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Direct numerical simulation of bubble-liquid mass transfer coupled with chemical reactions: influence of bubble shape and interface contamination

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Abstract

This work deals with the study of bubble-liquid mass transfer coupled with chemical reactions. The absorption of carbon dioxide in aqueous solution of sodium carbonate and bicarbonate is used as a reference case. The influences of the interface contamination state and of the ellipsoidal shape of the bubble on the mass transfer rate are studied using a two-dimensional (2-D) axisymmetric model. On the one hand, the case of a spherical bubble with a partially contaminated interface is investigated. It is assumed that a fixed stagnant cap lies on a part of the bubble surface in the rear. On the other hand, the case of an ellipsoidal bubble with a clean interface is investigated.

In a first stage, correlations to estimate the transfer rate without reaction are presented and compared to the 2-D model results. In a second stage, the mass transfer rate is computed with chemical reactions for several reaction rates. The influences of the coupling reactions - contamination state and the coupling reactions - ellipsoidal shape are then presented and discussed. These 2-D model results are also compared to mass transfer rate estimations based on classical one-dimensional (1-D) models. It is shown that 1-D approaches are useful to provide a rough estimation of the mass transfer rate but 2-D models have to be used when an accurate estimation of the mass transfer rate is required.
Keywords: bubble, mass transfer rate, interface contamination, bubble shape, chemical reactions

1. Introduction

A lot of chemical engineering processes are based on the absorption of gaseous component into a liquid phase. Bubble columns are simple but very effective gas-liquid systems. As a consequence, they are used in a variety of industries, such as in fine chemical production, oxidation and hydrogenation reactions, fermentation, etc [1, 2, 3].

It is commonly admitted that the global gas-liquid mass transfer rate is controlled by phenomena occurring in layers close to the gas-liquid interface [1, 2, 4, 5]. Therefore, a good understanding of these phenomena and their coupling is required to achieve an optimization of the processes.

This work is devoted to the bubble-liquid carbon dioxide (CO$_2$) absorption in aqueous solution of sodium carbonate and bicarbonate (Na$_2$CO$_3$ and NaHCO$_3$, respectively). This absorption is actually realized in the refined sodium bicarbonate production Solvay process.

For the CO$_2$-Na$_2$CO$_3$-NaHCO$_3$ system, it is generally assumed that the main resistance to the gas-liquid transfer is located in the thin liquid layer close to the interface [1, 6, 7]. There the convective transport of CO$_2$ by the liquid flow is actually coupled with its diffusive transport and with chemical reactions and it is a priori needed to take all these phenomena into account.

When bubble columns work in heterogeneous regime, such as in the Solvay bubble column, it has been shown that the main part of the bubble-liquid mass transfer takes place from the small bubbles [8]. Their mean diameter is between 1 and 6 mm. Therefore, this work is limited to the study of the bubble-liquid mass transfer from such small bubbles.

In water, the shape of bubbles with a diameter of 1 mm is nearly spherical. When the diameter increases, the bubble velocity increases and the inertial forces tend to cause a distortion: the bubbles get the shape of an oblate spheroid with the increase of their equivalent diameter [9, 10] (to simplify, this shape is often called ellipsoidal). It is known that such changes in interface shape can affect the mass transfer rate [10, 11, 12].

Furthermore, the aqueous solutions used in the industrial processes, such as the Solvay bubble columns, contain usually several surface active contaminant molecules which adsorb at the bubble interface. It is generally recognized that the bubble-liquid mass transfer rate can be strongly affected by
the presence of such adsorbed surfactants at the bubble surface [9, 12, 13, 14]. These surfactants indeed modify the overall bubble surface mobility, which affects the liquid flow field around the bubbles, and hence the coupling between convection and diffusion.

The goal of this work is to study the influences of the interface contamination state and of the ellipsoidal shape on the bubble-liquid mass transfer rate, when this transfer is coupled with chemical reactions in the liquid phase. Each influence is studied separately.

On the one hand, the case of a spherical bubble with a partially contaminated interface is investigated. It is generally admitted that the adsorbed surfactants are swept to the rear of the bubble, leaving the front uncontaminated [12]. The accumulated surfactants at the rear of the bubble tend to form a cap with immobile surface, which is called the stagnant cap, while the rest of the bubble surface remains mobile [13]. In this paper, it is assumed that the surface of the stagnant cap is fixed. The cap is characterized by the proportion of the bubble surface that is immobilized. The influence of this proportion on the bubble-liquid mass transfer rate, without and with chemical reactions, is studied.

On the other hand, the case of an ellipsoidal bubble with a clean interface is investigated. The bubble shape can be characterized by the major axis/minor axis ratio. The bubble-liquid mass transfer rate, without and with chemical reactions, is calculated for several values of this ratio.

The bubble-liquid mass transfer rate is computed by direct numerical simulation (DNS) of a two-dimensional (2-D) axisymmetrical model. The numerical procedure, which uses the COMSOL Multiphysics software to solve the equation system of this model, has been validated in a previous work devoted to the study of the bubble-liquid mass transfer from spherical bubbles [15]. It has been used to estimate the CO$_2$ transfer rate accompanied by chemical reactions in the liquid phase for spherical bubbles with a clean interface and with a fully contaminated interface. This work can therefore be considered as an extension of this previous study.

For both cases, the mass transfer rate is calculated from the CO$_2$ concentration field in the vicinity of the bubble interface, obtained by simulation of the model equations. In a first stage, the mass transfer rate is computed without chemical reaction. The DNS results are presented and compared to correlations proposed to estimate the mass transfer rate as a function of the contamination state and as a function of the shape. In a second stage, the DNS are realized with chemical reactions for several reaction rates. The
interactions between contamination state and reaction rate and between ellipsoidal shape and reaction rate are finally presented and discussed.

2. Modeling

2.1. Transport equations

A pure CO$_2$ bubble, moving upward at a steady velocity in a liquid at rest and of infinite extent, is considered. In the liquid phase, the transferred CO$_2$ takes part to the two following chemical reactions [1, 16, 17, 18, 19]:

\[
\begin{align*}
\text{CO}_2 + \text{OH}^- & \rightleftharpoons \text{HCO}_3^- \\
\text{HCO}_3^- + \text{OH}^- & \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}
\end{align*}
\]

The bubble velocity $G$, the bubble equivalent diameter $d_b$ (the diameter of a sphere of equivalent volume), and $\rho G^2$, where $\rho$ is the liquid density, are used as reference velocity, length and pressure, respectively. Notice that $G$ depends on $d_b$. In this work, the value of $G$ is let as constant and it is estimated using an experimental correlation for the chosen value of $d_b$.

The interfacial CO$_2$ concentration $[\text{CO}_2]_{\text{int}}$ is used as the reference concentration for CO$_2$. Whatever the contamination level at the interface, this concentration is determined by the Henry’s law from the CO$_2$ partial pressure in the bubble and is assumed to be uniform on the bubble interface [14]. The bulk concentrations $[\text{OH}^-]_{\text{bulk}}, [\text{HCO}_3^-]_{\text{bulk}}$ and $[\text{CO}_3^{2-}]_{\text{bulk}}$ are used as reference concentrations for OH$^-$, HCO$_3^-$ and CO$_3^{2-}$, respectively. These are the concentrations at an infinite distance from the bubble. Since H$_2$O is the solvent, its concentration is assumed not to be affected by the chemical reactions.

Let $\mathbf{u} = (u, v)$ be the dimensionless liquid velocity vector along $(r, z)$, $p$ the dimensionless pressure and $a, b, c, d$ the dimensionless concentrations of CO$_2$, OH$^-$, HCO$_3^-$ and CO$_3^{2-}$, respectively.

This work is limited to axisymmetric flows. Let $\text{Re}$ be the classical particle Reynolds number, defined as $\text{Re} = Gd_b/\nu$, where $\nu$ is the liquid kinematic viscosity. In the case of a clean spherical bubble, no vortex appears and the wake remains steady and axisymmetric if $\text{Re} < 500$ [14]. For a fully contaminated spherical bubble behaving as a solid sphere, the wake presents a steady axisymmetric vortex for $\text{Re} > 20$ and loses its axisymmetry at $\text{Re}=210$ [9, 14].
It is assumed that the density, the viscosity, the diffusion coefficients and the kinetic constants are not significantly affected by the mass transfer and chemical reactions. Therefore, these parameters are considered to be independent of composition. Temperature variations, although present, can be shown to remain small and are therefore assumed not to affect these physico-chemical parameters either. Moreover, the mass transfer rate is assumed slow enough compared to the characteristic time scale of the diffusion layer formation to neglect the bubble contraction due to the CO$_2$ absorption (constant bubble diameter). These assumptions are validated later on this paper.

The balance equations in the liquid phase are written in dimensionless form in an inertial reference frame located at the mass center of the bubble. Under the considered assumptions, the axisymmetric dimensionless form of the incompressible Navier-Stokes, the continuity and the convection-diffusion-reaction mass transport equations, read in cylindrical coordinates (and in the quasi-steady approximation) as follows [4, 14]:

\[
\begin{align*}
\frac{u}{r} \frac{\partial u}{\partial r} + v \frac{\partial u}{\partial z} &= -\frac{\partial p}{\partial r} + \frac{1}{Re} \left( \frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} - \frac{u}{r^2} + \frac{\partial^2 u}{\partial z^2} \right) \quad (3) \\
\frac{\partial v}{\partial r} + v \frac{\partial v}{\partial z} &= -\frac{\partial p}{\partial z} + \frac{1}{Re} \left( \frac{\partial^2 v}{\partial r^2} + \frac{1}{r} \frac{\partial v}{\partial r} + \frac{\partial^2 v}{\partial z^2} \right) \quad (4) \\
\frac{1}{r} \frac{\partial (ru)}{\partial r} + \frac{\partial v}{\partial z} &= 0 \quad (5) \\
u \frac{\partial a}{\partial r} + v \frac{\partial a}{\partial z} &= \frac{1}{Pe} \left( \frac{\partial^2 a}{\partial r^2} + \frac{1}{r} \frac{\partial a}{\partial r} + \frac{\partial^2 a}{\partial z^2} \right) - r_1 \quad (6) \\
u \frac{\partial b}{\partial r} + v \frac{\partial b}{\partial z} &= \frac{\beta_b}{Pe} \left( \frac{\partial^2 b}{\partial r^2} + \frac{1}{r} \frac{\partial b}{\partial r} + \frac{\partial^2 b}{\partial z^2} \right) - \chi_b (r_1 + r_2) \quad (7) \\
u \frac{\partial c}{\partial r} + v \frac{\partial c}{\partial z} &= \frac{\beta_c}{Pe} \left( \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} \right) - \chi_c (-r_1 + r_2) \quad (8) \\
u \frac{\partial d}{\partial r} + v \frac{\partial d}{\partial z} &= \frac{\beta_d}{Pe} \left( \frac{\partial^2 d}{\partial r^2} + \frac{1}{r} \frac{\partial d}{\partial r} + \frac{\partial^2 d}{\partial z^2} \right) + \chi_dr_2 \quad (9)
\end{align*}
\]

where Pe is the Peclet number, Pe = ReSc, in which Sc is the Schmidt number, defined as $\nu/D_{CO_2}$, where $D_{CO_2}$ is the CO$_2$ diffusion coefficient.
\( r_1 \) and \( r_2 \) are the chemical reaction rates. They read:
\[
\begin{align*}
  r_1 &= H_{a1}^2 (ab - \alpha c) \\
  r_2 &= H_{a2}^2 (bc - d)
\end{align*}
\] (10) (11)

\( \alpha = [\text{CO}_2]_{\text{bulk}}/[\text{CO}_2]_{\text{int}} \) is the ratio between the bulk and the interfacial \( \text{CO}_2 \) concentration. \( H_{a1} \) and \( H_{a2} \) correspond to the Hatta numbers for the reactions (1) and (2). They read as:
\[
\begin{align*}
  H_{a1}^2 &= k_{11} [\text{OH}^-]_{\text{bulk}} \frac{d_b}{G} \\
  H_{a2}^2 &= k_{21} [\text{OH}^-]_{\text{bulk}} \frac{[\text{HCO}_3^-]_{\text{bulk}} d_b}{[\text{CO}_2]_{\text{int}} G}
\end{align*}
\] (12) (13)

where \( k_{11} \) and \( k_{21} \) are the forward kinetic constants of reactions (1) and (2), respectively. \( H_{a1} \) and \( H_{a2} \) compare the characteristic contact time between gaseous and liquid phases, defined as \( d_b/G \), to the characteristic times of the reactions (1) and (2), respectively.

A Hatta number significantly lower than unity means that the reaction is slow compared to the mass transfer and therefore takes place mostly outside of the diffusion layer. When the Hatta number is of order one, the chemical reaction rate and the mass transfer rate have the same order of magnitude, and the reaction takes place inside and outside of the diffusion layer. Finally, when the Hatta number is large, the reaction is fast compared to the mass transfer and therefore mostly takes place inside of the diffusion layer (see e.g. [2]).

Other symbols appearing above are \( \beta_b = D_{\text{OH}^-}/D_{\text{CO}_2}, \beta_c = D_{\text{HCO}_3^-}/D_{\text{CO}_2} \) and \( \beta_d = D_{\text{CO}_2^-}/D_{\text{CO}_2} \) the ratios of diffusion coefficients and
\[
\begin{align*}
  \chi_b &= [\text{CO}_2]_{\text{int}}/[\text{OH}^-]_{\text{bulk}}, \chi_c &= [\text{CO}_2]_{\text{int}}/[\text{HCO}_3^-]_{\text{bulk}} \text{ and} \\
  \chi_d &= [\text{CO}_2]_{\text{int}}/[\text{CO}_2^-]_{\text{bulk}} \text{ the ratios of bulk concentrations.}
\end{align*}
\]

2.2. Flow domain and boundary conditions

The axisymmetric computational domain is presented in Figure 1 for a spherical bubble. A semi bubble is located at the center of a semi circular domain. The dimensionless domain diameter is 10.

The inlet is located at the upper boundary of the flow domain, where uniform downward velocity and bulk concentrations are imposed. Therefore, the inlet conditions read:
\[
u = 0, \quad v = -1 \] (14)
\[ a = \alpha, \quad b = 1, \quad c = 1, \quad d = 1 \]  \hspace{1cm} (15)

At the lower boundary of the domain, a stress-free condition is imposed and it is assumed that chemical equilibrium is reached and the flux of the different species is purely convective:

\[ \left( -p\mathbf{I} + \frac{1}{\text{Re}}\mathbf{\tau} \right) \cdot \mathbf{n} = 0 \]  \hspace{1cm} (16)

\[ \mathbf{n} \cdot \nabla a = 0, \quad \mathbf{n} \cdot \nabla b = 0, \quad \mathbf{n} \cdot \nabla c = 0, \quad \mathbf{n} \cdot \nabla d = 0 \]  \hspace{1cm} (17)

where \( \mathbf{n} \) is the unit vector normal to the boundary, \( \mathbf{I} \) is the identity matrix and \( \mathbf{\tau} = (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) \) is the dimensionless viscous stress tensor.

On the bubble surface, only the CO\(_2\) is able to diffuse through the interface. The CO\(_2\) concentration equals \([\text{CO}_2]_{\text{int}}\) and the flux of the other species equals zero. Therefore, the dimensionless boundary conditions read as follows:

\[ a = 1, \quad \mathbf{n} \cdot \left( -\frac{\beta_b \nabla b}{\text{Pe}} + b \mathbf{u} \right) = 0, \quad \mathbf{n} \cdot \left( -\frac{\beta_c \nabla c}{\text{Pe}} + c \mathbf{u} \right) = 0, \quad \mathbf{n} \cdot \left( -\frac{\beta_d \nabla d}{\text{Pe}} + d \mathbf{u} \right) = 0 \]  \hspace{1cm} (18)

\( \theta \) is the angle relative to the vertical axis. For the clean zone of the interface \((0 < \theta < (180^\circ - \varphi_{\text{cap}}))\), a slip condition is applied. Therefore the normal component of the velocity and the shear stress are equal to zero at the surface of the bubble:

\[ \mathbf{n} \cdot \mathbf{u} = 0, \quad \mathbf{t} \cdot \mathbf{\tau} \cdot \mathbf{n} = 0 \]  \hspace{1cm} (19)

where \( \mathbf{t} \) is the unit tangential vector.

For the contaminated zone of the interface \((\theta \geq (180^\circ - \varphi_{\text{cap}}))\), the surface is assumed to be rigid. Therefore, a no slip condition is applied:

\[ \mathbf{u} = 0 \]  \hspace{1cm} (20)
2.2.2. Ellipsoidal bubble characteristics

Let $l$ and $h$ be the major and the minor axis of the oblate ellipsoidal bubble, respectively. The ellipsoidal shape is then characterized by the major axis/minor axis ratio $W = l/h$. $l$ and $h$ are related to the spherical equivalent diameter (the diameter of a sphere of equivalent volume) by:

$$l = d_b \frac{\sqrt{W}}{W}$$

$$h = \frac{d_b}{\sqrt{W^2}}$$

The ellipsoidal bubble is illustrated in Fig. 2-b for $W=1.7$. As explained earlier, it is considered that all the surface of the ellipsoidal bubble is clean. Therefore, the condition applied at the interface is given by Eq.19.

2.3. Meshing

The boundary-value problem is solved numerically using the COMSOL Multiphysics software, enabling to solve partial differential equations using a finite element method. The domain therefore has to be meshed. Since the meshing procedure used in the previous work [15] has led to fully satisfactory results, the same procedure is used in this work.

A concentric structured rectangular mesh is used. For this domain configuration, it has been found that the rectangular shape of the mesh is one of the mesh quality criteria [20]. Indeed, it has been observed that such a mesh leads to a far better convergence and more accurate results for the convection-diffusion equations than an unstructured mesh, especially in the wake zone at the rear of the bubble.

As it is presented in Figure 3, two mesh zones are defined. A finer mesh is used in the vicinity of the interface. The dimensionless thickness of this finer mesh zone is 0.05. It can be demonstrated that the diffusion boundary layer normalized by the bubble diameter can be roughly estimated by $1/\sqrt{\text{Pe}}$ [21]. In this work, the smallest value of Pe is 5000. Therefore, it is ensured that the diffusion boundary layer always lies within this zone.

Different element sizes have been tested and it has been observed that these following meshing settings ensure that the solution does not depend on the mesh size anymore.

To mesh the domain, in a first stage the domain boundaries are meshed using the COMSOL mesh tool. 392 node points, regularly spaced, are imposed on the bubble surface. This number is chosen in order to get an
equivalent dimensional mesh size on the bubble surface close to 4 \( \mu \text{m} \). 392 regularly spaced node points are also imposed on the semi-circle between the two mesh zones and on the semi-circle corresponding to the domain boundary. On the symmetry axis, in the dense mesh zone, 30 points are defined above the bubble and below the bubble. The linear growth setting of the software is selected and the used linear growth factor is 3. In the coarse mesh zone of the symmetry axis, 80 points are defined above the bubble and below the bubble as well. A linear growth is also applied and the linear growth factor is 9.

In a second stage, the domain is meshed using the mapped mesh option of the COMSOL mesh tool, generating thereby rectangular mesh. The resulting mesh is made of 43120 elements.

2.4. Simulation procedure

The transport equations are solved by a finite element method (COMSOL Multiphysics). As a consequence of hypotheses made in writing the equations and boundary conditions, it turns out that the liquid flow is not influenced by the mass transfer and chemical reactions. Hence, the Navier-Stokes and continuity equations can be solved in a first stage (segregated solver).

The initial guess for the velocity field is:

\[ u = 0, \quad v = 0 \]  

(23)

The resulting computed flow is then stored. In a second step, the diffusion-convection problem is solved without chemical reactions using the flow field calculated at the previous step. The initial guesses for the concentration fields are:

\[ a = \alpha, \quad b = 1, \quad c = 1, \quad d = 1 \]  

(24)

The resulting concentration fields are stored in order to be used as new initial guesses. Finally, the convection-diffusion-reaction problem is solved. For this resolution, the initial guesses are the flow field determined in the first step and the concentration fields determined in the second step.

2.5. Parameters

In the previous work [15], a spherical bubble having a diameter \( d_b = 1 \) mm, rising in water, has been considered. The slip velocity of the bubble has been estimated at \( G = 0.2 \) m/s using the correlation of Clift et al. [9]. In these conditions, we obtain \( \text{Re} = 200 \) and \( \text{Sc} = 500 \). In order to compare
the influences of the partial contamination state of the interface and of the ellipsoidal shape on the mass transfer rate with the results of the previous work, the same value of Re and Sc are used.

The physico-chemical parameters (diffusion coefficients, kinetic constants, equilibrium constants and CO_2 solubility) have been calculated using correlations from Vas Bhat et al. [16]. The NaHCO_3 and Na_2CO_3 bulk concentrations are given by the operating conditions in a BIR column and the bulk concentrations of the other species can be calculated by the equilibrium constants. The CO_2 interfacial concentration is estimated from the CO_2 solubility and the CO_2 partial pressure in the gaseous phase, which is given by the BIR column operating conditions.

The obtained values for the dimensionless parameters are: \( \alpha = 0.003, \chi_b = 64, \chi_c = 0.03, \chi_d = 0.025, \beta_b = 4.1, \beta_c = 0.9, \beta_d = 0.7, \) Ha_1 = 0.19, Ha_2 = 902. Notice that from the Ha_2 value, it is expected that the chemical reaction (2) remains close to the equilibrium for the time scale considered here.

### 2.6. Post-processing

The bubble-liquid mass transfer rate is quantified by the Sherwood number Sh. It corresponds to the dimensionless average mass transfer rate from the bubble to the liquid. It is calculated as the total bubble-liquid mass transfer rate \( 2\pi \int_0^{\pi} (-D_{CO_2} \nabla [CO_2] \cdot n) \left( \frac{d_b}{2} \right)^2 \sin \theta d\theta, \) normalized by a reference mass transfer rate defined as \( \frac{D_{CO_2} d_b}{\rho_b} ([CO_2]_{int} - [CO_2]_{bulk}) \pi d_b^2. \) It is therefore calculated with COMSOL from the integration, along the bubble surface, of the projection of the dimensionless CO_2 flux on the normal to the interface:

\[
Sh = -\frac{1}{2(1 - \alpha)} \int_0^{\pi} (\nabla a \cdot n) \sin \theta d\theta \tag{25}
\]

Notice that the dimensional total bubble-liquid mass transfer rate (in mol/s) can be obtained by \( Sh(1 - \alpha) \pi d_b D_{CO_2} [CO_2]_{int} \)

Since Ha_2 is much larger than Ha_1, the mass transfer is not very sensitive to the value of Ha_2. This has been confirmed by a sensitivity analysis, which validates the expectation that the reaction 2 remains very close to the equilibrium. Therefore, the effect of the chemical reaction kinetics on the mass transfer rate is studied by computing the Sherwood number for different values of Ha_1.

The contribution of the chemical reactions on the global mass transfer rate is quantified by the enhancement factor \( E. \) It is defined as the ratio
of the transfer rate coupled with reactions to the transfer rate in the purely
diffusive regime [2]. It is calculated by:

\[
E = \frac{Sh}{Sh_0}
\]

where \(Sh_0\) is the Sherwood number without reaction.

3. Simulation results and discussion

Prior to the analysis, it has been verified that the physico-chemical para-
eters (density, viscosity, diffusion coefficients, kinetic constants and CO\(_2\) solubility) are not significantly affected by the mass transfer and the chemical reactions. From the numerically computed species concentration fields, it has been estimated that the variations of all the parameters are lower than 1%. Moreover, it has been estimated that the characteristic time of bubble con-
traction (due to the CO\(_2\) absorption) is between 1 and 2 order of magnitude
larger than the characteristic gas-liquid contact time of the mass transfer.

Therefore, the assumptions of constant physico-chemical parameters and
quasi steady bubble volume during the mass transfer are considered to be
validated.

3.1. Spherical bubble with partially contaminated interface

3.1.1. Concentration field

The CO\(_2\) concentration field, computed with \(Ha_1=0.19\) and \(\varphi_{cap} = 30^\circ\)
is presented in Figure 4.

It is observed that the diffusion boundary layer is very thin along the
clean zone and becomes abruptly thicker along the contaminated zone. This
thickness increase of the diffusion layer, that corresponds to lower CO\(_2\) con-
centration gradients, leads to a lower mass transfer rate below the bubble
than above the latter. However, the chemical reactions are expected to con-
sume CO\(_2\) and hence to enhance the CO\(_2\) concentration gradient. Therefore,
the resulting bubble-liquid CO\(_2\) transfer rate is the combination of these two
effects.

3.1.2. Mass transfer rate without reaction

Simulations are realized for several values of \(\varphi_{cap}\), from 0 to 180 \(^\circ\), with
\(Ha_1\) and \(Ha_2\) set to 0. For each simulation, the Sherwood number without
reaction for a spherical partially contaminated bubble, \(Sh_{0,pc}\), is evaluated.
The plot of $\text{Sh}_{0,\text{pc}}$ as a function of $\varphi_{\text{cap}}$ is presented in Fig. 5. As expected, it is observed that the Sherwood number decreases when the cap angle increases, because of the decrease of the convective mass transport.

This result is compared to this simple correlation [13, 14]:

$$\text{Sh}^*_{0,\text{pc}} = \frac{\text{Sh}_{0,\text{fc}} A_{\text{cap}} + \text{Sh}_{0,\text{cl}} (A - A_{\text{cap}})}{A}$$  \hspace{1cm} (27)$$

where $\text{Sh}_{0,\text{fc}}$ and $\text{Sh}_{0,\text{cl}}$ are the Sherwood numbers without reaction for the spherical fully contaminated bubble and for the spherical clean bubble, respectively. $A$ is the total surface area of the bubble and $A_{\text{cap}}$ is the surface area of the stagnant cap. In dimensionless form, $A = \pi$ and $A_{\text{cap}} = 0.5 \pi (1 - \cos(\varphi_{\text{cap}} \pi/180))$.

$\text{Sh}^*_{0,\text{pc}}$ is plotted in Fig. 5 and compared to $\text{Sh}_{0,\text{pc}}$. It is observed that this correlation provides a reasonably good estimation (maximum relative error of 13.4% at $\varphi_{\text{cap}} = 80^\circ$). Notice that Eq. 27 tends to underestimate $\text{Sh}_{0,\text{pc}}$ for $0 < \varphi_{\text{cap}} < 130^\circ$ and to overestimate $\text{Sh}_{0,\text{pc}}$ for $130 < \varphi_{\text{cap}} < 180^\circ$.

It is important to mention that $\text{Sh}_{0,\text{cl}}$ and $\text{Sh}_{0,\text{fc}}$ can be estimated using 1-D models [15]. Let $\text{Sh}_{0,\text{Higbie}}$ and $\text{Sh}_{0,\text{film}}$ be the estimation of $\text{Sh}_{0,\text{cl}}$ and $\text{Sh}_{0,\text{fc}}$, respectively. $\text{Sh}_{0,\text{Higbie}}$ is calculated with the 1-D Higbie model, using the ratio $d_b/G$ as the contact time, and $\text{Sh}_{0,\text{film}}$ is calculated with the 1-D film model, using $4 \sqrt{D_{\text{CO}_2} d_b / G}$ as the film thickness. Using these values, $\text{Sh}_{0,\text{Higbie}} = 2 \sqrt{\text{Pe} / \pi}$ and $\text{Sh}_{0,\text{film}} = \sqrt{\text{Pe} / 4}$ can be obtained by an analytical development. The Sherwood number $\text{Sh}^{**}_{0,\text{pc}}$, evaluated by injecting $\text{Sh}_{0,\text{Higbie}}$ and $\text{Sh}_{0,\text{film}}$ in Eq. 27, therefore reads:

$$\text{Sh}^{**}_{0,\text{pc}} = \frac{\sqrt{\text{Pe} A_{\text{cap}} / 4} + 2 \sqrt{\text{Pe} / \pi (A - A_{\text{cap}})}}{A}$$  \hspace{1cm} (28)$$

$\text{Sh}^{**}_{0,\text{pc}}$ is also plotted in Fig. 5. It is observed that $\text{Sh}_{0,\text{Higbie}}$ overestimates $\text{Sh}_{0,\text{cl}}$. Therefore, Eq. 28, based on 1-D models, provides a rough estimation of $\text{Sh}_{0,\text{pc}}$, but tends to overestimate $\text{Sh}_{0,\text{pc}}$, especially when $\varphi_{\text{cap}}$ tends to 0. This results shows the necessity to use the 2-D model when the Sherwood number has to be calculated accurately.

3.1.3. Mass transfer rate with reactions

In this section, simulations are realized for several values of $\varphi_{\text{cap}}$, from 0 to 180 °, and for several values of $\text{Ha}_1$, from 0.1 to 10. For each simulation, the Sherwood number with reaction, $\text{Sh}_{\text{pc}}$, and the chemical enhancement...
factor, $E_{pc}$, for a spherical partially contaminated bubble are evaluated. The contours of $Sh_{pc}$ and $E_{pc}$ as functions of $\varphi_{cap}$ and $Ha_1$ are presented in Figs. 6-a and 6-b, respectively.

Large variations of $Sh_{pc}$ are observed with $\varphi_{cap}$ and $Ha_1$. When $Ha_1 < 1$, it is observed that $Sh_{pc}$ is strongly influenced by the value of $\varphi_{cap}$. It increases when $\varphi_{cap}$ decreases. When $Ha_1 > 1$, the value of $Sh_{pc}$ is much less sensitive to $\varphi_{cap}$. Actually, for high values of $Ha_1$, it can be expected that the reactions occur very fast and close to the interface. Therefore, the mass transfer rate is mainly controlled by the reaction rate and it depends much less on the interface characteristics (affecting the convective mass transport), as observed in Fig. 6-a.

Concerning the chemical enhancement factor, it is observed in Fig. 6-b. that $E_{pc}$ is influenced by $Ha_1$, as expected, but it is also affected by $\varphi_{cap}$. For a given value of $Ha_1$, when $\varphi_{cap}$ increases, $E_{pc}$ is firstly constant for small values of $\varphi_{cap}$ and tends to increase for larger values of $\varphi_{cap}$. When $\varphi_{cap}$ increases, $Sh_{0,pc}$ and $Sh_{pc}$ both decrease, but $Sh_{pc}$ decreases less rapidly than $Sh_{0,pc}$ because the chemical reactions compensate the decrease of the convective mass transfer.

It has been shown in [15] that the Sherwood numbers for a fully contaminated interface and for a fully clean interface can be approached using the 1-D film and Higbie models, respectively, with chemical reactions. Let $Sh_{film}$ and $Sh_{Higbie}$ be these estimations, which are computed by the numerical resolution of these 1-D models, presented in [15]. The estimation of the Sherwood number with chemical reactions using the 1-D model estimation, noted $Sh_{pc}^{**}$, writes:

$$Sh_{pc}^{**} = \frac{Sh_{film}A_{cap} + Sh_{Higbie}(A - A_{cap})}{A}$$  \hspace{1cm} (29)

The contours of $Sh_{pc}^{**}$ as a function of $\varphi_{cap}$ and $Ha_1$ are presented in Fig. 7-a. The comparison with Fig. 6-a shows that Eq. 29 provides a reasonably good estimation of $Sh_{pc}$ when $Ha_1 < 1$, apart for small values of $\varphi_{cap}$, but underestimate $Sh_{pc}$ when $Ha_1 > 1$. The contours of the relative error (in %) made by using the Eq. 29 to estimate $Sh_{pc}$ are presented in Fig. 7-b. Again, this result shows that 1-D models are useful to provide a rough estimation of $Sh_{pc}$, but a 2-D model is required if accuracy is needed, especially when the reaction rates are important.
3.2. Ellipsoidal bubble with clean interface

3.2.1. Concentration fields

The CO$_2$ concentration field, computed with $Ha_1=0.19$ and $W=1.7$ is presented in Figure 8. It is observed that CO$_2$ is accumulated in the wake of the bubble, due to a recirculation that appears in this zone when the bubble is sufficiently flattened. It induces a decrease of the mass transfer as the CO$_2$ concentration gradient is decreased in this zone. Nevertheless, this decrease is partially compensated by the enhancement effect of the chemical reactions. It is observed that this enhancement effect becomes significant for $Ha_1 \geq 0.3$.

3.2.2. Mass transfer rate without reaction

Simulations are realized for several values of $W$, from 1 to 2, with $Ha_1$ and $Ha_2$ set to 0. For each simulation, the Sherwood number without reaction for an ellipsoidal bubble with a clean interface, $Sh_{0,ell}$, is evaluated. The plot of $Sh_{0,ell}$ as a function of $W$ is presented in Fig. 9.

As expected, it is observed that $Sh_{0,ell}$ decreases when $W$ increases. It is interesting to notice that this decrease is approximately proportional to the inverse of $W$. Therefore, the following simple correlation is proposed to evaluate it:

$$Sh^*_{0,ell} = \frac{Sh_{0,cl}}{W}$$

where $Sh_{0,cl}$ is the Sherwood number without reaction for a spherical bubble with a clean interface, and was calculated in the previous section.

$Sh^*_{0,ell}$ is also plotted versus $W$ in Fig. 9 and it is compared to $Sh_{0,ell}$ (computed with the 2-D model). It is observed that Eq. 30 leads to an excellent estimation of $Sh_0$ for an ellipsoidal shape bubble (maximum relative error of 1.2%). This point would be worth further investigations however. Moreover, as mentioned above, $Sh_{0,cl}$ can be estimated by $Sh_{0,Higbie}$ using the ratio $d_b/G$ as the contact time, leading to $Sh_{0,Higbie} = 2\sqrt{Pe/\pi}$ by an analytical development. Therefore, $Sh_{0,ell}$ can be approached by

$$Sh^*_{0,ell} = \frac{2}{W}\sqrt{\frac{Pe}{\pi}}$$

$Sh^*_{0,ell}$ is plotted in Fig. 9. It is observed that Eq. 31 reproduces the trend of $Sh_{0,ell}$ but overestimates $Sh_{0,ell}$ for all values of $W$, since $Sh_{0,Higbie}$ overestimates $Sh_{0,cl}$ by less than 11%.
3.2.3. Mass transfer rate with reactions

In this section, simulations are realized for several values of $W$, from 1 to 2, and for several values of $H_{a1}$, from 0.1 to 10. For each simulation, the Sherwood number with reaction, $S_{h_{ell}}$, and the chemical enhancement factor, $E_{ell}$, for an ellipsoidal bubble with a clean interface, are evaluated. The contours of $S_{h_{ell}}$ and $E_{ell}$ as functions of $W$ and $H_{a1}$ are presented in Figs. 10-a and 10-b, respectively.

Variations of $S_{h_{ell}}$ are observed and, as expected, $S_{h_{ell}}$ increases with $H_{a1}$. For a given value of $H_{a1}$, $S_{h_{ell}}$ decreases when $W$ increases, since the flattening of the bubble is unfavorable to the mass transfer. Even for the highest values of $H_{a1}$, $S_{h_{ell}}$ is influenced by $W$, though less than for small values of $H_{a1}$.

Concerning $E_{ell}$, it is observed in Fig. 10-b that it is not very sensitive to $W$. For $H_{a1} \lessapprox 0.8$, $E_{ell}$ is almost constant for $1 < W < 1.6$ and decreases slightly with $W$ beyond 1.6. For higher values of $H_{a1}$, $E_{ell}$ is almost insensitive to $W$. Therefore, $E_{ell}$ is mainly controlled by the reaction rate and it is not much affected by the shape of the bubble.

As shown in [15], the Sherwood number of a clean interface spherical bubble can be approached using the 1-D Higbie model, with chemical reactions. Let $S_{H_{igbie}}$ denote this estimation, which is computed by the numerical resolution of this 1-D model. An estimation of $S_{h_{ell}}$ using the 1-D model estimation, noted $S_{h_{ell}}^{**}$, is proposed on the basis of Eq. 30. It reads:

$$S_{h_{ell}}^{**} = \frac{S_{H_{igbie}}}{W}$$

The contours of $S_{h_{ell}}^{**}$ as a function of $W$ and $H_{a1}$ are presented in Fig. 11-a. The comparison with Fig. 10-a shows that Eq. 32 provides a reasonably good estimation of $S_{h_{ell}}$. It reproduces the tendencies of $S_{h_{ell}}$ but underestimate $S_{h_{ell}}$ for all values of $W$ and $H_{a1}$. The contours of the relative error (in %) made by using the Eq. 32 to estimate $S_{h_{ell}}$ are also presented in Fig. 11-b. Again, this result shows that 1-D models are useful to provide a rough estimation of the mass transfer rate but 2-D models are required when accuracy is needed.

4. Conclusions and perspectives

In this paper, the influences of the interface contamination state and of the ellipsoidal shape on the bubble-liquid mass transfer rate, when this
transfer is coupled with chemical reactions in the liquid phase, are studied. A 2-D axisymmetric model is used to investigate separately the influences of the ellipsoidal shape of a bubble with a clean interface and the interface contamination state of a partially contaminated spherical bubble. To consider the coupling with chemical reaction, the case of the \( \text{CO}_2 \) absorption in aqueous solution of \( \text{Na}_2\text{CO}_3 \) and \( \text{NaHCO}_3 \) is used as a reference. For both cases, it is observed that the mass transfer and the chemical reactions do not significantly affect the physico-chemical parameters. Therefore, to consider constant values for these parameters is a validated assumption.

For each case, simulations are first realized without chemical reaction. The Sherwood number without reaction is then estimated. In a second stage, simulations are realized with chemical reactions. The Sherwood number and the chemical enhancement factor are then estimated. For all cases, it can be observed that the estimation based on 1-D models are useful to provide a rough estimation of the mass transfer rate. It can be concluded that the 2-D model and the simulation procedure presented in this paper are needed when accurate estimations of the mass transfer rate are required.

For the case of the partially contaminated spherical bubble, the Sherwood number without reaction \( \text{Sh}_{0,pc} \) is computed as a function of the cap angle \( \varphi_{\text{cap}} \). It is shown that \( \text{Sh}_{0,pc} \) decreases when \( \varphi_{\text{cap}} \) increases, due to recirculation in the wake favoring the accumulation of \( \text{CO}_2 \). Moreover, it is shown that \( \text{Sh}_{0,pc} \) can be reasonably estimated by a simple area-weighted average of \( \text{Sh}_{0,fc} \) and \( \text{Sh}_{0,cl} \) (Eq. 27). \( \text{Sh}_{0,pc} \) can be also estimated by values obtained from the analytical solution of the 1-D Higbie and film models, using a similar area-weighted average (Eq. 28), but it leads only to a rough estimation.

The Sherwood number with reaction \( \text{Sh}_{pc} \) and the chemical enhancement factor \( E_{pc} \) are computed as functions of \( \varphi_{\text{cap}} \) and of the Hatta number of the first (slow) reaction \( \text{Ha}_1 \). For \( \text{Sh}_{pc} \), two regimes are observed. When \( \text{Ha}_1 < 1 \), \( \text{Sh}_{pc} \) decreases strongly when \( \varphi_{\text{cap}} \) decreases. When \( \text{Ha}_1 > 1 \), \( \text{Sh}_{pc} \) is less sensitive to \( \varphi_{\text{cap}} \). It is also shown that \( \text{Sh}_{pc} \) can be reasonably estimated using Eq. 29 but this estimation tends to underestimate \( \text{Sh}_{pc} \) when \( \text{Ha}_1 > 1 \). As far as chemical enhancement is concerned, it is observed that \( E_{pc} \) is influenced by \( \text{Ha}_1 \) and \( \varphi_{\text{cap}} \). For a given value of \( \text{Ha}_1 \), \( E_{pc} \) increases when \( \varphi_{\text{cap}} \) increases but is almost constant for small values of \( \varphi_{\text{cap}} \).

For the case of the ellipsoidal bubble with a clean interface, the Sherwood number without reaction \( \text{Sh}_{0,ell} \) is computed as a function of the major axis/minor axis ratio \( W \). It is observed that \( \text{Sh}_{0,ell} \) decreases when \( W \) increases, almost proportionally to the inverse of \( W \). It is shown that dividing
$\text{Sh}_{0,\text{cl}}$ by $W$ leads to a good estimation of $\text{Sh}_{0,\text{ell}}$ (Eq. 30). $\text{Sh}_{0,\text{ell}}$ can be also estimated by the value obtained from the analytical solution of the 1-D Higbie model (Eq. 31), but the latter leads to an overestimation of $\text{Sh}_{0,\text{ell}}$.

The Sherwood number with reaction $\text{Sh}_{\text{ell}}$ and the chemical enhancement factor $E_{\text{ell}}$ are computed as functions of $W$ and $\text{Ha}_1$. It is observed that $\text{Sh}_{\text{ell}}$ increases when $\text{Ha}_1$ increases and decreases when $W$ increases. It is also shown that $\text{Sh}_{\text{ell}}$ can be reasonably estimated by Eq. 32. Concerning the chemical enhancement, it is observed that $E_{\text{ell}}$ is mainly controlled by the reaction rate and it is not much affected by the shape of the bubble.

In a further generalization of this model, the model could be completed to investigate the mass transfer when it is coupled with a helical motion of the bubble. Typically, this motion is observed in air-water system when the bubble diameter is larger than 6 mm. This would require the investigation of the stability of the rectilinear bubble trajectory considered here. This could be performed by coupling the Navier-Stokes equation to a level set model, in order to predict the shape the motion trajectory for a given bubble volume. Moreover, this model could be generalized in order to predict the steady state contamination angle (which is considered as a parameter in this work), taking into account the coupling of the Marangoni flow (induced by the surfactant concentration gradient) at the interface and the flow due to the bubble motion.

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