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# Review on the mass transfer performance of CO<sub>2</sub> absorption by amine-based solvents in low- and high-pressure absorption packed columns

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The gas-phase volumetric overall mass transfer coefficient ( $K_G a_V$ ) plays a key role in the assessment of an absorption packed column's performance since it determines the height of an absorber column. The effective and useable data provided by  $K_G a_V$  is necessary for designing and scaling up absorption packed columns. This study provides the first comprehensive review of mass transfer performance in terms of  $K_G a_V$  for CO<sub>2</sub> ( $K_{GCO_2 a_V}$ ) absorption into amine solutions for absorber columns with random and structured packing. To date, researchers associated with the  $K_{GCO_2 a_V}$  parameter have focused on two main fields: experimental works and developing empirical correlations. For experimental works,  $K_{GCO_2 a_V}$  has been evaluated in the literature for a large number of conventional and improved amines over a range of operating parameters in laboratory-scale packed columns. In addition, researchers have developed empirical correlations for  $K_{GCO_2 a_V}$  based on operating parameters affecting  $K_{GCO_2 a_V}$  and physical properties. The details of research determining the  $K_{GCO_2 a_V}$  have been reviewed for low- and high-pressure absorption packed columns. Finally, directions for future research of the mass transfer performance for absorber packed columns in the CO<sub>2</sub> capture process have been discussed.

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## 1. Introduction

Today, fossil fuels play a major role in the production and supply of energy in the world. With global economic development and population growth, the utilization of these fuels has increased extensively. As a result, the consumption of fossil

fuels is causing a sharp increase of CO<sub>2</sub> emissions into the atmosphere.<sup>1,2</sup> CO<sub>2</sub> is the main greenhouse gas responsible for global warming and climate change. Although CO<sub>2</sub> is corrosive to exposed equipment and has a low heating value, it can be used in various industries after treatment.<sup>3</sup> Research has become essential in achieving an effective process of CO<sub>2</sub> removal from industrial exhaust gas streams.<sup>4</sup> CO<sub>2</sub> is usually produced in different concentrations by three main processes including pre-combustion, post-combustion, and oxyfuel

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combustion.<sup>5,6</sup> Currently, the only CO<sub>2</sub> separation process implemented at a fully commercial scale is the post-combustion CO<sub>2</sub> capture process. The foremost instances are post-combustion CO<sub>2</sub> capture in the TMC Mongstad in Norway, which can capture 300 000 tons of CO<sub>2</sub> per year and BD3 Sask Power in Canada, which can capture 1 million tons of CO<sub>2</sub> per year.<sup>6</sup> Depending on the conditions of the post-combustion capture process, different CO<sub>2</sub> separation technologies can be used such as absorption, adsorption, and membrane and cryogenic separation.<sup>7,8</sup> One of the most widespread and cost-effective processes in the capture of impurities from various gas streams is the absorption method using chemical solvents. Among chemical absorption processes, the amine processes are among the most important. They have been applied in numerous refineries worldwide for eliminating CO<sub>2</sub> and hydrogen sulfide from ammonia-synthesis gas, natural gas, crude hydrogen, fossil-fuel fired power plants, petroleum industry, and town gas streams.<sup>9</sup> Over the past decades, different separator devices for CO<sub>2</sub> capture processes, including columns with tray, spray, packing types, and membrane contactors have been extensively studied and have received significant attention.<sup>10–13</sup> Among these separators, packed columns (random or structured) are well known to have good mass transfer performance features. To accurately estimate the exact size of packed column height necessary for the mass transfer of CO<sub>2</sub> from the gas phase to the liquid phase in case of absorption with a chemical reaction, the accurate prediction of the mass transfer coefficients is very important.<sup>11</sup> To raise the designer's confidence and provide the best data for scaling up and designing packed columns in CO<sub>2</sub> capture plants, a good understanding of the basics of modeling and designing is fundamental.<sup>11</sup> Currently, CO<sub>2</sub> absorption into amine solutions in packed columns is considered to be one of the most complicated systems because of relationships between the mass/heat transfer, hydromechanics and thermodynamics.<sup>14</sup> To calculate the mass transfer rate in an absorber column, whether random or structured, empirical or semi-empirical correlations have been developed by researchers in terms of mass transfer coefficients in gas and liquid phases and interfacial areas. However, these developed correlations can be inaccurate in some case and sometimes they cannot be applied to specific systems such as CO<sub>2</sub>–amine systems. A review on several mass transfer correlations in packed columns has been performed in the literature.<sup>15,16</sup> Razi, *et al.*<sup>17</sup> have assessed these correlations in a rate-based model for CO<sub>2</sub> capture with a monoethanolamine (MEA) solution to show the uncertainty associated with using correlations in large-scale CO<sub>2</sub> capture plants. They concluded that the interactions among the transport parameters, mass transfer coefficients, effective interfacial areas and kinetics are too complex for the mass transfer correlations to be applied with a sufficient level of confidence.<sup>17</sup> So far, none of these reviews has provided a review of mass transfer performance in terms of the  $K_{\text{GCO}_2 a_v}$  parameter for CO<sub>2</sub> absorption into amine solutions in packed columns. In existing studies related to the  $K_{\text{GCO}_2 a_v}$  for CO<sub>2</sub> absorption at a laboratory scale, packed columns have been experimentally investigated for a large number of amine-based solvents across a range of

operating parameters. The base of researchers' studies was the prediction of  $K_{\text{GCO}_2 a_v}$ , the investigation of effects of operating parameters on it, and the correlation between  $K_{\text{GCO}_2 a_v}$  and operating process parameters. This study presents a review of studies of  $K_{\text{GCO}_2 a_v}$  parameter at low- and high-pressure packed columns for CO<sub>2</sub> absorption into amine solutions in packed columns. The advantage of directly using  $K_{\text{GCO}_2 a_v}$  when calculating the mass transfer rate is that it makes it unnecessary to calculate the individual mass transfer coefficients in gas and liquid phases and other parameters such as the enhancement factor and Henry's law solubility constant. In addition, the  $K_{\text{GCO}_2 a_v}$  can be applied to specific systems; for example, Ziari, *et al.*<sup>18</sup> have used such developed empirical correlation in a CO<sub>2</sub> capture simulation with MEA solution for an absorber packed column.

## 2. Overview of amine solvents used in the analysis of $K_{\text{GCO}_2 a_v}$

### 2.1. Conventional amines

Notable development in CO<sub>2</sub> capture processes using reactive solvents has been seen in the past decade due to their ability to offer near-full absorption and desorption of CO<sub>2</sub>. Among different reactive solvents such as amines, potassium carbonate, and ammonia, that have been studied for CO<sub>2</sub> capture processes, amines are considerably well-developed.<sup>19</sup>

MEA is the most well-known amine, with a high reaction rate with CO<sub>2</sub> and a low cost.<sup>20</sup> These advantages of MEA can decrease the height of an absorber column and facilitate large-scale operations.<sup>14,21</sup> However, MEA has some disadvantages such as high-energy consumption for its regeneration, low absorption capacity, and degradation and corrosion problems.<sup>7,22</sup> To overcome these disadvantages, a number of important amine solvents have been commercially utilized such as diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), and piperazine (PZ).<sup>23</sup>

As can be seen from Table 1, the aforementioned amines each have their advantages and disadvantages. Clearly, there is no particular amine solvent with all ideal characteristics for CO<sub>2</sub> capture processes. Studies have so far focused on the improvement of amine solvents in order to reach a high CO<sub>2</sub> capture performance and a low cost of operation.<sup>24</sup> In recent years, mixing of conventional amines has shown a considerable improvement of absorption and desorption in CO<sub>2</sub> capture processes.<sup>25</sup> The higher absorption capacity, faster kinetics and lower energy consumption for stripping of CO<sub>2</sub> are good characteristics of mixed amines. Research of mixed amines, such as MEA–MDEA and AMP–PZ, has demonstrated a great enhancement of the kinetics, thermodynamics, mass transfer, as well as energy consumption for regeneration.<sup>26–28</sup>

### 2.2. Newly developed amines

Recently, the focus of studies has turned to new and promising amines, such as *N,N*-diethylethanolamine (DEEA), 4-diethylamino-2-butanol (DEAB), diethylenetriamine (DETA), and 1-dimethylamino-2-propanol (1DMA2P).<sup>23,29–33</sup> DEEA is



Table 1 Properties of conventional and newly developed amines<sup>45</sup>

Chemical name	MEA	DEA	MDEA	AMP	PZ, anhydrous	PZ, 65%	1DMA2P	DETA	DEEA
Molecular formula	C <sub>2</sub> H <sub>7</sub> NO	C <sub>4</sub> H <sub>11</sub> NO <sub>2</sub>	C <sub>5</sub> H <sub>13</sub> NO <sub>2</sub>	C <sub>4</sub> H <sub>11</sub> NO	C <sub>4</sub> H <sub>10</sub> N <sub>2</sub>	C <sub>4</sub> H <sub>10</sub> N <sub>2</sub>	C <sub>5</sub> H <sub>13</sub> NO	C <sub>4</sub> H <sub>13</sub> N <sub>3</sub>	C <sub>6</sub> H <sub>15</sub> NO
Formula weight	61.08	105.14	119.16	89.14	86.13	86.13	103.16	103.17	117.19
Freezing point °C	10.3	28	-21.0	26.0	110	41	-85.0	-39.0	-70
Boling point °C	170	268	247.1	165	146	116	96.0	207	161
Density at 25 °C	1.01	1.092	1.03	0.934	0.877	1.03	0.913	0.952	0.884
Vapor pressure (at 20 °C) mm Hg	0.48	<0.01	0.01	<1	0.1	6.28	8	0.08	1
Water solubility	Miscible	Miscible	Miscible	Miscible	14 wt%	Miscible	Miscible	Miscible	Miscible
Absorption rate	High	Medium	Low	Medium	High	High	Low	Medium	Low
Absorption capacity	Medium	Medium	High	High	High	High	High	High	Medium
Heat of absorption	High	High	Medium	High	High	High	Medium	High	Medium

a tertiary-type amine, which is a potential candidate for CO<sub>2</sub> bulk removal.<sup>34</sup> This amine can be made from low-priced resources such as agricultural products and residues.<sup>33</sup> Kim and Savage,<sup>35</sup> Benitez-Garcia, *et al.*<sup>36</sup> and Li, *et al.*<sup>37</sup> have reported data of CO<sub>2</sub> absorption rates by DEEA at different temperatures and concentrations. Li, *et al.*<sup>37</sup> have concluded that the rate of absorption of CO<sub>2</sub> in a DEEA solution is higher than in an MDEA solution. Also, Vaidya and Kenig<sup>38</sup> have shown that the absorption capacity of a DEEA solution, in terms of CO<sub>2</sub> loading, approached a value of 1 mol CO<sub>2</sub>/mol DEEA. DEAB is an amino alcohol solvent which was synthesized based on a normal molecular design approach.<sup>39</sup> Sema, *et al.*<sup>40</sup> have studied and compared the CO<sub>2</sub> absorption capacity of DEAB with conventional amines such as MEA, DEA, AMP, and MDEA, and their results showed that the absorption of CO<sub>2</sub> in a DEAB solution requires a lower DEAB concentration for the same CO<sub>2</sub> removal efficiency as conventional amines. They also concluded that the rate of absorption of CO<sub>2</sub> in a DEAB solution is higher than in an MDEA solution and lower than in an MEA solution. DETA, a polyamine comprising two primary and one secondary amine groups, has shown to have a faster reaction rate and a higher absorption capacity compared with conventional amines.<sup>41,42</sup> Recently, Chowdhury, *et al.*<sup>43</sup> and Liang, *et al.*<sup>44</sup> have shown that a new tertiary amine, 1-dimethylamino-2-propanol (1DMA2P), has good potential for CO<sub>2</sub> absorption because of its superior performance. Kadiwala, *et al.*<sup>30</sup> have shown that 1DMA2P has a faster reaction rate than MDEA but slower than MEA. Chowdhury, *et al.*<sup>43</sup> have reported that the CO<sub>2</sub> loading of 1DMA2P (at low CO<sub>2</sub> partial pressures) is about twice as high as that of an MDEA solution. Table 1 shows a summary of conventional and newly developed amines' properties<sup>45</sup> used in analyses of  $K_{GCO_2}a_v$  in packed columns.

### 3. Mass transfer theory

At a particular point of an absorber column, mass transfer occurs because of a chemical potential gradient between gas and liquid phases. The mass transfer ends when equilibrium is reached. In other words, when the net mass transfer becomes zero.<sup>46</sup> Nevertheless, the question is at what rate can the mass be transferred? This problem can be associated with the mass

transfer coefficient.<sup>47</sup> The mass transfer coefficient is an important parameter in designing absorber columns.<sup>11,14</sup> Knowledge of this parameter can help a designer accurately calculate the height of an absorber column. In an absorber packed column in a post-combustion CO<sub>2</sub> capture plant, the removal efficiency of CO<sub>2</sub> absorption by amine solutions can be determined by the gas-liquid contact degree, physicochemical properties and hydrodynamics of the absorber column, amine reactivity degree and operating parameters related to the gas and amine solution.<sup>17</sup> Chemical absorption of CO<sub>2</sub> into an amine solution can be described by the two-film theory.<sup>48</sup> This theory proposes that there are two thin films near the gas and liquid phase interfaces, which separate them from the liquid and gas bulk phases. This theory assumes that bulk phases are in equilibrium and all resistances of mass and heat transfer exist in the two films.<sup>48</sup> In most cases, when CO<sub>2</sub> moves from the gas to the liquid phase, a chemical reaction between CO<sub>2</sub> and the amine solution can take place in the liquid film or liquid bulk.<sup>49</sup> According to Fig. 1 and based on the two-film theory, the reaction between CO<sub>2</sub> and the amine solution can be characterized as infinitely fast rate or very slow rate.<sup>48</sup> Depending on the relative values of the reaction rate constants, mass transfer coefficients of gas and liquid phases, concentration ratio of reactants and CO<sub>2</sub> equilibrium solubility, reactions occur in a narrow zone within the film or through the film and bulk of

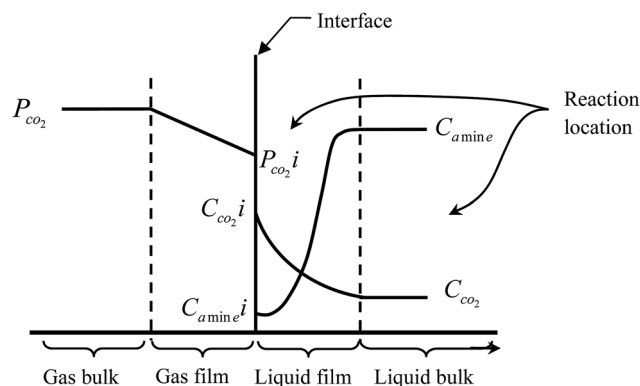


Fig. 1 Location of the chemical reaction between CO<sub>2</sub> and an amine solution based on the two-film theory.



the liquid. The two-film theory is prevalently used in rate-based models.<sup>49–55</sup> A significant number of them consider that the reaction takes place within the liquid film, when the reaction is assumed to be infinitely fast (*i.e.*, CO<sub>2</sub> absorption into the MEA solution).

### 3.1. Determination of $K_{GCO_2}a_v$ in an absorption packed column

At steady-state conditions, the absorbed mass flux of CO<sub>2</sub> ( $N_{CO_2}$ ) across the gas–liquid interface can be represented in terms of  $K_G$  and the difference between the CO<sub>2</sub> partial pressure in the gas bulk ( $P_{Y_{CO_2}}$ ) and the CO<sub>2</sub> partial pressure at the gas–liquid interface ( $P_{Y_{CO_2}^i}$ ), as shown in eqn (1).<sup>56,57</sup>

$$N_{CO_2} = K_G (P_{Y_{CO_2}} - P_{Y_{CO_2}^i}) \quad (1)$$

It is obvious from eqn (1) that  $N_{CO_2}$  is greatest when  $P_{Y_{CO_2}^i}$  approaches zero and  $P_{Y_{CO_2}}$  is at a maximum value. In the same way,  $N_{CO_2}$  is zero when  $P_{Y_{CO_2}}$  is equal to  $P_{Y_{CO_2}^i}$ . The significance of  $K_G$  can be seen from eqn (1)—for a given driving force, a greater  $K_G$  can give greater  $N_{CO_2}$  into the amine solution.<sup>58</sup> Since the driving force of mass transfer occurs at a small distance from the film, the concentration in the interface and, subsequently,  $K_G$  are difficult to measure in an absorption packed column because of the variations in the interfacial area with varying gas and liquid flow rates.<sup>59</sup> Therefore, it is more convenient and useful to express  $N_{CO_2}$  based on the unit volume of the absorption packed column rather than the interfacial area unit, as follows:<sup>59</sup>

$$N_{CO_2}a_v = K_Ga_v (P_{Y_{CO_2}} - P_{Y_{CO_2}^*}) \quad (2)$$

In eqn (2),  $N_{CO_2}a_v$  can be obtained from  $K_{GCO_2}a_v$  and the difference between  $P_{Y_{CO_2}}$  and the CO<sub>2</sub> partial pressure in the gas phase in equilibrium with the CO<sub>2</sub> concentration in the liquid bulk ( $P_{Y_{CO_2}^*}$ ). To calculate  $N_{CO_2}a_v$ , the mass balance according to the rate-based model, considering a small differential height of packing ( $dZ$ ) of the absorption packed column (Fig. 2), can be written as follow:<sup>59</sup>

$$N_{CO_2}a_v dZ A_C = G d \left( \frac{y_{CO_2}}{1 - y_{CO_2}} \right) \quad (3)$$

By substituting eqn (3) into eqn (2),  $K_{GCO_2}a_v$  can be determined using eqn (4):

$$K_{GCO_2}a_v = \left( \frac{G}{P(y_{CO_2} - y_{CO_2}^*) A_C} \right) \frac{dY_{CO_2}}{dZ} \quad (4)$$

Most researchers have used eqn (4) to determine  $K_{GCO_2}a_v$  from experiments on absorption packed columns.<sup>32,33,58–61</sup> In eqn (4), the gas flow rate ( $G$ ) and cross-section area of the column ( $A$ ) as well as the packed column pressure ( $P$ ) are known, and only two terms—the driving force and the derivative

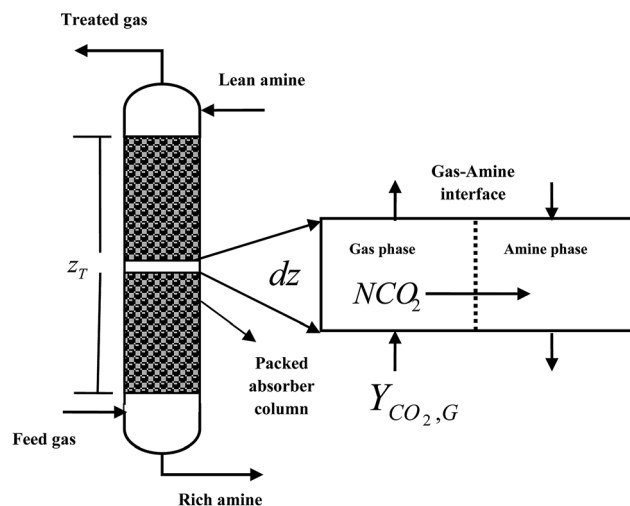


Fig. 2 Differential elements of packing for an absorption column.

of the CO<sub>2</sub> molar ratio—have to be determined. The term  $y_{CO_2}^*$  in eqn (4) can be obtained from the equilibrium solubility data of CO<sub>2</sub> into the amine solution. Often,  $y_{CO_2}^*$  is assumed to be zero due to a fast reaction between CO<sub>2</sub> and the amine solution.<sup>14,32,49,58,60–65</sup> The derivative of the CO<sub>2</sub> molar ratio ( $\frac{dY_{CO_2}}{dZ}$ ) can be determined by measuring the CO<sub>2</sub> concentration (molar fraction) profile in the gas phase along the height of the absorber packed column. By converting molar fraction values to molar ratio values of CO<sub>2</sub>, the term  $\frac{dY_{CO_2}}{dZ}$  is calculated by plotting  $Y_{CO_2}$  against the packing height of the absorber column ( $Z$ ), as shown in Fig. 3.<sup>59</sup>

When the CO<sub>2</sub> concentration is measured at the inlet and outlet of an absorber packed column, the average values of  $K_{GCO_2}a_v$  can be obtained from eqn (5) suggested by Dey and Aronowilas.<sup>66</sup>

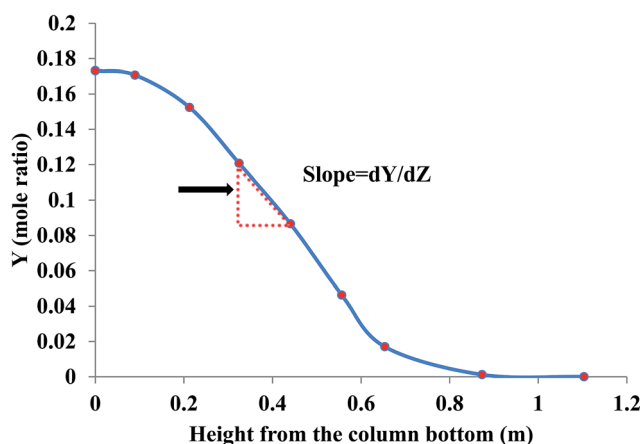


Fig. 3 Determination of the molar ratio slopes by measuring the CO<sub>2</sub> concentration profile in the gas phase along the height of an absorber column.



$$K_{\text{GCO}_2}a_{\text{v}} = \frac{\frac{G}{A_{\text{c}}}}{P \left( \frac{y_{\text{in}} - y_{\text{out}}}{\ln \frac{y_{\text{in}}}{y_{\text{out}}}} \right)} \left( \frac{Y_{\text{in}} - Y_{\text{out}}}{Z} \right) \quad (5)$$

The advantage of using directly  $K_{\text{GCO}_2}a_{\text{v}}$  when simulating the  $\text{CO}_2$  absorption process is avoiding the need to calculate the enhancement factor and individual mass transfer coefficients in liquid and gas phases. The correlations between individual mass transfer coefficients are dependent on dimensionless numbers such as the Reynolds and Schmidt numbers, as well as some hydrodynamic properties of the absorber column; mostly however, they were not developed to use in specific systems (*i.e.*, amine system and packing type). In our previous work,<sup>51</sup> we have applied mass transfer correlations from literature, which were not developed for amine systems, in the simulation of  $\text{CO}_2$  absorption in amine solutions. We have performed sensitivity analyses of individual mass transfer coefficients and kinetics constants of the  $\text{CO}_2$  reaction in amine solutions (the kinetic constant is used for calculating the enhancement factor). We concluded that two mass transfer correlations had the best prediction for an absorber column profiles compared with other applied mass transfer correlations from the literature. Therefore, when  $K_{\text{GCO}_2}a_{\text{v}}$  is used directly in modeling  $\text{CO}_2$  absorption into amine solutions, there is no need to evaluate the sensitivity of the absorber model.

## 4. Experimental studies determining $K_{\text{GCO}_2}a_{\text{v}}$ in low-pressure absorber packed columns

Several experimental works for obtaining  $K_{\text{GCO}_2}a_{\text{v}}$  for conventional and newly developed amines have been conducted by researchers for absorption columns packed with random and structured packing. The reason for determining the mass transfer coefficient based on the gas phase is easy and hassle-free measurement of the  $\text{CO}_2$  concentration along the height of the packed column. In most of these experimental studies, first  $K_{\text{GCO}_2}a_{\text{v}}$  was determined and then the effects of operating parameters on it. In addition, the empirical correlations for  $K_{\text{GCO}_2}a_{\text{v}}$  have been developed based on the effects of operating parameters in absorber columns. Table 2 provides a list of published works related to the determining of  $K_{\text{GCO}_2}a_{\text{v}}$  in absorber packed columns operated in low-pressure conditions. For each list, detailed information about the solvent type, packing type, the height and diameter of packed columns, and operating parameters is given. In the following, the review of the mass transfer performance in terms of  $K_{\text{GCO}_2}a_{\text{v}}$  by amine-based solvents operating in low-pressure absorber packed columns has been carried out.

### 4.1. $K_{\text{GCO}_2}a_{\text{v}}$ of conventional amines

Tontiwachwuthikul, *et al.*<sup>67</sup> have reported the mass transfer performance of  $\text{CO}_2$  absorption into MEA and AMP by

measuring the temperature and concentration along the height of the absorption packed column. They performed several experiments in a laboratory-scale absorber packed column with 12.7 mm ceramic Berl saddles packing type. The column was made of six packed bed sections with a total packing height of 6.55 m and a 0.1 m diameter. The profiles along the height of the packed column were obtained for different liquid to gas ratios, inlet  $\text{CO}_2$  concentration in feed of flue gas, and amine concentrations. They did not determine the  $K_{\text{GCO}_2}a_{\text{v}}$  values directly; rather, they modeled the packed column for  $\text{CO}_2$  absorption with an MEA solution by applying a rate-based model. Aroonwilas and Tontiwachwuthikul<sup>68</sup> have studied experimentally  $K_{\text{GCO}_2}a_{\text{v}}$  for  $\text{CO}_2$  absorption into AMP solution. They performed their experiments on a laboratory-scale absorption column of 1.1 m packing height and a 0.019 m diameter, packed with EX-type structured packing with a specific surface area of approximately  $1700 \text{ m}^2 \text{ m}^{-3}$ . Their experimental results showed that the values of  $K_{\text{GCO}_2}a_{\text{v}}$  at fixed operating parameters were unaffected by the  $\text{CO}_2$  partial pressure over a range of 3–15 kPa. They also compared the values of  $K_{\text{GCO}_2}a_{\text{v}}$  for two cases—columns packed with ceramic Berl saddles packing and EX-type structured packing at the same operating conditions. They found that the value of  $K_{\text{GCO}_2}a_{\text{v}}$  for EX-type structured packing was six times greater than for the ceramic Berl saddles packing. Afterwards, Aroonwilas and Tontiwachwuthikul<sup>63</sup> have studied experimentally the  $K_{\text{GCO}_2}a_{\text{v}}$  for  $\text{CO}_2$  absorption into AMP solution under operating conditions different from their previous work.<sup>68</sup> They found that the effect of the  $\text{CO}_2$  partial pressure on the values of  $K_{\text{GCO}_2}a_{\text{v}}$  changed slightly at pressures above 6 kPa and the values of  $K_{\text{GCO}_2}a_{\text{v}}$  reduced from 1 to 6 kPa. For flow rates in the absorber column, the  $K_{\text{GCO}_2}a_{\text{v}}$  was unaffected by the gas flow rate but the liquid flow rate had a pronounced effect on  $K_{\text{GCO}_2}a_{\text{v}}$ , which increased the values of  $K_{\text{GCO}_2}a_{\text{v}}$  by increasing the liquid flow rate in the range of  $6.1\text{--}14.8 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ . In addition, by increasing the  $\text{CO}_2$  loading of the AMP solution, the  $K_{\text{GCO}_2}a_{\text{v}}$  values decreased. Demontigny, *et al.*<sup>58</sup> have reported experimental data of  $\text{CO}_2$  absorption into ultra-highly concentrated MEA solutions (up to  $9 \text{ kmol m}^{-3}$ ) and investigated the effects of process parameters on  $K_{\text{GCO}_2}a_{\text{v}}$  in three pilot-scale absorption columns packed with random (16 mm Pall Ring and IMTP-15) and structured packing (Gempak 4A). The diameter and height of the absorption packed columns were 0.1 and 2.4 m, respectively. Their results showed that the values of  $K_{\text{GCO}_2}a_{\text{v}}$  increased with increasing liquid flow rates and were unaffected by the gas flow rate. By increasing the  $\text{CO}_2$  partial pressure and  $\text{CO}_2$  loading, the values of  $K_{\text{GCO}_2}a_{\text{v}}$  decreased. In relation to the MEA concentration, which was one of their important works, by increasing the MEA concentration up to  $4 \text{ kmol m}^{-3}$ , the values of  $K_{\text{GCO}_2}a_{\text{v}}$  decreased with a mild slope but increased in the range of  $4\text{--}9 \text{ kmol m}^{-3}$ . They also studied the effect of the packing type on the  $K_{\text{GCO}_2}a_{\text{v}}$  values, and found that structured packing (Gempak 4A) had a better performance compared with random packing (16 mm Pall Ring and IMTP-15). When comparing 16 mm Pall Ring packing with IMTP-15 packing, the IMTP-15 had greater  $K_{\text{GCO}_2}a_{\text{v}}$  values. Aroonwilas, *et al.*<sup>69</sup> have performed experiments on the performance of three types of





Table 2 Summary of operating parameters for absorber packed columns in low pressure for determining  $K_{\text{CO}_2}$

Solvent	Packing type	Packing height (m)	Column diameter (D)	Inlet CO <sub>2</sub> concentration (kPa)	Gas flow rate (mol m <sup>-2</sup> s <sup>-1</sup> )	Amine flow rate (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	Inlet liquid temperature (°C)	Inlet gas temperature (°C)	Amine concentration (mol L <sup>-1</sup> )	Inlet CO <sub>2</sub> loading (mol CO <sub>2</sub> /mol amine)	Ref.
MEA and AMP	Ceramic Berl saddles	6.55	0.1	11.5–19.5	11.1–14.8 (mol m <sup>-2</sup> s <sup>-1</sup> )	9.5–13.5 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	N/A	14–20	1.2–3.8	0.0–0.37	(Tontiwachwuthikul <i>et al.</i> , 1992)
AMP	EX	1.1	0.019	4.7–15.15	12.82 (mol m <sup>-2</sup> s <sup>-1</sup> )	9.73 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	N/A	N/A	1.14	0.027	(Aroonwilas and Tontiwachwuthikul, 1997)
AMP	EX	1.1	0.019	4–10	46.2–96.8 (kmol m <sup>-2</sup> h <sup>-1</sup> )	6.1–14.8 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	N/A	N/A	1.1–3	0.027–0.439	(Aroonwilas and Tontiwachwuthikul, 1998)
MEA	16 mm Pall rings	2.4	0.1	14.78–15.23	119.5–199.1 (L min <sup>-1</sup> )	0.971–2.093 (L min <sup>-1</sup> )	24.1–26	24.8–26.3	6–7	0.195–0.225	(Demontigny <i>et al.</i> , 2001)
MEA	IMTP-15	2.4	0.1	5–19.9	94.7–249.2 (L min <sup>-1</sup> )	0.867–3.134 (L min <sup>-1</sup> )	23.5–28	23.4–31.2	2.98–9.02	0.077–0.354	(Demontigny <i>et al.</i> , 2001)
MEA	Gempak 4A	2.4	0.1	14.90–20.30	119.7–191.9 (L min <sup>-1</sup> )	0.948–2.968 (L min <sup>-1</sup> )	22.5–28.7	24.4–28	3–7	0.12–0.227	(Demontigny <i>et al.</i> , 2001)
MEA and AMP	EX	1.1	0.019	Up to 15	30–97.5 (kmol m <sup>-2</sup> h <sup>-1</sup> )	4.9–29.3 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	20–37	N/A	1.1–5.2	N/A	(Aroonwilas <i>et al.</i> , 1999)
MEA and AMP	Gempak 4A	0.98–2.21	0.1	Up to 15	30–97.5 (kmol m <sup>-2</sup> h <sup>-1</sup> )	4.9–29.3 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	20–37	N/A	1.1–5.2	N/A	(Aroonwilas <i>et al.</i> , 1999)
MEA and AMP	BX	1.02	0.25	Up to 15	30–97.5 (kmol m <sup>-2</sup> h <sup>-1</sup> )	4.9–29.3 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	20–37	N/A	1.1–5.2	N/A	(Aroonwilas <i>et al.</i> , 1999)
MEA, AMP, DEA, MDEA and DIPA	DX	2	0.02	10	48.2 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	4.8–10 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	N/A	N/A	3	0–0.4	(Aroonwilas and Veawab, 2004)
MEA and MEA-MDEA	DX	0.165–0.825	0.02	5–15	7.26–10.13 (L min <sup>-1</sup> )	4.8–15.3 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	30–50	N/A	3–7	0–0.29	(Setameteekul <i>et al.</i> , 2006)
MEA-MeOH	DX	0.4	0.034	15	5 (L min <sup>-1</sup> )	0.02–0.1 (L min <sup>-1</sup> )	N/A	N/A	5	0–0.5	(Usubharatana <i>et al.</i> , 2006b)
MEA-AMP	DX	0.5	0.02	5–15	100 (kmol m <sup>-2</sup> h <sup>-1</sup> )	2.5–5 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	N/A	N/A	3–5	0–0.59	(Dey and Aroonwilas, 2009)
MEA, MEA-MDEA, DEAB and DEAB-MEA	DX	2.15	0.0275	14.4–14.9	4.5–5.7 (L min <sup>-1</sup> )	0.025–0.118 (L min <sup>-1</sup> )	20–41	19.6–30.3	1.1–7.17	0–0.3	(Naami <i>et al.</i> , 2012)
DETA	Dixon rings	1.14	0.028	14.8–15.8	28.78–46.62 (kmol m <sup>-2</sup> h <sup>-1</sup> )	2.65–7.56 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	30–50	N/A	1–4	0.05–0.819	(Fu <i>et al.</i> , 2012)
DETA	DX	1.2	0.028	8.8–14.1	22.2–40.4 (kmol m <sup>-2</sup> h <sup>-1</sup> )	1.95–4.87 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	30–50	N/A	1–4	0.184–0.826	(Fu <i>et al.</i> , 2013)
MEA-MeOH	DX	1.25	0.028	6.7–13.8	24.37–63.54 (kmol m <sup>-2</sup> h <sup>-1</sup> )	2.92–16.09 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	10	11–17	2.5–5	0–0.373	(Fu <i>et al.</i> , 2015)

Table 2 (Contd.)

Solvent	Packing type	Packing height (m)	Column diameter (D)	Inlet CO <sub>2</sub> concentration (kPa)	Gas flow rate	Amine flow rate	Inlet liquid temperature (°C)	Inlet gas temperature (°C)	Amine concentration (mol L <sup>-1</sup> )	Inlet CO <sub>2</sub> loading (mol CO <sub>2</sub> /mol amine)	Ref.
1DMA2P	DX	1.4	0.028	13.2–14.5	28.02 (kmol m <sup>-2</sup> h <sup>-1</sup> )	4.07 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	40	N/A	2	0.2–0.42	(Liang <i>et al.</i> , 2015a)
1DMA2P	Dixon rings	1.4	0.028	13.3–14.5	28.75–46.62 (kmol m <sup>-2</sup> h <sup>-1</sup> )	2.65–7.56 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	30–60	N/A	1–3	0–0.373	(Wen <i>et al.</i> , 2015)
NH <sub>3</sub>	N/A	2	0.015	2.8–8	1400–2300 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	20–30 (m <sup>3</sup> min <sup>-1</sup> )	27	N/A	0.27–0.72	N/A	(Li <i>et al.</i> , 2014)
MEA–MeOH	Sulzer BX 500, Mellapale y 500 and Pall rings	3	0.15	15	1.7–6.5 (m <sup>3</sup> h <sup>-1</sup> )	20–50 (L h <sup>-1</sup> )	20–50	N/A	5	0.2–0.4	(Gao <i>et al.</i> , 2016)
DEEA	DX and Dixon rings	1.7	0.028	3–15	30.5–43.52 (kmol m <sup>-2</sup> h <sup>-1</sup> )	3.9–11.7 (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	27–60	N/A	1–4	0.05–0.02	(Xu <i>et al.</i> , 2016)

structured packing (laboratory-scale (EX), pilot-scale (Gempak 4A), and industrial-scale (SulzerBX)) in terms of the  $K_{GCO_2}a_v$  coefficient. The experimental data was reported for CO<sub>2</sub> absorption into sodium hydroxide (NaOH), MEA and AMP solutions. The laboratory-scale absorption packed column was packed with 20 packing elements of EX and had a total packing height of 1.1 m and a 0.019 m diameter. The pilot-scale absorption packed column was packed with Gempak 4A stainless steel and the packing height varied between 0.98 and 2.21 m, and the absorber had a 0.1 m diameter. The third case was an industrial-scale absorption–desorption unit in which an absorber column was packed with six elements of Sulzer BX gauze structured packing, and the column had a total packing height of 1.02 m and a 0.25 m. Their results indicated that the values of  $K_{GCO_2}a_v$  increased with an increasing liquid flow rate and liquid concentration and were unaffected by the gas flow rate. The values of  $K_{GCO_2}a_v$  decreased with increasing CO<sub>2</sub> concentrations up to 15%. The values of  $K_{GCO_2}a_v$  increased with solvent temperature from 20 °C to 37 °C and decreased with temperatures from 40 °C to 65 °C. When comparing structured packing (Gempak 4A) and IMTP-25 packing, the Gempak 4A provided two times greater  $K_{GCO_2}a_v$  values. Aroonwilas and Veawab<sup>65</sup> have comprehensively investigated the performance of conventional amines such as MEA, DEA, DIPA (diisopropanolamine), MDEA, and AMP; in addition, they have investigated blends including MEA–MDEA, DEA–MDEA, MEA–AMP, and DEA–AMP. They performed the experiments in a laboratory-scale absorption column with a 2 m packing height and a 0.02 m diameter with 36 DX-type elements of structured packing. Their results were presented based on the CO<sub>2</sub> removal efficiency, absorber height requirement, effective mass-transfer area, and  $K_{GCO_2}a_v$ , under identical conditions for the liquid flow rate and CO<sub>2</sub> loading. Their result showed that the CO<sub>2</sub> removal efficiency in a CO<sub>2</sub> loading of zero was in the order MEA > DEA > AMP > DIPA > MDEA. The value of 100% of CO<sub>2</sub> removal efficiency was obtained for MEA, DEA, and AMP, requiring a 0.75, 1.75, and 2.0 m height of the packed column, respectively. Therefore, MEA showed a better performance in comparison with other studied amines. For blended amines, the value of 100% of CO<sub>2</sub> removal efficiency was obtained for MEA–AMP, DEA–AMP, MEA–MDEA, and DEA–MDEA, requiring a 1.2, 2.3, 3.3, and 5.4 m height of the packed column, respectively. The authors also assessed the performance in terms of the effective mass-transfer area under identical processing parameters and found that MEA provided the highest mass-transfer area among the tested amines, including DEA, DIPA, and MDEA. They also showed that the values of  $K_{GCO_2}a_v$  at different CO<sub>2</sub> loadings for MEA were higher compared with other tested amines such as DEA, AMP, DIPA, and MDEA. Setameteekul, *et al.*<sup>70</sup> studied the mass transfer performance for CO<sub>2</sub> absorption in a MEA and MDEA blended amine. The experiments were performed based on the factorial experimental design method (a statistical method), and conducted more than 106 tests with three replications in an absorption column packed with a DX-type packing. The packing height varied between 0.165 and 0.825 m, and the absorber had a 0.02 m diameter. The results of the work by Setameteekul, *et al.*<sup>70</sup> indicated that the solvent



temperature and solvent concentration have the largest effects on the  $K_{\text{GCO}_2 a_v}$  values and the other process parameters have smaller effects. Dey and Aronow<sup>66</sup> used the blended MEA–AMP amine to determine  $K_{\text{GCO}_2 a_v}$  by using only two data sampling points of  $\text{CO}_2$  concentrations at the bottom and top of an absorber column. In fact, they obtained the average values of  $K_{\text{GCO}_2 a_v}$  for an absorber column packed with a DX-type structured packing. Their results showed that the  $K_{\text{GCO}_2 a_v}$  values increased with an increasing liquid flow rate, temperature, and total amine concentrations, and decreased with increasing  $\text{CO}_2$  partial pressure of the feed gas and  $\text{CO}_2$  loading of the amines. The addition of higher concentrations of MEA in the mixed MEA–AMP amine led to an increase in the  $K_{\text{GCO}_2 a_v}$  values, except at high  $\text{CO}_2$  loadings. This was because of a lower reaction rate of  $\text{CO}_2$  with AMP compared with MEA.

Jeon, *et al.*<sup>71</sup> have studied the mass transfer performance and effect of adding ammonia ( $\text{NH}_3$ ) to AMP and MDEA. They determined the  $K_{\text{GCO}_2 a_v}$  values in an absorption packed column with a 1.5 m packing height and a 0.05 m diameter by testing two packing types including 6 mm ceramic Raschig rings, and a wire gauze laboratory-structured packing. They showed that the  $K_{\text{GCO}_2 a_v}$  values at a  $\text{CO}_2$  partial pressure of 15 kPa increased for both mentioned systems by using structured packing, and increased even more by adding  $\text{NH}_3$  from 1 wt% to 3 wt%. They also showed that the  $K_{\text{GCO}_2 a_v}$  values increased at lower  $\text{CO}_2$  partial pressure and higher liquid-to-gas ratios. The overall conclusion of their work was that adding  $\text{NH}_3$  to AMP and MDEA and using structured packing produced higher  $K_{\text{GCO}_2 a_v}$  values. Li, *et al.*<sup>72</sup> have performed experiments for  $\text{CO}_2$  absorption using an  $\text{NH}_3$  solution to determine the  $K_{\text{GCO}_2 a_v}$  values in an absorber column packed with a novel structured packing with diversion windows type. The height of the absorber column and column diameter were 2.4 m (packing height: 2 m) and 0.15 m, respectively. Their results showed that  $K_{\text{GCO}_2 a_v}$  was enhanced by increasing the liquid flow rate and its concentration. However, the  $K_{\text{GCO}_2 a_v}$  values decreased when the  $\text{CO}_2$  partial pressure increased to 8 kPa, and were unaffected by the gas flow rate. Kang, *et al.*<sup>73</sup> have tested various packing types including ceramic Raschig rings, Berl saddles, a structured gauze packing and a hybrid of Raschig rings and a structured packing in different ratios to investigate the mass transfer performance of a  $\text{CO}_2$ –MEA–AMP system. Their results showed that  $\text{CO}_2$  removal efficiencies of Raschig rings, Berl saddles, and the structured packing materials provided higher values for the MEA than the AMP solution, and that the structured packing had a greater efficiency than the random packing. They improved the performance of single random and structured packing materials by mixing them in ratios of 1 : 1, 2 : 1, and 1 : 2. The optimal performance was obtained for the 2 : 1 ratio (structured packing/Raschig rings). The  $K_{\text{GCO}_2 a_v}$  parameter decreased in the order 2 : 1 hybrid packing > structured packing > Raschig rings > Berl saddles.

#### 4.2. $K_{\text{GCO}_2 a_v}$ of hybrid amines

Usubharatana, *et al.*<sup>74</sup> have studied  $K_{\text{GCO}_2 a_v}$  for  $\text{CO}_2$  absorption by using a hybrid solution containing MEA and methanol. Their

experiments were carried out on a laboratory-scale absorption column with a 0.4 m packing height and a 0.034 m diameter, packed with DX-type structured packing with a specific surface area of around  $900 \text{ m}^2 \text{ m}^{-3}$ . They showed that by increasing the methanol concentration in the MEA solution,  $K_{\text{GCO}_2 a_v}$  increased. By increasing the liquid flow rate,  $K_{\text{GCO}_2 a_v}$  increased and led to a decrease of the methanol carryover because of its vaporization to the top of the absorber column. Fu, *et al.*<sup>60</sup> have obtained experimentally  $K_{\text{GCO}_2 a_v}$  by using a hybrid solution containing MEA and methanol. They performed the experiment on a structured absorber column (packing height 1.25 m; column diameter 0.028 m) packed with a DX packing. They reported the  $\text{CO}_2$  concentration and temperature data along the height of the packed column (seven points along column) for 33 tested runs. The effects of key process parameters including the MEA concentration,  $\text{CO}_2$  loading, amine flow rate and gas flow rate were investigated, and it was found that  $K_{\text{GCO}_2 a_v}$  decreased with increasing  $\text{CO}_2$  loading, gas flow rate (in higher concentrations of the MEA solution), and  $\text{CO}_2$  concentration in the inlet feed gas. The authors suggested using a high liquid-to-gas ratio and a low temperature of the feed gas and amine in the absorber column in order to prevent the vaporization of methanol at the top of the absorber column. Gao, *et al.*<sup>75</sup> have studied the effects of different process parameters on the  $K_{\text{GCO}_2 a_v}$  values using a hybrid solvent: MEA–methanol. The experiments performed on an absorber column (packing height 3 m; column diameter 0.15 m) packed with three different packing types including Sulzer BX500, Mellapale Y500, and Pall rings  $16 \times 16$ . Their results indicated that the Sulzer BX500 had higher  $K_{\text{GCO}_2 a_v}$  values than the Mellapale Y500. The reason for this was the good uniform distribution of gas and liquid on the packing surface. In addition, their results showed that (1) the  $K_{\text{GCO}_2 a_v}$  values increased as the  $\text{CO}_2$  lean loading decreased and the hybrid solution temperature, hybrid solution flow rate and gas flow rate increased, (2) the optimal temperature for reducing methanol evaporation was  $20 \text{ }^\circ\text{C}$ , and (3) operating at a high liquid-to-gas ratio led to a reduction of methanol evaporation as suggested by Fu, *et al.*<sup>60</sup> study.

#### 4.3. $K_{\text{GCO}_2 a_v}$ of new amines

Naami, *et al.*<sup>59</sup> have studied experimentally  $K_{\text{GCO}_2 a_v}$  for  $\text{CO}_2$  absorption using a DEAB solution. They also investigated absorption using MEA, MDEA, DEAB, and blended solutions including MDEA–MEA and DEAB–MEA. The authors performed their experiments on an absorber column packed with DX-type structured packing (height 2.15 m; diameter 0.0275 m). It was concluded that the presence of MEA in the DEAB solution increased the  $K_{\text{GCO}_2 a_v}$  values. The authors also investigated the effect of the liquid flow rate on the  $K_{\text{GCO}_2 a_v}$  values, and found that by increasing it in a narrow range,  $K_{\text{GCO}_2 a_v}$  values increased rapidly. Nevertheless, the  $K_{\text{GCO}_2 a_v}$  values were unaffected by the gas flow rate for the above-mentioned amines. The absorption capacity and cyclic capacity between DEAB and MDEA were also compared in the study, and it was found that the new amine, DEAB, has a higher  $\text{CO}_2$  absorption and cyclic capacity than MDEA, which causes a reduction in the amine circulation rate





and energy consumption for amine regeneration. Fu, *et al.*<sup>64</sup> have determined experimentally  $K_{\text{GCO}_2 a_v}$  for CO<sub>2</sub> absorption into a DETA solution. They performed the experiment on a random absorber column (packing height 1.14 m; column diameter 0.024 m) packed with Dixon rings which have a specific surface area of around 2400 m<sup>2</sup> m<sup>-3</sup>. Their results showed that the  $K_{\text{GCO}_2 a_v}$  values for DETA were higher compared with MEA, and the  $K_{\text{GCO}_2 a_v}$  values increased as the DETA flow rate, DETA concentration, and inlet temperature increased. However, the  $K_{\text{GCO}_2 a_v}$  values decreased when the CO<sub>2</sub> loading of DETA increased. Fu, *et al.*<sup>76</sup> have investigated the  $K_{\text{GCO}_2 a_v}$  parameter using a DETA solution. They performed the experiment on a structured absorber column (packing height 1.7 m; column diameter 0.028 m) packed with a DX packing which has a specific surface area of around 900 m<sup>2</sup> m<sup>-3</sup>. They compared the  $K_{\text{GCO}_2 a_v}$  values between DETA-CO<sub>2</sub> and MEA-CO<sub>2</sub> systems, and found that the  $K_{\text{GCO}_2 a_v}$  values of DETA were higher compared with MEA. In addition, they showed that by increasing the DETA flow rate, concentration, and inlet temperature, the  $K_{\text{GCO}_2 a_v}$  values increased. Nevertheless, the  $K_{\text{GCO}_2 a_v}$  values decreased as the CO<sub>2</sub> loading of DETA increased. Liang, *et al.*<sup>44</sup> have investigated the mass transfer performance of CO<sub>2</sub> absorption by a 1DMA2P solution. They obtained  $K_{\text{GCO}_2 a_v}$  for a structured absorber column (packing height 1.4 m; column diameter 0.028 m) packed with DX packing. The authors compared the  $K_{\text{GCO}_2 a_v}$  values for 1DMA2P-CO<sub>2</sub> with those for MEA-CO<sub>2</sub> and MDEA-CO<sub>2</sub> systems, and found that the  $K_{\text{GCO}_2 a_v}$  values of the MEA solution were higher compared with 1DMA2P and MDEA solutions. They ranked them as MEA > 1DMA2P > MDEA. In addition, they showed that by increasing the CO<sub>2</sub> loading for the three mentioned systems, the  $K_{\text{GCO}_2 a_v}$  values decreased. Following the study of Liang, *et al.*,<sup>44</sup> Wen, *et al.*<sup>77</sup> obtained the  $K_{\text{GCO}_2 a_v}$  values in an absorber column packed with Dixon rings for 1DMA2P-CO<sub>2</sub> system. They compared the  $K_{\text{GCO}_2 a_v}$  values for 1DMA2P-CO<sub>2</sub> with those for the MDEA-CO<sub>2</sub> system, and found that the  $K_{\text{GCO}_2 a_v}$  values of the new amine solution were higher compared with the MDEA solution. In addition, the effects of the gas flow rate, amine concentration, amine flow rate, CO<sub>2</sub> loading, and amine temperature on the  $K_{\text{GCO}_2 a_v}$  values were investigated and the results indicated that the  $K_{\text{GCO}_2 a_v}$  values increased with increasing amine concentrations and amine flow rates, but decreased with increasing CO<sub>2</sub> loading. The inert gas flow rate had little effect on the  $K_{\text{GCO}_2 a_v}$  values. For the amine temperature, the  $K_{\text{GCO}_2 a_v}$  values increased up to 323 K in temperature range of 303–333 K, and decreased as amine temperature went above 323 K. Xu, *et al.*<sup>33</sup> have conducted experiments for CO<sub>2</sub> absorption in a DEEA solution. The experiments were carried out for both random and structured packing columns, namely DX and Dixon rings. The authors obtained the  $K_{\text{GCO}_2 a_v}$  values in an absorber column with a 1.7 m packing height and a 0.028 m diameter. The effects of important process parameters on the  $K_{\text{GCO}_2 a_v}$  values were investigated. The results showed that the DEEA concentration, CO<sub>2</sub> loading, and liquid flow rate had the most pronounced effect on  $K_{\text{GCO}_2 a_v}$ , whilst the gas flow rate had a negligible effect. The authors compared the  $K_{\text{GCO}_2 a_v}$  values between MDEA-CO<sub>2</sub> and DEEA-CO<sub>2</sub> systems, and showed that

the  $K_{\text{GCO}_2 a_v}$  values for DEEA were higher compared with the MDEA solution. They also showed that the DX-type structured packing enhanced the  $K_{\text{GCO}_2 a_v}$  values and cyclic capacity compared with the Dixon rings packing. Chen, *et al.*<sup>78</sup> have used the experimental design method including the Taguchi method to select blended amines (MEA-DEAE, MEA-MDEA, MEA-DIPA, and MEA + AMP) as promising solvents for CO<sub>2</sub> capture in a packed column (packing height 1.2 m; column diameter 0.05 m). The optimum points and effects of three key process parameters including the liquid flow rate, gas flow rate and amine concentration on the absorption rate and  $K_{\text{GCO}_2 a_v}$  were studied. Sixteen runs were carried out by the Taguchi method at four levels for four factors to obtain the response values (absorption efficiency, absorption rate, scrubbing factor, and  $K_{\text{GCO}_2 a_v}$ ). In case of  $K_{\text{GCO}_2 a_v}$ , the values were obtained using a two-film model. The results of the study indicated that the gas flow rate and amine flow rate are significant parameters, while the type of amine and amine concentration showed little effect on the  $K_{\text{GCO}_2 a_v}$  values.

## 5. Experimental studies determining $K_{\text{GCO}_2 a_v}$ in high-pressure absorber packed columns

In the previous section, we reviewed the experimental studies for determining  $K_{\text{GCO}_2 a_v}$  in low-pressure absorber packed columns. The evaluation of the  $K_{\text{GCO}_2 a_v}$  coefficient under high pressure is essential for removing CO<sub>2</sub> from natural gas streams. Few studies are available in the literature for determining  $K_{\text{GCO}_2 a_v}$  in high-pressure absorber packed columns.

Abdul Halim, *et al.*<sup>62</sup> performed experiments in order to remove CO<sub>2</sub> from a mixture of CO<sub>2</sub> and methane using an MEA solution under a pressure of 50 bar. The experiments were performed in a packed column (packing height 2.04 m; column diameter 0.046 m) with a packing type of Sulzer gauze, which has a surface area of around 500 m<sup>2</sup> m<sup>-3</sup>. The aim of their work was to determine  $K_{\text{GCO}_2 a_v}$  and the CO<sub>2</sub> removal efficiency under high pressure. The  $K_{\text{GCO}_2 a_v}$  values were obtained at a fixed CO<sub>2</sub> concentration of 20% mol, an amine concentration range of 1–4 kmol m<sup>-3</sup>, an amine flow rate range of 4.51–8.1 m<sup>3</sup> m<sup>-2</sup> h<sup>-1</sup>, a gas flow rate range of 18.89–35.08 kmol m<sup>-2</sup> h<sup>-1</sup>, and feed temperature range of 27 °C to 45 °C. They validated their experiments' reliability by the work of Maneintr, *et al.*<sup>79</sup> under low-pressure conditions. Their results indicated that high pressure, amine flow rate, and amine concentration had a significant effect on  $K_{\text{GCO}_2 a_v}$ , and that by increasing these parameters, the  $K_{\text{GCO}_2 a_v}$  values would increase. They also showed that the  $K_{\text{GCO}_2 a_v}$  values were unaffected by the gas flow rate and that the optimal point for the temperature of the inlet amine to the absorption column was found to be 40 °C. Halim, *et al.*<sup>80</sup> performed their experiments for removing CO<sub>2</sub> from a mixture of CO<sub>2</sub> and methane using an AMP-PZ solution in a packed column (packing height 2.04 m; column diameter 0.046 m) with a packing type of Sulzer gauze. The aim of their work was to determine the  $K_{\text{GCO}_2 a_v}$  values under high pressures (10–40 bar). The  $K_{\text{GCO}_2 a_v}$  values were obtained at a fixed CO<sub>2</sub>



concentration of 40% mole, a total amine concentration of 30% wt (PZ with 7 wt% and AMP with 23 wt%), an amine flow rate range of 2.89–3.97 m<sup>3</sup> m<sup>-2</sup> h<sup>-1</sup>, a gas flow rate range of 33–51 kmol m<sup>-2</sup> h<sup>-1</sup>, and a feed temperature range of 30 °C to 35 °C. Their results indicated that high pressure, amine flow rate, and amine concentration had a large effect on  $K_{\text{GCO}_2}a_v$ , and; the  $K_{\text{GCO}_2}a_v$  values were unaffected by the gas flow rate. Following the work of Halim, *et al.*,<sup>80</sup> Hairul, *et al.*<sup>81</sup> performed experiments under different conditions of operating parameters. Their setup for an absorber column was similar the one in the work of Halim, *et al.*<sup>80</sup> They determined  $K_{\text{GCO}_2}a_v$  under different operating conditions over a pressure range of 10–50 bar, a CO<sub>2</sub> concentration range of 30% to 50% mol, an amine concentration range of 3–9 wt% for PZ and 23–30 wt% for AMP, an amine flow rate range of 2.89–4.33 m<sup>3</sup> m<sup>-2</sup> h<sup>-1</sup>, a gas flow rate range of 33–40 kmol m<sup>-2</sup> h<sup>-1</sup>, and feed temperature range of 30 °C to 35 °C. Their results showed that by increasing pressure above 20 bar,  $K_{\text{GCO}_2}a_v$  increased, and by increasing the CO<sub>2</sub> concentration in the feed gas,  $K_{\text{GCO}_2}a_v$  decreased. In addition, the performance of AMP in removing CO<sub>2</sub> from natural gas was compared with the AMP–PZ solution, and results showed the AMP–PZ system to be superior in terms of CO<sub>2</sub> removal efficiency.

## 6. General investigation of operating parameters affecting $K_{\text{GCO}_2}a_v$

In the above-mentioned reviewed works on  $K_{\text{GCO}_2}a_v$ , initially, the  $K_{\text{GCO}_2}a_v$  values were obtained experimentally using the concentration profile of CO<sub>2</sub> in the gas phase and the mass balance equation, and then the effects of process parameters on it were investigated. In previous sections, we have shown how are the response values affected by increasing and decreasing one operating parameter. An understanding of how  $K_{\text{GCO}_2}a_v$  of different amine-based solvents changes with different operating parameters and configurations of pilot-plant is significant in evaluating and optimizing CO<sub>2</sub> removal processes.<sup>14,82</sup> The variables affecting  $K_{\text{GCO}_2}a_v$  in the above-mentioned reviewed works have been described in detail as follows.

### 6.1. CO<sub>2</sub> partial pressure

Increasing the CO<sub>2</sub> partial pressure in the gas feed to the absorber column has two effects on  $K_{\text{GCO}_2}a_v$ . First, increasing the CO<sub>2</sub> partial pressure can lead to an increase of the partial pressure gradient<sup>83</sup> because of the consummation of more actively free-amine molecules and, as a result, a decrease of  $K_{\text{GCO}_2}a_v$  can occur (according to eqn (2)). Second, increasing the CO<sub>2</sub> partial pressure can intensify the gas flow turbulence in the absorber column and, as a result, increase  $K_{\text{GCO}_2}a_v$ .<sup>84</sup> In the above-mentioned reviewed works, researchers showed that by increasing the CO<sub>2</sub> partial pressure in the gas feed,  $K_{\text{GCO}_2}a_v$  decreased. This effect shows that amine solutions, especially those which have higher reaction kinetic constant values (such as MEA or PZ), have good performance under lower partial pressure than under higher partial pressure.<sup>85,86</sup> This effect

indicates that amine solutions have a high CO<sub>2</sub> removal efficiency in a lower partial pressure of CO<sub>2</sub> in the gas feed. This occurrence shows that the liquid phase resistance dominates the mass transfer performance of absorption into amine solutions.<sup>87</sup>

### 6.2. Gas flow rate

The turbulence increases in the gas phase because an increase in the gas flow rate can lead to an increase of  $K_{\text{GCO}_2}a_v$ .<sup>60,77,78</sup> However, experiments by many researchers, which were pointed out in previous sections, differed from the above-mentioned prediction by Fu, *et al.*<sup>60</sup> and Chen, *et al.*<sup>78</sup> works. They showed that the liquid film could control the process of CO<sub>2</sub> absorption in an amine solution and, as a result,  $K_{\text{GCO}_2}a_v$  in such a system is unaffected by the gas flow rate.

### 6.3. Liquid flow rate

One of the key parameters, which can affect the mass transfer performance, is the liquid flow rate. Many researchers showed that when the liquid flow rate increased,  $K_{\text{GCO}_2}a_v$  increased as well. The reasons for this effect are (1) an increase in the amine flow rate can cause an increase in free active molecules of amines for high CO<sub>2</sub> absorption, (2) an increase in the amine flow rate has the greatest effect on the surface of the packing, increasing the wet surface area between the amine and gas phases, and (3) an increase in the mass transfer coefficient in the liquid phase decreases the mass transfer resistance in the liquid phase and, as a result, increases the mass transfer coefficient in the gas phase.<sup>50,63,65,66,68</sup> However, increasing this factor above the optimum point can lead to a loss of amines and to high-energy consumption for amine regeneration.

### 6.4. Liquid concentration

In general, increasing the amine concentration causes an increase of the  $K_{\text{GCO}_2}a_v$  values. This is because of the availability of an extra amount of amine molecules for CO<sub>2</sub> absorption at the interface of the gas and liquid, and this increases the possibility for CO<sub>2</sub> to react with amines over a larger active surface area.<sup>33,60,76</sup> As mentioned before, the absorption of CO<sub>2</sub> in amine solutions is a process, which is controlled by the liquid phase. As a result, this phenomenon decreases the resistance in the liquid phase and increases the mass transfer coefficient in the gas phase. However, increasing the concentration leads to an increase of the viscosity, which can hinder the diffusion of CO<sub>2</sub> into amines. Under these conditions, the balance between increasing  $K_{\text{GCO}_2}a_v$  and the cost involved should be considered by increasing the amine concentration.

### 6.5. Liquid temperature

Another other key parameter is liquid temperature, which can have an effect on  $K_{\text{GCO}_2}a_v$ , the reaction kinetic, and equilibrium solubility. According to the Arrhenius equation,<sup>88</sup> the reaction kinetic constant for the reaction between CO<sub>2</sub> and an amine solution is temperature dependent, and by increasing the temperature a higher reaction rate constant is achieved.<sup>89</sup>



Consequently, the enhancement factor can be increased and consequently,  $K_{\text{GCO}_2 a_v}$  can be increased as well.<sup>90</sup> Under absorption conditions, this effect can be reversed at higher temperatures when the reaction between CO<sub>2</sub> and amines becomes reversible (it approaches desorption conditions), and it can decrease  $K_{\text{GCO}_2 a_v}$ . In addition, the higher temperature can lead to an increase in the vapor pressure of CO<sub>2</sub> above the amine solution's and this can cause an increase in the Henry's law solubility constant; as result, a decrease of  $K_{\text{GCO}_2 a_v}$  and the solubility of CO<sub>2</sub> in amine solutions can occur.<sup>91</sup> The balance between the above-mentioned parameters should be considered for increasing  $K_{\text{GCO}_2 a_v}$ .

### 6.6. CO<sub>2</sub> loading

An increase of CO<sub>2</sub> loading in amine solutions leads to a decrease in the existing active amine concentration, which consequently decreases  $K_{\text{GCO}_2 a_v}$ .<sup>33,71,74,76,77</sup> This is obvious when the amount of CO<sub>2</sub> loading in the lean amine solution is high, the mass transfer driving force from the gas phase to the liquid phase will decrease and, in these cases, increasing the liquid flow rate to compensate the low absorption rate is not an effective method. The optimum way for decreasing the CO<sub>2</sub> loading in amine solutions is heating the amine solution to increase  $K_{\text{GCO}_2 a_v}$ .

### 6.7. Absorption pressure

Increase of pressure in an absorber column can lead to a decrease of CO<sub>2</sub> concentration in equilibrium with the amine solution and, as a result, the driving force for mass transfer can increase. Halim, *et al.*<sup>80</sup> showed that the absorption of CO<sub>2</sub> (from natural gas) in an AMP–PZ solution under a pressure range of 20–40 bar increased  $K_{\text{GCO}_2 a_v}$ . However, the increasing absorber pressure in CO<sub>2</sub> capture post-combustion processes will increase the cost of operation.<sup>92</sup> Increasing  $K_{\text{GCO}_2 a_v}$  in CO<sub>2</sub> capture post-combustion processes by increasing pressure is not cost-effective.

### 6.8. Packing type

Packing is helpful in making more time for gas–liquid contact throughout the CO<sub>2</sub> absorption process, so it can increase the surface area and  $K_{\text{GCO}_2 a_v}$  in the packed column. Recently, researchers showed that using a structured packing in the absorption column could create higher surface area as compared with random packing.<sup>93</sup> This is because of greatly higher geometric wet surface areas per structured packing volume unit. However, the packing surface area should not be the only selection criteria for creating a higher  $K_{\text{GCO}_2 a_v}$  in the packed column.<sup>94</sup> The other parameters affecting packing, such as packing arrangement pattern, angle of corrugation, void fraction, and height of crimp, should be also considered when designing the absorption packed column, to minimize the pressure drop and capacity of the liquid entrainment.

## 7. Empirical correlations for $K_{\text{GCO}_2 a_v}$ in packed columns

Several mass-transfer coefficient correlations are available for absorber columns packed with random and structured packing.<sup>12,95–98</sup> These developed correlations differ in their accuracy and system-specific applicability. By having these correlations and calculating the enhancement factor,  $K_{\text{GCO}_2 a_v}$  can be obtained. However, these correlations can increase the error in calculations, for example in rate-based models, and one needs to perform a sensitive analysis for the mentioned correlations, which may not be applicable to CO<sub>2</sub>–amine systems.

The review on these correlations was done by Wang, *et al.*<sup>16</sup> for random and structured packing columns. Herein, we have reviewed the empirical correlations of  $K_{\text{GCO}_2 a_v}$  in absorber packed columns, which were obtained experimentally, mainly from analyzing the effects of operating parameters on  $K_{\text{GCO}_2 a_v}$  in CO<sub>2</sub>–amine systems. The reviewed correlations in this study are presented in Table 3 and the corresponding values of operating parameters for developed correlations have been listed in Table 2.

Kohl and Riesenfeld<sup>99</sup> have developed an empirical correlation of  $K_{\text{GCO}_2 a_v}$  for CO<sub>2</sub> absorption in an MEA solution. The correlation applies to an absorption column packed with random packing. In their study, the  $K_{\text{GCO}_2 a_v}$  correlation is as function of the amine flow rate ( $L$ ), amine loading ( $\alpha$ ), equilibrium loading ( $\alpha_e$ ), amine concentration ( $M$ ), viscosity ( $\mu$ ), CO<sub>2</sub> partial pressure, and amine temperature. Their empirical correlation is

$$K_G a_e = F \left( \frac{L}{\mu} \right)^{2/3} \left[ 1 + 5.7(\alpha - \alpha_e) \text{Me}^{0.00677 - 3.42P} \right] \quad (6)$$

In the above equation, the  $F$  value is the packing factor, and Kohl and Riesenfeld<sup>99</sup> have reported  $F$  values for some random packing types. For example, the  $F$  values have been reported as 0.0021 and 0.003 for 1 inch ceramic saddles and 3/8 inch ceramic saddles, respectively. Demontigny, *et al.*<sup>58</sup> have developed an empirical correlation of  $K_{\text{GCO}_2 a_v}$  for a CO<sub>2</sub>–MEA system based on the work of Kohl and Riesenfeld.<sup>99</sup> The correlation is as function of the same parameters developed by Kohl and Riesenfeld<sup>99</sup> except for the viscosity term as this term was not considered in the work of Demontigny, *et al.*<sup>58</sup> The developed equation in their work is

$$K_G a_e = 0.731(L)^{1/2} \left[ (\alpha - \alpha_e) \frac{M}{P_{\text{CO}_2}} \right] + 0.0061 \quad (7)$$

Demontigny, *et al.*<sup>58</sup> have reported that the eqn (7) had errors when predicting results using experimental data and is valid only up to a concentration of 3 kmol m<sup>-3</sup>. They reported that the errors arose from the CO<sub>2</sub> loading data. Despite of variations of CO<sub>2</sub> loading along the height of the packed column, the CO<sub>2</sub> loading value was assumed in its saturation point (0.5 mol CO<sub>2</sub>/mol amine). Aroonwilas and Tontiwachwuthikul<sup>63</sup> have developed an empirical correlation of  $K_{\text{GCO}_2 a_v}$  for a CO<sub>2</sub>–AMP system based on the work of Demontigny, *et al.*<sup>58</sup> The correlation



Table 3 Review of the developed empirical correlations of  $K_{GCO_2 a_v}$  in low-pressure absorber packed columns

Solvent	Packing type	Ref.	Correlations
MEA	Ceramic rings, glass rings, steel rings and ceramic saddles	(Kohl and Riesenfeld, 1985)	$K_G a_e = F \left( \frac{L}{\mu} \right)^{2/3} [1 + 5.7(\alpha - \alpha_e) M e^{0.00677 - 3.42P}]$
MEA	16 mm Pall rings, IMTP-15 and 4A Gempak	(Demontigny <i>et al.</i> , 2001)	$K_G a_e = 0.731(L)^{1/2} \left[ (\alpha - \alpha_e) \frac{M}{P_{CO_2}} \right] + 0.0061$
AMP	EX	(Aroonwilas and Tontiwachwuthikul, 1998)	$K_G a_e = 2.11(L)^{1/2} \left[ (\alpha - \alpha_e) \frac{M}{P_{CO_2}} \right] + 0.0193$
MEA	DX	(Setameteekul <i>et al.</i> , 2006)	$K_G a_e = 4.106 - 0.370A - 0.077B + 0.044C - 0.001758D - 4.74E + 0.00215A^2 + 0.004B^2 - 0.00162C^2 + 6.105E^2 - 0.02AC + \dots$
MEA-AMP	DX	(Dey and Aroonwilas, 2009)	$K_G a_e = k_{amine} e^{A \left( \frac{AMP}{MEA} \right)} e^{B\alpha} e^{C x_{CO_2}} L^D e^{E C_s} e^{F/T}$
DEAB	DX	(Sema <i>et al.</i> , 2013)	$K_G a_e = (L)^{0.65} \left[ (\alpha - \alpha_e) \frac{M}{P_{CO_2}} \right] + 0.0071$
MEA	Dixon rings	(Fu <i>et al.</i> , 2012)	$K_G a_e = (L/\mu)^{0.67} [0.00805(\alpha - \alpha_e) M] e^{(0.0067 - 3.4P_{CO_2})} - 0.0002213$
DETA	Dixon rings	(Fu <i>et al.</i> , 2012)	$K_G a_e = (L)^{0.67} (G)^{0.08} \left[ 0.752(\alpha - \alpha_e) \frac{M}{P_{CO_2}} \right] + 0.142$
MEA-MDEA	DX	(Naami <i>et al.</i> , 2013)	$K_G a_e = k_{amine} e^{A \left( \frac{MDEA}{MEA} \right)} e^{B\alpha} e^{C x_{CO_2}} L^D e^{E C_s} e^{F/T}$
1DMA2P	Dixon rings	(Wen <i>et al.</i> , 2015)	$K_G a_e = 0.023(L)^{0.44} \left[ 23.943(\alpha - \alpha_e) \frac{M}{P_{CO_2}} \right] + 0.2062$
NH <sub>3</sub>	Packing with diversion windows	(Li <i>et al.</i> , 2014)	$K_G a_e = 0.0767(L)^{0.42} (M)^{0.495} / P_{CO_2}^{0.194}$
DEEA	Dixon ring	(Xu <i>et al.</i> , 2016)	$K_G a_e = 0.2526(L)^{0.177} (\alpha - \alpha_e) \frac{M^{0.2451}}{P_{CO_2}^{0.173}} - 0.0074$
DEEA	DX		$K_G a_e = 0.5718(L)^{0.18} (\alpha_e - \alpha) \frac{M}{P_{CO_2}} + 0.0489$

obtained for an absorber column packed with a laboratory DX-type packing. The correlation is as function of the same parameters developed in the Demontigny, *et al.*<sup>58</sup> study. The developed correlation of  $K_{GCO_2 a_v}$  for a CO<sub>2</sub>-AMP system by Aroonwilas and Tontiwachwuthikul<sup>63</sup> is

$$K_G a_e = 2.11(L)^{1/2} \left[ (\alpha - \alpha_e) \frac{M}{P_{CO_2}} \right] + 0.0193 \quad (8)$$

They showed that the error between experimental data of  $K_{GCO_2 a_v}$  and results predicted by the above equation was 16.5%. Setameteekul, *et al.*<sup>70</sup> have developed a  $K_{GCO_2 a_v}$  correlation based on the experimental design factorial method. The  $K_{GCO_2 a_v}$  correlation was obtained for two systems including CO<sub>2</sub>-MEA and CO<sub>2</sub>-MEA-MDEA as a function of the amine flow rate, amine loading, amine concentration, amine temperature, and CO<sub>2</sub> partial pressure. The correlation is based on the results of interaction of operating parameters, and for the CO<sub>2</sub>-MEA system, it is obtained from the equation below.

$$K_G a_e = 4.106 - 0.370A - 0.077B + 0.044C - 0.001758D - 4.74E + 0.00215A^2 + 0.004B^2 - 0.00162C^2 + 6.105E^2 - 0.02AC + \dots \quad (9)$$

It should be noted that the above equation was obtained after truncation of insignificant parameters. Insignificant parameters were those, which had less probable values in the analysis of variance results. The results obtained by the factorial method had an error of 18.39% for the CO<sub>2</sub>-MEA system and

a high error reported for the CO<sub>2</sub>-MEA-MDEA system. Dey and Aroonwilas<sup>66</sup> have developed the  $K_{GCO_2 a_v}$  correlation for CO<sub>2</sub> absorption into a MEA-AMP solution in an absorber column packed with a laboratory DX-type packing as

$$K_G a_e = k_{amine} e^{A \left( \frac{AMP}{MEA} \right)} e^{B\alpha} e^{C x_{CO_2}} L^D e^{E C_s} e^{F/T} \quad (10)$$

In eqn (10), AMP/MEA is the molar ratio of the amine mixture,  $\alpha$  is the CO<sub>2</sub> loading,  $x_{CO_2}$  is the molar fraction of CO<sub>2</sub> in liquid,  $C_s$  is the amine concentration,  $L$  is the amine flow rate and  $T$  is the amine temperature. The regressed coefficients ( $K$ ,  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $E$ , and  $F$ ) were obtained for different AMP/MEA molar ratios of the amine mixture, and the errors were reported as 6.75%, 10.05%, 11.72% and 12.2% for MEA, MEA : AMP = 1 : 2, MEA : AMP = 1 : 1, and MEA : AMP = 2 : 1, respectively. Sema, *et al.*<sup>32</sup> have developed the  $K_{GCO_2 a_v}$  correlation for CO<sub>2</sub> absorption into a DEAB solution. They have reported that the correlation is valid for an absorber column packed with a DX-type packing. Their results showed that the reported error for the developed correlation (eqn (11)) against experimental data was 14.6%.

$$K_G a_e = (L)^{0.65} \left[ (\alpha - \alpha_e) \frac{M}{P_{CO_2}} \right] + 0.0071 \quad (11)$$

Fu, *et al.*<sup>64</sup> have developed a predictive correlation for  $K_{GCO_2 a_v}$  in a CO<sub>2</sub>-DETA system. This correlation is valid for an absorber column packed with Dixon rings. The developed correlation was



obtained based on the work of Demontigny, *et al.*<sup>58</sup> The correlation was validated the  $K_{GCO_2}a_v$ ; first, by developing the correlation according to the work of Kohl and Riesenfeld<sup>99</sup> for a CO<sub>2</sub>-MEA system, and then, the correlation was validated for a CO<sub>2</sub>-DETA system. These correlations are, for the CO<sub>2</sub>-MEA (eqn (12)) and CO<sub>2</sub>-DETA (eqn (13)) systems:

$$K_G a_e = (L/\mu)^{0.67} [0.00805(\alpha - \alpha_e M)] e^{(0.0067 - 3.4 P_{CO_2})} - 0.0002213 \quad (12)$$

$$K_G a_e = (L)^{0.67} (G)^{0.08} \left[ 0.752(\alpha - \alpha_e) \frac{M}{P_{CO_2}} \right] + 0.142 \quad (13)$$

The predicted results by the correlations above showed errors of 16% and 14%, for CO<sub>2</sub>-DETA and CO<sub>2</sub>-MEA systems, respectively, against experimental results. Fu, *et al.*<sup>76</sup> have applied an artificial neural network (ANN) in order to estimate of  $K_{GCO_2}a_v$  values for absorption of CO<sub>2</sub> into a DETA solution in an absorber column packed with laboratory Ex-type packing. In the ANN model, 8 parameters such as gas flow rate, CO<sub>2</sub> partial pressure, liquid flow rate, amine concentration, amine density, amine viscosity, diffusion of CO<sub>2</sub> in an amine solution, and the cycling loading of amines are defined as input parameters and  $K_{GCO_2}a_v$  as the output parameter. To develop the ANN model, 75% and 25% of the dataset were used for training and testing, respectively. Their results showed that the ANN model could predict experimental data very well, with an error of 7.6% for the CO<sub>2</sub>-DETA system in a packed column. Naami, *et al.*<sup>100</sup> have developed a correlation for the  $K_{GCO_2}a_v$  in a CO<sub>2</sub>-MEA-MDEA system in an absorber packed with a DX-type packing over MDEA-MEA concentrations of 27/3, 25/5, and 23/7 wt%. The developed correlation was based on the work of Dey and Aronowilas<sup>66</sup> (eqn (10)), and is

$$K_G a_e = k_{amine} e^{A \left( \frac{MDEA}{MEA} \right)} e^{B\alpha} e^{C x_{CO_2}} L^D e^{EC_s} e^{F/T} \quad (14)$$

In eqn (14), MDEA/MEA is the molar ratio of the amine mixture,  $\alpha$  is the CO<sub>2</sub> loading of the amine,  $x_{CO_2}$  is the molar fraction of CO<sub>2</sub> in the liquid,  $C_s$  is the amine concentration,  $L$  is the amine flow rate and  $T$  is the amine temperature. The regression coefficients ( $K$ ,  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $E$ , and  $F$ ) were obtained for different MDEA/MEA molar ratios of the amine mixture, and the errors were reported as 20.9%, 21.7%, and 22.8% for MEA/MDEA = 3/27 wt%, MEA/MDEA = 5/25 wt%, and MEA/MDEA = 7/23 wt%, respectively. Wen, *et al.*<sup>77</sup> have correlated the  $K_{GCO_2}a_v$  data in an absorber column packed with Dixon rings for a 1DMA2P-CO<sub>2</sub> system. Their developed correlation was based on the Demontigny, *et al.*<sup>58</sup> study:

$$K_G a_e = 0.023(L)^{0.44} \left[ 23.943(\alpha - \alpha_e) \frac{M}{P_{CO_2}} \right] + 0.2062 \quad (15)$$

Their results showed that the developed correlation had an error of 9.8% when predicting experimental data. Li, *et al.*<sup>72</sup> have developed the  $K_{GCO_2}a_v$  correlation in an absorber column

packing with diversion windows type in a NH<sub>3</sub>-CO<sub>2</sub> system. The correlation is based on important parameters such as the liquid flow rate ( $L$ ), NH<sub>3</sub> concentration and CO<sub>2</sub> partial pressure:

$$K_G a_e = 0.0767(L)^{0.42} (M)^{0.495} / P_{CO_2}^{0.194} \quad (16)$$

In addition, the modeling and simulation of absorption of CO<sub>2</sub> in a NH<sub>3</sub> solution was carried out using the computational mass transfer model with a developed correlation of  $K_{GCO_2}a_v$  (eqn (16)). The authors did not report the error values between the developed correlation and experimental data, but trends of the developed correlation showed that it had a small error in comparison with the experimental data. Xu, *et al.*<sup>33</sup> have developed two correlations of  $K_{GCO_2}a_v$  for absorber columns packed with Dixon rings and DX-type packing materials. They developed the correlation for a CO<sub>2</sub>-DEEA system based on the work of Demontigny, *et al.*<sup>58</sup> as follows:

$$K_G a_e = 0.2526(L)^{0.177} (\alpha - \alpha_e) \frac{M^{0.2451}}{P_{CO_2}^{0.173}} - 0.0074 \quad (17)$$

$$K_G a_e = 0.5718(L)^{0.18} (\alpha_{eq} - \alpha) \frac{M}{P_{CO_2}} + 0.0489 \quad (18)$$

Their results showed that the errors obtained by eqn (17) (Dixon rings packing) and eqn (18) (DX-type packing) were 3% and 8%, respectively.

## 8. Conclusions

In this study, a review has been provided on  $K_{GCO_2}a_v$  associated with amine-based solvents in absorption packed columns. As a first step, we have reviewed the experimental determination of  $K_{GCO_2}a_v$ , previously done by researchers. With measuring CO<sub>2</sub> concentrations in the gas phase along the height of absorber columns and using the two-film theory,  $K_{GCO_2}a_v$  was obtained by researchers for columns packed with random and structured packing materials. Details of pilot-plant data related to the determination of  $K_{GCO_2}a_v$  have been reported, and the determination of  $K_{GCO_2}a_v$  has been reviewed for various amine-based solvents (conventional amines, hybrid amines, newly developed amines) over a range of operating parameters of low- and high-pressure absorber columns. Second, we have reviewed and described the effects of operating parameters on the  $K_{GCO_2}a_v$  data in absorber packed columns. In most studies, authors showed that the  $K_{GCO_2}a_v$  values are unaffected by the gas flow rate, and by increasing the liquid flow rate, amine concentration, and column pressure, the  $K_{GCO_2}a_v$  values increased. Increasing the CO<sub>2</sub> loading of amines and the partial pressure of CO<sub>2</sub> in the gas feed lead to a  $K_{GCO_2}a_v$  decrease. Third, we have reviewed the developed empirical correlations of  $K_{GCO_2}a_v$  for absorber low-pressure columns. The most developed correlations are functions of operating parameters of the absorber column and somewhat depend on the physical properties such as viscosity. It should be noted that developed correlations, which were reviewed in this study, are only based on specific



systems (such as packing type and amine solvent). The advantages of these correlations are that one does not need to calculate the enhancement factor and perform a sensitivity analysis of mass transfer coefficients in both liquid and gas phases.

## 9. Prospects

In recent years, CO<sub>2</sub> removal using amine solutions has attracted extensive consideration by many researchers. One of the most important subjects is to evaluate the mass transfer performance in absorption packed columns in terms of mass transfer coefficients. As we have discussed in this study, the determination of the  $K_{\text{GCO}_2}a_v$  term can help the designer gain a deeper understanding of such a system because of the simplicity of using CO<sub>2</sub> concentration measurements in the gas phase for absorber columns. However, some attempts are needed to gain a better understanding of the mass transfer performance in terms of  $K_{\text{GCO}_2}a_v$ . Following are the possible future directions concerning the analysis and evolution of  $K_{\text{GCO}_2}a_v$  in absorption packed columns:

- Determination of  $K_{\text{GCO}_2}a_v$  for a pilot-plant and plant data.
- Determination of  $K_{\text{GCO}_2}a_v$  for a stripper column under high temperature.
- More analyses are needed of  $K_{\text{GCO}_2}a_v$  parameter in high-pressure conditions.
- Sophisticated equipment is required for high quality measuring of CO<sub>2</sub> along the packed column which is used for determination of  $K_{\text{GCO}_2}a_v$ .
- Considering other gases in the flue gas feed to the absorber when determining  $K_{\text{GCO}_2}a_v$ .
- Simultaneous effects of operating parameters on  $K_{\text{GCO}_2}a_v$  need to be investigated, for example using statistical methods.
- Determination of  $K_{\text{GCO}_2}a_v$  using an optimization technique such as the work of Ji, *et al.*<sup>101</sup> who did this for the mass transfer coefficient in the liquid phase.
- More research on mixed amines is needed; for example, the effects of activators on the amine solutions for the determination of  $K_{\text{GCO}_2}a_v$ .
- More research on the packing type for determination of  $K_{\text{GCO}_2}a_v$  is needed, especially for plant data.
- The empirically developed correlations should not depend only on the operating parameters but should also depend on physical properties, while for the CO<sub>2</sub>–amines systems reaction kinetics are also important.
- Applying the empirically developed correlation of  $K_{\text{GCO}_2}a_v$  directly in the rate-based model and considering the errors.
- Modeling and optimization  $K_{\text{GCO}_2}a_v$  are needed to find the optimum operating parameters effecting  $K_{\text{GCO}_2}a_v$ .

## Nomenclature

$a_v$	Effective interfacial area
$A_c$	Cross-sectional area of the column
AMP	2-Amino-2-methyl-1-propanol
$C$	Amine concentration

$C_{\text{CO}_2}^i$	CO <sub>2</sub> concentration at interface
DEA	Diethanolamine
DEEA	<i>N,N</i> -Diethylethanolamine
DEAB	4-Diethylamino-2-butanol
DETA	Diethylenetriamine
DMA2P	1-Dimethylamino-2-propanol
$F$	Packing factor
$g$	Gas
$G$	Gas flow rate
IMTP	Intalox metal tower packing
$K_G a_v$	Gas-phase volumetric overall mass transfer coefficient
$L$	Liquid flow rate
MEA	Monoethanolamine
MDEA	Methyldiethanolamine
PZ	piperazine
$P_{\text{CO}_2}^i$	Partial pressure of CO <sub>2</sub> at interface

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