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Predicting inter-phase mass transfer for idealized Taylor flow: A comparison of numerical frameworks

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ABSTRACT

Four numerical frameworks were derived to investigate the impact of underlying assumptions and numerical complexity on the predicted mass transfer between a Taylor bubble and liquid slug in circular capillaries. The separate influences of bubble velocity and film length, slug length, and bubble film thickness on $k_L a$ were compared to empirical and CFD-based predictions from existing literature. Reasonable agreement was obtained using a Slug Film model, which accounted for diffusion-limited mass transfer between the slug film and circulating bulk without the need for an iterative numerical solution. Subsequent investigation of the relative contributions of film and cap mass transport for industrially relevant conditions suggests that both mechanisms need to be accounted for during the prediction of $k_L a$.

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1. Introduction

Monolith reactors and capillary micro-reactors continue to receive attention from both industry and academia due to their low pressure drop, high mass transfer rates and ease of scale-up when compared to conventional reactor technology. Commonly considered for heat and mass transfer limited reactions such as hydrogenations, hydrodesulphurization, oxidations and Fischer–Tropsch synthesis, the monolith reactor's performance is highly dependent on the liquid-phase mass transfer coefficient, $k_L a$. Accurate predictions of this value are instrumental to the design and optimization of these systems.

The Taylor flow pattern (Fig. 1) is frequently observed in mini and micro-scale two-phase flow through monolith reactors and micro-reactors, consisting of alternating gas bubbles and liquid slugs flowing concurrently along a capillary length. While a diverse collection of numerical frameworks and empirical correlations appear in previous literature to describe mass transfer between the bubble, bubble film, liquid slug bulk and liquid slug film for both reacting and non-reacting systems (Irlandoust and Andersson, 1988; Irlandoust et al., 1992; Bercic and Pintar, 1997; van Baten and Krishna, 2004; Vandu et al., 2005; Nedelchev et al., 2007; Zheng et al., 2007; Pohorecki, 2007); the broad range of assumptions applied in the regression of mass transfer data

can limit the comparability of results from different sources of literature. The complexity of these numerical frameworks have ranged from simple homogeneous mixture models to detailed computational fluid dynamic (CFD) simulations, all with the intent of quantifying the effects of bubble and slug length, velocity, channel diameter and fluid properties on mass transfer. The range of assumptions applied in each of these studies has led to inconsistencies in the reported dependence of mass transfer on the aforementioned parameters, as well as the relative importance of transfer across the bubble film and cap. A systematic analysis of mass transfer models is needed to determine the minimum numerical complexity required to capture the dynamics of two-phase flow.

This work explores the effects of different simplifying assumptions on the predicted behavior of the volumetric gas–liquid mass transfer coefficient and the ratio of film to cap mass transfer for idealized Taylor flow. Four models are described here, representing numerical frameworks with levels of complexity between two extremes: the homogeneous mixture model and full CFD implementation. The homogeneous mixture model (Section 2.1) assumes that the slug bulk and bubble film are perfectly mixed, allowing for a constant concentration driving force to be applied for both film and cap mass transport. The perfectly mixed model (Section 2.2) introduces a separate concentration driving force for the bubble film, which flows into a perfectly mixed slug region. The slug film model (Section 2.3) separates the slug into a perfectly mixed bulk region surrounded by a slug film, where mass transfer between this film and the bulk is diffusion-limited.

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Fig. 1. Schematic of idealized Taylor flow, where shaded regions represent the liquid phase. For a moving frame of reference, the velocity at the capillary wall is set to $-U_b$, corresponding to movement from left to right.

The final model, the circulating slug model (Section 2.4), partitions the liquid slug into seven regions: two perfectly mixed regions near the leading and trailing bubble caps; and five discretized regions in which diffusive scalar transport equations are solved for the fully developed flow profile proposed by Thulasidas et al. (1997). These numerical frameworks are used to investigate the dependency of $k_L a$ on the characteristic parameters of Taylor flow, while determining the conditions under which film or cap mass transfer can reasonably be neglected.

2. Numerical simulation of inter-phase mass transfer

2.1. Homogeneous mixture model

Inter-phase mass transfer in Taylor flow involves complex interactions between a bubble's surface, the lubricating liquid film, and internal circulation within the liquid slug. Homogeneous mixture models attempt to simplify these interactions into a single term, $k_L a(1 - C_s)$, where C_s is the dimensionless cup-mixed average concentration within the liquid normalized against the saturation concentration of the gas phase within the liquid, and $k_L a$ is a weighted mass transfer term accounting for the different mass transfer mechanisms and specific surface area per unit cell volume. An example of one such model is that proposed by van Baten and Krishna (2004) and applied by Vandu et al. (2005) for gas–liquid mass transfer in square and circular capillaries

$$k_L a = k_{L,cap} a_{cap} + k_{L,film} a_{film} \quad (1)$$

The specific cap and film area per unit cell volume, a_{cap} and a_{film} , are determined based on the assumption of spherical caps for the leading and trailing bubble surfaces and a negligible film thickness relative to the bubble radius:

$$a_{cap} = \frac{A_{cap}}{V_{UC}} = \frac{\pi d^2}{0.25\pi d^2 L_{UC}} = \frac{4}{L_{UC}} \quad (2)$$

$$a_{film} = \frac{A_{film}}{V_{UC}} = \frac{\pi d L_{film}}{0.25\pi d^2 L_{UC}} = \frac{4 L_{film}}{d L_{UC}} \quad (3)$$

The cap mass transfer coefficient can be determined from the Higbie penetration model (Higbie, 1935) provided the gas diffusivity within the liquid, D , is known and a reasonable approximation can be obtained for the contact time of a liquid packet traveling across the cap of a bubble, $t_{C,cap}$. For a contact length of $0.25\pi d$ and a packet velocity equivalent to the centerline velocity of the liquid slug (Thulasidas et al., 1997), $k_{L,cap}$ can be expressed as

$$k_{L,cap} = \frac{4}{\pi} \sqrt{\frac{D[2(U_L + U_G) - U_b]}{d}} \quad (4)$$

The film mass transfer coefficient can also be determined directly from the Higbie penetration model, using L_{film} as the contact length and U_b as the packet velocity. However, the validity

of this approach is known to decrease with longer contact times as the interactions between the liquid packet and the film bulk can no longer be neglected. Mass transport theory for laminar falling films is thus applied in determining $k_{L,film}$. Based on Pigford's work on transient mass transfer for laminar falling films (summarized in Sherwood et al., 1975), and Thulasidas et al.'s (1995) characterization of bubble-train flow in capillaries; the mass transfer coefficient can be evaluated for both short and long contact times as

$$k_{L,film} = \begin{cases} 2 \sqrt{\frac{D}{\pi t_{C,film}}} \frac{\ln(1/\Delta)}{(1-\Delta)} & \text{for } Fo < 0.1 \\ 3.41 \frac{D}{\delta_b} & \text{for } Fo > 1.0 \end{cases} \quad (5)$$

where $\Delta = 0.7857 \exp(-5.212Fo) + 0.1001 \exp(-39.21Fo) + 0.0360 \exp(-105.6Fo) + \dots$

The Fourier number, $Fo = Dt_{C,film}/\delta_b^2$, acts as an indicator of the contact time between the bubble and film. Values of $Fo < 0.1$ correspond to short contact times, while values of $Fo > 1$ correspond to long contact times where the film approaches saturation. The film contact time can be approximated as $t_{C,film} = L_{film}/U_b$, while the thickness of the bubble film, δ_b , can be determined from the correlation of Aussillous and Quere (2000) for $10^{-3} < Ca_b = \mu U_b/\sigma < 1.4$:

$$\frac{2\delta_b}{d} = \frac{1.34Ca_b^{2/3}}{1 + 3.34Ca_b^{2/3}} \quad (6)$$

Note that many of these correlations require knowledge of the bubble velocity, U_b , before either $k_{L,cap}$ or $k_{L,film}$ can be determined. For the remainder of this analysis, the bubble velocity is approximated using the correlation proposed by Liu et al. (2005):

$$U_b = \frac{U_L + U_G}{1 - 0.61Ca_{LG}^{0.33}} \quad (7)$$

Combining Eqs. (1) through (7) produces a homogeneous mixture model theoretically capable of describing the effects of L_{film} , L_{UC} , Ca_{LG} , D and d on inter-phase mass transfer. While simple to implement, this approach has a number of key limitations which must be considered during application. Since the average liquid phase concentration is used to determine the driving force for mass transfer, concentration polarization near the interface is unaccounted for, potentially resulting in overestimates of mass transport. Likewise, the use of the unit cell volume when determining a_{cap} and a_{film} requires division of the resulting $k_L a$ by the liquid phase holdup when approximating the change in concentration within the liquid phase.

2.2. Perfectly mixed model

Similar to the homogeneous mixture models, the perfectly mixed model operates under the assumption that a single concentration can be used for the liquid slug. As such, it is reflective of very long liquid slugs, where the dissolved species in the

Fig. 2. Liquid flow region used in the derivation of the perfectly mixed model.

concentrated film has time to fully diffuse into the slug bulk. Fig. 2 illustrates the region over which a mass balance is performed to derive the numerical model.

Defining the dimensionless bulk concentration, C_S , and the film concentration entering the mixed region, C_{film} , the mass balance over the liquid slug is expressed for a moving frame of reference as

$$V_{slug} \frac{dC_S}{dt} = k_{L,cap} A_{cap} (1 - C_S) + (C_S - C_{film}) Q_{film,ref} \quad (8)$$

Using Eqs. (4) and (6), $k_{L,cap}$ can be determined along with δ_b for subsequent use in calculating the liquid slug volume and cap area:

$$V_{slug} = \pi d^2 (L_{UC} - L_{film}) - \pi (d - 2\delta_b)^3 / 6 \quad (9)$$

$$A_{cap} = \pi (d - 2\delta_b)^2 \quad (10)$$

The volumetric flow rate of the bubble film within a moving frame of reference, $Q_{film,ref}$, can be derived from the correlations of Thulasidas et al. (1995), where

$$Q_{film,ref} = \frac{\pi d^2}{4} \{ (U_L + U_G) - U_b \} \quad (11)$$

Determination of a reasonable value for C_{film} is non-trivial due to the time dependence of the bulk concentration entering the bubble film and the non-uniform radial velocity profile within the film. The concentration exiting the liquid film at the current time, t , is the result of mass transfer to liquid entering the bubble film at time, $t - t_{c,film}$, with a concentration of $C_{film, in}$. For the purpose of maintaining computational simplicity, the temporal variation of C_S was assumed to be minimal over a time frame of $t_{c,film}$ ($C_{film, in} = C_S$), with $k_{L,film}$ subsequently determined using Eq. (5) and an expression for $t_{c,film}$ accounting for the average velocity in the bubble film:

$$t_{c,film} = \frac{\pi (d^2 - (d - \delta_b)^2) L_{film}}{4 - Q_{film,ref}} = \frac{(1 - (1 - \delta_b/d)^2)}{U_b - (U_L + U_G)} L_{film} \quad (12)$$

Based on these assumptions, an analytical expression for C_{film} was derived:

$$C_{film} = 1 - (1 - C_S) \exp \left[\pi (d - 2\delta_b) \frac{k_{L,film} L_{film}}{Q_{film,ref}} \right] \quad (13)$$

Incorporating Eq. (13) into the overall mass balance for the mixed liquid region yields:

$$\frac{dC_S}{dt} = \left\{ \frac{k_{L,cap} A_{cap}}{V_{slug}} + \frac{Q_{film,ref}}{V_{slug}} \left(\exp \left[\pi (d - 2\delta_b) \frac{k_{L,film} L_{film}}{Q_{film,ref}} \right] - 1 \right) \right\} (1 - C_S) \quad (14)$$

Note that the cap mass transfer term is unchanged from that of the homogeneous mixture model, while the film mass transport term is modified to account for the difference in concentration driving force within the bubble film region.

While the perfectly mixed model accounts for mass transport within the bubble film, the mass transfer driving force is still overestimated, and the instantaneous mixing of the bubble film with the liquid slug ignores the time required for diffusion from the liquid film to the bulk of the slug. Regressions of experimental data using this model would fail to account for the effects of liquid slug length.

2.3. Slug film model

The slug film model is an extension of the perfectly mixed model, whereby the liquid slug is described as a perfectly mixed core surrounded by a thin film. This approach attempts to account for the effects of the liquid slug length while still avoiding the need for an iterative numerical solution. Fig. 3 illustrates the regions over which mass balances are performed.

Liquid flowing from the bubble film no longer mixes with the circulating bulk of the liquid slug. Instead, it continues to travel into the slug film region where diffusive transport occurs with the slug bulk. Similar to the perfectly mixed model, there would be time delays associated to the concentrations entering and exiting the bubble and slug films. For computational simplicity, the variation in concentration within these time periods is assumed to be negligible. As a result, the concentration entering the slug film, $C_{S,film, in}$, is assumed equal to the concentration leaving the bubble film, C_{film} . Likewise, the concentration entering the bubble film, $C_{film, in}$, is assumed equal to the concentration leaving the slug film, $C_{S,film, out}$.

Falling film theory is applied to both the bubble and slug films. The outlet concentration for the bubble film is easily obtained as in the perfectly mixed model

$$C_{film} = 1 - (1 - C_{S,film, out}) \exp \left[\pi (d - 2\delta_b) \frac{k_{L,film} L_{film}}{Q_{film,ref}} \right] \quad (15)$$

where the contact time used in the determination of $k_{L,film}$ is that of Eq. (12). A similar solution can be obtained for $C_{S,film, out}$, provided the slug bulk concentration, C_S , is assumed to remain fairly constant for the purpose of estimating the concentration driving force

$$C_{S,film, out} = C_S - (C_S - C_{film}) \exp \left[\pi (d - 2\delta_s) \frac{k_{L,slug, film} (L_{UC} - L_{film})}{Q_{film,ref}} \right] \quad (16)$$

Note that the length of the film is assumed equal to the slug length and the axial bubble cap lengths combined, or the difference between the unit cell length and bubble film length, $L_{UC} - L_{film}$.

The thickness of the film in the liquid slug, δ_s , is determined such that the flow rate in the film is equivalent to $Q_{film,ref}$. This is expressed in mathematical form as

$$\int_{r=d/2-\delta_s}^{r=d/2} 2\pi U(r) r dr = Q_{film,ref} \quad (17)$$

where $U(r)$ is the axial velocity at a radial distance, r , from the channel's center. Using the analytical solution for $U(r)$ proposed by Thulasidas et al. (1997), the value of δ_s which satisfies Eq. (17) is given by

$$U(r) = 2(U_L + U_G) \left(1 - \frac{4r^2}{d^2} \right) - U_b \quad (18)$$

$$\delta_s = \frac{d}{2} \left(1 - \sqrt{2 - \frac{U_b}{U_L + U_G}} \right) \quad (19)$$

Fig. 3. Liquid flow regions used in the derivation of the slug film model.

For the determination of $k_{L,slug\ film}$, the contact time is based on the slug film length and average velocity:

$$t_{C,slug\ film} = \frac{V_{slug\ film}}{-Q_{film,ref}} = \frac{(1-(1-\delta_S/d)^2)}{U_b-(U_L+U_G)}(L_{UC}-L_{film}) \quad (20)$$

where $V_{slug\ film} = \pi/4(d^2-(d-2\delta_S)^2)(L_{UC}-L_{film})$.

The overall mass balance for the perfectly mixed slug region requires an approximation of mass transport through the bubble caps and the boundary between the slug body and film. Mass transport through the bubble caps is determined from penetration theory, as was done in the homogeneous and perfectly mixed models. Mass transfer through the film is more difficult to estimate, as there are multiple concentration dependencies. One possible solution involves averaging the fluxes which would be necessary for the concentration drop predicted by Eq. (16) to occur

$$\left(\frac{dC_S}{dt}\right)_{film\ transport} = (C_{film}-C_{S,film\ out}) \frac{-Q_{film,ref}}{V_{slug}-V_{slug\ film}} \quad (21)$$

In order to express Eq. (21) solely as a function of C_S , C_{film} and $C_{S,film\ out}$ must be eliminated using Eqs. (15) and (16). Inter-substitution results in the following expressions:

$$C_{S,film\ out} = \frac{C_S(1-[B]) + [B](1-[A])}{1-[B][A]} \quad (22)$$

$$C_{film} = \frac{(1-[A]) + [A](1-[B])C_S}{1-[A][B]} \quad (23)$$

where

$$[A] = \exp\left[\pi(d-2\delta_b) \frac{k_{L,film}L_{film}}{Q_{film,ref}}\right] \quad (24)$$

$$[B] = \exp\left[\pi(d-2\delta_S) \frac{k_{L,slug\ film}(L_{UC}-L_{film})}{Q_{film,ref}}\right] \quad (25)$$

Substituting into Eq. (21) yields the contribution of film mass transport to the temporal change of C_S :

$$\left(\frac{dC_S}{dt}\right)_{film\ transport} = (1-C_S) \frac{(1-[A])(1-[B])}{(1-[B][A])} \frac{-Q_{film,ref}}{V_{slug}-V_{slug\ film}} \quad (26)$$

The overall change in C_S with respect to time can subsequently be determined:

$$\frac{dC_S}{dt} = \left\{ \frac{k_{L,cap}A_{cap}}{V_{slug}-V_{slug\ film}} - \left[\frac{(1-[A])(1-[B])}{1-[B][A]} \right] \frac{Q_{film,ref}}{V_{slug}-V_{slug\ film}} \right\} (1-C_S) \quad (27)$$

The slug film model provides the ability to determine the effect of liquid slug length on film mass transfer, albeit with a number of assumptions regarding the temporal variation in concentrations over a time frame comparable to the contact times, $t_{C,film}$ and $t_{C,slug\ film}$. The concentration driving force between the slug bulk and the film and cap regions is still overestimated due to the perfectly mixed assumption for the slug

bulk; however, it is closer to actual conditions than the perfectly mixed model. The slug film model represents one of the more comprehensive numerical frameworks for which a computationally simplistic analytical solution can be obtained. Subsequent elimination of assumptions necessitates the use of iterative solutions, eventually leading to full CFD simulations.

2.4. Circulating slug model

The circulating slug model is an intermediate step between highly simplified Taylor flow representations and full CFD simulations requiring the solution of the Navier–Stokes and convection–diffusion scalar transport equations. The model is designed based on analytical solutions for developed flow within the bubble film and liquid slug, and the use of perfectly mixed regions to transition between the fully developed flow patterns. While the proposed approach avoids the Navier–Stokes equation, it still requires the numerical solution of diffusive scalar transport equations describing mass transport in the slug film and bulk, and bubble film.

Fig. 4 illustrates the different regions of the idealized Taylor flow pattern, and the general discretization strategy used within each region. A complete description of the scalar transport equations, boundary conditions, discretization schemes, minimum mesh resolutions and solution procedures can be found in Appendix A.

3. Results and discussion

3.1. Numerical approximations of $k_L a$

In their work on gas–liquid mass transfer in 1.5, 2.5 and 3.1 mm diameter capillaries, Bercic and Pintar (1997) derived an empirical correlation for the average $k_L a$ measured during methane absorption into water along a 1.12 m capillary length

$$k_L a = 0.111 \frac{(U_G + U_L)^{1.19}}{[(1-\epsilon_G)L_{UC}]^{0.57}} \quad (28)$$

The values of $k_L a$ used to derive this correlation were obtained for long gas bubbles ($Fo > 1$), using the liquid concentration exiting the capillary length, C_{exit} :

$$k_L a = \frac{U_L + U_G}{1.12} \ln\left(\frac{1}{1-C_{exit}}\right) \quad (29)$$

A comparison between Eq. (28) and the instantaneous $k_L a$ values predicted by the four models discussed in this work was carried out to gauge the performance of each numerical framework. For the homogeneous mixture, perfectly mixed and slug film model, a direct comparison is possible. For the circulating slug model, simulations were carried out and the average $k_L a$ was determined from Eq. (29) using the cup-mix concentration for

Fig. 4. Liquid flow regions used in the derivation of the circulating slug model.

C_{exit} . The results are provided in Fig. 5 for $0.03 \leq U_L + U_G \leq 0.45$ m/s, $0.09 \leq \varepsilon_G \leq 0.9$, $L_{UC} = 0.017, 0.057, 0.11, 0.22$ m, and $d = 0.0015, 0.0025$ and 0.0031 m; assuming values of $D = 2 \times 10^{-9}$ m² s⁻¹, $\sigma = 0.072$ N m⁻¹ (assumed equivalent to air/water), and a liquid viscosity of $\mu = 0.00089$ kg m⁻¹ s⁻¹.

The homogeneous mixture model overestimated $k_L a$ for the majority of simulated conditions (Fig. 5a), only yielding similar predictions to Bercic and Pintar (1997) at low contact times ($Fo < 1$). For the longer contact times and short liquid slug lengths present in their experiments, significant concentration polarization of the bubble film would occur and the liquid slug concentration would approach saturation before exiting the 1.12 m reactor length. If the concentration rise within the bubble film is not accounted for, a reduction in $k_{L, film}$ is needed to achieve the same flux through the interface. As a result, many of the $k_L a$ values predicted by Eq. (28) will be lower than those obtained from the homogeneous mixture model. Likewise, as the concentration of the liquid slug approaches saturation, small errors in experimental measurement can result in significant under predictions of $k_L a$ when Eq. (29) is used.

The perfectly mixed model showed improved agreement with Eq. (28) (Fig. 5b) by accounting for the concentration rise in the bubble film. Nonetheless, a continued discrepancy between predicted $k_L a$ values was observed due to the absence of a resistance term for mass transfer from the slug film to the slug bulk, and over-estimation of the concentration driving force across the bubble cap. Both the homogeneous mixture model and perfectly

mixed model assume that the primary resistance to mass transfer is across the interface of the bubble, despite the fact that transfer between slug film and bulk is diffusion-limited. For short liquid slugs, there may be insufficient time for the species dissolved in the film to fully equilibrate with the slug bulk, creating a slug-length dependency for mass transport. A concentration gradient will also exist within the internal recirculation patterns of the liquid slug, whereby the liquid contacting the slug film and bubble cap is at a higher concentration than the average. All of these factors would contribute to an increase in $k_L a$ relative to experimental measurements derived from Eq. (29).

The slug film model incorporated the additional resistance term needed to account for diffusion-limited mass transport between the slug film and bulk. Subsequent $k_L a$ predictions (Fig. 5c), were closer in magnitude to those of Bercic and Pintar (1997) when compared to both the homogeneous mixture model and perfectly mixed model. Nonetheless, the predicted $k_L a$ continued to exceed that determined from Eq. (28).

The impact of assumptions applied in the development of the slug film model was assessed by comparing predicted $k_L a$ values (Fig. 5d, open symbols) to those obtained using the circulating slug model (Fig. 5d, closed symbols). One of the key limitations of the slug film model is the assumption that the slug concentration does not vary appreciably within a time scale comparable to $t_{C, film}$ and $t_{C, slug film}$. This assumption is avoided in the circulating slug model through discretization of the bubble film and slug and the subsequent solution of scalar transport equations. The $k_L a$ values

Fig. 5. Comparison of Bercic and Pintar (1997) correlation to $k_L a$ values predicted by the four models discussed in this work. (a) Homogeneous mixture model, (b) perfectly mixed model, (c) slug film model and (d) circulating slug model (vs. slug film model).

predicted by the circulating slug model was consistently lower than those predicted by the slug film model, suggesting that an iterative solution is needed when C_5 cannot be assumed constant due to extended contact times between the bubble and slug bulk with the film regions.

All of the aforementioned simulations were completed for gas and liquid bubble lengths many times that of the channel diameter. Industrially practical unit cell lengths are typically much smaller, 5–15 diameters, where $k_L a$ values are higher and $Fo < 0.1$. CFD simulations were performed in this operating region by van Baten and Krishna (2004) to determine the effects of U_b , L_{UC} , L_{film} , D , d , and δ_b on the overall mass transport coefficient. A similar analysis was completed using the four models presented here. It should be noted that for these simulations, δ_b and U_b were explicitly set, U_{LG} was determined from the velocity profiles reported in their work, and all $k_L a$ values were normalized against a reference volume equivalent to the unit cell volume.

Figs. 6a–c compare the predicted $k_L a$ values to those reported by van Baten and Krishna (2004) for specific variations in U_b , L_{UC} , L_{film} and δ_b . There are three significant observations which can be made from these results: the slug film model showed reasonable agreement with the CFD results for variations in U_b , L_{UC} and δ_b ; the circulating slug model underestimated most values of $k_L a$; and despite repeated validation of the homogeneous mixture model, the level of agreement reported by van Baten and Krishna (2004) could not be reproduced.

Another phenomenon of interest was the discrepancy between film length dependence of $k_L a$ values predicted by the CFD results and those predicted by the slug film and circulating slug models. As the length of the bubble film increases, $k_{L,film} a_{film}$ will also increase at a rate proportional to $L_{film}^{0.5}$. However, as L_{film} increases for a set L_{UC} , the length of the slug film must decrease accordingly, causing a similar reduction in $k_{L,slug} a_{slug}$. When the two lengths are comparable ($L_{film} = 0.02$ m), the variations in $k_{L,film} a_{film}$ and $k_{L,slug} a_{slug}$ are of a similar order of magnitude, resulting in minimal variations in the overall $k_L a$ with changes in L_{film} . While this was observed for both the slug film and circulating slug model, the CFD results reported by van Baten and Krishna (2004) did not appear to capture this interplay between bubble and slug film lengths.

3.2. Film vs. cap mass transfer

The ratio of film and cap mass transfer is an important parameter in determining if inter-phase mass transport can be improved through redistribution of cap and film area via bubble breakup and flow pattern transitions (Kirpalani et al., 2008; Fries and von Rohr, 2009; Donaldson et al., 2010). In the CFD simulations of van Baten and Krishna (2004), film mass transfer typically accounted for 60% of the overall transfer between the bubble and

liquid slug. In a subsequent experimental analysis of gas–liquid flow in a vertical capillary, Vandu et al. (2005) used a variation of the homogeneous mixture model to simulate mass transfer while assuming a dominance of film transport. As part of their analysis, the slug film contact time was identified as an appropriate indicator of the dominance of film mass transport. For values of $\sqrt{(U_L + U_G)/(L_{UC} - L_{film})}$ greater than $3 \text{ s}^{-0.5}$, the film contact times are fairly short, increasing the relative magnitude of film mass transfer. For values less than $3 \text{ s}^{-0.5}$, the long film contact times resulted in a reduced relative magnitude of film mass transfer. While this criteria does capture the reduced importance of film mass transport when long contact times are present, it fails to account for the reduction in mass transfer which would be observed when there is insufficient contact time for mass transport to occur between the bubble, bubble film, slug film and slug body.

The slug film model was used to explore the impact of key design parameters on the relative ratio of film and cap mass transport. From Eq. (27), the ratio of film to cap mass transport can be expressed as

$$R_{film/cap} = \frac{-(1-[A])(1-[B])/(1-[B][A])Q_{film,ref}}{k_{L,cap}A_{cap}} \quad (30)$$

By combining Eqs. (4)–(7), (11), (12), (19), (20), (24) and (25), an expression for $R_{film/cap}$ was derived which was only a function of four dimensionless parameters: Ca_{LG} , L_{film}/d , $(L_{UC} - L_{film})/d$, and a Peclet number accounting for the effects of diffusivity, $Pe = d(U_L + U_G)/D$:

$$R_{film/cap} = \frac{\pi}{16} \left[\frac{(1-[A])(1-[B])}{1-[B][A]} \right] \sqrt{Pe \left(\frac{0.61Ca_{LG}^{0.33}}{1-1.22Ca_{LG}^{0.33}} \right) \left(\frac{0.61Ca_{LG}^{0.33}}{1-0.61Ca_{LG}^{0.33}} \right)} \quad (31)$$

where

$$[A] = \exp \left[-4 \sqrt{\frac{4}{\pi Pe} \left(\frac{1-0.61Ca_{LG}^{0.33}}{0.61Ca_{LG}^{0.33}} \right) \left(\frac{1+4Ca_b^{2/3}+4Ca_b^{4/3}}{2.68Ca_b^{2/3}+7.1556Ca_b^{4/3}} \right) \frac{L_{film}}{d}} \right] [k]_{L,film} \quad (32)$$

$$[B] = \exp \left[-4 \sqrt{\frac{4}{\pi Pe} \left(\frac{1-0.61Ca_{LG}^{0.33}}{0.61Ca_{LG}^{0.33}} \right) \left(\frac{1-1.22Ca_{LG}^{0.33}}{0.61Ca_{LG}^{0.33}} \right) \frac{(L_{UC}-L_{film})}{d}} \right] [k]_{L,slug} \quad (33)$$

$$[k]_{L,film} = \begin{cases} \frac{\ln(1/[A])}{(1-[A])} & \text{for } Fo_{film} < 0.1 \\ 1.705 \frac{d}{\delta_b} \sqrt{\frac{4}{\pi Pe} \left(\frac{1-0.61Ca_{LG}^{0.33}}{0.61Ca_{LG}^{0.33}} \right) \left(1 - \left(\frac{1+2Ca_b^{2/3}}{1+3.34Ca_b^{2/3}} \right)^2 \right) \frac{L_{film}}{d}} & \text{for } Fo_{film} > 1.0 \end{cases} \quad (34)$$

Fig. 6. Comparison of CFD results by van Baten and Krishna (2004) to $k_L a$ values predicted by the four models discussed in this work. Unless otherwise specified simulations were carried out at $L_{UC} = 0.04$ m, $d = 0.003$ m, $L_{film} = 0.005321$ m, $D = 1 \times 10^{-9}$ m²/s, $U_b = 0.45$ m/s, and $\delta_b = 45$ μm.

$$[k]_{L,slug\ film} = \begin{cases} \frac{\ln(1/\Delta)}{(1-\Delta)} & \text{for } Fo_{slug\ film} < 0.1 \\ 1.705 \frac{d}{\delta_s} \sqrt{\frac{4(L_{UC}-L_{film})}{Pe d}} & \text{for } Fo_{slug\ film} > 1.0 \end{cases} \quad (35)$$

Note that δ_b/d , δ_s/d and Fo for the bubble and slug film can be determined once Ca_{LG} is known.

The sensitivity of $R_{film/cap}$ to each of the dimensionless parameters was explored for $10^{-4} \leq Ca_{LG} \leq 1$, $0.1 \leq (L_{UC}-L_{film})/d-1 \leq 10$, and $0.1 \leq L_{film}/d \leq 10$. For simplification purposes, a constant diffusivity was selected and Pe determined for $d=0.001$ m and the physical properties of an air/water system ($D=2 \times 10^{-9}$ m²/s, $\sigma=0.072$ N/m, $\mu=0.001$ kg/(m s)). The resulting variations in percentage total mass transfer attributed to the film are shown in Figs. 7–9 for a broad range of Ca_{LG} , L_{film} and $(L_{UC}-L_{film})/d-1$ values.

The effects of bubble and slug film length are illustrated in Fig. 7 for $Ca_{LG}=0.004$, where an increase in either parameter corresponds to an increased in the relevance of film mass transport. It is important to note that neither film nor cap mass transport can be neglected under these conditions. The interplay between capillary number and bubble film length is shown in Fig. 8 for a slug film length of approximately $4d$, or $(L_{UC}-$

Fig. 7. Percentage of total mass transport attributed to the film at different bubble and slug film lengths for $D=2 \times 10^{-9}$ m²/s, $Ca_{LG}=0.004$, $d=0.001$ m, $\sigma=0.072$ N/m, and $\mu=0.001$ kg/(m s).

Fig. 8. Percentage of total mass transport attributed to the film at different bubble film lengths and capillary numbers for $D=2 \times 10^{-9}$ m²/s, $(L_{UC}-L_{film})/d-1=3$, $d=0.001$ m, $\sigma=0.072$ N/m, and $\mu=0.001$ kg/(m s).

Fig. 9. Percentage of total mass transport attributed to the film at different bubble film lengths and capillary numbers for $D=2 \times 10^{-9}$ m²/s, $L_{film}/d=8$, $d=0.001$ m, $\sigma=0.072$ N/m, and $\mu=0.001$ kg/(m s).

$L_{film})/d-1=3$. Two interesting observations can be made from this graph: saturation of the comparatively thin bubble film led to minimal dependence between the film contribution to total mass transport and the bubble film length at low capillary numbers; and there is a maximum film contribution at $Ca_{LG} \sim 0.0003$ for $L_{film}/d=0.1$, ranging to $Ca_{LG} \sim 0.006$ for $L_{film}/d=100$. The location of the maxima represents the point at which an increase in Ca_{LG} resulted in insufficient contact time for mass transfer between the slug film and bulk. At higher values of Ca_{LG} , cap mass transfer was enhanced to a greater magnitude than film mass transfer, leading to the observed drop in the relative contribution of the film to total mass transport. Fig. 9 confirms this behavior, whereby the film mass transfer contribution became almost independent of Ca_{LG} at values comparable to the maxima observed in Fig. 8. As the slug film length increases, the minimum contact time required for transfer to the slug bulk was reached at greater values of Ca_{LG} .

4. Conclusions

In this work, four models predicting the overall inter-phase mass transfer coefficient for idealized Taylor flow were derived and the impacts of underlying assumptions discussed for a range of operating conditions. The homogeneous mixture model and perfectly mixed model consistently over-predicted mass transfer in idealized Taylor flow, and failed to account for the effects of slug length on the overall $k_L a$. The slug film model provided an analytical expression which accurately captured many of the parametric dependencies reported by van Baten and Krishna (2004), while avoiding the numerical complexity and time commitments associated to CFD simulations. While the circulating slug model provided insight into some of the interactions between the bubble film, slug film and slug bulk, the increased complexity associated to its implementation would only be justified for long slug film contact times, where the assumptions used in deriving the slug film model are no longer appropriate.

Subsequent analysis of the ratio of film to cap mass transfer using the slug film model for a broad range of operating conditions indicated that, for unit cell lengths practical in industrial applications, neither mechanism could be reasonably neglected. For the range of conditions discussed, the slug film model is recommended for practical estimation of $k_L a$. The use of this

correlation requires the estimation of additional properties relative to the homogeneous mixture model and perfectly mixed models, but yields comparable results to CFD simulations without the need for an iterative solution.

Nomenclature

a_{cap}	cap interfacial area per unit volume (m^{-1})
A_{cap}	cap interfacial area (m^2)
a_{film}	Bubble film interfacial area per unit volume (m^{-1})
A_{film}	bubble film interfacial area (m^2)
$[A]$	exponential term for bubble to bubble film mass transfer
$[B]$	exponential term for slug film to slug bulk mass transfer
Ca_b	capillary number, based on U_b
Ca_{LG}	capillary number, based on $U_L + U_G$
C_{exit}	concentration exiting a given capillary length
C_{film}	concentration exiting the bubble film
C_S	cup-mixed average concentration
$C_{S, cap, in}$	concentration within the mixed cap region in contact with the slug film inlet
$C_{S, cap, out}$	concentration within the mixed cap region in contact with the slug film outlet
$C_{S, film, in}$	concentration entering the slug film from the bubble film
$C_{S, film, out}$	concentration exiting the slug film
d	capillary diameter (m)
D	diffusivity ($\text{m}^2 \text{s}^{-1}$)
Fo	Fourier number
k_L	overall mass transfer coefficient (m s^{-1})
$k_{L, cap}$	gas bubble to slug bulk mass transfer coefficient (via the cap) (m s^{-1})
$k_{L, film}$	gas bubble to bubble film mass transfer coefficient (m s^{-1})
$k_{L, slug, film}$	slug body to slug film mass transfer coefficient (m s^{-1})
$[k]_{L, film}$	dimensionless bubble film mass transfer coefficient multiplier
$[k]_{L, slug, film}$	dimensionless bubble film mass transfer coefficient multiplier
L_{film}	bubble film length (m)
L_{UC}	unit cell length (m)
Pe	Peclet number
Q_{film}	volumetric flow rate of the film in the stationary reference frame ($\text{m}^3 \text{s}^{-1}$)
$Q_{film, ref}$	volumetric flow rate of the film in the moving reference frame ($\text{m}^3 \text{s}^{-1}$)
r	radial position from the capillary's centerline (m)
$R_{film/ cap}$	ratio of film to cap mass transfer
t	time (s)
$t_{C, cap}$	cap contact time (s)
$t_{C, film}$	bubble film contact time (s)
$t_{C, slug, film}$	slug film contact time (s)
U_b	bubble velocity (m s^{-1})
U_G	superficial gas velocity (m s^{-1})
U_L	superficial liquid velocity (m s^{-1})
U_{packet}	velocity of a liquid packet traveling along a bubble's surface (m s^{-1})
$U(r)$	axial velocity at position r (m s^{-1})
V_{film}	bubble film volume (m^3)
V_{slug}	volume of the slug bulk (m^3)
$V_{slug, film}$	volume of the slug film (m^3)
V_{UC}	unit cell volume (m^3)
δ_S	slug film thickness (m)
δ_b	bubble film thickness (m)
Δ	delta parameter for determining $k_{L, film}$ and $k_{L, S, film}$
ε_G	gas phase holdup
μ	liquid phase viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)
σ	surface tension (N m^{-1})

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Appendix A. Circulating slug model

The circulating slug model is based on analytical solutions for developed flow within the bubble film and liquid slug, and the use of perfectly mixed regions to transition between the fully developed flow patterns.

Fig. 4 illustrates the different regions of the idealized Taylor flow pattern, and the general discretization strategy used within each region. Three grid resolution parameters were utilized to ensure consistency between each of the regions: Number of radial cells within the film region, $N_{film, radial}$; number of radial cells within the slug bulk, $N_{bulk, radial}$; and number of axial cells per channel diameter length, N_{axial} , applicable to both the slug and bubble regions. The radial cell widths were determined such that the cross-section for flow was equivalent for each cell within a given region. Additional constraints were placed on the radial cells within the slug bulk, such that the forward flowing and backward flowing sub-regions contained an equal number of cells.

The velocity profile within the slug region (slug bulk and slug film) was determined from Eq. (18). The velocity profile within the bubble film, $U_{film}(r)$ was assumed to be parabolic, with a maximum velocity at the film's surface equivalent to $1.5Q_{film}L_{film}/V_{film} - U_b$:

$$U_{film}(r) = \frac{1.5Q_{film}L_{film}}{V_{film}} \left[1 - \frac{(r - 0.5d + \delta_b)^2}{\delta_b^2} \right] - U_b \quad (\text{A.1})$$

The predicted profile is consistent with the classical solution for falling films (Sherwood et al., 1975), and closely matches CFD results presented by van Baten and Krishna (2004).

For the bubble film region, the following scalar transport equation was applied in conjunction with the boundary conditions and indexing structure described in Fig. A1. Note that $U_{film, j}$ is negative for flow from left to right, and that an upwind scheme is applied

$$V_{b, (i, j)} \frac{dC_{film, (i, j)}}{dt} = U_{film, j} A_{b, conv, j} (C_{film, (i, j)} - C_{film, (i-1, j)})$$

Fig. A1. Circulating slug model indexing structure and boundary conditions applied within the bubble film.

$$+ D \left[\frac{A_{b,diff,j-0.5}}{L_{b,diff,j-0.5}} (C_{film,(i,j-1)} - C_{film,(i,j)}) - \frac{A_{b,diff,j+0.5}}{L_{b,diff,j+0.5}} (C_{film,(i,j)} - C_{film,(i,j+1)}) \right] \quad (A.2)$$

For $i=1$ to $N_{axial}(L_{film}/d)$ and $j=1$ to $N_{film,radial}$, the parameters required for the solution of the concentration within each cell of the film, $C_{film,(i,j)}$, are the convection and diffusion areas, $A_{b,conv,j}$ and $A_{b,diff,j}$, the diffusion lengths, $L_{b,diff,j}$, and the integrated axial velocity, $U_{film,j}$, and the cell volumes, $V_{b,(i,j)}$

$$A_{b,conv,j} = \pi (r_{b,j+0.5}^2 - r_{b,j-0.5}^2) \quad (A.3)$$

$$A_{b,diff,j} = 2\pi r_{b,j} \frac{d}{N_{axial}} \quad (A.4)$$

$$L_{b,diff,j} = \begin{cases} 0.25(r_{b,2.5} - r_{b,0.5}) & \text{for } j = 0.5 \\ 0.5(r_{b,j+1} - r_{b,j-1}) & \text{for } j \geq 1.5 \end{cases} \quad (A.5)$$

$$U_{film,j} = \frac{1.5Q_{film}L_{film}}{V_{film}} \left[1 - \frac{(0.5d - \delta_b)^2}{\delta_b^2} - \frac{(0.5d - \delta_b)^2}{2\delta_b^2} \left(\frac{r_{b,j+0.5}^3 - r_{b,j-0.5}^3}{(r_{b,j+0.5}^2 - r_{b,j-0.5}^2)} \right) + \frac{(r_{b,j+0.5}^2 + r_{b,j-0.5}^2)}{2\delta_b^2} \right] - U_b \quad (A.6)$$

$$V_{b,(i,j)} = \pi (r_{b,j+0.5}^2 - r_{b,j-0.5}^2) \frac{d}{N_{axial}} \quad (A.7)$$

where the radial positions of cell faces, r_j , are determined by

$$r_{b,j} = \frac{1}{2} \sqrt{\frac{j-0.5}{N_{film,radial}} [d^2 - (d-2\delta_b)^2] + (d-2\delta_b)^2} \quad (A.8)$$

A similar approach was taken in the slug body and film, resulting in the following scalar transport equation and associated parameters. Note that the $i + \text{sign}(U_{slug,j})$ subscript in the convection term enforces an upwind scheme for convective mass transport, where $\text{sign}()$ returns either 1 or -1 depending on value of $U_{slug,j}$

$$V_{S,(i,j)} \frac{dC_{slug,(i,j)}}{dt} = U_{slug,j} A_{S,conv,j} (C_{slug,(i,j)} - C_{slug,(i+\text{sign}(U_{slug,j}),j)}) + D \left[\frac{A_{S,diff,j-0.5}}{L_{S,diff,j-0.5}} (C_{slug,(i,j-1)} - C_{slug,(i,j)}) - \frac{A_{S,diff,j+0.5}}{L_{S,diff,j+0.5}} (C_{slug,(i,j)} - C_{slug,(i,j+1)}) \right] \quad (A.9)$$

$$A_{S,conv,j} = \pi (r_{S,j+0.5}^2 - r_{S,j-0.5}^2) \quad (A.10)$$

$$A_{S,diff,j} = 2\pi r_{S,j} \frac{d}{N_{axial}} \quad (A.11)$$

$$L_{S,diff,j} = \begin{cases} 0.25(r_{S,2.5} - r_{S,0.5}) & \text{for } j = 0.5 \\ 0.5(r_{S,j+1} - r_{S,j-1}) & \text{for } j \geq 1.5 \end{cases} \quad (A.12)$$

$$U_{slug,j} = 2(U_L + U_G) \left[1 - \frac{2}{d^2} (r_{S,j+0.5}^2 + r_{S,j-0.5}^2) \right] - U_b \quad (A.13)$$

$$V_{S,(i,j)} = \pi (r_{S,j+0.5}^2 - r_{S,j-0.5}^2) \frac{d}{N_{axial}} \quad (A.14)$$

$$r_{S,j} = \begin{cases} \frac{1}{2} \sqrt{\frac{j-0.5}{N_{bulk,radial}} (d-2\delta_S)^2} & \text{for } j < N_{bulk,radial} \\ \frac{1}{2} \sqrt{\frac{j-0.5-N_{bulk,radial}}{N_{film,radial}} [d^2 - (d-2\delta_S)^2] + (d-2\delta_S)^2} & \text{for } j > N_{bulk,radial} \end{cases} \quad (A.15)$$

Within the combined slug cap and film region, the axial and radial cell indices ranged from $i=1$ to $N_{axial}L_{slug}/d$ and from $j=1$ to $N_{bulk,radial} + N_{film,radial}$, respectively. The following boundary

conditions were applied to account for the flow direction of the circulating slug, symmetry along the centerline of the channel, and interaction with the mixed region transitions between the bubble film and slug bulk/film regions

$$C_{slug,(0,j)} = \begin{cases} C_{S,cap,in} & \text{for } j \leq N_{bulk,radial} \\ C_{S,film,in} & \text{for } j > N_{bulk,radial} \end{cases} \quad (A.16)$$

$$C_{slug,(1+N_{axial}L_{slug}/d,j)} = C_{S,cap,out} \quad (A.17)$$

$$\left. \frac{dC}{dr} \right|_{r=0, r=d/2} = 0 \quad (A.18)$$

The only remaining expressions required to complete the circulating slug model are the mass balances on the mixed slug inlet and outlet cap and film regions. Note that the cap mass transfer coefficient, $k_{L,cap}$, is approximated from Eq. (4)

$$V_{S,cap,in} \frac{dC_{S,cap,in}}{dt} = \sum_{j=1}^{N_{bulk,radial}/2} U_{slug,j} A_{S,conv,j} C_{slug,(1,j)} + \sum_{j=N_{bulk,radial}/2+1}^{N_{bulk,radial}} U_{slug,j} A_{S,conv,j} C_{S,cap,in} + \frac{DA_{cap,film}}{L_{diff,cap,film}} (C_{S,film,in} - C_{S,cap,in}) + k_{L,cap} A_{cap} (1 - C_{S,cap,in}) \quad (A.19)$$

$$V_{S,film,in} \frac{dC_{S,film,in}}{dt} = - \sum_{j=1}^{N_{film,radial}} U_{film,j} A_{b,conv,j} C_{film,(N_{axial}L_{film}/d,j)} + \sum_{j=N_{bulk,radial}+1}^{N_{bulk,radial}+N_{film,radial}} U_{slug,j} A_{S,conv,j} C_{S,film,in} + \frac{DA_{cap,film}}{L_{diff,cap,film}} (C_{S,cap,in} - C_{S,film,in}) \quad (A.20)$$

$$V_{S,cap,out} \frac{dC_{S,cap,out}}{dt} = - \sum_{j=1}^{N_{bulk,radial}/2} U_{slug,j} A_{S,conv,j} C_{S,cap,out} - \sum_{j=N_{bulk,radial}/2+1}^{N_{bulk,radial}} U_{slug,j} A_{S,conv,j} C_{slug,(N_{axial}L_{slug}/d,j)} + \frac{DA_{cap,film}}{L_{diff,cap,film}} (C_{S,film,out} - C_{S,cap,out}) + k_{L,cap} A_{cap} (1 - C_{S,cap,out}) \quad (A.21)$$

$$V_{S,film,out} \frac{dC_{S,film,out}}{dt} = \sum_{j=1}^{N_{film,radial}} U_{film,j} A_{b,conv,j} C_{S,film,out} - \sum_{j=N_{bulk,radial}+1}^{N_{bulk,radial}+N_{film,radial}} U_{slug,j} A_{S,conv,j} C_{slug,(N_{axial}L_{slug}/d,j)} + \frac{DA_{cap,film}}{L_{diff,cap,film}} (C_{S,cap,out} - C_{S,film,out}) \quad (A.22)$$

For each of these equations, the film and cap volumes and mass transfer areas for the inlet and outlet regions are equivalent, and can be expressed as

$$V_{S,film,out} = V_{S,film,in} = \pi [(d\delta_b - \delta_b^2)(0.5d - \delta_b) + (\delta_S - \delta_b)(0.5d - \delta_b)^2 - (\delta_S - \delta_b)^2(0.5d - \delta_b)/3] \quad (A.23)$$

$$V_{S,cap,out} = V_{S,cap,in} = \frac{\pi}{4} [d^2 - (d-2\delta_b)^2] - V_{S,film,in} \quad (A.24)$$

$$A_{cap,film} = \pi [(d-2\delta_b)^2 - (\delta_S - \delta_b)(d-2\delta_b)/2] \quad (A.25)$$

$$A_{cap} = \frac{\pi}{2} (d-2\delta_b)^2 \quad (A.26)$$

The circulating slug model was implemented in Matlab[®], using a Runge–Kutta–Fehlberg method for temporal discretization (ode45). The flux of gas dissolving into the bubble film and mixed cap region were monitored at each time step, and subsequently used to determine the overall k_La :

$$k_La = \frac{(\text{Cap flux} \times \text{Cap area}) + (\text{Bubble film flux} \times \text{Film area})}{1 - C_{\text{reference}}} \frac{1}{V_{\text{reference}}} \quad (\text{A.27})$$

The reference concentration and volume, $C_{\text{reference}}$ and $V_{\text{reference}}$, have varied in existing literature, significantly affecting the magnitude of the resulting k_La values. In van Baten and Krishna's work (2004), $V_{\text{reference}}$ was equated to the unit cell volume, $0.25\pi d^2 L_{UC}$, and a cup-mixed concentration was determined at the center of the liquid slug using the velocity field in the reference frame:

$$C_{\text{reference}} = \frac{\sum_{j=1}^{N_{\text{bulk,radial}} + N_{\text{film,radial}}} V_{S,j} U_{\text{slug},j} C_{\text{slug},(0.5N_{\text{axial}}L_{\text{film}}/d,j)} + \sum_{j=1}^{N_{\text{bulk,radial}} + N_{\text{film,radial}}} V_{S,j} U_{\text{slug},j}}{\sum_{j=1}^{N_{\text{bulk,radial}} + N_{\text{film,radial}}} V_{S,j} U_{\text{slug},j}} \quad (\text{A.28})$$

While Eq. (A.28) provides an accurate estimate of the average concentration experienced by the bubble within the moving frame of reference, it is difficult to directly compare to experimental data where the concentration measured at a channel's outlet is reflective of the cup-mix concentration in a stationary frame of reference. For the purpose of comparing the results obtained from circulating slug model to published data, the following reference concentration was used:

$$C_{\text{reference}} = \frac{\sum_{j=1}^{N_{\text{bulk,radial}} + N_{\text{film,radial}}} V_{S,j} (U_{\text{slug},j} + U_b) C_{\text{slug},(0.5N_{\text{axial}}L_{\text{film}}/d,j)} + \sum_{j=1}^{N_{\text{bulk,radial}} + N_{\text{film,radial}}} V_{S,j} (U_{\text{slug},j} + U_b)}{\sum_{j=1}^{N_{\text{bulk,radial}} + N_{\text{film,radial}}} V_{S,j} (U_{\text{slug},j} + U_b)} \quad (\text{A.29})$$

Likewise, a reference volume equivalent to the liquid volume is typically applied when regressing experimental data (Bercic and Pintar 1997), whereby

$$V_{\text{reference}} = 0.25(1 - \varepsilon_G)\pi d^2 L_{UC}$$

As the circulating slug approach requires discretization of the bubble film and slug regions, the minimum grid resolution needed for mesh-independent solutions was determined. The concentration profile and k_La were calculated using different values of N_{axial} , $N_{\text{bulk,radial}}$ and $N_{\text{slug,radial}}$ for the following simulation parameters: $L_{UC}=0.005$ m, $L_{\text{film}}=0.003$ m, $d=0.001$ m, $D=2 \times 10^{-9}$ m²/s, and two capillary numbers, $Ca_{LG}=0.00278$ and $Ca_{LG}=0.0278$. Based on the variation in the predicted k_La (Fig. A2), values of $N_{\text{axial}}=30$, $N_{\text{bulk,radial}}=40$ and $N_{\text{slug,radial}}=40$ were used for all of the subsequent simulations.

Fig. A2. Variation in k_La values predicted by the circulating slug model with increased mesh resolution.

Nomenclature

$A_{b,conv,j}$	area open to convective flow in computational cell (ij) in the bubble film (m ²)
$A_{b,diff,j}$	area open to diffusion in computational cell (ij) in the bubble film (m ²)
$A_{s,conv,j}$	area open to convective flow in computational cell (ij) in the slug (m ²)
$A_{s,diff,j}$	area open to diffusion in computational cell (ij) in the slug (m ²)
$C_{film,(ij)}$	concentration within computational cell (ij) in the bubble film
$C_{\text{reference}}$	reference concentration used to determine k_La in the circulating slug model
$C_{\text{slug},(ij)}$	concentration within computational cell (ij) in the slug
i	axial index used in circulating slug model
j	radial index used in circulating slug model
$L_{b,diff,j}$	diffusion length between cells ($ij-0.5$) and ($ij+0.5$) in the bubble film (m)
$L_{diff,cap,film}$	diffusion length between the mixed cap and film regions (m)
$L_{s,diff,j}$	diffusion length between cells ($ij-0.5$) and ($ij+0.5$) in the slug (m)
N_{axial}	axial cells per diameter length along the bubble film and slug
$N_{\text{film,radial}}$	number of radial cells within the bubble and slug film regions
$N_{\text{bulk,radial}}$	number of radial cells within the slug bulk region
r	radial position from the capillary's centerline (m)
$r_{b,j}$	radial position of cell center of cell (ij) in the bubble film (m)
$r_{s,j}$	radial position of cell center of cell (ij) in the slug (m)
$U_{film,j}$	axial velocity in computational cell (ij) in the bubble film (m s ⁻¹)
$U_{\text{slug},j}$	axial velocity in computational cell (ij) in the slug (m s ⁻¹)
$U(r)$	axial velocity at position r (m s ⁻¹)
$V_{b,(ij)}$	volume of computational cell (ij) in the bubble film (m ³)
$V_{\text{reference}}$	reference volume used to determine k_La in the circulating slug model (m ³)
$V_{s,(ij)}$	volume of computational cell (ij) in the slug (m ³)

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