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## Gas–Liquid Mass Transfer around a Rising Bubble: Combined Effect of Rheology and Surfactant

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1       GAS-LIQUID MASS TRANSFER AROUND A  
2       RISING BUBBLE: COMBINED EFFECT OF  
3       RHEOLOGY AND SURFACTANT

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7       **Abstract**

8       The influence of viscosity and surface tension on oxygen transfer was investigated by Planar  
9       Laser Induced Fluorescence with Inhibition (PLIF-I). The surface tension and the viscosity  
10       were modified using Triton X-100 and PolyAcrilAmide, respectively. Changes in the  
11       hydrodynamic parameters of millimetric bubbles were identified, and transfer parameters  
12       calculated. The results reveal a decrease in the mass transferred in presence of a contaminant.  
13       For modified viscosity, the decrease of mass transferred is allowed for by current correlations  
14       but the presence of surfactant leads to a sharp decrease in the liquid side mass transfer  
15       coefficient, which becomes even lower when polymer is added. An explanation for the gap  
16       between classical correlations and experimental values of  $k_L$  is discussed, and a hypothesis on  
17       the existence of an accumulation of contaminant in the diffusion layer is proposed. This leads  
18       to the possibility of a decrease of the diffusion coefficient and oxygen saturation  
19       concentration in the liquid film explaining the discrepancy between models and experience.

20 Adapted values of  $D_{O_2}$  and  $[O_2]^*$  in this layer are estimated. This original study unravels the  
21 complexity of mass transfer from an air bubble in a complex medium.

## 22 **1. Introduction**

23 Gas-liquid columns are applied extensively in systems involving a mass transfer, e.g. in  
24 chemical and biological processes <sup>1</sup>. Among these applications is the gas-liquid mass transfer  
25 that is particularly important in wastewater treatment plants, where oxygen is transferred into  
26 the water to keep the bacteria responsible for degradation of the pollutants alive <sup>2</sup>. Usually,  
27 this oxygen is provided by bubbly flow and is thus a key step for the performance of the  
28 process <sup>2</sup>. As a result, many studies have been carried out on both the hydrodynamic and  
29 mass transfer aspects of gas/liquid contactors. In the 1990s, research was first conducted using  
30 the global point of view of contactors <sup>3-6</sup> with global oxygen probes and gas hold-up. Then, to  
31 complement these studies, local phenomena and their physical effects on hydrodynamics and  
32 mass transfer were investigated <sup>7-11</sup>. At the same time, experimental data acquired at the  
33 scales of different contactors, such as bubble columns, agitated tanks or airlift contactors, led  
34 to the development of increasingly accurate analytical or numerical models. However,  
35 physicochemical phenomena occurring during the gas/liquid transfer are not yet fully  
36 understood because they are highly dependent on the nature of the liquid media. The presence  
37 of surfactants, amphiphilic molecules present in large amounts in wastewater, has been  
38 identified as an inhibitor of mass transfer <sup>12,13</sup>. This inhibition can occur for many reasons.  
39 Alves et al. <sup>14</sup> highlighted modification of the shapes and velocities of bubbles, leading to a  
40 decrease in the mass transferred when surfactants were added to water. However, the  
41 modification does not affect hydrodynamics alone, and the work of Caskey and Barlage <sup>15</sup>  
42 showed a decrease of the gas-liquid mass transfer coefficient of  $CO_2$  in presence of surfactant  
43 on a plane interface, linked to a decrease of surface tension. A study by Painmanakul <sup>11</sup>

44 focused on gas/liquid transfer in a liquid medium containing surfactants, highlighting the  
45 influence of physicochemical properties on the interfacial area by increasing the bubble size  
46 and the gas hold up. Painmanakul and Hébrard <sup>16</sup> underlined the direct link between  
47 physicochemical properties of the liquid phase and the liquid side mass transfer coefficient,  
48  $k_L$ , from bubbles. The effect of surfactant on mass transfer has also been studied by Gomez-  
49 Diaz et al. and Rosso et al. <sup>17,18</sup> and attributed to the accumulation of surfactant at the  
50 interface, leading to a “barrier effect”. A study by Sardeing et al. <sup>19</sup> supported the direct effect  
51 of surface recovery of surfactants on the liquid side mass transfer coefficient,  $k_L$ . They  
52 designed a model for predicting this coefficient, based on two values of  $k_L$ , with and without  
53 surfactant. A few years later, the work of Hébrard et al. <sup>6</sup> revealed the direct link between the  
54 liquid side mass transfer coefficient  $k_L$  and the diffusion coefficient of oxygen,  $D_{O_2}$ , in  
55 presence of surfactants.

56 For a better understanding of local effects during mass transfer from the bubble to the  
57 water, a few techniques for visualizing mass transfer directly have been developed in the last  
58 decade. Among them are techniques using redox dyes<sup>20–28</sup> or Laser Induced Fluorescence  
59 (LIF). LIF methods using a pH sensitive fluorescent dye<sup>29–33</sup> can be implemented to visualize  
60  $CO_2$  transfer, not only in pure water, but also in water contaminated with a surfactant<sup>34,35</sup> or  
61 having had its viscosity modified with glycerol<sup>36</sup>. This technique can also be applied to the  
62 visualization of oxygen transfer by means of Fluorescence Induced by Laser with Inhibition  
63 (PLIF-I), using a fluorescent dye quenched by the presence of oxygen (LIF-I)<sup>37</sup>, from plane  
64 interfaces<sup>38–40</sup>, from Taylor bubbles<sup>41–44</sup> or from free moving bubbles. (PLIF-I) has been  
65 used by Roy and Duke<sup>38</sup>, Bork et al.<sup>36</sup>, Dani et al.<sup>8</sup> and Francois et al.,<sup>37</sup> to visualize oxygen  
66 transfer into water from millimetric bubbles. This technique has also been coupled with  
67 Particle Image Velocimetry (PIV) measurement, to approach mass transfer and velocity of the  
68 liquid simultaneously<sup>48</sup>. In the work of Jimenez<sup>49</sup> the PLIF-I technique was used to study the

69 influence of a non-ionic surfactant (caprylic acid monoglyceride) on oxygen transfer by  
70 providing information about the hydrodynamic parameters of the bubbles studied, such as  
71 velocity and equivalent diameter, and also the liquid side mass transfer coefficient and the  
72 diffusion coefficient of oxygen. They demonstrated that, at a concentration lower than the  
73 Critical Micellar Concentration (CMC), the bubble undergoes a sharp decrease of velocity and  
74 mass transfer coefficient. A slight decrease of diffusion coefficient has also been observed.  
75 However, it has been clearly demonstrated that the physical dimensionless numbers generally  
76 used to model mass transfer, such as Schmidt and Reynolds numbers, are not sufficient to  
77 explain the decrease of oxygen transfer to the water in presence of surfactants. As a result, a  
78 discrepancy was observed between the theoretical  $k_L$  proposed by Frössling and Higbie <sup>50,51</sup>  
79 and experimental values. Recently, a study by Xu et al. <sup>52</sup> used the PLIF-I technique to study  
80 the mass transfer coefficient and diffusion of oxygen in polymer solutions (Newtonian and  
81 non-Newtonian fluids). This study highlighted a similar decrease of mass transfer in presence  
82 of polymer. A slight decrease of diffusion coefficient was observed, which was explained by  
83 the increase in the viscosity of the solution.

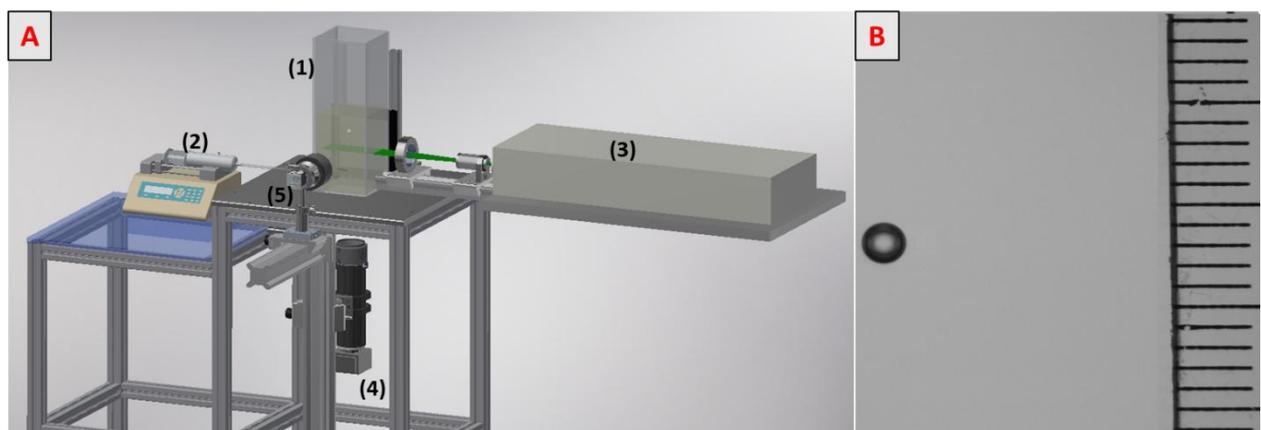
84 The present study proposes to apply PLIF-I to visualize and quantify the oxygen mass  
85 transfer from millimetric bubbles rising in different complex media at rest: a non-ionic  
86 surfactant, Triton X-100, and a solution containing both Triton X-100 and the non-Newtonian  
87 polymer PAAm (PolyAcrylAmide) in the same concentration as the one used by Xu et al. <sup>52</sup>.  
88 To the best of our knowledge, this is the first time that a complex medium, combining a  
89 change in viscosity and a change in surface tension, is studied in terms of oxygen mass  
90 transfer, with a local approach.

## 91 **2. Materials and Methods**

### 92 *2.1 Experimental set-up*

93 The experimental set-up is depicted in Figure 1A. The 30 x 10 x 10 cm<sup>3</sup> column (1) was  
94 filled with 1.5 L of the solution under study. The liquid was deoxygenized with nitrogen  
95 before each measurement and the oxygen concentration was verified with an oxygen probe  
96 (HACH, HQ40D). A single millimetric bubble was generated with a syringe pump  
97 (HARVARD Apparatus PHD 22/2000 programmable) (2) and injected through a 75 μm  
98 diameter needle. To excite fluorescence, a horizontal laser sheet was generated by an  
99 Nd:YAG laser (3) (DANTEC Dynamics Dualpower 200-15, 15 Hz, 2x200 mJ). A Charge-  
100 Coupled Device camera (4) (DANTEC Dynamics Flowsense CM, 12 bit, 15 Hz, 2048x2048)  
101 was located at the bottom of the column and focused on the laser sheet. A microlens (105 nm  
102 f/8, Canon) with an extension tube was applied to obtain a visualization window of 10.6 mm x  
103 10.6 mm. A 570 nm high-pass filter was also placed in front of the lens to block the laser light  
104 and to record only light emitted by fluorescence.

105 A high-speed camera (5) (Photon SA3, 8 bits, 2000 fps, 1024x1024) was placed in front of  
106 the bubble to record its shape, size and velocity. Each experiment was run 6 times in order to  
107 ensure the repeatability of measurements. The liquid temperature was 294±1°K.



109 Figure 1: (A) Experimental set-up. (B) Visualization of a bubble rising in water containing 0.02 g/L of  
110 Triton X-100 in solution

111

## 112 2.2 Material

113 The water used in each case was ultra-pure water having a conductivity of 0.054 mS/cm.  
114 The fluorophore used for this study was a ruthenium complex ( $C_{36}H_{24}Cl_2N_6Ru \cdot xH_2O$ , Sigma-  
115 Aldrich, CAS: 207802-45-7). The surface active agent of interest was Triton X-100 (Sigma-  
116 Aldrich, CAS: 9002-93-1) at a concentration of 0.02 g/L, so lower than the CMC (around 150  
117 mg/L at 293 K). The polymer used was PolyAcrylAmide-co-acrylic acid (PAAm, Sigma-  
118 Aldrich, CAS: 62649-23-4) at a concentration of 0.1 % (w/w). It was mixed with the solution  
119 of Triton X-100 to understand possible interactions in a medium when surface tension and  
120 viscosity are changed simultaneously. For all experiments, perfect solubilization of surfactant  
121 and polymer was observed in the water. A characterization of the mass transfer and the  
122 hydrodynamic parameters of a solution with PAAm 0.1% (w/w) without surfactant can be  
123 found in Xu et al.<sup>52</sup>. The principal results are recalled here.

## 124 2.3 Determination of hydrodynamic parameters

125 The velocities and sizes of bubbles were determined by means of the high-speed camera.  
126 An example of the images obtained is given in Figure 1B. The camera was calibrated so as to  
127 obtain  $(19.6 \pm 0.08)$   $\mu\text{m}/\text{pixel}$ , and the width (a) and length (b) of the bubble were thus  
128 deduced. The equivalent diameter was calculated by equation (1)

$$129 d_{\text{eq}} = (a^2 \times b)^{1/3} \quad (1)$$

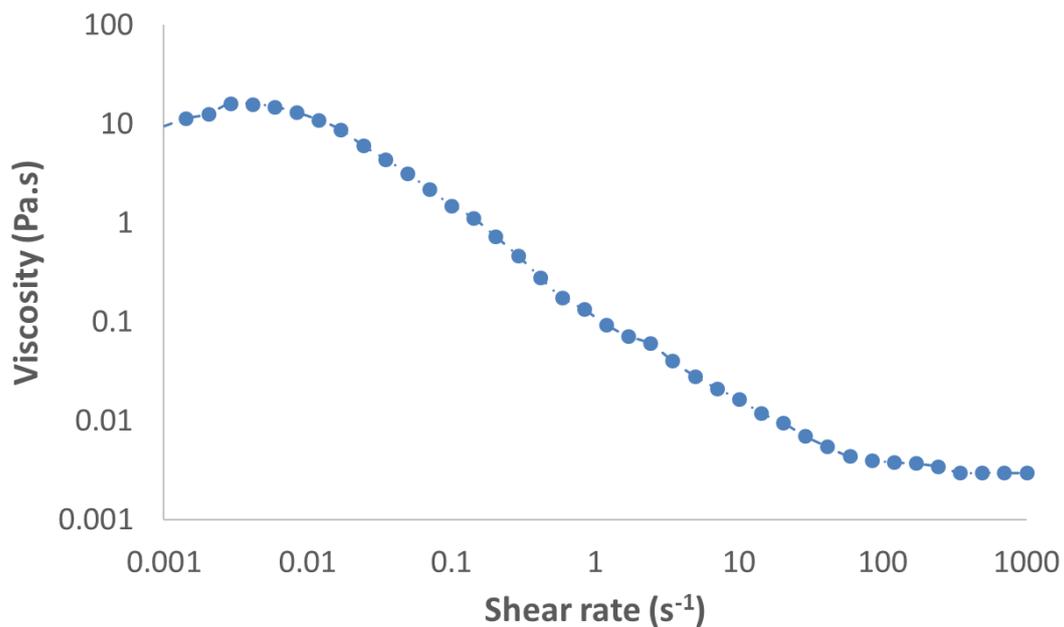
130 The speed of the camera was 2000 frames per second and the number of images recorded  
131 during the time the bubble was in the window allowed its velocity to be deduced.

132 Surface tensions were measured by the Noüy ring method, with a manual tensiometer  
133 (KRÜSS, K6). Viscosities of fluids were measured with a rheometer (HAKKE MARS III,  
134 Germany). Because PAAm is a polymer leading to a non-Newtonian fluid, its viscosity was  
135 measured for a large range of shear rates, between  $10^{-3}$  and  $10^3$  Pa.s. Figure 2 shows results  
136 obtained by Xu et al.<sup>52</sup> when measuring the viscosity of a solution of 0.1% by weight of

137 PAAm. Viscosity measurements in presence of Triton X-100 at the study concentration were  
138 found to be the same as for water (1 mPa.s). Thus, it was assumed that the presence of Triton  
139 X-100 did not affect the rheology of the medium at the concentration used. For our operating  
140 conditions, the shear rate was estimated according to the velocity of the bubble and its  
141 equivalent diameter, with equation (2). This is the characteristic shear rate near the equator of  
142 a spherical bubble<sup>53</sup> Since eccentricities found for bubbles containing PAAm were 1.04 and  
143 1.03, they were assimilated to spherical bubbles.

144  $\gamma = U/d_{eq}$ . (2)

145



146

147 Figure 2: Viscosity of a solution of 0.1% (w/w) PAAm in water, according to the shear rate.

148

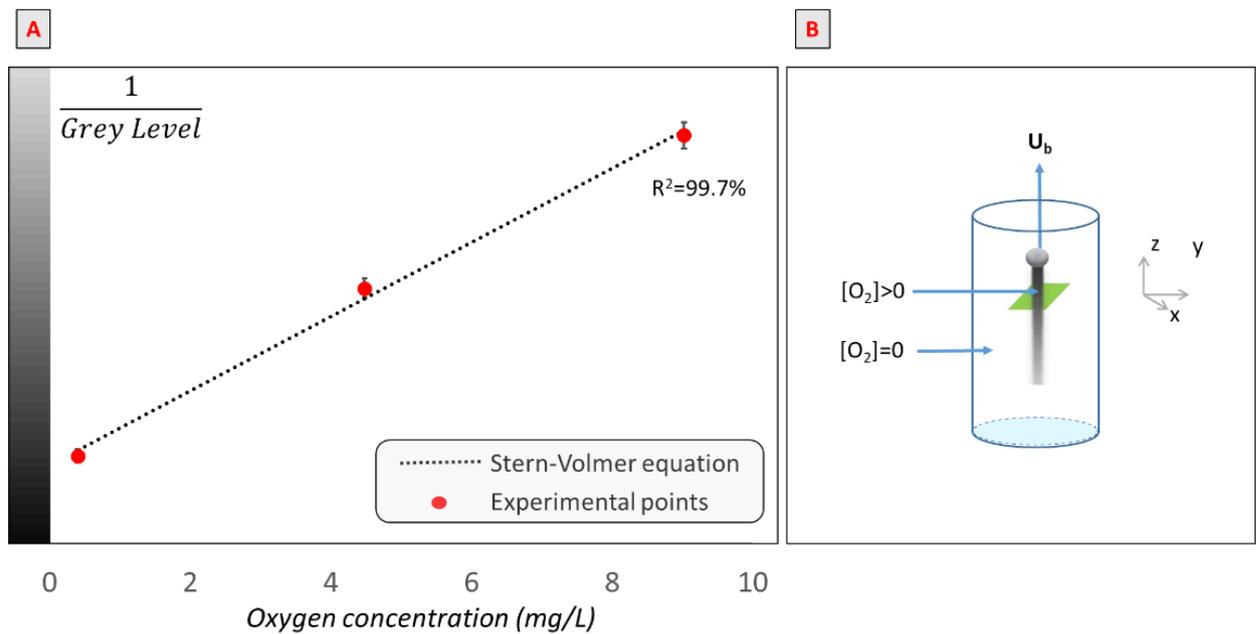
#### 149 2.4 Determination of transfer parameters

150 The mass transfer in the bubble wake was quantified using the PLIF-I technique. The basic  
151 aim of the PLIF-I experiment was to establish the relationship between the grey level and the

152 oxygen concentration, as the fluorescence of the ruthenium complex used is quenched in  
 153 presence of oxygen following Stern and Volmer's equation <sup>54</sup>:

$$154 \quad 1/G = 1/G_0 + K_{sv}/G_0 [O_2] \quad (3)$$

155 Note that, in this equation, G is the grey level in presence of oxygen, G<sub>0</sub> is the grey level  
 156 without oxygen, K<sub>sv</sub> is the Stern Volmer (L/mg) constant and [O<sub>2</sub>] (mg/L) is the oxygen  
 157 concentration. Thus, the calibration curve was established for each experiment, using an  
 158 optical oxygen probe (HACH, HQ40D), for oxygen concentrations between 0 and 9 mg/L. An  
 159 example of a calibration curve obtained is presented in Figure 3A.



160  
 161 Figure 3: (A) Example of calibration curve: Inverse of grey level of images obtained versus oxygen  
 162 concentration in a solution of water and ruthenium (III). (B) Schematic representation of the bubble  
 163 rising in its domain

164  
 165 Then, to calculate the mass transfer coefficient and diffusion coefficient, the assumption  
 166 was made that, far from the bubble rear, there was no convection and so no transfer in the z  
 167 direction (Figure 3B). François et al. <sup>46</sup> have shown that, considering that the liquid velocity is

168 negligible, after a certain distance, there is no diffusion of oxygen in the z direction because  
169 there is no concentration gradient. As a result, the mass of oxygen is constant in the (x,y)  
170 plane. Then,  $F_{O_2}$ , the mass flow rate, can be approximated by equation (4), where  $m_{O_2}$  is the  
171 total amount of oxygen transferred in a plane perpendicular to the wake ( $\text{mg}\cdot\text{m}^{-1}$ ).

$$172 \quad F_{O_2} = dm_{O_2}/dt \quad (4)$$

173 This assumption needs to be verified in each case and will be developed in the case of  
174 solutions containing polymer and surfactant since it is the first time these measurements have  
175 been carried out in this kind of medium. Experimentally, it is assumed that convection is  
176 negligible if  $m_{O_2}$  is constant with time. Furthermore, we determined a threshold criterion for  
177 exploiting images with a low signal. We assumed that the quality of the signal was sufficient  
178 if the signal/noise ratio was above 10, according to equation (5)

$$179 \quad (I - I_0)/\sigma_n > 10 \quad (5)$$

180 where  $I$  and  $I_0$  are the maximal and minimal intensities, respectively, and  $\sigma_n$  is the standard  
181 deviation of the background noise.

182 Once these criteria had been verified after a sufficient length in the bubble wake, the mass  
183 transferred in a horizontal plane was considered constant and so the change in the size of this  
184 spot structure would be due only to molecular diffusion of oxygen. In previous studies by  
185 Francois et al.<sup>37</sup>, Jimenez et al.<sup>47</sup> and Dietrich et al.<sup>46</sup>, it was observed that, for quasi-  
186 spherical bubbles, the diffusion spot was circular and presented a Gaussian profile. As a  
187 result, the diffusion spot could be fitted by equation (6), where the concentration  $[O_2]$  in each  
188 pixel  $x_p, y_p$  is estimated as

$$189 \quad [O_2](x,y) = A \exp(-((x_p - X)^2 + (y_p - Y)^2)/B + C) \quad (6)$$

190 Parameters were found by fitting the equation with the raw image using the `fminsearch`  
191 solver (Matlab R2017a). Note that  $A$  and  $B$  are parameters, and  $(X, Y)$  is the centre of the  
192 spot. The parameter  $C$ , representing the background, was removed for further calculations.

193 Once the image had been processed, it was possible to calculate the flux transferred by the  
194 bubble by using equation (7)

$$195 F_{O_2} = U_b \times \iint_{\delta D_{spot}} [O_2](x, y) dx dy \quad (7)$$

196 with x and y horizontal coordinates. Then, the mass transfer coefficient could be calculated  
197 by equation (8) as long as the surface area of the bubble was deduced from the equivalent  
198 diameter.

$$199 k_L = F_{O_2} / (S_b ([O_2]^* - [O_2])) \quad (8)$$

200 Finally, a method developed by Xu et al.<sup>57</sup> allowed the diffusion coefficient of oxygen to  
201 be determined assuming that the surface area of the spot  $S_{spot}$  increased with time according to  
202 equation (9)

$$203 S_{spot} = 2\pi D_{O_2} t \eta_D \quad (9)$$

204 where  $\eta_D$  is a constant that can be fixed following the procedure described by Xu et al.<sup>57</sup>.

### 205 **3. Results**

#### 206 *3.1 Hydrodynamic parameters of bubbles*

207 The surface tension and viscosity of each medium are given in Table 1. Concerning the  
208 surface tension measured with the Nouÿ ring method, addition of Triton X-100 to the water  
209 leads to a decrease of surface tension from 71.25 mN/m to 48.38 mN/m. When polymer is  
210 added to Triton X-100 and water, the surface tension decreases by 1.18 mN/m to reach 47.20  
211 mN/m. This decrease is slight but significant considering the precisions of the measurements.  
212 A similar slight decrease of surface tension with addition of PAAm was also found in a study  
213 by Xu et al.<sup>52</sup>. Concerning the viscosity, addition of PAAm led to a marked decrease but  
214 Triton X-100 did not affect viscosity in the operating conditions of the present experiment.

215 The hydrodynamic parameters of bubbles were measured and are reported in Table 1. These  
216 parameters are clearly affected by physicochemical modifications of the medium but it should  
217 be noted that the injection needle used in Xu's study<sup>52</sup> was smaller than that used in the work

218 presented here. Thus the smaller bubble diameter in the case of addition of PAAm was not  
 219 due to the physicochemistry but to a change in the injection needle. Concerning  
 220 hydrodynamic parameters, the addition of contaminant affected the velocity of the bubble.  
 221 The bubble velocity was 321 mm/s in ultra-pure water but the addition of surfactant halved  
 222 this value to 142 mm/s, a velocity that decreased again, to reach 118.1 mm/s, when polymer  
 223 was added to Triton X-100 and water.

224

225

|  | $\sigma$<br>(mN/m) | $\rho$<br>(kg/m <sup>3</sup> ) | $\eta$<br>(Pa.s)                  | $d_{eq}$<br>(mm) | $U_b$<br>(mm/s) | $\chi$<br>(-) |
|--|--------------------|--------------------------------|-----------------------------------|------------------|-----------------|---------------|
| Water  | 71.25±0.16         | 998.00±0.09                    | (1±0.001)<br>$\times 10^{-3}$     | 1.27±0.04        | 321±2           | 1.4           |
| PAAm 0.1% in water<br><sup>52</sup>                | 69.80              | 998.00                         | $13\gamma^{-0.35}$                | 1.00±0.04        | 81±1            | 1.04          |
| Triton X-100 0.02<br>g/L in water                  | 48.38±0.26         | 997.63±0.04                    | (1.001±0.001)<br>$\times 10^{-3}$ | 1.25±0.04        | 142±1           | 1.05          |
| PAAm 0.1% and<br>Triton X-100 0.02<br>g/L in water | 47.20±0.25         | 997.92±0.05                    | $13\gamma^{-0.35}$                | 1.44±0.04        | 118±1           | 1.03          |

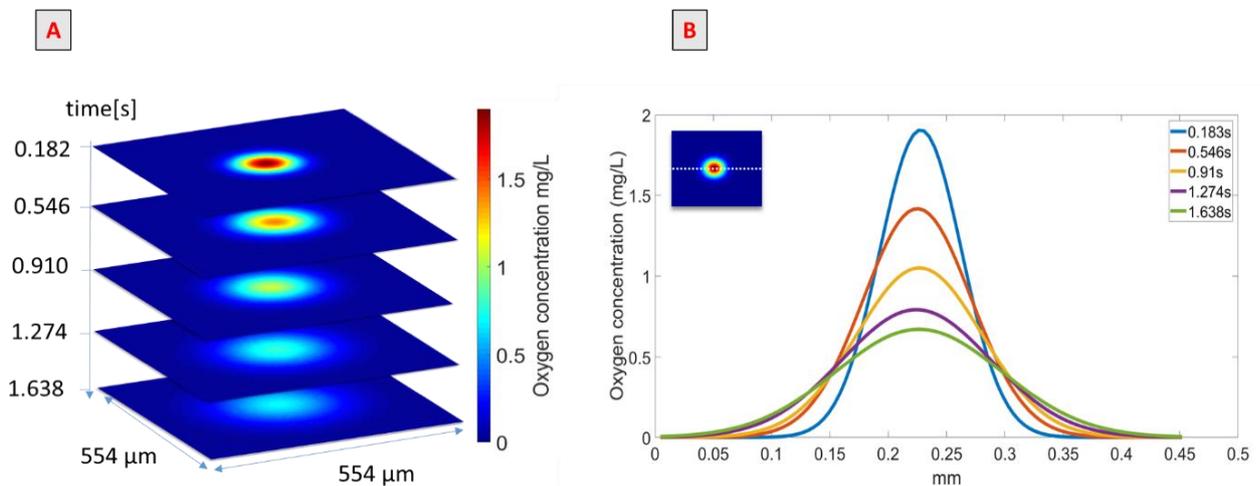
226 Table 1: Physical properties of fluids and hydrodynamic parameters of bubbles

227 It can, first, be seen that addition of Triton X-100 to water affects, not the bubble size, but its  
 228 shape. The bubble, which is ellipsoidal in the case of water, with an aspect ratio of 1.4, tends  
 229 to become more spherical with the surfactant, reaching an aspect ratio of 1.05. When polymer  
 230 is added, in the case reported by Xu et al. <sup>52</sup> and in this study, the bubble generated is  
 231 spherical. In the case of the present study, addition of PAAm led to bigger bubbles. Finally,  
 232 the bubble trajectories were found to be straight lines and these values are in good agreement  
 233 with the literature <sup>58</sup>.

234

### 235 3.2 Visualization of oxygen concentration field

236 The use of the PLIF-I technique to quantify the oxygen transferred has been validated for  
237 the situation when rheology and surface tension are modified simultaneously. Figure 4A  
238 presents images obtained at different times after the passage of the bubble; the spots in the  
239 centres of the images represent the oxygen transferred by the bubble. The first image was  
240 taken 0.182 s after the bubble passage and the oxygen concentration field in the spot varies  
241 between 0 and 1.8 mg/L. The oxygen field concentration seems to increase with time while  
242 the oxygen concentration in the centre of the spot decreases.



243

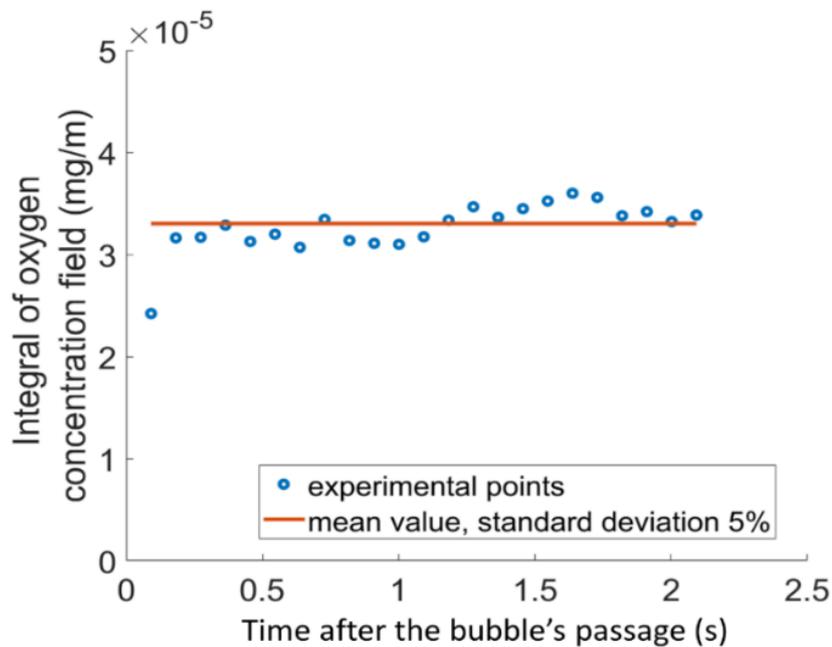
244 Figure 4: (A) Images obtained after the bubble's passage in the PAAm/TritonX-100 mixture  
245 in water. (B) Representation of oxygen concentration along an x-line.

246 This effect is depicted in Figure 4B, which represents oxygen concentration along an x-line  
247 (shown in the insert as a dotted white line) crossing the centre of the spot, at different times  
248 after the bubble's passage. These continuous lines were obtained with the Gaussian model  
249 presented in equation (6). Each curve has a Gaussian shape but successive curves tend to be  
250 more spread out: between 0.183 seconds and 1.638 seconds after the bubble's passage, the  
251 maximum oxygen concentration, which is the concentration in the centre of the spot,

252 decreases from 1.8 to 0.6 mg/L and the diameter of the spot increases approximately from  
 253 0.21 mm to 0.38 mm. The integrals of these curves correspond to the amount of mass  
 254 transferred in the x-line, and so, if the mass transferred is conserved between images, the  
 255 integral over the surface studied has to be conserved. To verify the mass conservation  
 256 assumption, the integral of each image, calculated in mg/m according to equation (10), was  
 257 determined and the results are given in Figure 5.

$$258 \text{ Integral} = \iint_{\delta D_{\text{spot}}} [\text{O}_2](x,y) dx dy \quad (10)$$

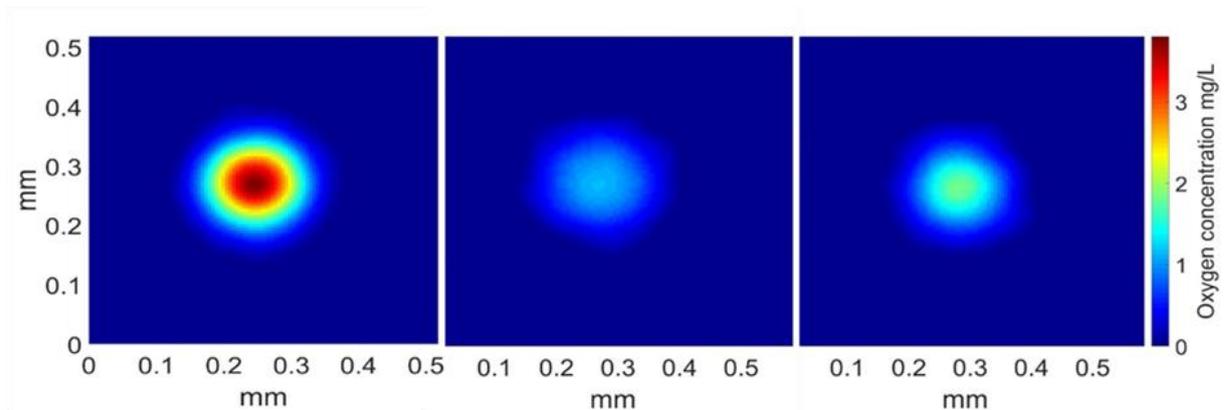
259 The first point representing the integral after the bubble's passage (91 ms) is lower than the  
 260 rest of the values as the bubble wake is convecting oxygen. From 182 ms after its passage  
 261 onwards, the bubble is far enough away to have no effect on the amount of oxygen in the  
 262 wake, and conservation of the mass transferred in the wake is observed. The red line  
 263 represents the mean value of the conservative points, equal to  $3.2 \times 10^{-5}$  mg/m for this  
 264 experiment. The conservation of the mass transferred is thus confirmed with good precision  
 265 for measurements taken after a time of 182 ms (standard deviation from the mean value is  
 266 about 5%).



267

268 Figure 5: Integral of the oxygen concentration field according to the time after the bubble's  
269 passage in solution of PAAm and Triton X-100

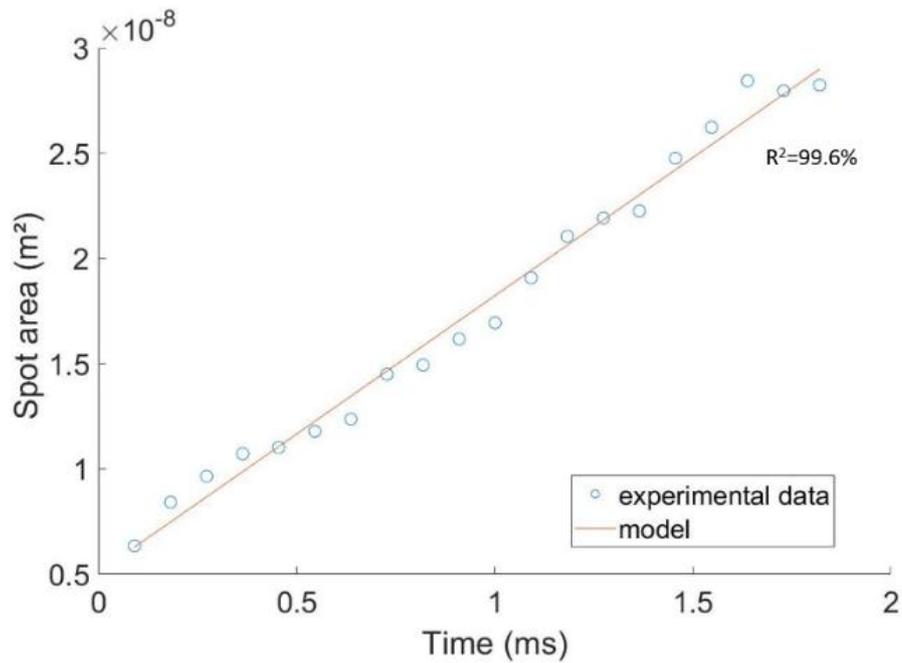
270 The method for calculating the mass transfer coefficient has thus been validated for a  
271 medium containing 0.02 g/L of Triton X-100 and 0.1% (w/w) of PAAm; its feasibility had  
272 already been validated in the case of water and surfactant by previous studies <sup>49,52</sup>. For  
273 comparison of the amount of mass transferred in the three different media, images 182 ms  
274 after the bubble's passage are shown in Figure 6.



275  
276 Figure 6 : Representation of the oxygen concentration in a plane perpendicular to the bubble  
277 wake, 182 ms after the bubble's passage. Medium from left to right: water, water+ Triton X-  
278 100, water+Triton X-100+PAAm

279 According to the spots displayed, the amount of mass transferred seems highest in the case  
280 of water, then decreases in presence of Triton X-100 and PAAm and is the lowest for the  
281 bubble rising in the solution of water and surfactant. Values of the integrals were calculated  
282 and are presented in Table 2, confirming the trend displayed in Figure 6. Finally, in order to  
283 calculate the diffusion coefficient of oxygen, the linearity of the expansion of the mass  
284 transfer spot with time needed to be verified. It was verified for the whole experiment, and  
285 Figure 7 presents this linearity in the case of water with polymer and surfactants, as the

286 diffusion coefficient has never been calculated in this kind of medium with the PLIF-I  
287 technique.



288

289 Figure 7 : Area of the spot as a function of time after the bubble's passage in a solution  
290 containing PAAm and Triton X-100

291 The area of the spot was calculated and is reported versus time, between 0.182 s and 2 s.  
292 Blue circles represent experimental points and the red line is a linear model determined from  
293 the experimental points, which fits the curve at 99.6%. The linearity of expansion of the spot  
294 area with time is thus verified. This assumption checked, the mass transfer coefficient was  
295 calculated using equation (8).

296

297

298

299

|   | Integral<br>( $10^{-5}$ mg/m) | $k_L$<br>( $10^{-4}$ m/s) | $D_{O_2}$<br>( $10^{-9}$ m <sup>2</sup> /s) | Re<br>(-) | Sc<br>(-) | Sh<br>(-) |
|---|-------------------------------|---------------------------|---|-----------|-----------|-----------|
| Water   | 7.0±0.2                       | 4.9±0.07                  | 2.13±0.06                                   | 407       | 470       | 290       |
| PAAm 0.1% in water<br>52                        | 3.48                          | 1.06±0.09                 | 1.88±0.02                                   | 30        | 1490      | 60        |
| Triton X-100 0.02 g/L in water                  | 2.41±0.13                     | 0.76±0.02                 | 1.82±0.14                                   | 177       | 550       | 50        |
| PAAm 0.1% and Triton X-100<br>0.02 g/L in water | 3.1±0.2                       | 0.62±0.02                 | 1.75±0.13                                   | 68        | 1580      | 50        |

301 Table 2: Transfer parameters for different media

## 302 4. Discussion

### 303 4.1 Comparison with models

304 Values calculated for integrals, mass transfer and diffusion coefficients are summed up in  
305 Table 2. It is interesting to note, first, that the mass transfer coefficient decreases when  
306 surfactant is added to the solution. It decreases even more when PAAm 0.1% (w/w) is added  
307 to this solution. However, when spots are compared in terms of integrals, in other words, the  
308 total masses transferred (see Figure 6 and Table 2), it is observed that the mass transferred in  
309 the water containing the PAAm 0.1% (w/w) and Triton X-100 is higher than the mass  
310 transferred in the water containing only Triton X-100. It is important to underline that the  
311 velocity of a bubble in water containing Triton X-100 is higher, while the size of the bubble is  
312 smaller. When these parameters are taken into account (see equations (7) and (8)), the mass  
313 transfer coefficient calculated is higher with just surfactant in the water than with surfactant  
314 and PAAm.

315 Experimental values obtained for the mass transfer coefficient can be compared with two  
316 models describing two extreme cases. The first is the Higbie model <sup>51</sup>, usually used for  
16

317 bubbles of large diameter, associated with a mobile interface, and the second is the Frössling  
318 model<sup>50</sup>, describing small bubbles with a rigid interface. These two models are given by  
319 equations (11), for Higbie, and (12), for Frössling, and the values calculated are presented in  
320 Table 3.

$$321 \quad k_{L\text{Higbie}} = D_{O_2}/d_{eq} \times (1.13\text{Re}^{0.5}\text{Sc}^{0.5}) \quad (11)$$

$$322 \quad k_{L\text{Frössling}} = D_{O_2}/d_{eq} \times (2 + 0.66\text{Re}^{0.5}\text{Sc}^{0.33}) \quad (12)$$

323 For the case of transfer in pure water, as expected, the experimental value of the mass  
324 transfer coefficient is between the two extreme cases. The bubble is not contaminated, so the  
325 value should be higher than the  $k_L$  predicted by Frössling but, for Higbie's model, the bubble  
326 is too small to be considered as a clean bubble according to the definition. Concerning the  
327 value for the transfer of oxygen in a solution of water containing 0.1% of PAAm presented in  
328 Xu et al.<sup>52</sup>, the decrease of mass transfer coefficient is represented by models and the  
329 experimental value still lies between the two extreme cases. However, concerning values for  
330 the solution containing the surfactant, the mass transfer coefficient  $k_L$  is overestimated for  
331 each correlation. Such a result has also been observed in the work of Jimenez<sup>49</sup> for transfer in  
332 a solution of caprylic acid monoglyceride in water. The overestimation of the mass transfer  
333 coefficient is also found for the solution containing Triton X-100 and PAAm. However,  
334 probably due to the change of viscosity, the mass transfer coefficients predicted are lower and  
335 closer to the experimental values. From these results, we can conclude that the decrease of  
336 mass transfer coefficient is still predictable by the current dimensionless Reynolds and  
337 Schmidt numbers when only viscosity changes, because hydrodynamic parameters were  
338 strongly modified and taken into account by the models. However, if these models are applied  
339 to solutions containing surfactant, they lead to an overestimation.

340 Another point of discussion from these results concerns the thickness of the diffusion layer.  
341 The double film theory proposed by Lewis and Whitman<sup>59</sup> defined the thickness of the liquid

342 film as in equation (13). Later, a model proposed by Moore<sup>60</sup> calculated the thickness of the  
 343 film with the Péclet number according to equation (14).

$$344 \quad \delta_{df} = D_{O_2} / k_L \quad (13)$$

$$345 \quad \delta_{Pe} = d_{eq} Pe^{-0.5} \quad (14)$$

346 The calculation of these two theoretical thicknesses is presented in Table 3. First, it can be  
 347 seen that the diffusion layer thickness predicted with Moore's<sup>60</sup> model, by equation (14), is  
 348 almost the same for all the media, between 2.9  $\mu\text{m}$  and 4.8  $\mu\text{m}$ . This layer is the thinnest for  
 349 the bubble rising in water, increases in presence of the surfactant, and increases more when  
 350 surfactant and polymer are both in solution, to reach a value of 4.6  $\mu\text{m}$ .

|  | $k_L$<br>( $10^{-4}$ m/s) | $k_{L\text{Frössling}}$<br>( $10^{-4}$ m/s) | $k_{L\text{Higbie}}$<br>( $10^{-4}$ m/s) | $\delta_{df}$<br>( $\mu\text{m}$ ) | $\delta_{Pe}$<br>( $\mu\text{m}$ ) |
|--|---------------------------|---|--|------------------------------------|------------------------------------|
| Water  | 4.91±0.07                 | 1.73  | 8.32                                     | 4.3                                | 2.9                                |
| PAAm 0.1% in water<br>52                         | 1.06±0.09                 | 0.79  | 4.40                                     | 17.7                               | 4.8                                |
| Triton X-100 0.02 g/L in<br>water                | 0.76±0.02                 | 1.06  | 5.13                                     | 23.9                               | 4.0                                |
| PAAm 0.1% and Triton X-<br>100 0.02 g/L in water | 0.62±0.02                 | 0.74  | 4.27                                     | 28.2                               | 4.6                                |

351

352 Table 3 : Results for experimental  $k_L$ , theoretical  $k_L$  and diffusion layer thickness.

353 Concerning the diffusion layer thickness predicted with the double layer model by equation  
 354 (13), the value for a bubble rising in pure water is of the order of magnitude of the one  
 355 predicted by the Péclet number. However, for the solution containing 0.1% of PAAm, it is  
 356 about 4 times the value predicted for water. The thickness of the layer of solutions containing  
 357 surfactants with and without polymer is more than 5 times that predicted for the water with  
 358 the same model and for the same solution with Moore's<sup>60</sup> model. It is assumed that the  
 18

359 calculation of the layer thickness by Lewis and Whitman in presence of contaminant is  
360 overestimated.

361 To sum up, the comparison of experimental results with models reveals an overestimation  
362 of the mass transfer coefficient with the Frössling model or an overestimation of the thickness  
363 of the layer by the double layer theory model.

#### 364 *4.2 Physicochemical modifications in the vicinity of the interface*

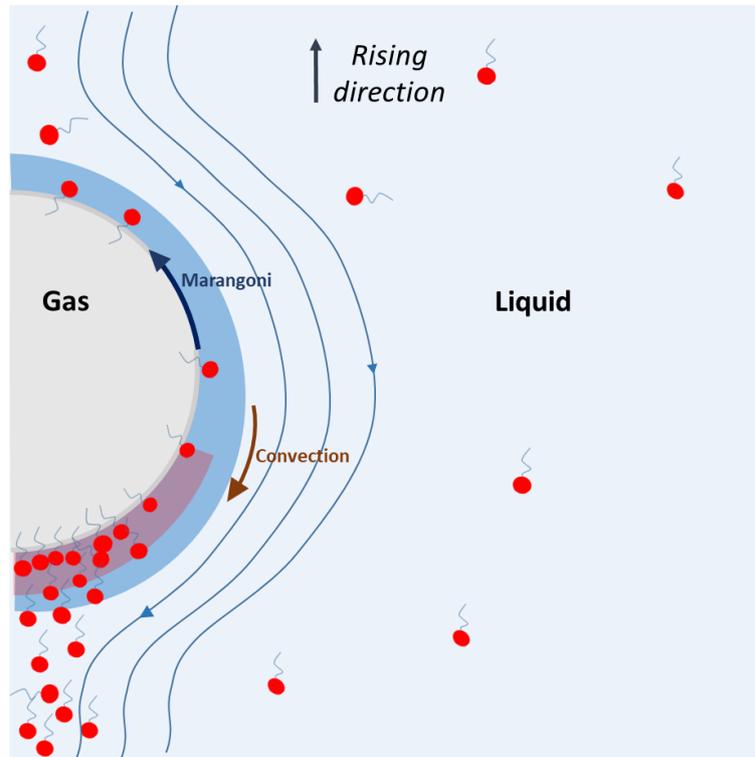
365 These overestimations can be explained by modifications of the hydrodynamics. It has  
366 been shown by Weiner et al. <sup>61</sup> that the flow around the bubble is strongly affected by the  
367 presence of surfactants. These authors observe a change in the trailing vortex, in which  
368 oxygen is transported only by diffusion. Such a change can strongly affect the mass transfer  
369 coefficient.

370 Here, we propose that the presence of surfactant affects not only the hydrodynamics but  
371 also the physicochemical properties in the vicinity of the interface. It is important to keep in  
372 mind that one of the properties of surfactants is to accumulate at interfaces. This accumulation  
373 could lead to a higher concentration close to the bubble, in the liquid film.

374 The physical phenomenon that can explain these overestimations is presented in Figure 8.  
375 On this figure, a single bubble is rising in a solution containing surfactants. During the rise,  
376 the surfactants are adsorbed on the bubble, on the interface, and they will feel two opposite  
377 forces: (i) convection, which will sweep surfactants towards the rear of the bubble, and (ii) the  
378 Marangoni stress, which tends to bring surfactant towards the nose of the bubble to avoid a  
379 surface tension gradient. The assumption is that, due to the convection, which exceeds the  
380 Marangoni stress, surfactants are first adsorbed at the nose of the bubble, then swept towards  
381 the rear. Since the nose of the bubble is surfactant free, new surfactant molecules are adsorbed  
382 and swept, and an accumulation of surfactant appears at the rear of the bubble, in the diffusion  
383 layer. The result of this higher concentration can lead to two phenomena: a decrease of the

384 diffusion coefficient of oxygen and a change in the saturation concentration of oxygen  $[O_2]^*$ .

385 These two assumptions will be discussed below.



386

387 Figure 8: Representation of physical phenomenon occurring during the rising of a bubble in  
388 surfactant solution, according to the theory presented in this study

#### 389 4.2.1. Estimation of a modified diffusion coefficient for oxygen

390 First, we can wonder whether the diffusion coefficient in the liquid film is the same as the  
391 one calculated in the bulk, far from the bubble, and, so, if the diffusion coefficient in the  
392 Schmidt number used to predict  $k_L$  is overestimated when water is contaminated. Hereafter,  
393 this modified diffusion coefficient will be estimated using the theoretical values determined  
394 with equation (13). The values of diffusion coefficient inside the layer were estimated by  
395 modifying the coefficient until the two thicknesses of the diffusion layers, predicted by  
396 equations (13) and (14), reached exactly the same value. It is important to keep in mind that

397 this calculation is not intended to give a precise diffusion coefficient but just to estimate its  
 398 range of magnitude, according to the model described previously.

399 The diffusion coefficient in the layer thus estimated is presented in

400 Table 4. This diffusion coefficient in the layer was also calculated in the case of polymer  
 401 because the assumption that there is an accumulation of polymer close to the interface cannot  
 402 be excluded even if it would be very much smaller than in the case of surfactants. It is  
 403 possible to assume that this decrease of the diffusion coefficient needs to be taken into  
 404 account in the calculation of the theoretical mass transfer coefficient. As shown in Table 4,  
 405 the diffusion coefficient estimated in the diffusion layer is half that in the bulk. In a solution  
 406 containing surfactant, it is estimated to be divided by a factor of at least five. So, the value of  
 407 the theoretical mass transfer coefficient was also estimated with the diffusion coefficient in  
 408 the diffusion layer. With these new values, presented in

409 Table 4, experimental values found for mass transfer coefficient are between the two

|  | $k_L$<br>experimental<br>( $10^{-4}$ m/s) | $D_{O_2}$ in the<br>diffusion layer<br>( $10^{-10}$ m <sup>2</sup> /s) | $k_{L\text{Frössling}}$ modified<br>( $10^{-4}$ m/s) | $k_{L\text{Higbie}}$ modified<br>( $10^{-4}$ m/s) |
|--|---|--|--|---|
| PAAm 0.1% in<br>water<br>52                        | 1.06±0.09                                 | 5.1  | 0.21   | 2.29  |
| Triton X-100 0.02<br>g/L in water                  | 0.76±0.02                                 | 3.04   | 0.18   | 2.1   |
| PAAm 0.1% and<br>Triton X-100 0.02<br>g/L in water | 0.62±0.02                                 | 2.84   | 0.12   | 1.74  |

410 theoretical values.

411

412

413 Table 4: Diffusion coefficient estimated in the diffusion layer and corrected theoretical  $k_L$

414 *4.2.1. Estimation of a modified value of oxygen saturation  $[O_2]^*$*

415 Another point of discussion is the value of the oxygen saturation. If the **diffusion** layer  
416 reached a high concentration, the saturation concentration of oxygen in this layer could  
417 decrease. Thus, the value of the experimental mass transfer coefficient calculated from  
418 equation (8) would underestimate this experimental mass transfer coefficient. In the same way  
419 as for the diffusion coefficient in the previous part, a modified value of oxygen saturation  
420 concentration was estimated here. The objective was to modify the value of oxygen saturation  
421 concentration until the calculation of experimental mass transfer reached the same value as  
422 the mass transfer coefficient predicted by the Frössling model. Results are presented in Table  
423 5. They show that, to reach the value predicted by Frössling, the oxygen saturation value  
424 should be 6.59 mg/L in the layer instead of the 9.18 mg/L measured in the bulk for the  
425 solution with only Triton X-100. For the solution with PAAm and Triton X-100, it should be  
426 7.61 mg/L instead of 9.15 mg/L.

|  | $k_L$<br>experimental<br>( $10^{-4}$ m/s) | $k_{L\text{Frössling}}$<br>( $10^{-4}$ m/s) | $[O_2]^*$<br>experimental<br>(mg/L) | $[O_2]^*$ modified<br>(mg/L) |
|--|---|---|-------------------------------------|------------------------------|
| Triton X-100 0.02<br>g/L in water                  | 0.76±0.02                                 | 1.06  | 9.18±0.02                           | 6.59                         |
| PAAm 0.1% and<br>Triton X-100 0.02<br>g/L in water | 0.62±0.02                                 | 0.74  | 9.15±0.02                           | 7.61                         |

427 Table 5 : Modification of the value of oxygen saturation

428 It is obvious that, if the higher concentration appears in the double layer as has been  
429 assumed here, the two effects, on diffusion coefficient and oxygen saturation, would both be

430 involved and isolated calculations could not be made. The aim of this discussion was to  
431 highlight some effects and give an order of magnitude for them. Measurements close to the  
432 diffusion layer would be very interesting for a better prediction of the mass transfer  
433 coefficient in presence of contaminants and, as the calculated thicknesses of layers are in the  
434 range of possible visualization by microscopy, this opens up the promising perspective of  
435 building an accurate model for predicting mass transfer in the future.

436

## 437 **5. Conclusion**

438 The effect of surfactant and polymer on mass transfer from a single bubble rising in a liquid  
439 has been studied. It has been demonstrated that addition of surfactants and polymers decreases  
440 the velocity of bubbles and a combination of the two leads to an even greater decrease.  
441 Moreover, although little change is noticed in the size of the bubble when Triton X-100 is  
442 added, the bubble tends to become more spherical. This effect is also highlighted when  
443 polymer is added to the mixture of surfactant and water, but with an increase in the size of the  
444 bubble. These hydrodynamic changes have an impact on the mass transferred in the liquid.  
445 The liquid side mass transfer coefficient is reduced from  $4.9 \times 10^{-4}$  m/s in the case of water to  
446  $0.76 \times 10^{-4}$  m/s when surfactant is added, and addition of PAAm 0.1% in the latter solution  
447 causes the mass transfer coefficient  $k_L$  to decrease to  $0.62 \times 10^{-4}$  m/s. A part of this decrease in  
448 mass transfer coefficient can be explained by changes in the hydrodynamic parameters of the  
449 bubble, but correlations used in the literature to predict the mass transfer coefficient  $k_L$  by  
450 taking hydrodynamic parameters and physicochemical parameters of the bulk into account are  
451 not sufficient and lead to an overestimation of the mass transfer coefficient. To explain the  
452 overestimation, and the sharp decrease of mass transfer coefficient, it has been proposed that  
453 an accumulation of contaminants in the diffusion layer may lead to a higher concentration of  
454 surfactant and to physicochemical modifications, such as decreases in diffusion coefficient

455 and oxygen saturation. However, in order to propose a model, some information about the  
456 thickness of the diffusion layer, the concentration of contaminant and the associated diffusion  
457 coefficient and oxygen saturation concentration found experimentally are required.

458

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461 **Nomenclature**

462 *Notation*

463 a Width of bubble (mm)

464 A Parameter representing the Gaussian distribution of the oxygen field concentration  
465 (mg/L or mg/m<sup>3</sup>)

466 b Length of bubble (mm)

467 B Parameter representing the Gaussian distribution of the oxygen field concentration  
468 (pixel<sup>2</sup>)

469 CMC Critical Micellar Concentration

470 C Parameter representing the background noise of the image (-)

471  $d_{eq}$  Equivalent diameter of bubbles (mm or m)

472  $D_{O_2}$  Diffusion coefficient of oxygen (m<sup>2</sup>/s)

473  $F_{O_2}$  Flux of oxygen transferred (mg/s)

474 G Grey level of image in presence of oxygen

475  $G_0$  Grey level of image without oxygen

476 I maximum signal intensity

477  $I_0$  minimum signal intensity

478  $k_L$  Mass transfer coefficient of oxygen in the liquid side (m/s)

|     |               |   |
|-----|---------------|---|
| 479 | $k_{LF}$      | Mass transfer coefficient of oxygen in the liquid side predicted by the Frössling                         |
| 480 |               | correlation   |
| 481 |               | (m/s)   |
| 482 | $K_{sv}$      | Stern-Volmer constant (L/mg)  |
| 483 | $m_{O_2}$     | Total amount of oxygen transferred in a plane perpendicular to the wake ( $\text{mg}\cdot\text{m}^{-1}$ ) |
| 484 | $[O_2]$       | Oxygen concentration in the liquid ( $\text{mg/L}$ or $\text{mg/m}^3$ )                                   |
| 485 | $[O_2]^*$     | Oxygen concentration when the liquid is saturated with oxygen ( $\text{mg/L}$ or $\text{mg/m}^3$ )        |
| 486 | $S_b$         | Surface area of the bubble ( $\text{mm}^2$ or $\text{m}^2$ )  |
| 487 | $S_{spot}$    | Area of the diffusion spot ( $\text{mm}^2$ or $\text{m}^2$ )  |
| 488 | $U_b$         | Velocity of the bubble (m/s or mm/s)  |
| 489 | $x_p$         | Number of the line of the image (pixel)   |
| 490 | $x$           | Horizontal position (m)   |
| 491 | $X$           | Number of the line in the centre of the spot (pixel)  |
| 492 | $y_p$         | Number of the column of the image (pixel)   |
| 493 | $y$           | Vertical position (m)   |
| 494 | $Y$           | Number of the column in the centre of the spot (pixel)  |
| 495 |               | <i>Greek letters</i>  |
| 496 | $\gamma$      | Shear rate ( $\text{s}^{-1}$ )  |
| 497 | $\delta_{df}$ | Thickness of the diffusion layer estimated with the double film theory ( $\mu\text{m}$ )                  |
| 498 | $\delta_{df}$ | Thickness of the diffusion layer estimated with Péclet Number ( $\mu\text{m}$ )                           |
| 499 | $\eta$        | Viscosity (Pa.s)  |
| 500 | $\eta_D$      | Fixed parameter for determination of the diffusion coefficient (-).                                       |
| 501 | $\sigma$      | Surface tension (mN/m)  |
| 502 | $\sigma_n$    | Standard deviation of the background noise  |
| 503 | $\rho$        | Density ( $\text{kg/m}^3$ )   |

504 *Dimensionless numbers*

505 Pe Péclet number ( $Pe=d_{eq}\times U_b/D$ )

506 Re Reynolds number ( $Re=U_b\times d_{eq}\times\rho/\eta$ )

507 Sc Schmidt number ( $Sc=\eta/(\rho\times D)$ )

508 Sh Sherwood number ( $Sh=k_L\times d_{eq}/D$ )

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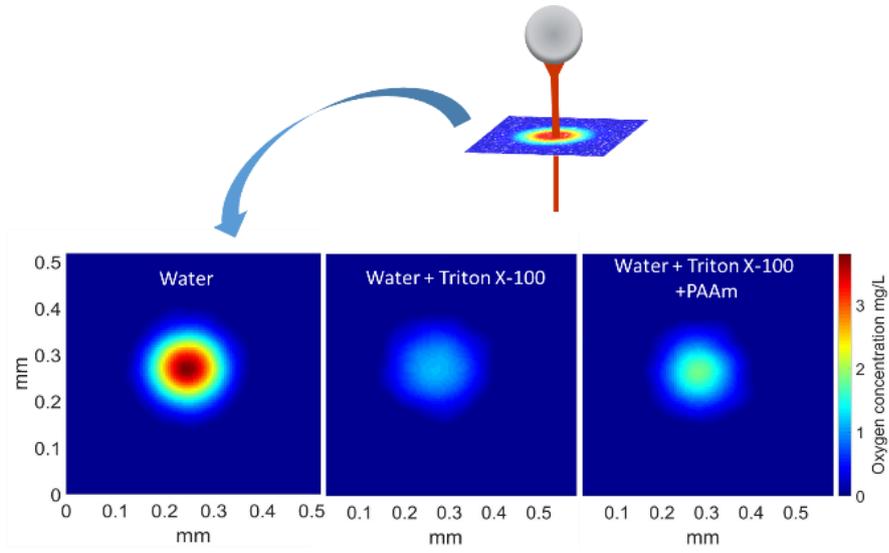
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695 Graphical abstract



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