Effect of liquid viscosity on the liquid phase mass transfer coefficient of packing

Di Song, A. Frank Seibert, Gary T. Rochelle*

Abstract

There are many correlations of liquid phase mass transfer coefficient ($k_L$) for packings in the literature; most were developed without data that vary liquid viscosity ($\mu_L$) significantly (< 5 cP). In CO$_2$ capture by amine scrubbing, $\mu_L$ of aqueous amine may be significantly greater than water, which makes it important to know how mass transfer is affected by $\mu_L$. A research plan is proposed to measure the effective mass transfer area ($a_e$) and $k_L$ in a pilot-scale packed column with $\mu_L$ from 1 to 100 cP. Glycerol was chosen as the viscosity enhancer for its complete solubility in water and the Newtonian behavior of its aqueous solution. Models were built to estimate the physical properties ($\mu_L$, $\rho$, $D_{CO_2}$, $H_{CO_2}$, $\gamma$) of CO$_2$/NaOH/H$_2$O/glycerol based on literature data. Kinetic data ($k_g'$) for the system were obtained with a wetted wall column (WWC). The kinetic data, $k_g'$, was found to initially increase with glycerol concentration because of the catalytic effect of glycerol, then decrease rapidly because of the increase in $\mu_L$. The overall reaction rate constant ($k_{Alk}$) was determined from $k_g'$ data, and was found to increase with glycerol concentration until it becomes asymptotic. This model for $k_g'$ will be used for future measurement of $a_e$ and $k_L$ in a pilot-scale column.

1. Introduction

CO$_2$ capture and storage (CCS) is an important technology for greenhouse gas control. Post-combustion amine scrubbing is by far the most feasible technique for large scale point source CO$_2$ capture because of its maturity and
tail-end characteristic. The \( \mu_L \) of concentrated and CO\(_2\)-loaded amine solution can be 10-30 times more viscous than water, which makes it important to know how mass transfer in packed columns is affected by \( \mu_L \). Most of the existing \( k_L \) (\( k_{L,a} \)) correlations in the literature examined only water or dilute aqueous solutions with \( \mu_L \) close to 1 cP. In these correlations, the dependence of \( k_L \) on \( \mu_L \) was indirectly obtained from the dependence on dimensionless numbers such as \( Re \) and \( Sc \). A more reliable prediction can only be made when \( \mu_L \) is varied directly in \( a_e \) and \( k_L \) measurements.

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_e )</td>
<td>effective mass transfer area of packing per volume of column, m(^2)/m(^3)</td>
</tr>
<tr>
<td>( a_p )</td>
<td>specific (dry) area of packings, m(^2)/m(^3)</td>
</tr>
<tr>
<td>( C )</td>
<td>constant in correlation</td>
</tr>
<tr>
<td>( d )</td>
<td>characteristic length, m</td>
</tr>
<tr>
<td>( D )</td>
<td>diffusion coefficient, m(^2)/s</td>
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<tr>
<td>( g )</td>
<td>gravitational acceleration, m/s(^2)</td>
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<tr>
<td>( H )</td>
<td>Henry’s constant, atm·L/mol</td>
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<td>( h )</td>
<td>WWC tube length, m</td>
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<tr>
<td>( k )</td>
<td>reaction rate constant</td>
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<td>( k_{L,CO_2} )</td>
<td>overall reaction rate constant for CO(_2)/NaOH/H(_2)O/glycerol, L/mol·s</td>
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<td>( k_g' )</td>
<td>liquid phase mass transfer coefficient with chemical reactions expressed in gas unit, mol/m(^2)·Pa·s</td>
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<td>( k_G )</td>
<td>gas phase mass transfer coefficient, mol/m(^2)·Pa·s</td>
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<td>( k_L )</td>
<td>liquid phase mass transfer coefficient, m/s</td>
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<td>( K )</td>
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<td>( L )</td>
<td>liquid volumetric flow rate, cm(^3)/s</td>
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<td>( N )</td>
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<tr>
<td>( q )</td>
<td>pure-component Van der Waals surface area parameter</td>
</tr>
<tr>
<td>( r )</td>
<td>pure-component Van der Waals volume parameter</td>
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<tr>
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<td>temperature, °C or K</td>
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<tr>
<td>( u )</td>
<td>fluid velocity, m/s</td>
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<td>( w )</td>
<td>weight fraction</td>
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<tr>
<td>( x )</td>
<td>mole fraction</td>
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<tr>
<td>( Z )</td>
<td>coordination number in UNIQUAC model</td>
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### Greek Letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( \alpha )</td>
<td>dependence of ( k_L ) on ( \mu_L )</td>
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<tr>
<td>( \beta )</td>
<td>non-randomness parameter in NRTL model</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>dependence of ( k_L ) on ( D )</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>activity coefficient</td>
</tr>
<tr>
<td>( \delta )</td>
<td>dependence of ( D ) on ( \mu_L )</td>
</tr>
<tr>
<td>( \eta )</td>
<td>liquid film thickness, m</td>
</tr>
<tr>
<td>( \eta )</td>
<td>parameter in Pigford mass transfer model, defined in Eq. A11</td>
</tr>
<tr>
<td>( \theta )</td>
<td>area fraction in UNIQUAC model</td>
</tr>
<tr>
<td>( \Theta )</td>
<td>dimensionless concentration change, defined in Eq. A10</td>
</tr>
<tr>
<td>( \mu )</td>
<td>viscosity, cP</td>
</tr>
<tr>
<td>( \rho )</td>
<td>density, kg/m(^3)</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>surface tension, N/m</td>
</tr>
<tr>
<td>( \tau )</td>
<td>exposure time of liquid surface, s</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>segment fraction in UNIQUAC model</td>
</tr>
</tbody>
</table>
Dimensionless numbers

$Ha$  Hatta number, $(k_1D)^{0.5}/k_L$

$Sc$  Schmidt number, $\mu/\rho D$

$Sh$  Sherwood number, $kd/D$

$Re$  Reynolds number, $u_D/\mu$

Subscripts

$L$ liquid phase

$G$ gas phase

$g$ glycerol

$w$ water

$Alk$ alkalinity

Superscripts

$b$ bulk solution

$i$ fluid interface

2. Literature review

2.1. Effect of $\mu_L$ on $k_L$

In packed columns, $\mu_L$ affects $k_L$ in two ways: directly through affecting the turbulence in the liquid phase, and indirectly via its influence on the diffusion coefficient, $D$, of mass transfer species. The total influence of $\mu_L$ on $k_L$ is the sum of the two effects.

To illustrate the two effects, assume a $k_L (k_L a)$ correlation of the simplified form of Eq. 1, and $D$ is a function of $\mu_L$ in the form of Eq. 2. Combining the two equations gives Eq. 3, in which $(\alpha+\beta\gamma)$ refers to the total influence of $\mu_L$ on $k_L$, while $\alpha$ and $\beta\gamma$ refer to the direct and indirect effects of viscosity respectively. The value $(\alpha+\beta\gamma)$ can be correlated from empirical data with varying $\mu_L$. To obtain separate values of $\alpha$ and $\beta\gamma$, a reliable relationship between $D$ and $\mu_L$ is required.

$$k_L (k_L a) = C_1 \mu^a D^\beta$$  \hspace{1cm} (1)

$$D = C_2 \mu^\gamma$$  \hspace{1cm} (2)

$$k_L (k_L a) = C_1 C_2^{\beta\gamma} \mu^{a+\beta\gamma} = C_3 \mu^{a+\beta\gamma}$$  \hspace{1cm} (3)

A comprehensive overview of liquid phase mass transfer properties in packed columns can be found in the literature [1,2]. Au-yeung and Ponte made a detailed review of $k_L (k_L a)$ models for packed columns before the 1980s [1]. They pointed out that the lack of data for high viscosity liquids impedes a thorough understanding of $k_L$. Wang et al. discussed $k_L$, $k_G$, and $a_e$ correlations for both random and structured packing in the literature, but they did not focus on the effect of $\mu_L$ [2].

2.2. $k_L (k_L a)$ correlations for random packing

A number of $k_L (k_L a)$ correlations have been developed to predict the mass transfer in columns with random packing. Sherwood and Holloway were the first to systematically measure $k_L a$ of several aqueous systems [3]. Van Krevelen and Hoftijzer include the effect of gas-liquid chemical reaction in their $k_L$ correlation for different random packings [4]. Data from a technical plant together with other literature data were used for the correlation. $k_L$
and $\alpha$ were separated by simply assuming that $a_\alpha$ is equal to $a_p$. $\alpha$ was found to vary with $Ha$ with an approximate value of $-1/3$.

Shulman and co-workers, using a 0.25 m diameter (i.d.) column, measured $k_G$ by vaporization of naphthalene packing with known surface area [5,6]. The $k_G$ correlation was used in conjunction with $k_{G\alpha}$ data from Fellinger [7] to obtain $a_\alpha$, which was then used to separate $k_L$ from $k_{L\alpha}$ data from several investigators [3,8-10]. Though $\alpha$ was an unreasonable positive value (0.05) for this correlation, their attempt to separate $k_L$ and $k_G$ from $a_\alpha$ by experimentally measuring $a_\alpha$ is an important contribution to the understanding of mass transfer in packed columns.

Knoedler and Bonini measured $k_{L\alpha}$ through vacuum desorption of oxygen from water with triangular packing in a 0.15 m diameter (i.d.) column [11]. The direct dependence of $k_{L\alpha}$ on $\mu_L$ was found to be 0.52. The unrealistic positive value of $\alpha$ proves the unreliability of the model, which incorporates no variance in $\mu_L$.

Davidson were the first to propose a theoretical $k_{L\alpha}$ model for random packing with the assumption of laminar flow and complete liquid mixing [12]. The packing surface was assumed to consist of a number of inclined surfaces with random angles and length. The model was later adopted and modified by several authors [13-15]. The power, $\alpha$, was determined to be $-1/6$.

After comparing $k_{L\alpha}$ data from multiple sources [3,16-18], Norman concluded that the influence of types of random packing on $k_{L\alpha}$ is remarkably small and a universal $k_{L\alpha}$ correlation can be used for random packing [19].

Norman and Sammak measured $k_L$ by absorption of sulphur dioxide into water and carbon dioxide into different aqueous and organic solutions [20,21]. They were the first to vary $\mu_L$ over a relatively large range (0.4-20 cP). $k_L$ and $\alpha$ were separated by a preliminary experiment observing the wetted percentage of packing surface as a function of liquid flow rate. Though the packing they examined (vertical disc packing) is not commonly used, their endeavor to examine the specific influence of $\mu_L$ on $k_L$ was a step forward.

Onda et al. developed widely-accepted models of $a_\alpha$ and $k_L$ of random packing by correlating extensive literature data and their own experimental data for gas absorption into water and organic solutions [22-25]. The liquid viscosity was not significantly varied in any of the data sources.

Mohunta and Laddha measured $k_L$ with a few experimental runs performed with increased $\mu_L$ by adding glycerol to water [26]. Data with increased $\mu_L$ fitted well with the bulk of the literature data. While this was the first reported attempt to vary $\mu_L$ using aqueous glycerol, the range of $\mu_L$ was still small (0.73-1.48 cP).

Cornell and co-workers developed a $k_{L\alpha}$ correlation based on some reported data [27,28]. The databank size was limited and an empirical packing-specific factor was introduced for data fitting. Bolles and Fair modified the model by significantly expanding the databank with a larger range of column size, operating conditions, and packing types [29]. However, the range of $\mu_L$ was still limited (0.09-1.5 cP).

Mangers and Ponter were the first to systematically investigate the effect of $\mu_L$ on $k_{L\alpha}$ [30]. By the addition of glycerol, the $\mu_L$ range (0.9-26 cP) was significantly larger than previous investigators. They found a sharp transition point in the relation between $k_{L\alpha}$ and $L/\mu_L$. The transition was believed to result from whether the packing surface was fully wetted. $k_{L\alpha}$ correlations at both sides of the transition point were provided. The values of $\alpha$ were different before and after the transition point, but both were close to -0.6. Ponter and Au-yeung modified the model by introducing a mixing factor with more empirical data [14].

Linek et al. measured $k_{L\alpha}$ of random packings by desorption of oxygen from water into pure nitrogen [31]. Effective mass transfer area was determined by absorption of carbon dioxide into sodium hydroxide solutions. The overall mass transfer coefficient for this system with fast chemical reaction was known in a theoretical form [32], and was confirmed by experiments with the same system at packing surface with known interfacial area. This approach to measure $a_\alpha$ with a fast reaction system with known mass transfer rates sheds light upon future study of mass transfer in pilot-scale experiments to separate $a_\alpha$ from empirical data of $k_{L\alpha}$ and $k_{G\alpha}$. The $k_L$ data showed good agreement with the correlation of Onda et al. [25].

Echarte et al. examined the desorption of carbon dioxide from water and aqueous glycerol solutions for $k_L$ in a 0.4-m I.D. column [15]. The effective mass transfer area, $a_{cp}$, were obtained in the same column by water cooling. The use of $a_{cp}$ data obtained from water for $k_L$ of the much more viscous system of water/glycerol is based on the assumption that $a_\alpha$ is not a function of $\mu_L$, which might not be correct. Compared to the experiment of Mangers and Ponter, the $\mu_L$ range (0.9-6.1 cP) is smaller but the column size is larger. The correlation is a modification of the theoretical model of Davidson.
Delaloye et al. studied the effect of \( \mu_L \) on \( k_{La} \) of random packings by stripping oxygen from aqueous solutions of different viscosity enhancers including sodium alginate, glycerol, and polyethylene glycol (PEG) [33]. The \( \mu_L \) range of was 0.8-9.6 cP. The authors pointed out that, despite the large number of \( k_L \) correlations in the literature, few of them gave reliable prediction for \( \alpha \). This was illustrated by the fact that even correlations which agreed for water-like viscosities diverged by an order of magnitude for \( \mu_L \) of only 10 cP. For sodium alginate and glycerol, \( \alpha \) was found to be -0.52, which was in good agreement with the result of Echarte et al. For PEG, \( \alpha \) was found to be -0.26. The authors attributed the discrepancy to the inaccuracy of diffusion coefficient, \( D \), model for PEG and the fact actual physical properties of PEG sample might be different from those indicated by the manufacturer.

Billet and Schultes [34,35] developed a semi-theoretical \( k_L \) correlation based on penetration theory [36]. The model was correlated by examining an extensive data set involving different packings and systems. However, the range of \( \mu_L \) was small (0.3-1.66 cP), and the correlation requires knowledge of a packing-specific shape constant, which is not readily available for all packings. The model was updated by further enlarging the data base [37]. The model may provide good prediction for mass transfer properties if shape constants of packing are known and when \( \mu_L \) is close to water, but its reliability for viscous liquids is doubtful.

Maćkowiak also developed a semi-theoretical \( k_L \) model based on penetration theory [38]. Liquid was assumed to flow down along the packing surface in the form of thin rivulets, but change to droplets between individual packing elements. Both rivulets and droplets were believed to provide \( \alpha_e \). Multiple reported data which covered a variety of random packings were used for the correlation. However, the data used only include water-like liquids, and a packing-specific parameter is needed for the correlation.

### 2.3. \( k_L (k_{La}) \) correlations for structured packing

Since the 1960s structured packing has been applied in industrial distillation and absorption columns [39]. The majority of these studies focused on distillation (e.g., [40-44]), where mass transfer resistance is often thought to be controlled by the vapor phase which makes deducing \( k_L \) unreliable.

Bravo et al. were the first investigators to systematically examine mass transfer for structured packings [45]. The model for \( k_L \) was derived theoretically based on penetration theory. No parameter for \( k_L \) was correlated by empirical data. Though the calculated HETP showed good agreement with extensive literature data from distillation, its use is not recommended for prediction of \( k_L \) or \( \alpha \). This model was modified [40,41,46] to include effects of characteristic packing dimension, effective fluid velocity, and contact time. However the correlation of \( k_L \) remained in the same form.

The \( k_L \) correlation of Billet and Scheltes [34,35,37] for structured packing is the same as with random packing.

Weiland and co-workers measured \( a_e \) and \( k_{La} \) by absorption of carbon dioxide into solutions of sodium hydroxide and sodium carbonate/bicarbonate [47]. Though different parameters were assigned to different packings in the correlations, the correlations were the first to be obtained by a system controlled by liquid phase mass transfer resistance. The power, \( \alpha \), was found to be a positive value around 0.5, which is likely a result from the limited range of \( \mu_L \).

Hanley et al. developed a theoretical \( k_L \) model from an analogy to electrical percolation on a conductor/insulator lattice [48]. In the model, \( k_L \) was independent of \( \mu_L \).

The \( k_{La} \) correlation of Brunazzi and Paglianti obtained from an aqueous system was verified by data obtained from absorption of chlorinated compounds into solvent with elevated \( \mu_L \) (mixture of polyethylene glycol dimethylethers with \( \mu_L \) of 4 cP and 7.7 cP) [49,50]. \( a_e \) was measured in a previous study by absorption of 1,1,1-trichloroethane into the same liquid in the same column [51]. Similar to Weiland et al., this correlation also contains packing-specific parameters and gives a positive value of \( \alpha \) (0.7) for Mellapak 250Y. This might be caused by the assumption that packing height affects \( k_L \), which is more likely to be the result of liquid maldistribution.

Maćkowiak measured \( k_L \) of an aqueous system [52]. The experimental data, together with literature data were used for correlating the model. An assumption was made that \( a_e \) is equal to \( a_{ep} \), \( \alpha \) was found to be -0.93, which is unreliable because \( \mu_L \) was not varied.

Murrieta et al. developed a \( k_L \) model derived from penetration theory [53]. A packing-specific correction factor was introduced to fit the empirical data. The effective mass transfer area, \( a_e \), was estimated by a previous model [41]. It should be noted that the column diameter is the similar to that to be used in the current study.
Valenz et al. measured $k_{La}$ of an aqueous system with $a_c$ obtained from absorption of carbon dioxide into sodium hydroxide solution [54]. Strikingly large differences were found between $k_{La}$ and $a_c$ measured in the work and those predicted by three well-established correlations for structured packings [37,40,55]. No property other than superficial liquid velocity was correlated for the model.

Hanley and Chen [56,57] developed a model for $k_L$ by correlating a large set of literature data for distillation and absorption/desorption systems. Dependence on physical properties was regressed by dimensional analysis and by the least square rule. Data for various packing families were individually analyzed. A universal value of $\alpha$ (-0.67) was found for all packing families examined. The correlation is more of an overall mathematical summary of previously reported data from various sources than an empirical inspection.

2.4. Limitations of existing $k_L$ ($k_{La}$) models in the prediction of $\alpha$

Despite the large number of $k_L$ ($k_{La}$) models in literature, few of them provide reliable prediction on how $\mu_L$ will affect $k_L$ because of two major problems:

- The total effect of $\mu_L$ ($\alpha + \beta \gamma$) was not correlated from actual variance of $\mu_L$ in the experiment;
- The direct ($\alpha$) and indirect ($\beta \gamma$) part of the effects of $\mu_L$ were not correctly separated.

To illustrate the first problem, assume $k_L$ correlation takes the form of Eq. 4, which is equivalent to Eq. 5 when dimensionless groups are expanded. In Eq. 5, the total influence of $\mu_L$ on $k_L$ is $(b-a)$, which is determined by exponents on $Re$ ($a$), and $Sc$ ($b$). Typically $a$ is correlated by varying the liquid flowrate, and $b$ is directly assigned the value of 0.5 in order to satisfy the 0.5 dependence on $D_L$ dictated by penetration theory [36]. As a result, the $\mu_L$ term only appears in Eq. 4 as a part of dimensionless groups without being empirically varied. The $\alpha$ obtained this way is obviously not reliable.

$$Sh = Sh_0 \left( \frac{Re}{Re_0} \right)^a \left( \frac{Sc}{Sc_0} \right)^b$$  \hspace{1cm} (4)

$$k_L = k_L^0 \left( \frac{d}{d_0} \right)^{a-1} \left( \frac{\rho}{\rho_0} \right)^{a-b} \left( \frac{\mu}{\mu_0} \right)^{b-a}$$  \hspace{1cm} (5)

The second problem arises from the assigned 0.5 dependence on $D_L$. 26 of the 29 authors assume that $\beta$ is equal to 0.5 (see Appendix A.1). Since inaccuracy of $\beta$ will lead to inaccuracy of $\alpha$, a reliable value for $\beta$ is of critical importance. Though the 0.5 dependence has been partly confirmed by Vivian and King via desorption of different gases from water in a packed column [58], the conclusion might not necessarily hold for non-aqueous systems or a system with an even larger change in $D_L$ due to a large change in $\mu_L$. Therefore, instead of direct assignment, the reliable approach to obtain $\beta$ is to determine $D_L$ empirically or to resort to literature that examined $D_L$ for the specific system used in the $k_L$ experiment.

Fig. 1 summarizes the predicted value of $\alpha$ in the $k_L$ ($k_{La}$) correlations mentioned earlier. The drastic disagreement on $\alpha$ (-1.03 to +0.7) implies the unreliability of the existing models. For the few correlations in which $\mu_L$ was varied over a relatively large range (solid points in Fig. 1), either the column size is too small to avoid the wall effect/entrance effect and to be representative of an industrial scale situation, or only random packings were investigated. Therefore, a systematic investigation of the effect of $\mu_L$ on $k_L$ in columns with random and structured packings is necessary.
3. Experimental details & data analysis

3.1. Overall research plan

A research plan (Table 1) was proposed to systematically investigate the influence of $\mu_L$ on $k_L$ in columns with several random and structured packings. The proposed range of $\mu_L$ is 1-100 cP. Glycerol was chosen as the liquid viscosity enhancer for its ease of dissolution and complete solubility in water. Aqueous glycerol is Newtonian [59], which guarantees that the $\mu_L$ measured by the viscometer is identical with the actual $\mu_L$ of the liquid film on the packing surface, and that the fluid exhibits the same $\mu_L$ in the WWC and pilot column experiments regardless of the shear rate.

Table 1. Project plan

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<td>Target data</td>
<td>$k'_{g'}$</td>
<td>$a_e$</td>
<td>$k_L$</td>
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<tr>
<td>System</td>
<td>CO$_2$ + (NaOH/water/glycerol)</td>
<td>CO$_2$ + (NaOH/water/glycerol)</td>
<td>Toluene + (water/glycerol)</td>
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<tr>
<td>Equipment</td>
<td>WWC</td>
<td>Pilot column (0.46 m I.D.)</td>
<td>Pilot column (0.46 m I.D.)</td>
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<tr>
<td>Packing</td>
<td>N/A</td>
<td>Various random and structured packings</td>
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<tr>
<td>Approx. range of $\mu_L$</td>
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<td>0.9-100 cP</td>
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<td>wt% of glycerol</td>
<td>0-89</td>
<td>0-90</td>
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</table>

3.2. Experimental equipment, methods, and materials

The WWC was used to measure the $k'_{g'}$ of CO$_2$/NaOH/H$_2$O/glycerol. The bench-scale gas-liquid contactor has a known interfacial area, based on which $k'_{g'}$ can be obtained from flux and concentration data by countercurrent gas-liquid contact. The details of the apparatus have been reported by Cullinane [60], Tsai [61], and Chen [62]. The packed column to be used for future measurement of $a_e$ and $k_L$ has been described by Tsai et al. [61,63].
The inorganic carbon (CO$_3^{2-}$ or its equivalent) was measured by total inorganic carbon analysis (TIC) to account for bulk depletion of alkalinity. pH and concentration of total alkalinity were measured by acid titration with a Titranod series titrator (Metrohm, Riverview, FL, USA). A Physica MCR 300 cone and plate viscometer (Anton Paar GmbH, Graz, Austria) was used for liquid viscosity measurement. A Mettler Toledo DE40 densitometer (Mettler-Toledo, Inc., Columbus, OH) was used for density measurement of liquid samples. Details about this equipment and related experimental methods can be found in Rochelle et al. [64].

Distilled and deionized (DDI) water, 1N sodium hydroxide solution (Fisher), 1N sodium carbonate solution (Fisher), and glycerol (Fisher, 0.995-0.998 purity) were used in solution preparation.

3.3. Data analysis

$k_g'$ was obtained from the slope of the flux-driving force plot forced through zero [61]. The empirical $k_g'$, together with other calculated/measured properties ($H_{CO2}, D_{CO2}$, alkalinity concentration), were used to determine the overall reaction rate constant ($k_{Alk}$) from Eq. 6 [61]. After the correlation of $k_{Alk}$ has been developed, Eq. 6 will be used to calculate $\alpha_e$ from $k_g'a$ data obtained from pilot column.

\[ k_g = \sqrt{\frac{k_{Alk} D_{CO2 L}}{H_{CO2}}} \]  

(6)

Models were built to estimate the physical properties ($\mu_L, \rho, D_{CO2}, H_{CO2}, HCO2$) of CO$_2$/NaOH/H$_2$O/glycerol based on literature data. The correlations used for $\mu_L$ and $\rho$ were described by Cheng for H$_2$O/glycerol [65]. The effect of sodium hydroxide (nominally 0.1 N) and dissolved carbon dioxide on $\mu_L$ and $\rho$ was small, which was confirmed by comparing measured and calculated values. Parameters of NRTL and UNIQUAC activity coefficient models (Table 2) for H$_2$O/glycerol were correlated based on literature data [66]. Predicted values of $\gamma$ are shown in Fig. 2. It was assumed that sodium hydroxide and dissolved carbon dioxide had insignificant influence on $\gamma$. Several sources [67-72] reported that $H_{CO2}$ for CO$_2$/NaOH/H$_2$O/glycerol was correlated by Eq. 7 & 8. Parameters in Eq. 7 are summarized in Table 3. The effect of sodium hydroxide and dissolved carbon dioxide on $H_{CO2}$ was neglected because the influence of ions is less than 5% for the worst case scenario using methods of Pohorecki and Moniuk [73]. Predicted and literature values of $H_{CO2}$ are shown in Fig. 3. Correlation of mutual diffusion coefficient of H$_2$O/glycerol $D_{g-w}$ is shown in Eq. 9. Calculated and literature data [74-80] are shown in Fig. 4(a). Correlation of diffusion coefficient of CO$_2$ in H$_2$O/glycerol $D_{CO2 g-w}$ is shown in Eq. 10. Calculated and literature data [81-87] are shown in Fig. 4(b).

\[
\log \frac{H_{CO2 g-w}}{H_{CO2 w}} = (A_{g} + B \ln(w_g + 1) + C \ln^2(w_g + 1)) \times \left( \frac{D}{T(\circ C)} + E + FT(\circ C) + G \ln T(\circ C) \right)
\]  

(7)

\[
\log H_{CO2 w} = -7.8857 \times 10^{-5} T(K)^2 + 5.9044 \times 10^{-2} T(K) - 9.1229
\]  

(8)

$D_{g-w} = 0.3403 T(\circ C)^{0.3134} \mu^{-0.5557}$  

(9)

$D_{CO2 g-w} = 0.3169 T(\circ C)^{0.5206} \mu^{-0.7407}$  

(10)

Sterilization experiments were performed to check if bacteria growth is a problem in glycerol-rich solutions [88]. It was found that the use of biocide is unnecessary. To check if the mass transfer resistance is still dominated by the liquid phase for toluene/H$_2$O/glycerol, $\gamma_{Toluene}$ was calculated by correlation of Carrillo-Nava et al. [89] and was found to remain high enough (> 100) at the proposed range of glycerol concentration.

### Table 2: NRTL and UNIQUAC parameters for water/glycerol (see Appendix A.2 for details)

<table>
<thead>
<tr>
<th>Model</th>
<th>$A_{12}$</th>
<th>$A_{21}$</th>
<th>$B_{12}$</th>
<th>$B_{21}$</th>
<th>$a_{12}$</th>
<th>$Z$</th>
<th>$\sigma^2$</th>
<th>AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRTL</td>
<td>0.0933</td>
<td>-0.8763</td>
<td>752.1</td>
<td>-193.3</td>
<td>0.4757</td>
<td>-</td>
<td>0.00103</td>
<td>2.93%</td>
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<tr>
<td>UNIQUAC</td>
<td>-0.0101</td>
<td>1.9212</td>
<td>537.9</td>
<td>-284.4</td>
<td>-</td>
<td>10</td>
<td>0.7181</td>
<td>1.39%</td>
</tr>
</tbody>
</table>
Table 3. Parameters in Eq. 7

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>3.28</td>
<td>-3.43</td>
<td>-2.26</td>
<td>14.6</td>
<td>-7.09</td>
<td>-0.00416</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Fig. 2. Activity coefficients of H₂O/glycerol at 20 °C

Fig. 3. $H_{CO_2}$ of CO₂/NaOH/H₂O/glycerol
4. Results & Discussion

4.1. $k_g'$ & reaction kinetics

The $k_g'$ of the CO$_2$/NaOH/H$_2$O/glycerol system obtained from the WWC experiments is shown in Fig. 5. As expected, the $k_g'$ increases with increasing temperature. When glycerol concentration increases, $k_g'$ initially increases and then decreases rapidly.

Several equilibria and reactions are proposed to represent the system:

$$\text{Glycerol} + OH^- \overset{K}{\rightleftharpoons} \text{Glycerol}^- + H_2O$$

(R1)

$$CO_2 + 2OH^- \overset{k_{OH}}{\rightarrow} CO_3^{2-} + H_2O$$

(R2)

$$CO_2 + 2\text{Glycerol}^- + H_2O \overset{k_{\text{Glycerol}}}{\rightarrow} CO_3^{2-} + 2\text{Glycerol}$$

(R3)

The overall reaction rate results from the combined effects of R2 and R3, and can be expressed as Eq. 11 & 12. The trend of $k_g'$ as a function of glycerol concentration could be explained by the assumption that $k_{\text{Glycerol}}$ is larger than $k_{OH}$. When the glycerol concentration is low ($< 10$ wt %), the increase in $\mu_L$ and $H_{CO_2}$ is small, so the overall effect of glycerol leads to a higher $k_g'$ because of the catalytic effect of glycerol. When glycerol concentration is further increased, the increase in $\mu_L$, subsequent decrease in $D_{CO_2}$, and increase in $H_{CO_2}$ starts to impede the mass transfer and decrease $k_g'$. 

$$k_{\text{Alk}} = k_{OH^-} \left( \frac{[OH^-]}{[Alk]} \right) + k_{\text{Glycerol}} \left( \frac{[\text{Glycerol}^-]}{[Alk]} \right)$$

(11)

$$[Alk] = [OH^-] + [\text{Glycerol}^-]$$

(12)
Three parallel WWC experiments were performed for reproducibility. Experiments with different liquid flow rates were performed to confirm that $k_g'$ is not a function of $L$. Experiments with different presaturator temperature (i.e., different partial pressure of water of inlet gas) were performed to investigate the effect of water mass transfer on $k_g'$. Experiments with 0.05 N sodium carbonate were performed to check the effect of ionic strength and carbon dioxide loading on $k_g'$. None of these factors was found to be significant.

The $k_{Alk}$ determined from $k_g'$ is shown in Fig. 6. Despite the discrepancy between different experiments, $k_{Alk}$ increases with temperature and glycerol concentration, and finally becomes asymptotic. The trend in Fig. 6 proves the previous assumption that $k_{Glycerol}$ is larger than $k_{OH}$.
4.2. Change in \( \mu_L \) & alkalinity depletion

The \( \mu_L \) of the WWC samples are shown in Fig. 7. The change of \( \mu_L \) before and after the experiments is insignificant, and both are close to calculated values. This guarantees that there is no change of \( \mu_L \) for bulk solution due to mass transfer of water.

Bulk depletion of alkalinity is about 10% for the worst case scenario, which is acceptable considering the square root dependence of \( k'_{Alk} \) on alkalinity concentration.

Surface depletion of alkalinity was calculated for each WWC experiment. The pseudo-first-order assumption central to this work is only valid when there is no appreciable depletion of alkalinity at the liquid surface. Flux of alkalinity can be calculated by Eq. 13 through reaction stoichiometry. The interface concentration of alkalinity can be calculated by Eq. 14 with \( k'_{Alk} \) estimated by theory from Pigford [90,91] (see Appendix A.3). The worst case scenario calculated at the highest partial pressure of CO\(_2\) shows an average ratio of surface depletion of 7.6%.

\[
N_{Alkaliity} = 2N_{CO_2} \tag{13}
\]

\[
N_{Alkaliity} = k'_{Lk} ([Alk]^b - [Alk]^1) \tag{14}
\]

5. Conclusions

Prediction of \( \alpha \) of existing \( k_L (k_{L,A}) \) correlations of packing is scattered (-1.03 to +0.7) and unreliable. Models have been built to estimate the physical properties (\( \mu_L, \rho, D_{CO_2}, H_{CO_2}, \gamma \)) of CO\(_2/NaOH/H_2O/glycerol\) based on literature data. The \( k'_{Alk} \) of the system were measured by WWC experiments with \( \mu_L \) range 0.9-60 cP. The \( k'_{Alk} \) was found to initially increase about 25% when glycerol increases to 10 wt % because of the catalytic effect of glycerol, and then decreases about 75% when glycerol increases to 89 wt % because of the impeding effect of elevated \( \mu_L \) on mass transfer. \( k_{Alk} \) was estimated from \( k'_{Alk} \), and was found to increase with glycerol concentration until it becomes asymptotic to a value about five times greater. After \( k_{Alk} \) is correlated as a function of \( K_w, K_{glycerol}, k_{OH^-}, \) and \( k_{glycerol} \), this model for \( k'_{Alk} \) will be used for future measurement of effective mass transfer area (\( a_e \)) and liquid phase mass transfer coefficient (\( k_L \)) using a 42.8 cm diameter (i.d.) packed column.
Acknowledgements

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The authors declare the following competing financial interest(s): One author of this publication consults for Southern Company and for Neumann Systems Group on the development of amine scrubbing technology. The terms of this arrangement have been reviewed and approved by the University of Texas at Austin in accordance with its policy on objectivity in research. The authors have financial interests in intellectual property owned by the University of Texas that includes ideas reported in this paper.
## Appendix A. Detailed information for figures, tables, and equations

### A.1. Detailed information for Fig. 1

<table>
<thead>
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<th>Author, Year</th>
<th>System Description</th>
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<th>$k_i$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>I.D. (cm)</th>
<th>Packing</th>
<th>$\Delta \mu &gt; 5$ cP?</th>
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<td>Sherwood &amp; Holloway, 1940</td>
<td>CO$_2$/O$_2$/H$_2$ + H$_2$O + Air</td>
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<td>Van Krevelen and Hoftijzer, 1947</td>
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<td>Davidson et al., 1960</td>
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<td>$\beta$</td>
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<td>O$_2$ + (H$_2$O+sodium alginate/glycerol/polyethylene glycol) + Air</td>
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<td>CO$_2$ + NaOH/(Na$_2$CO$_3$+NaHCO$_3$) solution + Air</td>
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<td>1997</td>
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<td>0.70</td>
<td>~0.2</td>
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<td>structured</td>
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<td>CO$_2$ + H$_2$O + Air; chlorinated compounds + mixture of polyethylene glycol dimethylethers</td>
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<tr>
<td>1999</td>
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<td>2011</td>
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<td>2012</td>
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</table>
A.2. Detailed information for Table 2

The models of NRTL and UNIQUAC for binary systems are described by Eq. A1-A4 and Eq. A5-A9, respectively.

\[
\ln y_i = x_i^2 \left[ \ln \left( \frac{G_{ij}}{x_i + x_j G_{ij}} \right) + \frac{\tau_{ij} G_{ij}}{(x_i + x_j G_{ij})^2} \right] \\
\ln G_{ij} = -\alpha_{ij} \tau_{ij} \\
\alpha_{ij} = \alpha_{ji} \\
\tau_{ij} = A_{ij} + \frac{B_{ij}}{T} \\
\ln y_i = \ln \left( \frac{\Phi_i}{x_i} \right) + \left( \frac{z_j}{z_i} \right) q_i \ln \left( \frac{\theta_j}{\Phi_j} \right) \left( l_i - \frac{r_i}{r_j} l_j \right) - q_i \ln(\theta_i + \theta_j \tau_{ij}) + \theta_j q_i \left( \frac{\tau_{ji}}{(\theta_i + \theta_j \tau_{ij})} - \frac{\tau_{ij}}{\theta_j + \theta_i \tau_{ij}} \right) \\
\Phi_i = \frac{r_i \kappa_i}{r_i \kappa_i + r_j \kappa_j} \\
\theta_i = \frac{q_i \kappa_i}{q_i \kappa_i + q_j \kappa_j} \\
\ln \tau_{ij} = A_{ij} + \frac{B_{ij}}{T} \\
l_i = \left( \frac{z_j}{z_i} \right) (r_i - q_i) - (r_i - 1)
\]

Van der Waals parameters were obtained from Aspen Plus®: \( q_1 = 1.4, q_2 = 3.06, r_1 = 0.92, r_2 = 3.385 \).

Subscript 1 = water; 2 = glycerol.

\[
\sigma^2 = \sum \frac{(y_{calc} - y_{exp})^2}{(\text{no. of data points}) \times (\text{no. of parameters})}.
\]

\[
AAD = (100\% / (\text{no. of data points})) \times \Sigma \left( \left| \frac{y_{calc} - y_{exp}}{y_{exp}} \right| \right).
\]

A.3. Detailed information for Eq. 13 (\( k_0^L \) calculation)

The physical mass transfer coefficient in the liquid phase was calculated by the following equations.

\[
\left\{ \begin{array}{l}
\Theta = 0.7857 \exp(-5.1219\eta) + 0.1001 \exp(-39.21\eta) \\
+ 0.036 \exp(-105.6\eta) + 0.0181 \exp(-204.7\eta), \text{ for } \eta > 0.01 \\
\Theta = 1 - 3 \sqrt{\frac{\eta}{\pi}}, \text{ for } \eta < 0.01
\end{array} \right.
\]

\[
\eta = \frac{D_{Alk} \tau}{\delta^2}
\]

\[
\tau = \frac{h}{u_{surf}}
\]

\[
\delta = \sqrt{\frac{3 \mu_{L} u_{L}}{\rho_{L} \beta P}}
\]
\[ u_{\text{surf}} = \frac{\rho_L g \delta^2}{2 \mu_L} \]  
(A14)

\[ k^0_L = \left( \frac{Q_L}{a} \right) (1 - \Theta) \]  
(A15)

Since \( D_{\text{OH}^-} \) is larger than \( D_{\text{glycerol}^-} \), and \( D_{\text{glycerol}^-} \) is approximately equal to \( D_{\text{glycerol}^+} \), the mutual diffusion coefficient of \( \text{H}_2\text{O}/\text{glycerol} \) (Eq. 9) was used for the \( k^0_L \) calculation.

References


