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DIRECT MEASUREMENT OF MASS TRANSFER AROUND A SINGLE BUBBLE BY MICRO-PLIFI

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Abstract

In this paper, an original direct and non-intrusive technique using Planar Laser Induced Florescence with Inhibition (PLIFI) is proposed to quantify the local mass transfer around a single spherical bubble rising in a quiescent liquid. The new set-up tracks the mass transferred in the bubble wake for a plane perpendicular to the bubble trajectory instead of a parallel plane as in previous works, thus avoiding optical reflection problems. A spherical bubble is formed in a glass column containing fluorescent dye. A camera with a microscopic lens is placed underneath the column to record cross sections of the transferred oxygen. A high-speed camera is located far from the column to simultaneously record the bubble position, size, shape and velocity. The dissolved gas inhibits the fluorescence so that oxygen concentration fields can be measured. From this, a calculation method is developed to determine mass transfer on the micro-scale. Experimental results are compared to the Sherwood numbers calculated from the Frössling and Higbie models used for fully contaminated and clean spherical bubbles respectively. Results show that all experimental Sherwood numbers occur between the two models, which gives credence to the measurements. The new technique is then developed for bubble diameters ranging from 0.7 to 2 mm in six hydrodynamic conditions ($1 < Re < 10^2$, $10^2 < Sc < 10^6$).

1. Introduction

Gas-liquid reactors play an important role in engineering processes, where they have many applications, including wastewater treatment and chemical or biochemical processes. Their efficiency is directly linked to their design, which requires a profound understanding of mass transfer phenomena. In chemical engineering, mass transfer is the limiting step that governs the design procedure. An accurate prediction of mass transfer phenomena is thus essential to improve the performance of such reactors.

The mechanisms of gas-liquid mass transfer are controlled by an interplay between molecular diffusion and convective transport. In a thin film around the interface that corresponds to the mass boundary layer, the transport is controlled by molecular diffusion. This process tries to reduce non-equilibrium of chemical activities on either side of the interface. At this level, the mass transfer can be affected by the presence of surfactants on the interface. Next to the mass boundary layer, transport results from a combination of molecular diffusion and convection of the flow around the inclusion. In the case of a bubble, the transfer then depends on the diffusion between the two phases, on the bubble contamination and also on the convective effects expressed by the Reynolds number ($Re = \frac{U_B \cdot d_B \rho}{\mu}$), the bubble shape and the hydrodynamic conditions of the liquid at the bubble interface.

Although the mechanisms of gas-liquid transfer have been widely studied (Jähne and Haussecker 1998, Turney and Banerjee 2008), it is still difficult to accurately predict them, especially when the transfer occurs in complex media. Currently, six methods are mainly used to measure the transfer in gas-liquid reactors (Gogate and Pandit 1999). These methods consist in determining a mass transfer coefficient that globally characterizes the transfer in a

given operating condition. For example, the dynamic methods measure the time-varying concentration of the oxygen dissolved in the liquid phase using probes while the oxygen concentration of the inlet gas is changed stepwise. As for the steady state sulphite method, it determines mass transfer coefficients by measuring the absorption of oxygen in a sulphite solution. Chemical and electrochemical methods are also widely used to describe the transfer in industrial reactors. However, they all give an indirect measurement due to the interpretation of the signal produced by the probes and/or the use of correlations for calculating the mass transfer coefficient from experimental data (sensor, pressure, volume, etc.). These methods are also intrusive, using probes and adding sulphite or peroxide to the liquid. Moreover, they only give a global estimation of the transfer between the two phases whereas the transfer occurs at very thin gas-liquid interfaces. The implementation of a local method suited to micro-scales is therefore necessary to increase the accuracy of mass transfer measurements. Generally idea is to develop a direct measurement without any modelling assumption and experimental interferences.

In this perspective, optical techniques have been developed based on the use of a fluorescent dye sensitive to dissolved oxygen molecules or pH, to measure the oxygen or carbon dioxide concentration, respectively, at a gas-liquid interface. When the solution containing fluorescent dye is illuminated by a 2D-laser sheet and the local data are acquired by digital cameras, the technique is named PLIF (Planar Laser Induced Fluorescence). This technique has been adapted to visualize oxygen concentration by studying the fluorescence of an oxygen-sensitive dye (Münsterer and Jähne 1998, Mühlfriedel *et al.* 2000, Herlina and Jirka 2004, Falkenroth *et al.* 2007, Walker and Peirson 2008). The inhibition of the fluorescence is used to quantify the oxygen concentration. This technique is called PLIFI (Planar Laser Induced Fluorescence with Inhibition). Studies concerning mass transfer around a single bubble have

also been performed, to provide qualitative measurements of oxygen mass transfer around a single bubble (Roy and Duke 2000, 2004, Bork *et al.* 2001, 2002, Dani *et al.* 2007), as have local measurements of concentration distributions around a carbon dioxide droplet (Samoya *et al.* 2005) and bubble wake structure using a pH-sensitive dye (Stöhr *et al.* 2009).

These works demonstrate the relevance of using the PLIFI technique for observing mass transfer phenomena. However, the technique has limitations for quantifying mass transfer around a bubble. In the presence of a bubble, the fluorescence is disturbed by light reflections and refractions on its surface. A white ring is then systematically observed around the bubble as well as the bubble shadow, and there is an intensity contrast between the solution to the left of the bubble and the solution to the right (Fig. 1). The optical issues require heavy image processing leading to less precise information. Furthermore, the mass transfer is only observed in a 2D-plane parallel to the bubble trajectory. The information collected is then only valid for a longitudinal section of the bubble and can obviously not be extended to the whole bubble, thus preventing any mass transfer quantification. No mass transfer quantification by non-intrusive laser technique has been presented in the literature and, to the best of our knowledge; there is no reported work on PLIF measurement at micro-scale.

This present paper introduces a new approach for reaching quantitative mass transfer values. By means of the PLIFI technique at micro-scale, oxygen mass transfer between a single rising bubble and a liquid is investigated in order to gain new insight into the gas-liquid transfer mechanism.

2. Mass transfer in a bubble wake: mathematical analysis

2.1. General mass balance

Oxygen mass transfer around a single bubble is related to both convective and diffusive phenomena. These phenomena are commonly studied through a mass balance defined on a closed geometric contour $\partial\mathcal{D}$ as described in Eq. (1).

$$\frac{dm_{O_2}}{dt} = -\iint_{\partial\mathcal{D}} (\vec{U} - \vec{U}_{\partial\mathcal{D}}) [O_2] \cdot \vec{n} \cdot dS - \iint_{\partial\mathcal{D}} \vec{j}_{O_2} \cdot \vec{n} \cdot dS \quad (1)$$

The first term corresponds to the mass accumulation of the oxygen in the studied domain $\partial\mathcal{D}$ during a time dt , the second term corresponds to the net convective transport through the domain and the third term to the diffusive transport of the oxygen molecules. This last term can be expressed with a Fick law for the flux density $\vec{j}_{O_2} = -D_{O_2} \frac{\partial[O_2]}{\partial\vec{n}}$ (Fig. 2 (a)). $[O_2]$ is the oxygen local concentration, U is the local velocity, $\vec{U}_{\partial\mathcal{D}}$ is the contour velocity.

2.2. Mass balance applied to a bubble rising in a quiescent liquid

The experimental configuration described in this paper concerns a single spherical bubble rising linearly at a velocity U_B . The mass balance is taken on a closed contour delimited by the bubble surface $\partial\mathcal{D}_B$, by a wake contour $\partial\mathcal{D}_W$ and by a static contour $\partial\mathcal{D}_S$ where the oxygen concentration and the velocity are null, as depicted on Fig. 2 (b). The geometric contour is decomposed into three surfaces: the upper cross-section $\partial\mathcal{D}_N$, the lower cross-section $\partial\mathcal{D}_W$ and the middle section $\partial\mathcal{D}_{GN}$. In this configuration, the mass balance can be developed as:

$$\begin{aligned} \frac{dm_{O_2}}{dt} = & -\iint_{\partial\mathcal{D}_B} (\vec{U} - \vec{U}_{\partial\mathcal{D}_B}) [O_2] \cdot \vec{n} \cdot dS - \iint_{\partial\mathcal{D}_S} (\vec{U} - \vec{U}_{\partial\mathcal{D}_S}) [O_2] \cdot \vec{n} \cdot dS - \iint_{\partial\mathcal{D}_W} (\vec{U} - \vec{U}_{\partial\mathcal{D}_W}) [O_2] \cdot \vec{n} \cdot dS \dots \\ & \dots - \iint_{\partial\mathcal{D}_B} \vec{j}_{O_2} \cdot \vec{n} \cdot dS - \iint_{\partial\mathcal{D}_S} \vec{j}_{O_2} \cdot \vec{n} \cdot dS - \iint_{\partial\mathcal{D}_W} \vec{j}_{O_2} \cdot \vec{n} \cdot dS \end{aligned} \quad (2)$$

The contour $\partial\mathcal{D}_S$ is immobile ($\vec{U}_{\partial\mathcal{D}_S} = 0$) while the bubble contour $\partial\mathcal{D}_B$ moves at the same speed as the bubble. Due to the continuity on the bubble interface, the liquid velocity \vec{U} on the bubble contour $\partial\mathcal{D}_B$ is equal to the bubble velocity \vec{U}_B . On the lower cross-section $\partial\mathcal{D}_W$, the velocity field is disturbed by the passing of the bubble, which sets the initially quiescent liquid in motion ($\vec{U} = \vec{U}_W$). The oxygen concentration $[O_2]$ and then the oxygen flux is null ($\vec{j}_{O_2} = 0$) everywhere except on the bubble contour $\partial\mathcal{D}_B$ where the transfer occurs and on the lower cross-section $\partial\mathcal{D}_W$ of the contour where the oxygen dropped off by the bubble is still present. The bubble transfers oxygen throughout its ascension, thus accumulating a certain amount of mass in the domain, leading to $\frac{dm_{O_2}}{dt} > 0$. Then the Eq. (2) can be reduced to:

$$\frac{dm_{O_2}}{dt} = - \iint_{\partial\mathcal{D}_W} \vec{U}_W \cdot [O_2] \cdot \vec{n} \cdot dS - \iint_{\partial\mathcal{D}_B} \vec{j}_{O_2} \cdot \vec{n} \cdot dS - \iint_{\partial\mathcal{D}_W} \vec{j}_{O_2} \cdot \vec{n} \cdot dS \quad (3)$$

The flow rate of mass transferred by the bubble F_{O_2} corresponds to the term $-\iint_{\partial\mathcal{D}_B} \vec{j}_{O_2} \cdot \vec{n} \cdot dS$ (which is positive, Fig 2.a). It can be expressed in a more explicit way as:

$$F_{O_2} = \frac{dm_{O_2}}{dt} + \iint_{\partial\mathcal{D}_W} \vec{U}_W \cdot [O_2] \cdot \vec{n} \cdot dS + \iint_{\partial\mathcal{D}_W} \vec{j}_{O_2} \cdot \vec{n} \cdot dS \quad (4)$$

At a distance z sufficiently far from the bubble, the effects on the wake of the bubble passing are significantly attenuated. At this distance, the velocity field in the wake \vec{U}_W becomes negligible. Assuming that the diffusive flux of the oxygen in the bubble wake \vec{j}_{O_2} is relatively low at this distance in comparison to the interfacial transfer F_{O_2} , the mass flow rate can be approximated as:

$$F_{O_2} = \frac{dm_{O_2}}{dt} \quad (5)$$

The oxygen transfer by a single bubble can then be tracked by the oxygen accumulation in the distant wake.

2.3. Mass transfer quantification

In the case of a rectilinear bubble trajectory, the accumulation term can be written in a cylindrical volume dV as:

$$\frac{dm_{O_2}}{dt} = \lim_{\Delta t \rightarrow 0} \frac{\Delta m_{O_2}}{\Delta t} = \lim_{\Delta z \rightarrow 0} \frac{\iiint_V [O_2](r, \theta, z) \cdot dV}{\int_z \frac{dz}{U_B}} = \lim_{\Delta z \rightarrow 0} U_B \frac{\iiint_V [O_2](r, \theta, z) \cdot r \cdot dr \cdot d\theta \cdot dz}{\int_z dz} \quad (6)$$

The oxygen concentration field is necessarily axis-symmetric due to the sphericity of the bubble and to its linear trajectory. The oxygen concentration in the bubble wake then depends only on the radius r and the distance z . However, at a large enough distance z the oxygen concentration field in the bubble wake varies only slightly with the height. Considering a large distance z , the following assumption is then made:

$$\frac{\partial [O_2]}{\partial r} \gg \frac{\partial [O_2]}{\partial z} \text{ which implies } [O_2](r, z) \approx [O_2](r) \quad (7)$$

From this assumption, Eq. (6) can be simplified to:

$$\frac{dm_{O_2}}{dt} = \lim_{\Delta t \rightarrow 0} U_B \cdot 2\pi \cdot \Delta z \cdot \frac{\int_r [O_2](r) \cdot r \cdot dr}{\Delta z} = U_B \cdot 2\pi \cdot \int_r [O_2](r) \cdot r \cdot dr \quad (8)$$

The flux is deduced from the previous correlation by dividing by the bubble surface area:

$$\langle \bar{j}_{O_2} \rangle = \frac{2 \cdot U_B}{d_B^2} \cdot \int_r [O_2](r) \cdot r \cdot dr \quad (9)$$

Finally the average flux density $\langle \bar{j}_{O_2} \rangle$ can be estimated by knowing the radial profile of oxygen concentration $[O_2](r)$ in a cross-section (Fig. 2.c) of the bubble wake taken at a

distance z sufficiently far from the bubble, and knowing the bubble velocity U_B and diameter d_B . The next step is to characterize the three parameters through experimental measurements in order to calculate the mass transferred.

3. PLIFI technique to assess oxygen concentration field

3.1. General principles of the PLIF technique

PLIF is based on the excitation of a fluorescent dye by a laser sheet at a wavelength λ_a that the fluorescent dye is capable of absorbing. A part of the energy absorbed by the fluorescent dye is re-emitted a few nanoseconds later in the form of light at a wavelength λ_f different from λ_a , the remaining part being dissipated in the form of non-radiative energy. The general principle of the PLIF technique is to light a solution containing a fluorescent dye with a laser sheet and record the fluorescence of the solution in the illuminated plane with an optical system.

3.2. Application to gas-liquid mass transfer measurements: PLIFI technique

The PLIF technique has been widely used for direct two-dimensional visualization of scalar transport in aqueous flows (Crimaldi 2008). Concerning the study of gas-liquid mass transfer, an additional property, specific to certain fluorescent dyes only, is taken into account. Some fluorescent dyes are sensitive to molecules called quenchers. In presence of these molecules, the fluorescence is inhibited due to an increase of the energy dissipated in the form of non-radiative energy. In this case, the intensity of fluorescence is inversely proportional to the quencher concentration (Albani 2001, Geddes 2001) as described by the Stern-Volmer equation:

$$\frac{I_Q}{I_0} = \frac{1}{1 + K_{SV}[Q]} \quad (10)$$

where K_{SV} is the Stern-Volmer constant ($\text{L}\cdot\text{mg}^{-1}$), $[Q]$ the quencher concentration ($\text{mg}\cdot\text{L}^{-1}$), I_Q the fluorescence intensity in the presence of the quencher and I_0 in the absence of the quencher.

3.3. Application to oxygen concentration measurements

The PLIFI technique applied to oxygen concentration measurements requires the use of a fluorescent dye sensitive to the presence of oxygen molecules. The Ruthenium complex, of chemical formula $C_{72}H_{48}N_8O_6Ru$ (Nanomeps, France) was chosen for PLIF measurements. As the tracer was not directly soluble in water, it was systematically dissolved in a small amount of ethanol. A first set of experiments with the ruthenium complex enabled the optimal dye concentration to be defined as 30 mg.L^{-1} . From the Stern-Volmer equation, the inverse of the oxygen concentration, measured by probes, should vary linearly with the fluorescence intensity of the solution. This property was checked for a solution composed of 30 mg.L^{-1} of ruthenium complex, 20 % by mass of ethanol and 80 % by mass of deionized water. An example of calibration curve obtained is presented in Fig. 3 for a given experience. The experimental points correlate with a linear equation, enabling the determination of the Stern-Volmer constant $K_{sv} = 0.189 \text{ L.mg}^{-1}$ matching the specific operating conditions for this example.

4. Experimental set-up and procedure

From the analysis developed in section 2, three parameters are necessary to calculate the flux transferred by a rising bubble: the concentration field in a cross section of the bubble wake $[O_2](r)$, the bubble velocity U_B and its size d_B . The experimental set-up implemented here aimed to access this information using a PLIF system to capture concentration fields and a high-speed camera to define the bubble velocity, size and shape. The experimental set-up was quite similar to the one developed by Dani *et al.* (2007). However, here, the oxygen wake behind the bubble was observed in a plane perpendicular to the bubble trajectory whereas it was visualized in a plane parallel to the bubble trajectory in the previous work. This new configuration allowed the acquisition of successive cross sections of the bubble wake and

eliminated optical issues due to the presence of the bubble on the fluorescence images. In the new configuration, an additional camera was added to gather information on the rising bubble.

4.1. Experimental set-up

The experimental set-up consisted of a transparent column fitted with a bubble injection system, and optical equipment designed to produce a laser sheet and to acquire fluorescence as well as bubble rising images. The experimental set-up is depicted in Fig. 4. The 100 x 100 x 300 mm³ column had a square cross-section [1]. It had three transparent glass sides and one PMMA side where the injection system was set. The base was made of glass and the top of the column was open. The injection system [2] was placed 20 mm from the bottom of the column. It was composed of a very thin glass capillary with an inner diameter ranging from 0.01 to 0.1 mm connected to an automatically controlled syringe (Harvard Apparatus PHD 2000). The syringe was filled with pure oxygen and the flow rate was chosen to produce only a single bubble at a time. Bubbles were formed at the centre of the column in a solution containing a fluorescent dye [3]. A drain tap [4] was fitted at the bottom of the column to evacuate the liquid easily after each experiment.

The PLIF system consisted of a laser and an image acquisition system provided by LaVision. The laser sheet [5] was produced by a Nd: Yag laser [6] (Quantel, $\lambda_a = 532$ nm, 10 Hz, 200 x 2 mJ) driven by a synchronization system [7] (Programmable Trigger unit, LaVision). The laser sheet crossed the column horizontally – in the xy plane - at approximately 80 mm from the bottom of the column and was focused at the centre of it. A CCD (Charge-Coupled-Device) camera [8] (Imager Intense, LaVision, Germany, 12 bits, 1040 x 1376 pixels²) was placed vertically under the column - on the z axis - and was focused on the laser sheet at the centre of the column. The digital camera was fitted with a 105 mm objective (Micro-Nikkor 105 mm f/2.8, Nikon) and with three teleconverters (Nikon) to reach a high spatial resolution on the

focused area of approximately 0.0023 mm/pixel. This optical system was surmounted by a 570 nm high-pass filter [9] intended to block the laser light and only acquire the fluorescence light emitted by the solution. The PLIF images were acquired through specific software (Davis 7.2, LaVision) that triggered and stopped both laser and digital camera simultaneously. In addition to the PLIF acquisition system, a high-speed camera [10] (PCO 1200, 10bits, 770 Hz, 1024 x 1280 pixels²) was placed horizontally – along the y axis – to film the rising bubble. A 60 mm objective (Micro-Nikkor 60 mm f/2.8, Nikon) was added to the camera to obtain a spatial resolution of 0.056 mm/pixel. A backlight was placed behind the column to film the bubble by shadowgraph.

4.2. Experimental procedure

For each series of measurements, the first step was to focus the CCD camera on the laser sheet in presence of the fluorescent dye solution. This step was of prime importance since the refractive index changes with the composition of the solution. The second step was to record a set of fluorescence images to define the calibration curve specific to the operating condition. The calibration curve was defined from three points as the fluorescence intensity varied linearly with the oxygen concentration. The solution containing the fluorescent dye was firstly fully oxygenated by streaming with pure oxygen. The oxygen concentration $[O_2]_{ref}$ was measured with an oxygen sensor (FiveGoTm, Do meter FG4, Mettler Toledo). Then a set of 50 fluorescence images GV_{ref} was taken with the CCD camera. The solution was then partially deoxygenated by streaming with helium. An oxygen concentration measurement $[O_2]_{ref-2}$ and a set of fluorescence images GV_{ref-2} were taken in this condition. Then a set of images was acquired with the solution fully deoxygenated ($[O_2]_{ref-3}$, GV_{ref-3}). A last set of PLIF images was recorded in the absence of fluorescent dye to obtain the background noise GV_{bn} . The last step was to form a single bubble in the deoxygenated solution and simultaneously start the

CCD camera - laser system and the high speed camera. This step was repeated several times with a time lapse between recordings sufficiently long for the liquid to be again at rest when a new single bubble was formed.

4.3 Experimental conditions

The solutions were all initially prepared with 30 mg.L⁻¹ of the ruthenium complex dissolved in ethanol. A certain amount of ethanol was then systematically added to reach 20 % of the total solution by mass. Then a variable amount of glycerol was added to the solution (ranging from 0 % to 80 % by mass) and it was completed with deionized water. The experiments were carried out with four different solutions (see Table I). The physical properties of the different solutions were measured with a Haake VT550 Viscotester (Thermo Scientific, Thermo Fisher Scientific Inc) for the viscosity and a pycnometer (Brand Duran, $V = 25 \text{ cm}^3$) for the density.

The bubbles formed by the injection system were spherical and moved in a straight line. The bubble diameter was changed by using different sizes of glass capillary. The diameters ranged from 0.7 mm to 1.9 mm. The velocity of the bubble in a given solution depended on its size and on the physical properties of the solution. The velocities reached during the experiments were between 0.03 m.s⁻¹ and 0.20 m.s⁻¹. Details concerning the characterization of the diameter and velocity are given in section 5.1. All experiments were carried out at a constant pressure and temperature of 293K.

5. PLIFI and shadowgraph results

5.1 Bubble diameter, velocity and position

The bubble diameter d_B and velocity U_B were determined by exploiting the shadowgraph images acquired with the high speed camera (Fig. 5). The diameter d_B was defined from a single image. The time between images was known (0.0013 s between two successive images) so the velocity could be deduced. The bubble position z was determined knowing the initial position, the laser flash frequency and the bubble velocity.

5.2. Mass transfer visualization

Mass transfer was visualized thanks to the fluorescence images acquired with the CCD camera. The bubble transferred a mass of oxygen over its complete rise time. The oxygen wake left behind the bubble was crossed horizontally by the laser sheet as shown in Fig. 2. At each laser flash, a PLIF image was recorded. On it, a horizontal cross-section of the oxygen wake at a distance z from the bubble was visualized. An illustration of a raw fluorescence image obtained with the CCD camera is provided in Fig. 6. The dark area visible on Fig. 6 indicates the presence of oxygen in the wake of the bubble. The information displayed on the fluorescence image is expressed in grey values, GV . The darker the grey value, the higher the oxygen concentration in the solution.

The conversion of grey values into oxygen concentration $[O_2]$ was done in two steps. First the raw image was processed to compensate for the irregularity of the laser power and the spatial inhomogeneity of the lighting. The processing approach used here was the same as the one developed by Dani *et al.* (2007). The overall correction to reduce spatial dispersion and temporal irregularities is given by the following equation:

$$GV^*(x, y, t) = \frac{GV(x, y, t) - \overline{GV}_{bn}(x, y)}{\overline{GV}_{ref}(x, y) - \overline{GV}_{bn}(x, y)} \frac{\overline{E}}{E(t)} \quad (11)$$

where $GV(x,y,t)$ is the grey value of a pixel with coordinates (x,y) of a raw image taken at time t , $GV^*(x,y,t)$ is the corrected grey value of this same pixel, $\overline{GV}_{bn}(x,y)$ is the average grey value of 50 background noise images, $\overline{GV}_{ref}(x,y)$ is the average grey value of several reference images, \overline{E} is the average laser intensity received on the reference images, and $E(t)$ is the laser intensity received on the image taken at time t . The intensities \overline{E} and $E(t)$ are estimated from the fluorescence intensity of the reference images and from the fluorescence intensity of the image taken at time t respectively. The oxygen concentration field $[O_2](x,y,t)$ was deduced from the normalized grey value $GV^*(x,y,t)$ using Eq. (12):

$$[O_2](x,y,t) = a \left(\frac{1}{GV^*(x,y,t)} \right) + b \quad (12)$$

The a and b coefficients were calculated from the linear interpolation of three experimental points of coordinates $(1/GV^*_1(x,y), [O_2]_{ref})$, $(1/GV^*_2(x,y), [O_2]_{ref-2})$ and $(1/GV^*_3(x,y), [O_2]_{ref-3})$.

An illustration of the oxygen concentration field $[O_2]$ captured in a cross-section of the bubble wake is depicted in Fig. 7. It corresponds to the processed and converted image previously seen on Fig. 6. It can be observed that the concentration profile is circular with concentric gradient of oxygen from 0 to 9 mg.L⁻¹ and it appears clearly symmetric. For the observed bubble ($d_B = 0.72$ mm), the oxygen spot is around 100 μ m, confirming the micro-scale size of the convective transfer. The high spatial resolution of the fields allows good confidence to be placed in the transfer estimation from Eq. 9.

2D-cross-sections of the bubble wake were obtained at successive distances z between the oxygen wake and the bubble. The size of the spots seemed to diffuse very progressively, from 100 μ m to 200 μ m in 300 d_B (z direction). By exploiting these successive PLIF images, the oxygen wake of the bubble could be reconstructed to obtain the oxygen-3D field $[O_2](r,z)$

(see Fig. 8). It was then possible to view the concentration wake behind the bubble by reconstruction in a vertical plane including the bubble trajectory.

6. Mass transfer quantification by μ -PLIFI

6.1. Determination of the flux

From a PLIFI image (Fig. 7) a radial profile of the oxygen concentration can be extracted as shown in Fig. 9. As in Fig. 8, the diffusion of the oxygen spot is expressed by the flattening of the oxygen profiles. These profiles, which are similar to a Gaussian curve, are well defined and strongly continuous. In order to determine the flux, the centre of the oxygen patch was defined and an orthoradial average concentration value was calculated for each radius r of the oxygen disc. The oxygen concentration profile obtained was well fitted with a Gaussian profile as described in Eq. (13):

$$[O_2](r) = A \cdot \exp\left(-\left(\frac{r}{s}\right)^2\right) \quad (13)$$

where A and s are parameters for the multi-criteria optimization. The aim of establishing a Gaussian fit was to eliminate the experimental noise observed at large radius r . An oxygen concentration profile was associated to the successive PLIF images acquired during the rise of the bubble. A radial profile of the oxygen wake was then obtained at successive distances z from the bubble. At each distance z , a flux was determined by integrating the oxygen concentration profile as described in Eq. (9). Given the high quality of profile measurement, the integration of these points was certainly precise.

6.2. Standard deviation and symmetry quantification

The expression of the flux established in Eq. (9) assumes an axis-symmetric oxygen concentration field. The symmetry of the oxygen concentration field captured on fluorescence images was verified through the standard deviation σ and the skewness coefficient γ_1 of the distribution. The standard deviation σ evaluates the deviation of the discrete values present on a given radius r of the oxygen disc. A definition is given below:

$$\sigma(r) = \sqrt{\frac{\int_0^{2\pi} ([O_2](r, \theta) - \overline{[O_2]}(r))^2 r \cdot d\theta}{\int_0^{2\pi} r \cdot d\theta}} \quad (14)$$

where $[O_2](r, \theta)$ is the oxygen concentration at a pixel with coordinates (r, θ) , and $\overline{[O_2]}(r)$ is the average oxygen concentration on the radius r . An illustration of the standard deviation associated with an oxygen concentration profile is provided in Fig. 10. In this example the average deviation is 5 %. The skewness coefficient γ_1 evaluates the asymmetry of the oxygen concentration distribution. A zero value indicates that the values are evenly distributed on both sides of the mean, implying a symmetric distribution. The skewness coefficient is defined as described in Eq. (15):

$$\gamma(r) = \frac{\mu_3(r)}{\sigma^3(r)} = \frac{\int_0^{2\pi} ([O_2](r, \theta) - \overline{[O_2]}(r))^3 r \cdot d\theta}{\int_0^{2\pi} r \cdot d\theta \cdot \sigma^3(r)} \quad (15)$$

The average skewness coefficient γ_1 calculated from Eq. 15 is around 7% and confirms the quasi-axisymmetry of the concentration fields.

Eq. (9) was established by considering a variation of the concentration with z to be clearly negligible relative to the variation with r (Eq. (7)) when z is large. The study of the experimental oxygen concentration profiles at different z corroborated the hypothesis (Fig. 9). Lastly, the validity of Eq. (9) was assumed if the velocity in the bubble wake was negligible. Measurements of velocity field in the bubble wake could not be implemented during the experiments. However, the behaviour of the flux values plotted against z (Fig. 11) tends to prove this assumption as the flux values first increase with z to then reach a steady state around an average flux density value $\overline{\langle j_{O_2} \rangle}$. This asymptotic behaviour demonstrates that the

effects of the bubble passing are seen in the close wake and are absent at a large enough distance z from the bubble. The distance z at which the velocity field in the bubble wake becomes negligible is the critical distance z_C . In the next parts of this paper, the flux is systematically estimated from this critical distance z_C .

6.3. Coherence of the flux values

The coherence of the flux values was firstly checked regarding the reproducibility of the flux values calculated at successive cross-sections of the same bubble wake. Considering only the flux values estimated from the critical distance z_C , the standard deviation was calculated as follows:

$$\sigma = \sqrt{\frac{1}{n} \sum_{j=1}^n \left(\langle \bar{j}_{O_2} \rangle_j - \overline{\langle \bar{j}_{O_2} \rangle} \right)^2} \quad (16)$$

where $\langle \bar{j}_{O_2} \rangle_j$ is the flux density value at z_j ($z_j \geq z_C$), $\overline{\langle \bar{j}_{O_2} \rangle}$ the average flux density calculated from z_C , and n the number of flux values included between z_C and z_F . In the example shown in Fig. 11, the calculation provides a deviation of $2.35 \times 10^{-4} \text{ g.m}^{-2}.\text{s}^{-1}$. Thus, once the bubble passing effects become negligible, the discrete flux density values only deviate by 3 %.

In our study the value of the critical distance z_c varies from 20 diameter of the bubble (d_B) for $Re = 1$ to $200 d_B$ for $Re = 100$. Then we propose a simple criterion that helps the estimation of this distance: $z_c \approx 20\sqrt{Re}$ (where z_c is expressed in bubble diameter, standard deviation of 7.5%).

The coherence of the flux density was also checked regarding the repeatability of the mass transfer measurements obtained in the same operating conditions. The standard deviation of

the flux density values was calculated from three different experiments all performed in the same conditions. Considering the results displayed in Table II, the standard deviation σ was always less than 5%. The good reproducibility and repeatability of the flux measurements attests the strength of the PLIFI technique developed here.

7. Direct measurement of mass transfer for several bubble sizes and several fluids

A qualitative analysis of the concentration field in the bubble wake obtained in different hydrodynamic conditions is depicted in Fig. 12. As previously shown, the concentration field shape is circular with a concentric concentration gradient for all hydrodynamic conditions. The size and the intensity of the oxygen spot increase with Reynolds number. This can be explained by the impact of viscosity, which reduces the mass transfer of the bubble. At high Reynolds numbers, the intensity of the convective effects renews the interface better. Fig. 12 also shows the evolution of the concentration field in the bubble wake at different distances from the bubble. In all cases, diffusion is observed between $z = 10 d_B$ and $z = 70 d_B$ and this effect is amplified as Schmidt numbers ($Sc = \frac{\mu}{\rho \cdot D_{O_2}}$) decrease. These observations are in a good agreement with physical expectations.

In order to validate the experimental data, the drag coefficients C_D associated with the six operating systems were compared to the drag coefficients for clean C_D^m (from Mei *et al.*, 1994) and fully contaminated C_D^{im} (Schiller and Nauman, 1933) bubbles. The results are presented in Fig. 13 and are consistent with the experimental data and models presented in the literature. It can be observed that the small bubbles (points 3-5-6) are near the contaminated bubble model whereas large bubbles (1-2-4) are very close the clean bubble model. In the case of small bubble, we can also observe that the level of contamination is increased with glycerol fraction as proximity of point 3 (80% glycerol) is superposed on contamination curve

while point 6 (0 % glycerol) is far from it. This figure 13 validates the hydrodynamic measurements of bubble size d_B and velocity U_B on a large scale of Reynolds numbers ($1 < \text{Re} < 100$). This point is of great importance because the mass flow estimation depends strongly of these values (equation 9).

The experimental mass transfer coefficients can be deduced from the experimental flux values as described in the following equation:

$$k_{L_E} = \frac{\langle \bar{j}_{O_2} \rangle}{[O_2]_{sat} - [O_2]_{ref}} \quad (17)$$

where $[O_2]_{sat}$ is the oxygen concentration at saturation in the liquid and $[O_2]_{ref}$ the residual oxygen concentration in the quiescent liquid. The oxygen concentration at saturation $[O_2]_{sat}$ is estimated from the definition of the oxygen solubility in an aqueous solution containing different molecules (Schump *et al.*, 1978):

$$[O_2]_{sat} = \frac{[O_2]_{pure\ water}}{10 \sum c_i C_i} \quad (18)$$

where i are the different molecules present in the aqueous solution, c_i are coefficients specific to each molecule ($c_{ethanol} = 0.015$, $c_{glycerol} = 0.025$), and C_i are the concentrations in mol.L^{-1} of each species in the solution.

In order to validate the order of magnitude of the experimental values obtained in terms of mass transfer, the experimental results are compared to those obtained from established theories. Two models are especially renowned for predicting the mass transfer of a free rising bubble: the Frössling model (1938) and the Higbie model (1935). The Frössling model considers that the surface of the bubble is fully contaminated (presence of surfactants at the interface). The Higbie model considers that the surface of the bubble is totally clean. The Frössling mass transfer coefficient is defined as presented in the following equation:

$$k_{L_F} = \frac{D_{O_2}}{d_B} \left(2 + 0.6 \text{Re}^{0.5} Sc^{0.33} \right) \quad (19)$$

and the Higbie mass transfer coefficient is calculated as below:

$$k_{L_H} = \frac{D_{O_2}}{d_B} (1.13 \text{Re}^{0.5} \text{Sc}^{0.5}) \quad (20)$$

The bubble velocity U_B , its diameter d_B , the viscosity μ and the density ρ of the liquid were all experimentally determined, only the diffusion coefficient D_{O_2} was estimated from the correlation of Wilke and Chang (1955). The experimental mass transfer coefficients are systematically between those of the Frössling and Higbie models (Table II). In the experiments shown, the bubble surface is partially contaminated due to the presence of ethanol, glycerol or fluorophore particles. These molecules could be accumulated on the gas – liquid interface as surfactants thus disturbing the bubble mass transfer especially for small bubbles (Fig. 13) in high glycerol concentration. This contamination of the bubble is very difficult to quantify and is not estimated in this work. Nevertheless the real mass transfer is always greater than the mass transfer described by the Frössling theory (contaminated bubbles) and lower than that of the Higbie theory (clean bubbles). The comparison of experimental data with theoretical relations requires a lot of physicochemical data with a precision in the same order of mass transfer measurement (about 5% of standard deviation). As it is really difficult to measure these data (diffusivity, contamination), this result is quite consistent and definitely validates the relevance of the PLIFI experimental measurements.

Fig. 14 represents the variation of the Sherwood number depending on the Peclet number ($Pe = \text{Re} \text{Sc}$). For the graphic representation, the model of Takemura and Yabe (1998) was preferred to the Higbie model since its mass transfer prediction is more appropriate for small clean bubble ($d_B < 2.5$ mm). The Takemura and Yabe Sherwood number is defined as:

$$Sh^m = \frac{2}{\sqrt{\pi}} \left(1 - \frac{2}{3} \frac{1}{\left(1 + 0.09 \text{Re}^{2/3} \right)^{3/4}} \right)^{1/2} \times \left(2.5 + (\text{Re} \text{Sc})^{1/2} \right) \quad \text{Re} \leq 100 \quad (21)$$

The Sherwood number Sh^m for a clean spherical bubble (Takemura and Yabe, 1998) is plotted by the dashed line while the Sherwood number Sh^{im} ($Sh^{im} = \frac{k_{L_F} d_B}{D_{O_2}}$) for a contaminated bubble (Frössling) is the continuous line. As demonstrated in Fig.14, experimental Sherwood numbers are between the two models from the literature, corroborating the pertinence of the quantification. It is observed that small bubbles have similar behaviour and give lower Sherwood numbers than large bubbles. This classical result can be explaining by the dependence of the Sherwood with $Re^{1/2}$ for a given Sc number (Fig. 14).

8. Conclusion and perspectives

This paper introduces an original approach for directly and accurately measuring the mass transfer around a single rising bubble. Although the mass transfer from a bubble into a liquid occurs at the gas-liquid interface, the approach developed here provides a definition of the flux where only the oxygen concentration field present in a bubble wake cross-section, the bubble velocity and size are required.

The PLIFI technique is used to track the oxygen field present in the bubble wake while the bubble velocity and size are defined from high-speed camera images. The acquisition of fluorescence images in a plane perpendicular to the bubble trajectory is a new technique that avoids the optical issues encountered in previous works and gives pertinent information for mass transfer quantification.

The observation of axis-symmetric oxygen concentration fields on the fluorescence images demonstrates the relevance of the PLIFI measurements and suggests that significant flux values can be obtained by exploiting PLIFI images. The constancy of the flux calculated for a single bubble at successive cross-sections once the oxygen wake is at rest and the repeatability of the flux values obtained for identical bubbles in the same hydrodynamic

conditions demonstrates the consistency of the method. The comparison of the mass transfer coefficients determined in six hydrodynamic conditions ($1 < Re < 10^2$, $10^2 < Sc < 10^6$) with the mass transfer coefficients that would theoretically be obtained in the same conditions also gives encouraging results. Even if the experimental set-up requires transparent media and the addition of fluorophore molecules, this technique has the advantage to visualize the oxygen spot leaved by bubble transfer.

The method presented not only gives new insight into the complex mechanism of bubble mass transfer that could help to develop rigorous theoretical models and numerical simulations, but also provides a means of measuring mass transfer coefficients from rising single bubbles, opening intriguing possibilities for further research.

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Notation

$C_D = \frac{4}{3} \cdot g \cdot \frac{d_B}{U_B^2}$	Drag coefficient, dimensionless
$Pe = Re \cdot Sc$	Peclet number, dimensionless
$Re = \frac{U_B \cdot d_B \rho}{\mu}$	Reynolds number, dimensionless
$Sc = \frac{\mu}{\rho \cdot D_{O_2}}$	Schmidt number, dimensionless
$Sh = \frac{k_L d_B}{D}$	Sherwood number, dimensionless
d	diameter, m
D	diffusion coefficient, $m^2 \cdot s^{-1}$
E	laser energy, dimensionless
F_{O_2}	masse flow rate, $g \cdot s^{-1}$
g	gravity, $m \cdot s^{-2}$
GV	gray level, dimensionless
I	laser intensity, arbitrary unit
j	flux density, $g \cdot m^{-2} \cdot s^{-1}$
k_L	mass transfer coefficient, $m \cdot s^{-1}$
K_{sv}	Stern-Volmer constant, $L \cdot mg^{-1}$
m	mass, g
$[O_2]$	oxygen concentration, $mg \cdot L^{-1}$
$[Q]$	quencher concentration, $mg \cdot L^{-1}$
r	radius, m
S	surface area, m^2
$S_{O_2, water}$	oxygen solubility in pure water, $g \cdot m^{-3}$
t	time, s
U	velocity, $m \cdot s^{-1}$
z	distance, d_B
z_C	critical height, d_B

Greek letters

λ_a	absorption wavelength, nm
λ_f	fluorescence wavelength, nm
σ	standard deviation, $mg \cdot L^{-1}$
γ_1	skewness coefficient, dimensionless
μ_3	third moment, $(mg \cdot L^{-1})^3$
μ	viscosity, Pa.s
ρ	density, $kg \cdot m^{-3}$
θ	grade, dimensionless

Subscripts

$\partial \mathcal{D}_B$	bubble contour
$\partial \mathcal{D}_{Gu}$	upper geometric contour
$\partial \mathcal{D}_{Gm}$	middle geometric contour
$\partial \mathcal{D}_{Gd}$	lower geometric contour
B	bubble

<i>W</i>	bubble wake
<i>Q</i>	quencher
<i>0</i>	in the absence of quencher
<i>bn</i>	background noise
<i>ref</i>	totally deoxygenated solution (experimental value)
<i>ref_2</i>	half oxygen saturated solution (experimental value)
<i>ref_3</i>	oxygen-saturated solution (experimental value)
<i>sat</i>	oxygen-saturated solution (theoretical value)

Superscripts

\overline{X}	average of the X values
*	normalized value
<i>m</i>	clean bubble surface
<i>im</i>	fully contaminated bubble surface

Captions list

Fig. 1. (a) PLIF image of a rising air bubble obtained by Dani et al. (2007). (b) Successive PLIF images of a rising carbon dioxide bubble obtained by Stöhr et al. (2009).

Fig. 2. (a) Zoom on the bubble and definition of the vector \vec{n} . (b) Description of the mass balance domain $\partial\mathcal{D}$. (c) Zoom on the lower cross-section $\partial\mathcal{D}_{Gd}$ in the (r,θ) plane.

Fig. 3. Calibration curve ($[\text{Ru}] = 30 \text{ mg.L}^{-1}$, $[\text{Ethanol}] = 20 \text{ w/w\%}$, $[\text{H}_2\text{O}] = 80 \text{ w/w\%}$). \diamond : experimental points, \square : fitting curve.

Fig. 4. Experimental set-up.

Fig. 5. Raw image acquired with the high speed camera of a rising bubble flashed by the laser sheet.

Fig. 6. Raw fluorescence image acquired with the CCD camera ($[\text{Ru}] = 30 \text{ mg.L}^{-1}$, $[\text{Ethanol}] = 20 \text{ w/w\%}$, $[\text{H}_2\text{O}] = 80 \text{ w/w\%}$, $d_B = 0.72 \text{ mm}$, $U_B = 0.110 \text{ m.s}^{-1}$, $z = 3 d_B$). The image is displayed in grey values GV.

Fig. 7. Oxygen concentration field in a cross-section of the bubble wake ($[\text{Ru}] = 30 \text{ mg.L}^{-1}$, $[\text{Ethanol}] = 20 \text{ w/w\%}$, $[\text{H}_2\text{O}] = 80 \text{ w/w\%}$, $d_B = 0.72 \text{ mm}$, $U_B = 0.110 \text{ m.s}^{-1}$, $z = 3 d_B$). The image is displayed in mg.L^{-1} .

Fig. 8. Reconstructing of the oxygen wake from three PLIF images ($[\text{Ru}] = 30 \text{ mg.L}^{-1}$, $[\text{Ethanol}] = 20 \text{ w/w\%}$, $[\text{H}_2\text{O}] = 80 \text{ w/w\%}$, $d_B = 0.72 \text{ mm}$, $U_B = 0.110 \text{ m.s}^{-1}$). The image is displayed in mg.L^{-1} .

Fig. 9. Oxygen concentration profile in the bubble wake from experimental points at different distances z from the bubble.

Fig. 10. Standard deviation of the oxygen concentration profile on a cross-section of the oxygen wake ($[\text{Ru}] = 30 \text{ mg.L}^{-1}$, $[\text{Ethanol}] = 20 \text{ w/w\%}$, $[\text{H}_2\text{O}] = 80 \text{ w/w\%}$, $d_B = 0.72 \text{ mm}$, $U_B = 0.110 \text{ m.s}^{-1}$, $z = 22 d_B$).

Fig. 11. Flux quantified at successive distances z from the bubble. \mathcal{K} : experimental points, - -: average flux (from $z_C = 220 d_B$ to $z = 700 d_B$). ($[\text{Ru}] = 30 \text{ mg.L}^{-1}$, $[\text{Ethanol}] = 20 \text{ w/w\%}$, $[\text{H}_2\text{O}] = 80 \text{ w/w\%}$, $d_B = 0.72 \text{ mm}$, $U_B = 0.110 \text{ m.s}^{-1}$).

Fig. 12. Qualitative comparison of mass transfer in different hydrodynamic conditions.

Fig. 13. Drag coefficients vs. Reynolds numbers. - -: clean spherical bubble C_D^m , \square : contaminated spherical bubble C_D^{im} . \blacksquare : $[\text{glycerol}] = 80 \text{ w/w\%}$ glycerol, $d_B = 1.88 \text{ mm}$, \bullet : $[\text{glycerol}] = 60 \text{ w/w\%}$, $d_B = 1.29 \text{ mm}$, \circ : $[\text{glycerol}] = 60 \text{ w/w\%}$, $d_B = 0.72 \text{ mm}$, \blacklozenge : $[\text{glycerol}] = 40 \text{ w/w\%}$, $d_B = 1.30 \text{ mm}$, \diamond : $[\text{glycerol}] = 40 \text{ w/w\%}$, $d_B = 0.78 \text{ mm}$, Δ : $[\text{glycerol}] = 0 \text{ w/w\%}$, $d_B = 0.72 \text{ mm}$.

Fig. 14. Sherwood numbers vs. Peclet numbers. - -: Takemura and Yabe (1998) model (clean bubble), \square : Frössling model (contaminated bubble). \blacksquare : $[\text{glycerol}] = 80 \text{ w/w\%}$ glycerol, $d_B = 1.88 \text{ mm}$, \bullet : $[\text{glycerol}] = 60 \text{ w/w\%}$, $d_B = 1.29 \text{ mm}$, \circ : $[\text{glycerol}] = 60 \text{ w/w\%}$, $d_B = 0.72 \text{ mm}$, \blacklozenge : $[\text{glycerol}] = 40 \text{ w/w\%}$, $d_B = 1.30 \text{ mm}$, \diamond : $[\text{glycerol}] = 40 \text{ w/w\%}$, $d_B = 0.78 \text{ mm}$, Δ : $[\text{glycerol}] = 0 \text{ w/w\%}$, $d_B = 0.72 \text{ mm}$.

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