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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 (2D) 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 2D 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 2D model results are also compared to mass transfer rate estimations based on classical one-dimensional (1D) models. It is shown that 1D approaches are useful to provide a rough estimation of the mass transfer rate but 2D models have to be used when an accurate estimation of the mass transfer rate is required.

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, and fermentation [1–3].

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 [1–5]. 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_2CO_3 and $NaHCO_3$, respectively). This absorption is actually realized in the refined sodium bicarbonate production Solvay process.

For the CO_2–Na_2CO_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 [10–12].

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 [9,12–14]. 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.

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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 (2D) 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 [1,16–19]:

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \tag{1}$$

$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O \tag{2}$$

The bubble velocity G, the bubble equivalent diameter d_b (the diameter of a sphere of equivalent volume), and ρG^2, where ρ 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 $[CO_2]_{int}$ 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 $[OH^-]_{bulk}$, $[HCO_3{}^-]_{bulk}$ and $[CO_3{}^{2-}]_{bulk}$ 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_2O 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, and d the dimensionless concentrations of CO_2, OH^-, $HCO_3{}^-$ and $CO_3{}^{2-}$, respectively.

This work is limited to axisymmetric flows. Let Re be the classical particle Reynolds number, defined as $Re = Gd_b/\nu$, where ν is the liquid kinematic viscosity. In the case of a clean spherical bubble, no vortex appears and the wake remains steady and axisymmetric if $Re < 500$ [14]. For a fully contaminated spherical bubble behaving as a solid sphere, the wake presents a steady axisymmetric vortex for $Re < 20$ and loses its axisymmetry at $Re = 210$ [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]:

$$u\frac{\partial u}{\partial r} + v\frac{\partial u}{\partial z} = -\frac{\partial p}{\partial r} + \frac{1}{Re}\left(\frac{\partial^2 u}{\partial r^2} + \frac{1}{r}\frac{\partial u}{\partial r} - \frac{u}{r^2} + \frac{\partial^2 u}{\partial z^2}\right) \tag{3}$$

$$u\frac{\partial v}{\partial r} + v\frac{\partial v}{\partial z} = -\frac{\partial p}{\partial z} + \frac{1}{Re}\left(\frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r} + \frac{\partial^2 v}{\partial z^2}\right) \tag{4}$$

$$\frac{1}{r}\frac{\partial (ru)}{\partial r} + \frac{\partial v}{\partial z} = 0 \tag{5}$$

$$u\frac{\partial a}{\partial r} + v\frac{\partial a}{\partial z} = \frac{1}{Pe}\left(\frac{\partial^2 a}{\partial r^2} + \frac{1}{r}\frac{\partial a}{\partial r} + \frac{\partial^2 a}{\partial z^2}\right) - r_1 \tag{6}$$

$$u\frac{\partial b}{\partial r} + v\frac{\partial b}{\partial z} = \frac{\beta_b}{Pe}\left(\frac{\partial^2 b}{\partial r^2} + \frac{1}{r}\frac{\partial b}{\partial r} + \frac{\partial^2 b}{\partial z^2}\right) - \chi_b(r_1 + r_2) \tag{7}$$

$$u\frac{\partial c}{\partial r} + v\frac{\partial c}{\partial z} = \frac{\beta_c}{Pe}\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2}\right) - \chi_c(-r_1 + r_2) \tag{8}$$

$$u\frac{\partial d}{\partial r} + v\frac{\partial d}{\partial z} = \frac{\beta_d}{Pe}\left(\frac{\partial^2 d}{\partial r^2} + \frac{1}{r}\frac{\partial d}{\partial r} + \frac{\partial^2 d}{\partial z^2}\right) + \chi_d r_2 \tag{9}$$

where Pe is the Peclet number, $Pe = ReSc$, in which Sc is the Schmidt number, defined as ν/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:

$$r_1 = Ha_1^2(ab - \alpha c) \tag{10}$$

$$r_2 = Ha_2^2(bc - d) \tag{11}$$

$\alpha = [CO_2]_{bulk}/[CO_2]_{int}$ is the ratio between the bulk and the interfacial CO_2 concentration. Ha_1 and Ha_2 correspond to the Hatta numbers for the reactions (1) and (2). They read as:

$$Ha_1{}^2 = k_{11}[OH^-]_{bulk}\frac{d_b}{G} \tag{12}$$