

Applicability of enhancement factor models for CO₂ absorption into aqueous MEA solutions

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Abstract

In many chemical industrial processes, mass transfer across gas-liquid interfaces accompanied by chemical reaction is the governing phenomena. In case of mass transfer accompanied by a chemical reaction in the liquid phase, the reaction will enhance mass transfer and generally the mass transfer enhancement is quantified in terms of an enhancement factor. Large number of enhancement factor models have been developed in literature and used without critical analysis for analyzing pilot data for CO₂ absorption into aqueous amines. In order to perform such a critical analysis, 24 models are tested using lab-scale experimental data from four independent apparatuses for CO₂ absorption into MEA solutions covering a range of different conditions such as short and long contact times, with and without gas phase resistance, high and low CO₂ loadings and temperatures. Of the 24 enhancement factor models tested only six models were found to satisfactorily predict the experimental CO₂ fluxes. These were the models based on the simple pseudo-first order reaction assumption, Emodels 1, 2 and 3 by Hatta [2] and Dankwerts [4] respectively, Emodel 20, the deCoursey and Thring [44] model based on Danckwert's surface renewal theory with unequal diffusivities, Emodel 24, the recently published generalized model by Gaspar and Fosbøl [51] and Emodel 21, the Tufano et al. [67] model based surface renewal theory. All these models were found to work equally well to the discretized penetration model. No significant difference was found between Emodels 1, 2 and 3, indicating that whether one uses as basis a film, penetration or surface renewal model, is of insignificant importance.

The success of the simple models is attributed to the short contact times in the experiments used as basis and the accuracy of the kinetic model. Contact times of the same magnitude between mixing points is also encountered in industrial packings and it is believed that the simple enhancement factor models may work well also in these cases if an accurate kinetic model is used.

Keywords

Enhancement factor model; mass transfer; chemical reaction; CO₂ absorption; Aqueous Alkanolamines

1 Introduction

Gas diffusion into a liquid phase, either with or without chemical reaction, is a frequently encountered separation method in many chemical industrial processes. In gas scrubbing operations, polymer processing, homogeneous and heterogeneous catalysis, as well as other chemical processes, important steps are governed by mass transfer across gas/liquid interfaces, often accompanied by a chemical reaction. Carbon dioxide removal from a gas stream using a chemical absorbent is a simultaneous mass transfer process with chemical reaction taking place in the liquid phase. The phenomena governing the mass transfer occurring at the interface are of both theoretical and practical importance, and are the drivers in the overall capture process. In a conventional temperature swing process such as in post-combustion CO₂ capture from flue gas from a fossil fuel power plant, CO₂ in the combustion gas stream is absorbed in an absorber using a chemical solvent and is released in a stripper at elevated temperature. As the partial pressure of CO₂ is low, requiring chemical absorbents for capture, the gas-liquid interface can be described as

a mass transfer/mixing system accompanied by chemical reactions. Furthermore, as these reactions are reversible and with finite rates, the reaction kinetics are of main importance for both absorption and desorption, and should be known when analyzing the governing mass transfer mechanisms at the gas/liquid interface. The performance of a given absorbent for CO₂ capture can thus be understood by a description of the mass transfer phenomena involved as well as the description of the enhancement of the mass transfer due to chemical reaction. An improved understanding of these processes may lead to the discovery of new solvents with improved performance for example for acid gas cleaning processes. The mass transfer phenomenon is mainly dependent on the diffusivities of the transferring components, the hydrodynamic properties like fluid mixing and geometry of the equipment used and the kinetics as given by the type of chemical absorbent used [1]. All these described phenomena can be modelled.

CO₂ capture using aqueous alkanolamines is the most mature technology among the existing technologies for CO₂ removal. Main challenges for industrial implementation of post-combustion CO₂ capture are high energy requirement for regeneration, aerosol formation and degradation of the amine. Due to the high-energy penalty and aerosols emissions challenge for successful implementation of CO₂ capture technologies, a great number of researchers are working in developing the new low-energy penalty solvents, aerosols emissions control, optimization and integration and scale-up of the process [2–15]. Rate-based models have been used for the simulation of CO₂ absorption process. Process simulators capable of modelling CO₂ absorption typically have several sub-models describing physico-chemical and transport properties, mass and energy balances, gas-liquid interface transfer models accounting for chemical reaction (require reaction kinetics) and a thermodynamic model describing the chemical and vapor-liquid equilibria. If the sub-models used are rigorous, then the full-scale process model becomes computationally very heavy and will require substantial computational power and time. Thus, a goal pursued in the literature has been to identify simplified models which can capture the most important phenomena in the most simple and numerically efficient way.

In the case of mass transfer accompanied by a chemical reaction with CO₂ in the liquid phase, the reaction will enhance mass transfer. Often, the chemical reactions are complex and reversible in nature. This mass transfer enhancement is generally expressed as the ratio of the liquid side mass transfer coefficient with chemical reaction to that without any reaction and can be expressed as shown in eq. (1). From the design point of view, for example for modeling of such systems, an accurate quantification of the fluxes of the transferred components across the gas-liquid interface, as a function of gas and liquid phase compositions, column packing type, flow properties and temperature, is crucial. Traditionally, mass transfer phenomena have been studied using mainly three different models, i.e., the film-, penetration- and surface renewal theories [16]. The mass balance equations for the reacting systems yield non-linear partial differential equations and analytical solutions of these sets of equations for all reaction regimes is not possible. In these chemical systems, interpretation of the rate data measured may be difficult to incorporate into a general model that also considers convective and diffusive phenomena, even with models with major simplifications. An absorption process with mass transfer with an irreversible first-order reaction is simple and can be solved analytically for all mass transfer models. For all other process scenarios, only a limited number of approximate solutions are possible, thus numerical solutions must be obtained [17,18]. Mass transfer rates can in certain reaction regions be calculated with

satisfactory accuracy with approximate or linearized solutions to the models. As noted, the mass transfer enhancement due to chemical reaction can be assessed through an enhancement factor (E), which depends on the rate of reaction (kinetics and stoichiometry), diffusivities of reactants and products as well as concentrations.

$$E_A = \frac{\text{Liquid side mass transfer coefficient with reaction}}{\text{Liquid side mass transfer coefficient without reaction}} \Bigg|_{\text{same driving force } (C_{Ai} - C_{Ab})} = \frac{k_l}{k_{l0}} \quad (1)$$

The objective of this work is to compare the performance of different, commonly used, enhancement models and identify the models most suitable for modelling of CO₂ absorption into MEA. We compare 24 different enhancement factor models used to calculate mass transfer rates into aqueous MEA solutions. The models are compared with four different experimental data sets from the literature covering a relatively wide range of MEA concentration (0.5-9 moles /L), CO₂ loadings (0-0.5 moles CO₂ /mole MEA) and temperatures (293-343K). Validation of enhancement factor models against experimental data has, to our knowledge, not been performed systematically in the literature.

1.1 Literature review

Enhancement factor models for predicting transfer rates of gases into liquids were described in literature almost a century ago [19] and a large variety of models have been developed over the years. The underlying mathematics behind the development of the enhancement factor expressions is not presented here as it is deemed outside the scope of this paper and can be found in the referred papers. Therefore, only the final expressions are given here.

As noted, gas-liquid mass transfer models are commonly described with a convective term, a diffusion term, and a reaction term. For a stagnant reaction film where concentrations of transferring components are low, the convective term is usually disregarded. This is also done in this work. For a species A in an element, the general mass balance equation can be given according to eq. (2).

$$\left(\begin{array}{c} \text{Rate of accumulation of} \\ \text{mass of species A} \end{array} \right) = \left(\begin{array}{c} \text{Rate of mass of} \\ \text{species A in} \end{array} \right) - \left(\begin{array}{c} \text{Rate of mass of} \\ \text{species A out} \end{array} \right) + \left(\begin{array}{c} \text{Rate of production of mass of} \\ \text{species A due to reaction} \end{array} \right) \quad (2)$$

The general mass balance equation for a component A in the liquid phase is written as shown in eq. (3) where C is the concentration (mol/L), D_{AB} is the diffusivity of species A in B (m²/s) and r_A is the source term (reaction rate, mol/m³-s).

$$\frac{\partial C_A}{\partial t} = \left(D_{AB} \frac{\partial^2 C_A}{\partial x^2} + r_A \right) \quad (3)$$

In film-theory, the transient term in eq. (3) is assumed zero while in both penetration and surface renewal theories, it is not disregarded.

Derivation of various solutions to this system, based on selected "validity regimes", yield different enhancement factor models. The most frequently used expressions in the literature will be reviewed in this section.

When solving this system of equations, eq. (3), for all components, in the so-called pseudo-first order reaction regime, a special solution arises where the liquid side mass transfer coefficient is canceled out. An important dimensionless number known as the Hatta number [19] is used to characterize the significance of the reaction rate versus diffusional rate. The Hatta number is expressed as the ratio between diffusion time and reaction time. For the reaction scheme $A + \nu_B B \rightarrow$ products, and with a first order reaction in A (the reaction rate $r_A = k_1 C_A$), the Hatta number is defined as:

$$\begin{aligned}\phi_A^2 &= \frac{\text{maximum theoretical conversion rate due to reaction in the film per unit area of the film}}{\text{maximum theoretical mass transfer rate through the film in the absence of reaction}} \\ &= \frac{k_1 D_A}{k_{L0}^2} = \frac{k_1}{D_A} \delta^2 = \frac{k_1 C_{Ai} \delta}{\frac{D_A}{\delta} (C_{Ai} - 0)} \\ &= \frac{\delta^2 / D_A}{1/k_1} = \frac{t_D}{t_R} = \frac{\text{diffusion time}}{\text{reaction time}}\end{aligned}\quad (4)$$

Here k_1 is the reaction rate constants, δ is the film thickness, D_A is the diffusivity of A, k_{L0} is the liquid side physical mass transfer coefficient and ν_B is the stoichiometric coefficient for reactant B when the stoichiometric coefficient of reactant A is 1.

The Hatta number value can be used as an indication whether the reaction occurs in the bulk liquid phase, therefore requiring a large volume of liquid, or completely in the film, which demands contacting devices that provide large interfacial area. If $Ha \gg 1$, the reaction occurs primarily within the liquid film and when $Ha \ll 1$, most of the reaction occurs in the liquid bulk, i.e., beyond the film [20]. For pseudo-first order irreversible reactions, the enhancement factor is given for the film- [19], penetration- and surface renewal theories[21] respectively as shown in eq.s (5) -(7).

$$E_{A,ps}^{film} = \frac{\phi_A}{\tanh \phi_A} \quad (5)$$

$$E_{A,ps}^{pen} = \phi_A \left[\left\{ 1 + \frac{\pi}{8\phi_A^2} \right\} \operatorname{erf} \left[\sqrt{\frac{4\phi_A^2}{\pi}} \right] + \frac{1}{2\phi_A} \exp\left(-\frac{4\phi_A^2}{\pi}\right) \right] \quad (6)$$

$$E_{A,ps}^{surf} = \sqrt{1 + \phi_A^2} \quad (7)$$

Here, ϕ_A is the Hatta-number for a 1st order reaction as given in eq. (4).

The enhancement factor, for cases with reaction order higher than one, is a function of both Hatta number and the enhancement factor for an instantaneous reaction i.e., the infinite enhancement factor. Mass transfer model choice (film, penetration) will affect the infinite enhancement factor model and it can be given as [22]:

$$E_{A,\infty} = \left(1 + \frac{C_{B,bulk} D_B}{\nu_B C_{Ai} D_A} \right) \left(\frac{D_A}{D_B} \right)^n \quad (8)$$

For film theory $n=0$ and for penetration theory $n=0.5$ [22].

In 1948 Van Krevelen and Hoftijzer [23] developed the first approximate analytical relation based on film theory for absorption with irreversible second order chemical reaction. The developed

relation is implicit in nature and was developed for equal diffusivities of reactants but later applied for other diffusivity ratios also. The Van Krevelen and Hoftijzer [23] correlation is considered as the pioneering work in the development of approximate analytical models. Their expression is given as shown in eq. (9).

$$E_A = \frac{\phi_{A,2} \sqrt{\frac{E_{A,\infty}^{film} - E_A}{E_{A,\infty}^{film} - 1}}}{\tanh\left(\phi_{A,2} \sqrt{\frac{E_{A,\infty}^{film} - E_A}{E_{A,\infty}^{film} - 1}}\right)} \quad (9)$$

Here, $\phi_{A,2}$ is the Hatta-number for a 2nd order reaction and $E_{A,\infty}^{film}$ is the infinite enhancement factor for film theory as given in eq. (11).

$$\phi_{A,2} = \frac{\sqrt{D_A k_2 C_B}}{k_{L0}} \quad (10)$$

$$E_{A,\infty}^{film} = 1 + \frac{D_B C_{B,L}}{v_B D_A C_{A,Li}} \quad (11)$$

Eq.(8) and eq.(11) are the equations for infinite enhancement factor for irreversible reactions and are taken from the literature. This equations are applicable only irreversible reactions and should be modified or derived for reversible reactions. As the present work is mainly focusses on the testing and validation of existing models in the open literature, the derivation for reversible reactions is not considered.

Santiago and Farina [24] reported the maximum error between using an enhancement factor for second order irreversible reaction and a numerical solution of the film model to be less than 3 percent. In 1960, Olander at al. [25] developed enhancement factor models for instantaneous reversible reactions for the film and surface renewal theories. Later Secor and Beutler [26] solved the penetration theory equations representing mass transfer accompanied by reversible chemical reactions using a finite difference method. Numerical enhancement factor values obtained with penetration theory and film theory are quite close to each other when the diffusivities ratio of reactants is near to 1. Olander at al. [25], Secor and Beutler [26] and Danckwerts [27] considered instantaneous reversible reaction by assuming that the reaction is fast enough to maintain equilibrium at every point and time and the reaction kinetics are irrelevant under these conditions [27].

For the reaction scheme $v_A A + v_B B \rightleftharpoons v_C C + v_D D$ with reaction rate $R_A = v_A k_1 \left(A B^2 - \frac{C D}{K_{eq}} \right)$, the infinite enhancement factor equation given by Secor and Beutler [26] for penetration theory is shown in eq. (12).

$$E_{A,\infty} = 1 + \frac{m q \left(\sqrt{\frac{p}{q}} - \frac{2p}{q} \right)}{\left(1 - \frac{4p}{q} \right)} \quad (12)$$

where $m=1$, $p = \phi_A^2$ and $q = \frac{B_{bulk}}{A_i}$

For CO₂ absorption into partially loaded MEA solutions, with reaction scheme given by eq. (13), the infinite enhancement factor was given by Danckwerts [27] as shown in eq. (14).



$$E_{A,\infty} = 1 + \frac{\frac{D_{MEACOO^-}}{D_{CO_2}} \sqrt{K_{eq,CO_2}} C_{MEA}}{\left[\left(1 + 2 \frac{D_{MEACOO^-}}{D_{MEA}} \right) \sqrt{K_{eq,CO_2}} C_{CO_2,free,b} + \sqrt{C_{CO_2,free,in}} \right]} \quad (14)$$

where $K_{eq,CO_2} = \frac{C_{MEAH^+} C_{MEACOO^-}}{C_{CO_2} (C_{MEA})^2}$

Brian and co-workers [28,29] generalized the Van Krevelen and Hoftijzer [23] expression for Higbie's penetration theory by using the infinite enhancement factor corresponding to penetration theory given in eq. (15) and showed the agreement between the numerical solution of the partial differential equations and the enhancement factor expression for a second-order chemical reaction are within 6% when the diffusivity ratio of the reactants is one. As can be seen from both eq.s (9) and (15), the enhancement factor correlation is still implicit and needs iterative calculations.

$$E_{A,\infty}^{pen} = \sqrt{\frac{D_A}{D_B}} + \sqrt{\frac{D_B}{D_A}} \frac{C_{B,L}}{v_B C_{A,Li}} \quad (15)$$

Hikita and Asia [30] gave a general method for the calculation of the Hatta number for irreversible (m,n)th order reaction and the expression is given as,

$$\phi_A = \frac{\sqrt{\frac{2}{m+1} k_{m,n} C_{Ai}^{m-1} C_{B,bulk}^n D_A}}{k_{L0}} \quad (16)$$

Where $k_{m,n}$ are the reaction rate constants, C_{Ai} , $C_{B,bulk}$ and m , n are interfacial and bulk concentrations and reaction orders of A and B respectively. For Higbie's penetration model, the enhancement factor equation is given as:

$$E_A^{pen} = (\gamma + \pi/8\gamma) \operatorname{erf}(2\gamma/\sqrt{\pi}) + 1/2 \exp(-4\gamma^2/\pi) \quad (17)$$

where $\gamma = \sqrt{M(E_{A,\infty}^{pen} - E_A)/(E_{A,\infty}^{pen} - 1)}$

where $M = \phi_A^2$ and ϕ_A is expressed as shown in eq. (16).

Using the Hatta number expression given by eq. (16), enhancement factors can be estimated for any reaction order by using the available enhancement factor expressions in the literature. Kishinevskii and Armash [31] and Kishinevskii et al. [32] developed an explicit enhancement factor expression for irreversible second order reaction and for film theory as given in eq. (18):

$$E_A^{film} = 1 + (\phi_{A,2}/\alpha) [1 - \exp(-0.65\phi_{A,2}\sqrt{\alpha})] \quad (18)$$

where $\alpha = [\phi_{A,2}/(E_{A,\infty}^{film} - 1)] + \exp[0.68/\phi_{A,2} - 0.45\phi_{A,2}/(E_{A,\infty}^{film} - 1)]$

Similarly, Santiago and Farina [24] developed an explicit equation by following a different approach than DeCoursey [33] and the equation was given by Santiago and Farina [24] for $E_A > 3$ as:

$$E_A^{film} = \sqrt{[\phi_{A,2}^4/4(E_{A,\infty}^{film} - 1)^2] + [\phi_{A,2}^2/(E_{A,\infty}^{film} - 1)] + \phi_{A,2}^2} - [\phi_{A,2}^2/2(E_{A,\infty}^{film} - 1)] \quad (19)$$

Yeremian et al. [34] developed explicit enhancement factor expressions for second order irreversible reactions by generalizing the Van Krevelen and Hoftijzer expression to penetration and surface renewal theories. For the penetration theory, the explicit expression for the enhancement factor is given as shown in eq. (20)

$$E_A^{pen} = \frac{E_{A,ps}^2}{2(E_{A,\infty}^{pen} - 1)} + \left\{ \left[1 + 4 \frac{E_{A,\infty}^{pen} (E_{A,\infty}^{pen} - 1)}{E_{A,ps}^2} \right]^{0.5} - 1 \right\} \quad (20)$$

Where $E_{A,ps}$ is the enhancement factor for a pseudo first order reaction given in eq. (6) for the penetration theory.

For surface renewal theory, the result is shown in eq. (21).

$$E_{A,\infty}^{surf} = \frac{\phi_A^2}{2(E_{A,\infty}^{pen} - 1)} \left\{ \left[1 + \frac{4[(E_{A,\infty}^{pen} - 1)^2 + E_{A,\infty}^{pen} \phi_A^2 (E_{A,\infty}^{pen} - 1)]}{\phi_A^4} \right]^{0.5} - 1 \right\} \quad (21)$$

Here ϕ_A is the Hatta number for a 1st order reaction as given in eq. (4).

Porter [35] also developed an explicit correlation for the enhancement factor for a second order irreversible reaction given as:

$$E_A^{film} = 1 + (E_{A,\infty}^{film} - 1) \left\{ 1 - \exp[-(\sqrt{\phi_{A,2}^2} - 1)/(E_{A,\infty}^{film} - 1)] \right\} \quad (22)$$

Baldi and Sicardi [36] modified Porter's eq. (22) and gave an expression for the enhancement factor as:

$$E_A^{pen} = 1 + (E_{A,\infty}^{pen} - 1) \left\{ 1 - \exp[-(\sqrt{1 + \phi_{A,2}^2} - 1)/(E_{A,\infty}^{pen} - 1)] \right\} \quad (23)$$

For Danckwert's surface renewal theory with second order irreversible reaction, DeCoursey[37] presented an explicit enhancement factor expression as shown in eq. (24).

$$E_A^{surf} = -\frac{\phi_A^2}{2(E_{A,\infty}^{film} - 1)} + \sqrt{\left[\frac{\phi_A^4}{4(E_{A,\infty}^{film} - 1)^2} + \frac{E_{A,\infty}^{film} \phi_A^2}{(E_{A,\infty}^{film} - 1)} + 1 \right]} \quad (24)$$

Onda et al. [38–41] presented an approximate solution for the enhancement factor for penetration and surface renewal theories for absorption with reversible, consecutive and parallel chemical reactions using the Hikita and Asai approximation [30] under the condition of equal diffusivities. To manifest generalized enhancement factor models as applicable to all theories, they also compared the approximate solutions with a numerical solutions based on film theory and found the numerical and approximate solutions to be in good agreement within a few per cent. Onda et al. [38–41] confirmed that Hikita and Asai's approximation [30] is valid not only at steady state conditions but also at unsteady state conditions. Wellek et al. [42] developed a relatively simple explicit expression for the enhancement factor calculation for a second order irreversible reaction based on asymptotic solutions to the film model. The enhancement factor correlation is given as shown in eq. (25).

$$E_A = 1 + \left\{ 1 + \left(\frac{(E_{A,\infty}^{film} - 1)}{(\phi_{A,2} - 1)} \right)^{1.35} \right\}^{\frac{1}{1.35}} \quad (25)$$

Karlsson and Bjerle [43] developed expressions for the enhancement factor for irreversible second order reactions for both film and penetration theories by also taking the gas phase resistance into account. DeCoursey [33] developed an enhancement factor expression using surface renewal theory for a second order reversible reactions using the equal diffusivities condition. Later, DeCoursey and Thring [44] extended it to unequal diffusivities. Hikita et al. [45] developed an expression for the enhancement factor calculation for a reversible reaction based on penetration theory and applied it for estimation of kinetic constants for CO₂ reaction with aqueous sodium sulfite solutions.

The approximate solutions of Onda [38] and DeCoursey [33] were checked and verified by De Lind van Wijngaarden et al. [46] and Versteeg et al. [47]. Later in 1992, Winkelman et al. [48] compared a numerical solution and the DeCoursey and Thring [44] enhancement factor model with unequal diffusivities, and found that the approximate solution was in good agreement with numerical solutions with a maximum deviation of 14%. Van Swaaij and Versteeg [18] presented an overview of the approximate expressions and detailed numerical absorption models used for reversible reactions till then. However, the validity of the enhancement factor models and the accuracy of the models in predicting the absorption rates were not discussed.

In 1997, Hogendoorn et al. [49] proposed a new explicit expression for the enhancement factor for reversible reactions with finite rate in CO₂ loaded solutions and applicable for unequal diffusivities also based on Higbie's penetration theory. They developed a correlation by combining the DeCoursey [33] correlation for irreversible reaction of finite rate and the Secor and Beutler [26] model for instantaneous reversible reactions. In order to apply the film theory model of Secor and Beutler [26] to penetration theory, the diffusivity ratios were replaced by the square roots of these ratios. The enhancement factor model solutions were compared to numerical enhancement factor models obtained from a penetration theory model. They found that the deviations increased

substantially for high loadings in combination with unequal diffusivities. Last and Stichlmair [50] developed an explicit equation for irreversible second order fast reactions as shown in eq. (26). Using this enhancement factor equation, they determined the effective interfacial area and liquid side mass transfer coefficient.

$$E_A = \frac{1}{\left\{ \left(1 - (1/E_{A,\infty}^{film}) / \phi_{A,2}^{3/2} \right) + (1/(E_{A,\infty}^{film})^{3/2}) \right\}^{2/3}} \quad (26)$$

Recently, Gaspar and Fosbøl [51] developed a general enhancement factor model for the (m+n)th order reversible reactions and validated with the numerical solution of the two-film model for absorption, desorption and pinch conditions [51]. It was shown that the GM model predicts the rigorous two-film model within 2% accuracy and the surface renewal model within 10% accuracy for the reaction between CO₂ and MEA. The expression is given as:

$$E_A = 1 + (E_{A,\infty}^{film} - 1) \frac{1 - y_B^i}{1 - y_{CO_2}^b} \quad (27)$$

$$y_{CO_2}^b = \frac{C_{CO_2}^b}{C_{CO_2}^i} \quad \text{and} \quad y_B^i = \frac{C_B^i}{C_B^b}$$

In addition to the development of enhancement factor models, de Santiago and Farina [24], Wellek et al. [42] and Winkelman et al. [48] performed comparative studies of the existing correlations with numerical solutions for some asymptotic conditions. The most frequently used enhancement factor correlations in the literature for experimental absorption data interpretation and for comparison with numerical solutions of mass transfer with chemical reaction models are listed in table 1.

Table 1. Overview of the enhancement factor models used in the literature

Source	Reaction condition	Mass transfer theory	Limitations/Remarks
Hatta [19]	Pseudo first order reaction	Film theory	
van Krevelen and Hoftijzer [23]	2 nd order bi-molecular irreversible reaction	Film theory	Implicit correlation
Olander [25]	Instantaneous reversible reactions	Film, surface-renewal theories	Equilibrium exists at all points in the liquid phase
Brian et al. [28]	Irreversible 2 nd order reaction	Penetration theory	Implicit correlation
Hikita and Asai [30]	(m,n) th irreversible reaction	Film theory	Can be applied for reactions with any order and implicit in nature
Secor and Beutler [26]	Instantaneous reversible reactions	Penetration and film theories	Valid only for instantaneous reactions
Danckwerts [27]	Instantaneous reversible reactions	Surface renewal theory	Valid only for instantaneous reactions

Kishinevskii et al. [31,32]	2 nd order irreversible reaction	film theory	Explicit correlation
Porter [35]	2 nd order irreversible reaction	film theory	Explicit correlation
Onda et al. [38]	Reversible reaction	Film theory	Iterative procedure and Diffusivities all species must be equal
Danckwerts [21]	Pseudo-first order irreversible reaction	Penetration and surface renewal theories	
Yeramian et al. [34]	2 nd order irreversible reaction	Penetration and surface-renewal theories	Explicit correlation
DeCoursey [37]	2 nd order irreversible reaction	Surface-renewal theory	Explicit correlation
Baldi and Sicardi [36]	2 nd order irreversible reaction	Penetration theory	Explicit correlation
Wellek et al. [42]	2 nd order irreversible reaction	film theory	Explicit correlation
DeCoursey [33]	Reversible reaction	Surface-renewal theory	Diffusivities all species must be equal
Hikita et al. [45]	Reversible reaction	Penetration theory	Solute loading is close to zero
Astarita et al. [52]	Reversible reaction	Film theory	
DeCoursey and Thring [44]	Reversible 2 nd order reaction	Surface-renewal theory	Diffusivities do not need to be equal
Hogendoorn et al. [49]	Reversible reaction in CO ₂ loaded amine solutions	Penetration theory	Explicit correlation
Last and Stichlmair [50]	2 nd order irreversible reaction	Surface-renewal theory	Explicit correlation
Gaspar and Fosbøl [51]	2 nd order reversible reaction	Film theory	Implicit correlation

In addition to the expressions discussed above, researchers also used different combinations of these correlations for modeling a pilot laboratory absorption/desorption rig for CO₂ capture. Tobiesen et al. [53] used the explicit correlation of DeCoursey [37] in combination with the Weiland et al. infinite enhancement factor model [54], for modeling the pertinent reaction regimes in an absorber.

The correlations developed in the literature have the following limitations.

- i. All the enhancement factor equations in the literature except the DeCoursey and Thring [44] and Hogendoorn et al. [49] correlations, were developed using the assumption of equal diffusivities of reactants, which may not be valid for CO₂ absorption using aqueous amines.
- ii. Enhancement factor models were compared with numerical solutions from film, penetration or surface renewal models based on arbitrarily chosen transport and kinetic parameters. They were not tested against experimental mass transfer data.
- iii. Temperature effects were not considered in the development of the models.
- iv. All the authors assumed negligible gas phase mass transfer resistance in the enhancement factor models development except the Karlsson and Bjerle [43] model.
- v. All the analytical enhancement factor equations were developed for unloaded systems except the Hogendoorn et al. [49] model.
- vi. The concentration of the solvent solutions considered in the numerical solutions were less than 1 mol/L.
- vii. None of the models considered the thermodynamic non-idealities of solvents in the development.
- viii. All the models were developed using arbitrary reaction schemes and kinetics and were not developed for CO₂ capture using a particular aqueous solvent.

As there are numerous enhancement factor models available in the literature, many of which were developed for vastly different applications and developed with different base assumptions. In order to use these models with confidence, there is a strong need for quantitative analysis and comparison with experimental data of good quality. As mentioned enhancement factor models have often been evaluated based on artificial models or used when interpreting pilot plant data. When using pilot plant data one important very uncertain parameter is introduced, namely the specific interfacial area. Interfacial area correlations available in the literature have been found to have very large uncertainties [55–57]. The active area and enhancement factor are interrelated in the sense that they both affect directly the measured or calculated mass transfer rate. In order to perform a more stringent evaluation of only the enhancement factor models, the analysis must be based on data where the interfacial area is a priori well defined. Such data are available from laboratory experiments with wetted wall columns, laminar jet absorbers and string of discs apparatuses. In Putta et al. [46] data sets from four different apparatuses were compared, validated and used for developing an improved kinetic model for CO₂ absorption into MEA solutions. These data sets are also ideally suited for evaluating the accuracy of the various enhancement factor models.

2 Methodology

As mentioned above, in this work, we compare 24 different enhancement factor models used to calculate mass transfer rates into aqueous MEA solutions. In order to avoid uncertainties regarding determination of interfacial area, the models are compared with four different experimental data sets from the literature where the interfacial area is well defined and a priori known.

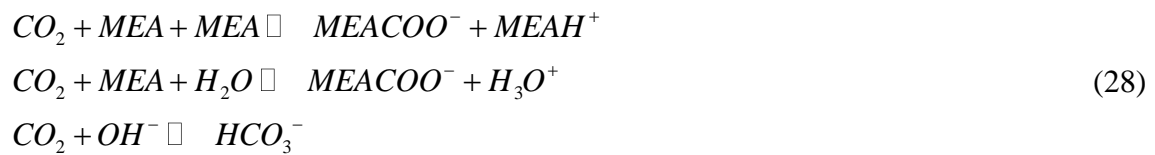
For CO₂ absorption into aqueous MEA solutions, two reaction mechanisms, namely the zwitterion and the direct (termolecular) mechanisms, have been proposed. From the studies of Luo et al. [58,59] and Aboudheir et al. [60], it was proposed that the direct (termolecular) reaction mechanism was able to represent the kinetic phenomena more precisely compared to the zwitterion

mechanism. Putta et al. [61,62] developed both concentration based and activity based kinetic models by numerical solution of a discretized penetration theory based mass transfer model coupled with global optimization using a set of wetted wall mass transfer rate data for parameter fitting. The developed kinetic models were validated with data from three other independent experimental set-ups covering a wide range of conditions.

Both the concentration and activity based reaction kinetic models by Putta et al. [61–63] are used in the present work for analyzing the performance of the 24 different enhancement factor models from the literature. To analyze the accuracy and validity of the enhancement factor models quantitatively, the resulting mass transfer rates from the various models are compared with 601 laboratory scale experimental cases and with the numerical solution to the penetration model used for fitting the kinetic model. The experimental cases used cover a wide range of conditions such as short and long contact times, with and without gas phase resistance, high and low CO₂ loadings and temperatures.

It is previously shown that modifying the rate models to include activities of species instead of species concentrations, will lead to a more thermodynamically consistent representation of the solvent system when activity based thermodynamics also are used [61,62,64].

The reaction kinetic models developed by Putta et al. [62], using the direct (termolecular) reaction mechanism, is used in the present work and a summary is given here:



The kinetics based on concentrations and activities were given as shown in eq. (29):

concentration based kinetics:

$$r_{CO_2_MEA,c} = k_{MEA,c}^T [MEA] [CO_2] \frac{\frac{\partial}{\partial t} [MEA] + \frac{\partial}{\partial t} [MEACOO^-]}{K_{eq_MEA,c}^T} - \frac{\partial}{\partial t} [MEAH^+] + \frac{\partial}{\partial t} [MEACOO^-]$$

$$r_{CO_2_H_2O,c} = k_{H_2O,c}^T [H_2O] [MEA] [CO_2] \frac{\frac{\partial}{\partial t} [H_2O] + \frac{\partial}{\partial t} [MEACOO^-]}{K_{eq_H_2O,c}^T} - \frac{\partial}{\partial t} [H_3O^+] + \frac{\partial}{\partial t} [MEACOO^-]$$

$$r_{CO_2_OH^-} = k_{OH^-,c}^T [CO_2] [OH^-] \frac{\frac{\partial}{\partial t} [CO_2] + \frac{\partial}{\partial t} [HCO_3^-]}{K_{eq_CO_2_OH^-,c}^T} - \frac{\partial}{\partial t} [HCO_3^-] + \frac{\partial}{\partial t} [CO_2]$$

activity based kinetics:

$$r_{CO_2_MEA,a} = k_{MEA,a}^T g_{MEA}^2 [MEA]^2 g_{CO_2} [CO_2] \frac{\frac{\partial}{\partial t} [MEA] + \frac{\partial}{\partial t} [MEACOO^-]}{K_{eq_MEA,a}^T} - \frac{\partial}{\partial t} [MEAH^+] + \frac{\partial}{\partial t} [MEACOO^-]$$

$$r_{CO_2_H_2O,a} = k_{H_2O,a}^T g_{H_2O} [H_2O] g_{MEA} [MEA] g_{CO_2} [CO_2] \frac{\frac{\partial}{\partial t} [H_2O] + \frac{\partial}{\partial t} [MEACOO^-]}{K_{eq_H_2O,a}^T} - \frac{\partial}{\partial t} [H_3O^+] + \frac{\partial}{\partial t} [MEACOO^-]$$

where

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

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

$$k_{OH^-,c}^T = 4.137 \times 10^{12} \exp\left(-\frac{6005.9}{T}\right)$$

and

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

$$k_{H_2O,a}^T = 2.1105 \times 10^6 \exp\left(-\frac{2382.4}{T}\right)$$
(29)

Where the subscripts *c* and *a* are used for the concentration based and activity kinetic models respectively. The direct reaction between OH⁻ and CO₂ is taken to be the same both in the case of concentration and activity basis.

Here $k_{MEA,c}^T, k_{H_2O,c}^T, k_{OH^-,c}^T, k_{MEA,a}^T, k_{H_2O,a}^T$ were kinetic constants and expressed as Arrhenius-type temperature equations:

$$k_{i,b}^T = k_{0i,b} \exp\left(-\frac{E_{i,b}}{RT}\right) \quad \text{where } b = c, a \quad (30)$$

The equilibrium constants are expressed as

$$\begin{aligned}
K_{eq_MEA,c}^T &= \frac{[MEA][CO_2]}{[MEA][CO_2]} \\
K_{eq_H_2O,c}^T &= \frac{[H_2O][MEA][CO_2]}{[H_2O][MEA][CO_2]} \\
K_{eq_CO_2_OH^-,c}^T &= \frac{[CO_2][OH^-]}{[CO_2][OH^-]} \\
K_{eq_MEA,a}^T &= \frac{[MEA][CO_2]}{[MEA][CO_2]} \\
K_{eq_H_2O,a}^T &= \frac{[H_2O][MEA][CO_2]}{[H_2O][MEA][CO_2]}
\end{aligned} \tag{31}$$

The equilibrium concentrations and activity coefficients were obtained by solving an e-NRTL based vapor-liquid equilibrium model which accounts for the liquid non-idealities [62]. When using concentration based kinetic model, the concentration based equilibrium constants given in eq. (31) were calculated individually for each experiment by setting the bulk liquid reaction rates to zero and using the equilibrium concentrations from the e-NRTL model. This ensures that thermodynamic model is used in a consistent way. Kinetic models developed by Putta et al. [62] and used here, have previously been shown to be able to represent experimental mass transfer data over a wide range of temperatures, concentrations, CO₂ loadings and CO₂ partial pressures. According to these models the overall reaction rates for CO₂ are given as

$$\begin{aligned}
R_{CO_2,c} &= r_{CO_2_MEA,c} + r_{CO_2_H_2O,c} + r_{CO_2_OH^-} \\
R_{CO_2,a} &= r_{CO_2_MEA,a} + r_{CO_2_H_2O,a} + r_{CO_2_OH^-}
\end{aligned} \tag{32}$$

In order to use these reaction rates in the various enhancement factor models of general order, we need to equate the reaction rate from eq. (32) with the corresponding rate equation used in the given enhancement factor model and then estimate an effective kinetic constant. This implies that the reversibility of the absorption reaction will be taken into account even though the original enhancement factor model may not have considered this.

The reaction rate equations used in the various enhancement factor models can be given as shown below. For the pseudo-first order reaction assumption, the reaction rate is given as

$$R_{CO_2} = k_{ov1}[CO_2] \tag{33}$$

For second order reaction, the reaction rate equation is given as

$$R_{CO_2} = k_{ov2}[MEA][CO_2] \tag{34}$$

Pseudo-first order reaction rate constant and second order reaction rate constant are related as [65]:

$$k_{ov1} = k_{ov2}[MEA].$$

For reversible reactions with second order, the reaction rate equation is given as

$$R_{CO_2} = k_{ov2_rev} [CO_2] [MEA] \frac{[MEA] [H^+] [MEA] [CO_2]}{K_{eq_MEA,c}^T} \quad (35)$$

The equilibrium constant $K_{eq_MEA,c}^T$ is calculated for each experiment such that the reaction rate in the bulk liquid is zero. For any given type of reaction rate equation (for any order, reversible, irreversible), the effective overall kinetic constant is calculated by the following eq. (36).

$$\begin{aligned} R_{CO_2} &= R_{CO_2,c} && \text{for concentrations based model} \\ R_{CO_2} &= R_{CO_2,a} && \text{for activity based model} \end{aligned} \quad (36)$$

The k_{ov} for all 3 cases can then be found as given in eq.s (37)-(39). Only the concentration based equations are given as the activity based ones look in principle the same.

For enhancement factor models based on pseudo-first order reaction assumption, the effective overall rate constant is given as:

$$k_{ov1,c} = \frac{k_{MEA,c}^T [MEA]^2 [CO_2] \frac{[MEA] [H^+] [MEA] [CO_2]}{K_{eq_MEA,c}^T} + k_{H_2O,c}^T [H_2O] [MEA] [CO_2] \frac{[H_3O^+] [MEA] [CO_2]}{K_{eq_H_2O,c}^T} + k_{OH^-,c}^T [CO_2] [OH^-] \frac{[CO_2] [OH^-] [CO_2]}{K_{eq_CO_2_OH^-,c}^T}}{[CO_2]} \quad (37)$$

Similarly, for enhancement factor models based on irreversible second order reaction assumption, the effective rate constant is given as shown in eq. (38).

$$k_{ov2,c} = \frac{k_{MEA,c}^T [MEA]^2 [CO_2] \frac{[MEA] [H^+] [MEA] [CO_2]}{K_{eq_MEA,c}^T} + k_{H_2O,c}^T [H_2O] [MEA] [CO_2] \frac{[H_3O^+] [MEA] [CO_2]}{K_{eq_H_2O,c}^T} + k_{OH^-,c}^T [CO_2] [OH^-] \frac{[CO_2] [OH^-] [CO_2]}{K_{eq_CO_2_OH^-,c}^T}}{[MEA] [CO_2]} \quad (38)$$

For enhancement factor models based on reversible second order reactions, the overall reaction rate constant is given as:

$$k_{v2_rev,c} = \frac{k_{MEA,c}^T [MEA]^2 [CO_2] + k_{H_2O,c}^T [H_2O] [MEA] [CO_2] + k_{OH^-,c}^T [CO_2] [OH^-]}{K_{eq_MEA,c}^T [MEA] + \frac{k_{MEA,c}^T [MEA] [CO_2]}{K_{eq_MEA,c}^T} + \frac{k_{H_2O,c}^T [H_2O] [MEA] [CO_2]}{K_{eq_H_2O,c}^T} + \frac{k_{CO_2_OH^-,c}^T [CO_2] [OH^-]}{K_{eq_CO_2_OH^-,c}^T}} \quad (39)$$

All the enhancement factors were tested using both concentration and activity based kinetics from Putta et al. [62].

Enhancement factors were experimentally determined using the effective overall kinetic constants corresponding to the given rate equation order and were then used to calculate the interphase CO₂ mass transfer flux using the equation given below:

$$N_{CO_2} = K_G \times LMPD = \frac{LMPD}{\frac{1}{k_g} + \frac{H_{CO_2}}{E_A \times k_l}} \quad (40)$$

Where LMPD is the logarithmic mean pressure difference between the inlet and outlet of the reactor.

In order to assess the performance of different enhancement factor models in predicting the mass transfer rates from 4 different experimental set-ups, some statistical measures were calculated.

The relative deviation between experimental and enhancement factor model predicted CO₂ fluxes were estimated using

$$dev = \left(\frac{N_{CO_2,E_{model}} - N_{CO_2,exp}}{N_{CO_2,exp}} \right) * 100 \quad (41)$$

Using these relative deviations, the average relative deviation (ARD) was calculated as shown in eq. (42).

$$ARD = \frac{1}{n} \sum_i^n \left(\frac{N_{CO_2,E_{model}} - N_{CO_2,exp}}{N_{CO_2,exp}} \right)_i * 100 = \frac{1}{n} \sum_i^n dev_i \quad (42)$$

Absolute average (relative) deviation (AARD) was estimated using eq. (43).

$$AARD = \frac{1}{n} \sum_i^n \left| \frac{N_{CO_2,E_{model}} - N_{CO_2,exp}}{N_{CO_2,exp}} \right|_i * 100 = \frac{1}{n} \sum_i^n |dev_i| \quad (43)$$

These performance measure indicators give a measure of the difference between predictions and experimental values. The average relative deviation (ARD) tells how large the average discrepancy

is but says nothing about the spread. The absolute average relative deviation (AARD) describes better the scatter in the differences. If ARD is low and AARD is high this indicates large scatter in the differences but that the average is close to the experimental. Both a large ARD and AARD will indicate a systematic deviation between model and experiments.

3 Results and discussion

All 24 enhancement factor models were tested for 601 experiments taken from four independent laboratory apparatuses covering the temperature range 293-343 K, amine concentrations between 0.5 – 9 M, CO₂ loadings between 0 – 0.5 molesCO₂/mole MEA , CO₂ partial pressures between 0.4 – 99 kPa and with and without the presence of gas-side mass transfer resistance, i.e., with dilute or pure CO₂. The enhancement factor model CO₂ flux predictions are compared with experimental data and, as a base case, results from the discretized penetration theory model given in Putta et al. [62] are also included.

To understand better the predictive ability of the different enhancement factor models given in the literature, the results are divided into three CO₂ loading ranges for the data from each experimental apparatus i.e., CO₂ loading < 0.2, 0.2 < CO₂ loading ≤ 0.4 and CO₂ loading > 0.4.

In tables, A1-A2 given in Appendix A, results from the 24 enhancement factor models tested for the aqueous CO₂- MEA system are given. The predicted fluxes are compared to experimental mass transfer rates and accuracies (ARD and AARD) are given both for the concentration based and activity based reaction kinetic models. In order to better evaluate the various enhancement factor models ability to predict the CO₂ fluxes, the results from the discretized penetration theory model [62] are also shown in the figures as model number zero (0). In order to simplify the referencing to the various enhancement factor models, the authors of the individual enhancement factor models and corresponding assumptions are only mentioned in the tables given in Appendix A. In the following, the enhancement factor models are referred by model number only. For example, the enhancement factor model developed by Brian et al. [28] based on penetration theory with a 2nd order irreversible reaction assumption will be referred to as Emodel 6 and the corresponding kinetic model (concentration or activity based) will also be indicated.

3.1 Experimental data from WWC apparatus reported by Luo et al. [58,59]

Experimental mass transfer data from a wetted wall column apparatus (WWC) (Luo et al. [58,59]) were used by Putta et al. [62] for the development of both concentration and activity based kinetic models using a discretized penetration model. These models are used in this work as a benchmark (Emodel 0). The results given in Appendix A for the WWC experiments by Luo et al. [58,59] are shown in figures 1 and 2.

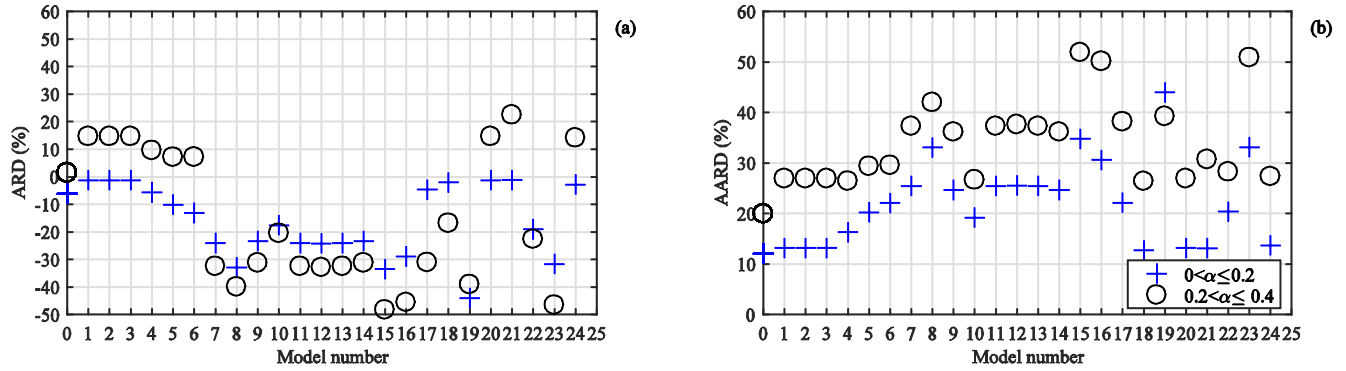


Fig. 1. Mass transfer rates prediction performance of different enhancement factor models using concentration based reaction kinetics for WWC data in terms of (a) average relative deviation (ARD) and (b) average absolute relative deviation (AARD)

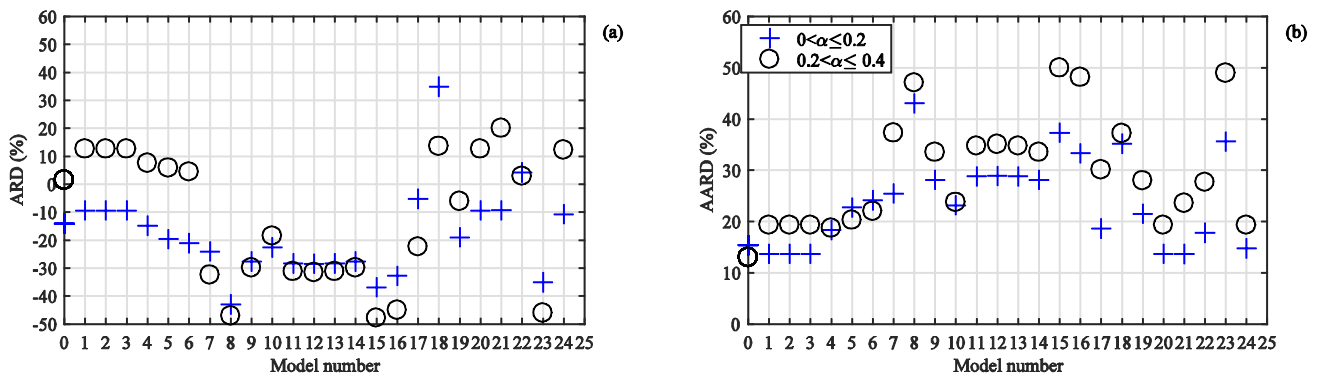


Fig. 2. Mass transfer rates prediction performance of different enhancement factor models using activity based reaction kinetics for WWC data in terms of (a) average relative deviation and (b) average absolute relative deviation.

For CO₂ loadings ≤ 0.2 in WWC, we see that the Emodels 1-3, 20 and 21 under-predict the CO₂ transfer fluxes with the same ARDs and give ARDs of 1% and 9% with the concentration and activity based kinetic models respectively. The AARD for these models are also quite similar, being about 12-13%. This indicates that even though the average is good there is some scatter in the results. Emodel 17 under-predicts the CO₂ fluxes with 5% ARD with both the concentration and activity based kinetic models. Here the AARD is above 20% also indicating scatter. Emodel 24 under predicts the CO₂ mass transfer fluxes with 3% and 11% ARD with concentration and activity based kinetic models respectively and is very similar to Emodels 1- 3 and 21 regarding AARD. With concentration based kinetics, Emodel 4 under predicts with 6% ARD and AARD 18% and Emodel 18 under predicts with 2% ARD and 12% AARD. However, with activity based kinetics Emodel 4 predictions give 15% ARD (under-predicted) and 16% AARD whereas Emodel 18 over-predicts with 35% ARD and about 35% AARD. In comparison, the discretized penetration theory model (Emodel 0) under-predicts with 6% and 14% ARDs and 12% and 13% AARD for CO₂ loadings ≤ 0.2 with concentration based and activity based kinetics respectively. This shows that the best enhancement factor models mimic the performance of the discretized model.

For data with $0.2 < \text{CO}_2 \text{ loading} \leq 0.4$, Emodels 1-3, 20 and 24 over-predict the CO₂ fluxes with ARDs of 15% and 13% with concentration and activity based kinetics respectively. The AARDs are also very similar at about 23% for concentration and 19% for activity based kinetics. Emodels 4-6 over-predict the CO₂ fluxes with less than 10% ARDs with both concentration and activity

based kinetics but have AARDs above 20%. With activity-based kinetics, Emodel 19 under-predicts CO₂ fluxes with 6 % ARD but has an AARD of nearly 30%. Emodel 22 with activity based kinetics over-predicts with 3% ARD but also here the AARD is nearly 30%. In this range the discretized penetration theory model (Emodel 0) gives an over-prediction with 1% ARD for both concentration and activity based kinetics and also the AARDs are reasonable at 20 and 13% respectively for concentration and activity based kinetics..

It thus seems that the enhancement factor models generally perform less satisfactorily for this set of data.

Generally, since the AARDs are larger than the ARDs, there is scatter in the calculated predictions. This also found for the discretized model used for fitting and may be an indication of uncertainties or scatter in the data. Some of the E models like 7, 8, 9, 11-16, 19, 23 always under-predict the mass transfer rates irrespective of operating conditions. This may indicate that there is a systematic error in these Emodel predictions.

3.2 Experimental data from SDC apparatus reported by Luo et al. [58,59]

The results of enhancement factor models given in the appendix A for the string of discs (SDC) apparatus are shown in figures 3 and 4. For SDC data with CO₂ loadings ≤ 0.2 , Emodels 1-3, 20-21 and 24 over-predict CO₂ transfer fluxes with same ARDs and give ARDs around 3-4% and 0.2-1% with the concentration and activity based kinetic models respectively. The AARDs for these models are also quite similar, being around 7-9%. This gives an indication about the scatter in the results as the average is good. Emodels 4-7 and 10 under predict the CO₂ fluxes with ARDs around 7-14% and also have quite similar AARDs about 10-16%. Here both the average and absolute averages are in the same order and the scatter in the results is less but have large deviations than Emodels 1-3, 20-21 and 24. Emodel 17 under predicts CO₂ fluxes with 3% ARD and over-predicts with 1% ARD with concentration and activity based kinetic models respectively. Here the AARD is around 16-19% also indicates the scatter in results. With concentration based kinetic model, Emodel 18 under-predicts CO₂ fluxes with 2% ARD and 9% AARD and Emodel 22 also under-predicts with 9% ARD and 12% AARD. However, with activity based kinetic model, Emodel 18 over-predicts with 44% ARD and around 46% AARD and also Emodel 22 over-predicts with 28% ARD and about 31% AARD. In comparison, the discretized penetration theory model (Emodel 0) over-predicts with 5% and 2% ARDs and 8% and 9% AARD for CO₂ loadings ≤ 0.2 with concentration and activity based kinetic models respectively. This indicates that the best enhancement factor models mimic the performance of the discretized penetration theory model.

For data with $0.2 < \text{CO}_2 \text{ loading} \leq 0.4$, Emodels 1-3, 20 and 24 over-predict CO₂ fluxes with same ARDs and give ARDs of 29% and 41% with concentration and activity based kinetics respectively. The AARDs are also same for these Emodels and are about 31% and 42% with concentration and activity based kinetics respectively. Emodel 4 over-predicts the CO₂ transfer fluxes with ARDs 22% and 32% and gives AARD of 25% and 34% with concentration and activity based kinetics respectively. The difference in ARD and AARD indicated the scatter in results.

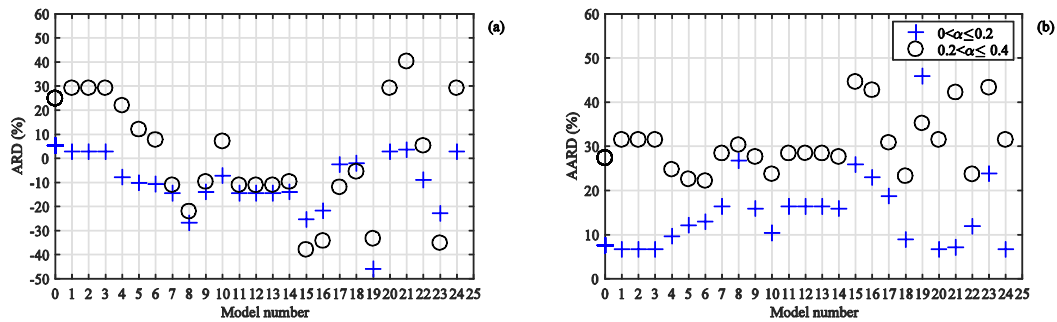


Fig. 3. Performance of different enhancement factor models using concentration based reaction kinetics for mass transfer rates prediction from SDC in terms of (a) average relative deviation (b) average absolute relative deviation

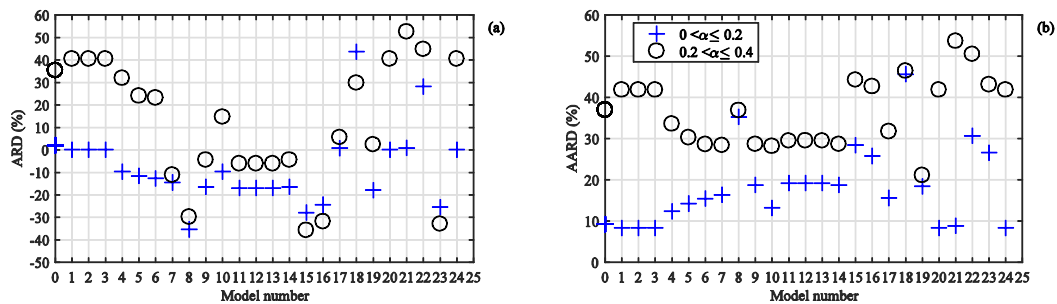


Fig. 4. Performance of different enhancement factor models using activity based reaction kinetics for mass transfer rates prediction from SDC in terms of (a) average relative deviation (b) average absolute relative deviation

Emodels 5 over-predicts with ARDs of 12% and 24% and gives AARDs of 23% and 30% with concentration and activity based kinetic models respectively. Emodel 6 over-predicts CO₂ fluxes with 8% and 23% ARDs and has AARD of 22% and 29% respectively with concentration and activity based kinetic models. Emodels 7-9, 11-16 and 23 under predict the CO₂ fluxes with both kinetic models. Emodel 7 under predicts with 11% ARD and 28% AARD with both concentration and activity based kinetics. Emodel 9 under predicts with 10% and 4% ARD and with 28% and 29% AARD with concentration and activity based kinetics respectively and there is scatter in results. Emodels 11-14 under predicts CO₂ fluxes with almost the same ARDs and give 10-11% and 4-6% with concentration and activity based kinetics respectively. The AARDs are also the same and are about 28-30%. Emodel 10 over-predicts with 7% and 15% ARD and with 24% and 28% AARD with concentration and activity based kinetic models respectively. Emodel 17 under predicts with 12% ARD with concentration based kinetics and over predicts with 6% ARD with activity based kinetics and gives around 31-32% AARD with both kinetic models. Emodel 18 gives under predictions with 6% ARD and 23% AARD and Emodel 22 over predicts with 5% ARD and 24% AARD with concentration based kinetic model. Emodel 19 over-predicts with 2% ARD and 21% AARD with activity based kinetic model. Discretized penetration theory model over predicts CO₂ transfer fluxes with 25% and 35% ARDs and 27% and 37% AARDs with concentration and activity based kinetics.

For SDC data with $0.2 < \text{CO}_2 \text{ loading} \leq 0.4$, all the 24 models with both kinetic models give AARDs more than 20% and this can be explained by the experimental uncertainty associated with measurements with low driving forces $\text{LMPD} \approx 0.35\text{-}2.8 \text{ kPa}$ (with more than 70% of the data with $\text{LMPD} < 2 \text{ kPa}$) and long contact time between the gas and liquid (3-4 sec). So, the high

uncertainty seen in the Emodels predicted CO₂ fluxes in the medium CO₂ loading range ($0.2 < \text{CO}_2 \text{ loading} \leq 0.4$) is expected and also the same has been observed in the discretized penetration theory model predictions.

3.3 Experimental data from WWC apparatus reported by Puxty et al. [66]

WWC data reported by Puxty et al. [66] were obtained for only 5 M MEA solution at different loadings at 40 and 60 °C with negligible gas phase mass transfer resistance operating conditions. The data also have some cases where desorption of CO₂ occurs at 60 °C and CO₂ loading 0.5 moles CO₂/mole MEA. The results given in appendix A and are shown in figures 5 and 6.

The Emodels 1-3, 20, 21 and 24 predict CO₂ fluxes with the same ARDs for the given kinetic model and CO₂ loadings ≤ 0.2 . The concentration based kinetic model gives over-predictions with 2 % ARD while activity based kinetic model gives under predictions with 1% ARD. The AARDs are also the same for these models at about 6% and 4% with concentration and activity based kinetics respectively. Emodel 4 gives under-predictions with 8% and 10% ARDs and 12% AARD with concentration and activity based kinetics. Emodel 18 with concentration based kinetics gives over-predictions with 1% ARD and 6% AARD whereas with activity based kinetics the same model over predicts with ARD and AARD of 43%. All the remaining models give under-predictions with ARDs varying from 11-46% and AARDs varying from 13-46%. In comparison, the discretized penetration theory model over-predicts with 6% and 3% ARDs and 7% and 5% AARDs with concentration and activity based kinetic models respectively. In this low loading region, Emodels 1-3, 20, 21, 24 with both kinetic models and Emodel 18 with concentration based kinetics give slightly better predictions than the discretized model.

For Puxty et al. [66] WWC data with $0.2 < \text{CO}_2 \text{ loading} \leq 0.4$, the calculated CO₂ fluxes using Emodels 1-3 and 20 are under-predicted with the same ARDs and AARDs whereas for data with CO₂ loading > 0.4 these models give over predictions with both concentration and activity based kinetic model. These Emodels under-predict CO₂ fluxes in the $0.2 < \text{CO}_2 \text{ loading} \leq 0.4$ range with 12% and 5% ARD and with 12% and 5% AARDs. For CO₂ loading > 0.4 data the predictions have 26% and 51% ARDs and 28% and 51% AARDs with concentration and activity based kinetics respectively. The Emodel 4 gives under-predictions with 16% and 9% ARDs and have the same AARDs as ARDs in the $0.2 < \text{CO}_2 \text{ loading} \leq 0.4$ range and give over predictions with 15% and 50% ARDs and 28% and 50% AARDs for CO₂ loading > 0.4 with concentration and activity based kinetics respectively. Emodel 18 with concentration based kinetics under-predicts CO₂ fluxes with 8% ARD 31% AARD in the $0.2 < \text{CO}_2 \text{ loading} \leq 0.4$ range and over predicts with 87% ARD and AARD for CO₂ loading > 0.4 . Emodel 21 gives, for concentration and activity based kinetic models respectively, under-predictions with ARD of 8% and 1% for $0.2 < \text{CO}_2 \text{ loading} \leq 0.4$ and over-predictions with ARDs $> 70\%$ for CO₂ loading > 0.4 regardless of kinetic model basis. For the same Emodel 21, the AARDs are 10% and 7% in $0.2 < \text{CO}_2 \text{ loading} \leq 0.4$ with concentration and activity based kinetic models respectively and more than 150% in CO₂ loading > 0.4 with both kinetic models. Emodel 24 under-predicts with the same ARDs and AARDs as Emodels 1-3 and 20 in the $0.2 < \text{CO}_2 \text{ loading} \leq 0.4$ range and also under-predicts for CO₂ loading > 0.4 with 18% and 2% ARDs and 48 and 64% AARDs with concentration and activity based kinetic models respectively. The discretized penetration model (Emodel 0) under predicts with 7% and 0.3% ARD

in the medium CO₂ loading range ($0.2 < \text{CO}_2 \text{ loading} \leq 0.4$) and over predicts with 31% and 54% in CO₂ loading > 0.4 range with concentration and activity based kinetics respectively.

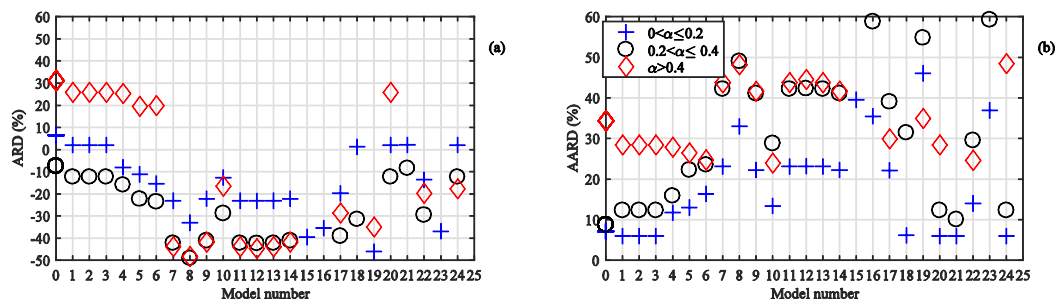


Fig. 5. Performance evaluation of different enhancement factor models using concentration based reaction kinetics for mass transfer rates prediction from WWC reported by Puxty et al. [66] in terms of (a) average relative deviation (b) average absolute relative deviation

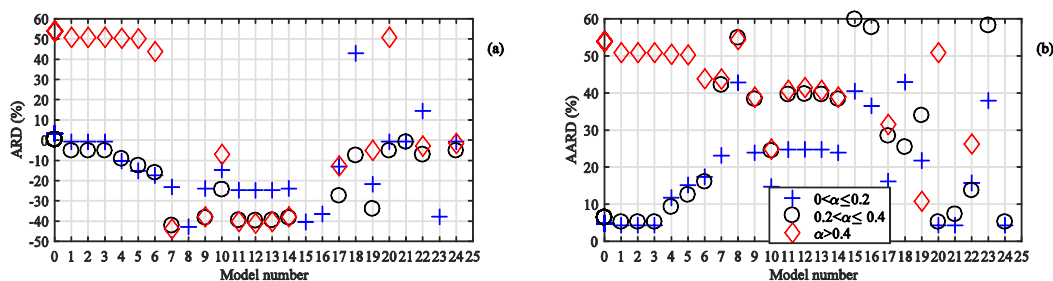


Fig. 6. Performance evaluation of different enhancement factor models using activity based reaction kinetics for mass transfer rates prediction from WWC reported by Puxty et al. [66] in terms of (a) average relative deviation (b) average absolute relative deviation

The higher ARDs and AARDs for CO₂ loading > 0.4 can, at least partly, be explained by the experimental uncertainty in the measurements themselves and also by uncertainties in the thermodynamic model when predicting the equilibrium vapor pressure at high temperature and at CO₂ loading > 0.4 . In addition, very low driving forces also gives additional uncertainty in the experimental CO₂ flux measurements themselves.

3.4 Experimental data from laminar jet absorber (LAMJET) apparatus reported by Aboudheir et al. [60]

From the figures 7 and 8 and the results given for laminar jet absorber (LAMJET) apparatus in table A1-A2 in Appendix, it is seen that the Emodels 1-3, 20, 21 and 24 under-predict the CO₂ fluxes with the same ARDs of 12% and 10-11% for CO₂ loadings ≤ 0.2 and give 15% and 7% ARDs for $0.2 < \text{CO}_2 \text{ loading} \leq 0.4$ with concentration and activity based kinetic models respectively. The AARDs for these models are also quite similar, being about 11-13% for CO₂ loadings ≤ 0.2 and 9-17% for $0.2 < \text{CO}_2 \text{ loading} \leq 0.4$. At high CO₂ loadings (CO₂ loadings > 0.4), Emodels 1-3, 20 and 24 under-predict fluxes with 11-13% and 3-5% ARDs and 13-14% and 6% AARDs with concentration and activity based kinetics respectively. With concentration and activity based kinetics, Emodel 21 gives predictions with 9% and 0.1% ARDs and 11% and 4% AARDs respectively. Emodel 18 with concentration based kinetics give under-predictions with ARDs 12%, 16% and 26% and AARDs 13%, 18% and 26% for CO₂ loadings ≤ 0.2 , $0.2 < \text{CO}_2$

loading ≤ 0.4 and CO_2 loadings > 0.4 respectively. With concentration based kinetics, Emodel 22 gives under-predictions ARDs about 19-27% in the three loading regimes and with activity based kinetics, the model over-predicts with 23%, 14% and 1% ARDs for CO_2 loadings ≤ 0.2 , $0.2 < \text{CO}_2$ loading ≤ 0.4 and CO_2 loadings > 0.4 respectively. The AARDs are about the same as ARDs for concentration based kinetics at 25%, 23% and 11% with activity based kinetics in the three loading ranges respectively.

The discretized penetration model under-predicts with ARDs around 5-6% in the low CO_2 loading range (CO_2 loadings < 0.2), about 8-15% in the medium CO_2 loading range ($0.2 < \text{CO}_2$ loading ≤ 0.4) and about 19-25% in the high CO_2 loading range (CO_2 loadings > 0.4). The AARDs are also in the same range as ARDs in the corresponding loading regime. The discretized model gives better predictions in the low loading range (CO_2 loadings ≤ 0.2) than all the Emodels and with almost the same accuracy as Emodels 1-3, 20, 21 and 24 for $0.2 < \text{CO}_2$ loading ≤ 0.4 and with less accuracy than Emodels 1-3, 20, 21 and 24 for loadings > 0.4 with both kinetic models.

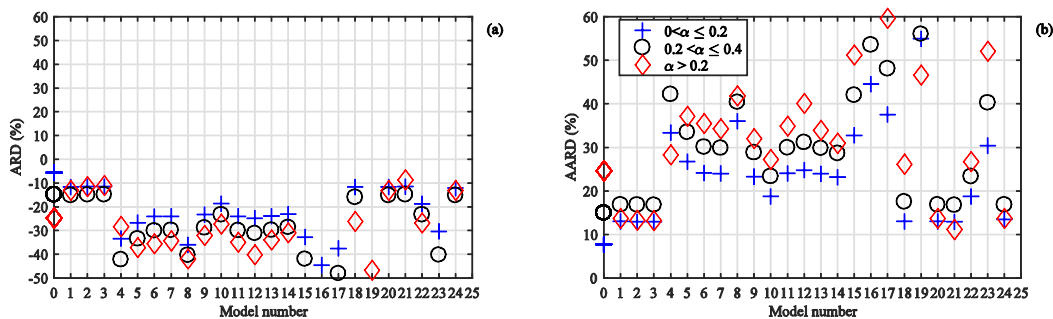


Fig. 7. Performance evaluation of different enhancement factor models using concentration based reaction kinetics for mass transfer rates prediction from laminar jet absorber reported by Aboudheir et al. [60] in terms of (a) average relative deviation (b) average absolute relative deviation

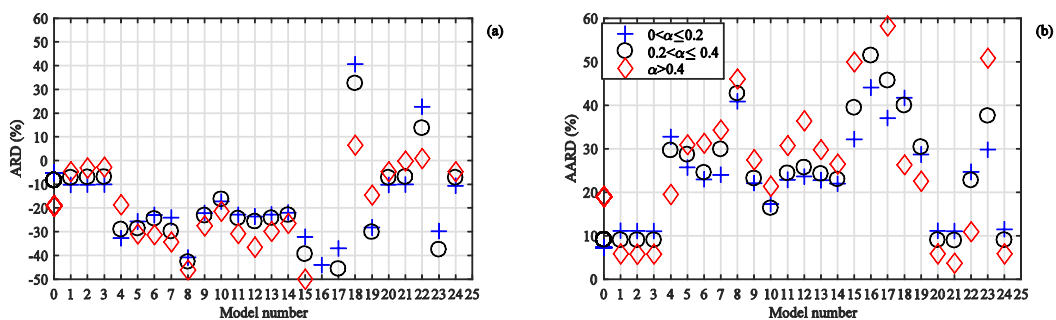


Fig. 8. Performance evaluation of different enhancement factor models using activity based reaction kinetics for mass transfer rates prediction from laminar jet absorber reported by Aboudheir et al. [60] in terms of (a) average relative deviation (b) average absolute relative deviation

By observing both tables A1 and A2, it is seen that some of the enhancement factor models give systematic deviations and also large deviations in flux predictions (ARDs and AARDs). A few models i.e., Emodels 1-3, 20, 21 and 24 with both kinetic models seem to predict fluxes without any systematic deviations and with good accuracy and precision when keeping in mind the uncertainties in the experimental measurements. With concentration based kinetics Emodel 18, also gives predictions with almost the same accuracy as the best performing models in both the low and medium loading ranges.

4 Overall model performance and summary discussion

In the previous sections, the different Emodels performances in calculating the CO₂ fluxes from 4 different experimental data sources (set-ups) were evaluated and it was found that the models give predictions with different accuracies for data from different sources and in different loading ranges.

The performance of the Emodels for the combined data from all sources, but still split in the different loading regimes is shown in Figures 9 and 10 and in Table A3 in Appendix A for all 24 Enhancement factor models.

It is seen that the Emodels 1-3 and 20 predict mass transfer rates for the combined data with CO₂ loading ≤ 0.2 , $0.2 < \text{CO}_2$ loading ≤ 0.4 and CO₂ loading > 0.4 with ARDs less than 10% with both concentration based and activity based kinetics. With concentration based kinetics, these Emodels under-predict in the low loading range (≤ 0.2), over-predict in the medium loading range (0.2-0.4) and again under-predict in the high loading range (> 0.4). However, with activity based kinetics, the models under-predict in the low loading regime and over predict in both the medium and high loading regimes. The AARDs are in the range 10-22%, showing that the models estimations have good accuracy but that there is some scatter in the results.

Emodel 21 gives ARDs less than 7% for loadings ≤ 0.2 , around 10-16% for $0.2 < \text{CO}_2$ loading ≤ 0.4 and around 11-19% in the high loading range with both kinetic models. Emodel 24 gives ARDs of 4% in the low and medium loading ranges and 14% in high loading regime with both kinetic model. Both Emodel 21 and 24 perform very similar to Emodels 1-3 and 20.

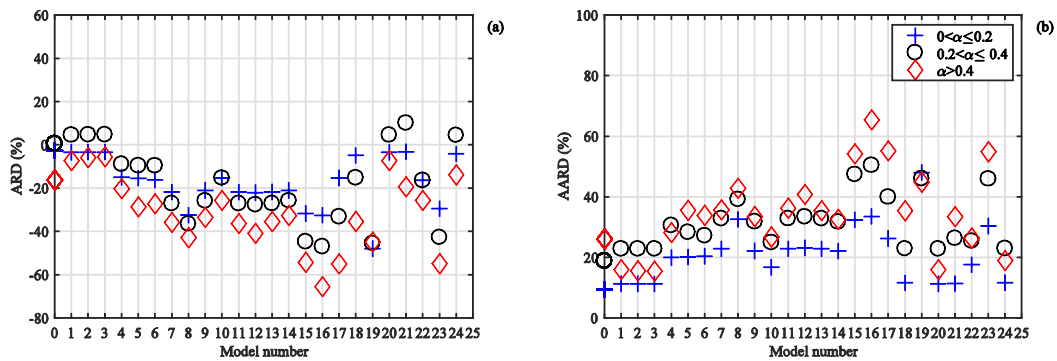


Fig. 9. Performance evaluation of different enhancement factor models using concentration based reaction kinetics for mass transfer rates prediction for data from all 4 experimental set-ups in terms of (a) average relative deviation (b) average absolute relative deviation

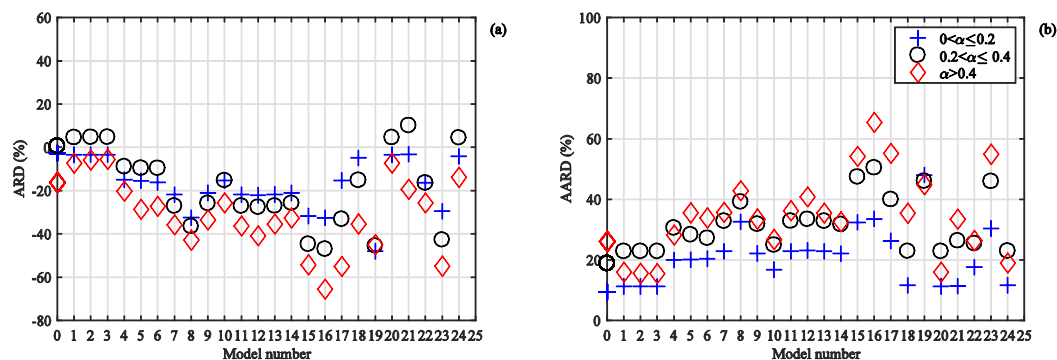


Fig. 10. Performance evaluation of different enhancement factor models using activity based reaction kinetics for mass transfer rates prediction for data from all 4 experimental set-ups in terms of (a) average relative deviation (b) average absolute relative deviation

ARDs and AARDs were calculated for all data points without any sub-division in loading ranges and the results are shown in Figure 11 and given in table A4 in Appendix A. For the full data set, the ARDs of the calculated CO₂ fluxes are less than 3% for all the Emodels (1-3, 20, 21 and 24) focused in the previous section. The AARDs of the predicted fluxes are around 14-18% for the data set which is quite good in terms of accuracy with simplified or linearized models which do not require excessive computational time. These Emodels give predictions with similar accuracy as the discretized penetration theory model.

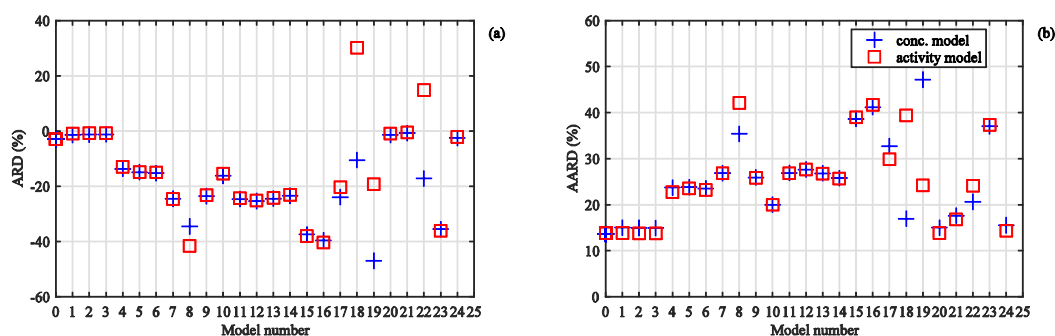


Fig. 11. Emodels predictive performance in terms of (a) average relative deviation (b) average absolute relative deviation for total 601 data points.

The results in section 3 show that six enhancement factor models perform significantly better than the others and on the same level as the discretized penetration model, Emodel 0. Among these are Emodels 1-3 which are simple pseudo first order models, respectively film-, penetration- and surface renewal-based. Of the 4 data sets the models have been tested on are three from apparatuses with low gas-liquid contact time. The WWC apparatuses typically have contact times of about 0.3-0.7 seconds and for the laminar jet absorber the contact time is less than 0.1 seconds. In these cases the depletion of free amine (MEA) close to the gas-liquid interface is very limited regardless of initial CO₂ loading, driving force and temperature. It is thus not surprising that these simple models perform well in these cases. For the SDC data all models perform less satisfactorily, but still reasonably well. In the SDC apparatus the contact time is in the range of 3-5 seconds and some depletion can occur. However in this case, as mentioned, the driving forces were very small and the experimental uncertainty larger than for the other apparatuses. It thus seems that the simplicity of the enhancement factor model is not important and it does not matter whether it is based on the film-, penetration- or surface renewal theory. What is important is that the kinetic model is accurate. In a real industrial absorber fitted with a modern random or structured packing, the liquid flows as a film on the packing elements, or along the structured packing. With short intervals, after one packing element or when a structured packing bends, mixing points are created before the liquid again spreads out as a film. The distance between mixing points in a random packing is very low, of the order 0.2-0.4 seconds. In a structured packing it may be slightly higher, 0.3-0.7 seconds. In both cases these contact time is of the same order of magnitude as found in typical wetted wall columns (WWC) and the assumption of insignificant depletion of free amine close to the interface may be reasonable. Thus the simple first order enhancement factor models probably will also work

well under industrial conditions as long as an accurate kinetic model is used and implemented correctly to obtain the effective rate constant for the enhancement factor model in question.

Emodels 20 and 24 also work as well the simple pseudo first order models. These are 2nd order models based on respectively surface renewal and film theory. Again the basic theory seems not to play a role. The two models do not implement the equal diffusivity concept, but it is uncertain why these models work better than the other models of similar complexity.

It can be speculated why many of the tested enhancement factor models show high deviations for in the case of the reversible reactions. One reason could be that the original models were basically developed for cases with very low amine concentrations and for unloaded amine solutions with equal diffusivities assumption. When applying those models for high amine concentrations and for CO₂ loaded solutions, they might fail due to application outside their range. The model by Gasper and Føsbøl [51] was developed for reversible reaction by taking into account the CO₂ loadings and it was found to be one of the best performing models. Similarly, the model by DeCoursey and Thring [44] was developed for reversible reaction with unequal diffusivities found to represent the experimental data with acceptable accuracy and is one among the best performing enhancement factor models.

Several enhancement factor models tested in the present work, also the rigorous penetration model, show higher deviations from experimental data at high loadings. This could be due to several reasons. Firstly, all mass transfer models rely on a thermodynamic model for driving force calculations. The uncertainty of the equilibrium model is higher in the high loading range than for lower loadings making the driving force estimation more uncertain. Secondly, the experimental data, both equilibrium and mass transfer rate data, are normally more uncertain at high loadings, in particular under conditions of low driving forces. Finally, just modelling the high loading range is more difficult than for lower loadings because of larger departures from ideality. This emphasizes the need for quality experimental equilibrium and mass transfer rate data with less uncertainty for the improvement of existing models in the high loading regime.

5 Conclusions

The mass transfer rate prediction performance of 24 different enhancement factor models was evaluated against 601 data points in four data sets from two wetted wall columns, a laminar jet contactor and a string of discs contactor. Predictions were also compared with results from a discretized penetration model used in developing concentration based and activity based reaction kinetic models for MEA by Putta et al. [62]. The data sets cover MEA concentrations from 0.5 - 9 moles/L, CO₂ loadings from 0 - 0.5 moles CO₂/mole MEA and temperatures from 293-343K. It is deemed important to use data from experiments where the interfacial area is well defined in order to avoid uncertainties in area predictions.

Of the 24 enhancement factor models tested only six models were found to satisfactorily predict the experimental CO₂ fluxes. These were the models based on the simple pseudo-first order reaction assumption, Emodels 1, 2 and 3 by Hatta[2] and Danckwerts[4] respectively, Emodel 20, the deCoursey and Thring [44] model based on Danckwert's surface renewal theory with unequal

diffusivities, Emodel 24, the recently published generalized model by Gaspar and Fosbøl [51] and Emodel 21, the Tufano et al. [67] model based surface renewal theory. All these models were found to work equally well to the discretized penetration model. No significant difference was found between Emodels 1, 2 and 3, indicating that whether one uses as basis a film, penetration or surface renewal model, is of insignificant importance.

The success of the simple models is attributed to the short contact times in the experiments used as basis and the accuracy of the kinetic model. Contact times of the same magnitude between mixing points is also encountered in industrial packings and it is believed that the simple enhancement factor models may work well also in these cases if an accurate kinetic model is used.

ACKNOWLEDGEMENT:

The authors thank Diego Pinto for reviewing and commenting the manuscript.

Nomenclature

ARD Absolute relative deviation

AARD Absolute average relative deviation

C Concentration of species, mol.L⁻¹

CO₂ Carbon dioxide

D Diffusivity, m²·s⁻¹

dev Deviation (relative)

e-NRTL Electrolyte- non-random two liquid

E Activation energy, kJ.kmol⁻¹

E_a Enhancement factor

erf Error function

g Gravitational acceleration, m.s⁻²

kg Gas side mass transfer coefficient,

kl Liquid side mass transfer coefficient with chemical reaction,

kl0 Liquid side physical mass transfer coefficient,

KG_{ov} Overall gas-side mass transfer coefficient, kmol·m⁻²·s⁻¹·kPa⁻¹

k_{ov1} Effective overall rate constant for pseudo-first order reaction

k_{ov2} Effective overall rate constant for second order reaction

k_{ov2_rev} Effective overall rate constant for reversible second order reaction

k_{H2O} Third order kinetic rate constant of H₂O, m⁶·kmol⁻²·s⁻²

k_{MEA}	Third order kinetic rate constant of MEA, $\text{m}^6 \cdot \text{kmol}^{-2} \cdot \text{s}^{-2}$
k_{OH^-}	Second order kinetic rate constant of $\text{CO}_2\text{-OH}^-$ reaction, $\text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{s}^{-2}$
K_{eq}	Equilibrium constant
LAMJET	Laminar jet absorber
LMPD	Logarithmic mean pressure difference between the inlet and outlet of the reactor, kPa
M	Molarity, $\text{kmol} \cdot \text{m}^{-3}$
MEA	Monoethanolamine
N	Molar flux, $\text{kmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$
P	Pressure, kPa
r	Reaction rate, $\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$
R_{CO_2}	Reaction rate of CO_2 , $\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$
R	Universal gas constant, $\text{kJ} \cdot \text{kmol}^{-1} \cdot \text{K}^{-1}$
SDC	String of discs column
T	Temperature, K

WWC	Wetted wall column
WWCP	Wetted wall column reported by Puxty et al.[49]
x	Position in the liquid film from the gas-liquid interface
Greek letter	
δ	Liquid film thickness, m
γ	Activity coefficient
ϕ	Hatta number
ν	Stoichiometric coefficient
Superscripts	
∞	Infinite
Film	Film theory
i	at interface

Model	Discretized penetration model
Pen	Penetration theory
Solution	In aqueous MEA solution
Surf	Surface renewal theory
T	Temperature dependence
Subscripts	
0	Initial
2	second order
*	at equilibrium

a	Activity based model
A	Component A
A _i	Component A at the gas-liquid interface
∞	Infinite
B	Component B
bulk	liquid bulk region
c	Concentration based model
CO ₂	Carbon dioxide
eq	Equilibrium
Exp	Experimental
Flux	CO ₂ absorption flux, kmol·m ⁻² ·s ⁻¹
H ₂ O	Water
HCO ₃ ⁻	Bicarbonate
l	Liquid phase
MEA	Monoethanolamine
MEAH ⁺	Protonated monoethanolamine
MEACOO ⁻	Carbamate
m,n	Stoichiometric coefficient
ps	pseudo-first order

R	Reaction
Surf	Surface renewal theory
WWC	Wetted wall column

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