activity coefficients, and Henry's law constant of CO<sub>2</sub> in MEA solutions and diffusivities, density and viscosity). In addition to the literature kinetic models, the recently developed kinetic model by Putta et al. [33] was also tested.

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

Reaction rate kinetic model	Case name	AARD (%)			
		Luo et al. [36,37]		Puxty et al. [35]	Aboudheir [3]
		SDC	WWC	WWC	LAM.JET
Hikita et al. [95,96]	SP1	28	23	71	14
Versteeg et al. [88]	SP2	31	22	79	14
Aboudheir et al. [34]	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. [33] Concentrations based	SP6	23	16	33	11
Putta et al. [33] activities based	SP7	18	16	23	7

From table 11, it can be seen that when the Hikita et al. [95,96] model (SP1) is used in combination with the thermodynamic model and other properties from Aspen Plus V8.6, the simulation predictions show higher deviations than in the base case except for the Aboudheir [3] laminar jet absorber data. For the Puxty et al. [35] WWC data the simulation predictions have an AARD above 70%. When comparing the ability of the same kinetic model (Kin1) but in combination with the Putta et al. [33] thermodynamic model and corresponding physical properties correlations (Table 9, Kin1), the deviations (AARDs) were smaller for the Luo et al. [36,37] SDC and Puxty et al. [35] WWC data. The model SP1 predicts with the same accuracy for the Luo et al. [36,37] WWC data as the base case. Furthermore, as shown in Table 11, the same trend was observed for the Versteeg et al. [86] kinetic model (SP2) giving predictions similar to the model SP1. In case of the Aboudheir et al. [34] kinetic model (SP3), the predictions are better with the Aspen plus thermodynamic model and properties than with the ones used in the base case. The same trend was seen for the Aspen Plus kinetic models (SP4 and SP5), for both the concentration based and activity based kinetic models. The concentration based kinetic model by Putta et al. (2016) (SP6) together with the Aspen Plus thermodynamic model and properties gave deviations (AARDs) of 9% and 21% higher than the base case (Table 9, Kin6) for the Luo et al. [36,37] SDC and Puxty et al. [35] WWC data respectively. The Luo et al. [36,37] WWC data were predicted with almost same the accuracy as in the base case (difference in AARD is less than 5%). The Putta et al. [33] activity-based kinetic model (SP7) in combination with the Aspen Plus thermodynamic model and properties predicts experimental absorption rates from Luo et al. [36,37] SDC and WWC with the same accuracy as the base case (Table 9, Kin6). The deviations (AARD) are 10% higher than that of the base case for the Puxty et al. [35] WWC data. Both kinetic models by Putta et al. [33] (SP6 and SP7) together with the Aspen Plus thermodynamic model and properties predicted data from

Aboudheir [3] laminar jet absorber with better accuracy than the base case. From these, it can be concluded that by using kinetic models along with Aspen Plus thermodynamic model and properties, the simulation predictions can be improved for some of the kinetic models whereas the predictions became worse for other kinetic models when compared with the same predictions based on the Putta et al. [33] e-NRTL model and properties mentioned in table 6.

All the parameter models and correlations studied in the present study have a varying degree of impact on the rate-based model predictions. Among all, the CO<sub>2</sub> Henry's law constant correlations or models have the highest impact on the predicted CO<sub>2</sub> absorption rates. The kinetic model selection affects the simulation predictions more than the thermodynamic model and the diffusivity correlations for CO<sub>2</sub> in amine solutions. Thermodynamic models selection has a lower impact on the predicted results than CO<sub>2</sub> diffusivity correlations selection.

#### 4 Conclusions

In the present study, different thermodynamic models, CO<sub>2</sub> Henry's law constant correlations, reaction kinetic models and CO<sub>2</sub> diffusivity correlations were applied to a rate-based mass transfer model and used to compare with available laboratory mass transfer rate data sets. The impact of using different models and correlations for the same property on the model predictions was studied in detail. Experimental data from four different well-characterized laboratory apparatuses with a wide range of process conditions were used to assess the impact of different models and correlations. When the thermodynamic model is changed, it was seen that model prediction performance can vary significantly. The effect is stronger at high loadings and low CO<sub>2</sub> partial pressures. By keeping all other parameters as in the base case and only changing the CO<sub>2</sub> Henry's law constant estimation correlation/method, it was seen that the error in model predictions can be

very large depending on the correlation used. Thus, the predictive ability of any given correlation should be assessed or validated before employing in the simulations. From this study, we can clearly see that one should always be careful when using only a “foreign” kinetic model from published literature in in-house or commercial process simulators without also using all other parameters (physico-chemical and thermodynamic properties) used in the “foreign” kinetic model. In the study of evaluating the different kinetic models predictive capacity, it was seen that most of the kinetic models existing in the literature fail to represent the experimental CO<sub>2</sub> absorption data from all the sources with the same accuracy. In most of the cases, the models are able to predict the experimental data from one source with good accuracy but fail to predict with the same accuracy from other sources. Also when evaluating the impact of CO<sub>2</sub> diffusivity correlations on the model performance, it was seen that those based on the N<sub>2</sub>O analogy give a better representation of the experimental data compared to modified Stokes-Einstein correlations. From the present study, it is observed that there is a risk of introducing large errors to model predictions just by simply using different physical property correlations other than those used in the original model development. Great caution is required when selecting the correct combination of property methods/correlations, kinetic model and thermodynamics. The following steps should be followed in order to evaluate the additional errors in the model predictions:

- (a) The deviations in the particular property value due to a new correlation should be quantified over a wide range of process conditions
- (b) The developer should quantify the error introduced to the predictions due to a property correlation selection
- (c) The model should be validated with experimental data
- (d) Steps (a)-(c) should be followed for every property correlation changed

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