Simultaneous 2-Tracer-LIF and PIV for the study of mass transfer around single CO$_2$-bubbles

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**ABSTRACT**

Bubble column reactors are used for different chemical and biological processes in industry. Dispersed gas comes into reaction with the liquid phase through gas-liquid mass transfer. Often mass transfer is the limiting factor for the reaction and its investigation and characterization becomes important for the optimization of a reactor. In the literature, mass transfer experiments use typically two types of reaction systems. In the first, oxygen is dissolved in a sulphite solution, and the oxygen concentration in the liquid is measured by means of a specific fluorescent dye. In the other reaction system, CO$_2$ gas is dissolved in an aqueous liquid. Here, the pH of water is changing during the reaction and with a pH sensitive fluorescent dye, this change is traceable through the fluorescence intensity. To gain more information about the liquid flow and the mass transfer around a single bubble, in this study three types of measurements are presented. First of all, high-speed LIF measurements of CO$_2$ transfer from the bubbles to the liquid are analysed. Then high speed PIV measurements were carried out to investigate the flow around the bubbles. At last simultaneous measurements of liquid velocity and pH around single rising ellipsoidal CO$_2$ bubbles in a round column using PIV and 2-Tracer LIF were implemented. The zig-zagging bubbles of 2-3 mm diameter are examined using uranine as fluorescent pH-tracer. Since the generated bubbles in this size regime have a three dimensional rising path, the combined PIV-LIF images were taken before the first inflection point of the bubble path, where bubble motion is still more or less two dimensional. The reflections on the bubble surface and the bubble shadows were reduced by the help of a simultaneously recorded live background.

**1. Introduction**

Bubble column reactors are used for different chemical and biological processes in industry. Dispersed gas comes into reaction with the liquid phase through gas-liquid mass transfer. Often mass transfer is the limiting factor for the reaction and its investigation and characterization becomes important for the optimization of a reactor.

Mass transfer from single bubbles, rising in a liquid is studied in a wealth of research groups. In the past, mostly gas probes have been used for the determination of mass transfer. Here we will concentrate on optical methods (direct observation, shadowgraphy and LIF) used for the determination of local gas concentrations. The absorption of oxygen is studied by the quenching
of laser-induced fluorescence of ruthenium complexes in the group of Cockx, Guiraud and Hébrard in Toulouse [1-3]. Dani [1] describes in detail the method used for a single rising bubble in a quadratic column. Due to the difficulties encountered e.g. from reflections on the bubble surface, Francois [2] changed the observation direction from a vertical laser light sheet to a horizontal one, with an observation of fluorescence from the bottom of the quadratic column. Thus they can reconstruct the complete oxygen wake of a rising bubble. The mass transfer is quantified as fluxes from the bubble to the liquid for different bubble sizes (0.7-1.9mm) and ethanol-water-glycerol mixtures. Simultaneously the bubble size and trajectory is monitored by shadowgraphy, using a high-speed camera. Jimenez [3] then used this set-up for the analysis of mass transfer from ellipsoidal, zigzagging bubbles and different surface tension and viscosity liquids, also with simultaneous high-speed imaging of the bubbles.

The groups of Räbiger and Schlüter in Bremen and Hamburg also use oxygen quenching of the fluorescence of ruthenium complexes for the determination of mass transfer from single bubbles under counter current conditions [4, 5]. In [5] they combine their LIF-System with simultaneous PIV measurements of the flow field around bubbles with 1-2.5mm diameter. Provided that the bubbles have strictly vertical trajectories and thus axisymmetric concentration and velocity fields, the authors derive from these measurements the convective mass transfer from the bubble to the fluid. Superimposed chemical reaction of oxygen, transferred from freely rising 1mm bubbles in a sulphite solution is analysed by the same groups in [6]. Here they also acquire the simultaneous velocity field around the bubbles and compare with numerical simulations. The mass transfer from CO, Taylor bubbles in microchannels is determined in [7]. Here the bubble shrinkage is visualised directly and used for the determination of ka-values.

Oxygen transfer from bubbles in organic solutions has been studied by Maceiras [8] in a quadratic column and counterflowing liquid. They observe the bubbles by direct observation, mass transfer is only monitored by an oxygen meter. In the study of Sharifullin [9] mass transfer is quantified by an optical probe in a counter-current loop reactor. They thus study the influence of surfactants on mass transfer.

Mass transfer from single CO₂-bubbles has been examined in the group of Saito [10, 11]. They developed a photoelectric optical fibre probe for the simultaneous determination of bubble cord length, velocity, void fraction and local CO₂-concentration in the liquid [11]. Zigzagging bubbles of 2.9 mm in diameter are used in an LIF experiment based on the fluorescent pH-Tracer HPTS in a square column [10]. Bubble shapes and trajectories, as well as mass transfer are observed in these measurements.
Bubbles in the same size range are also examined by Nock et. al. [12] by high speed imaging and a pH-meter to determine global mass transfer. In [13] the authors determine the shrinkage of small (0.3 mm) CO₂ bubbles in different alkaline solutions and calculate dissolution rates. The effect of surfactants and other contaminations on mass transfer from single CO₂ bubbles is examined by Aoki et. al. [14, 15]. They use Taylor bubbles from 5 to 25 mm and evaluate the kₐ-value from the decrease of bubble diameter.

In this paper we present high-speed and simultaneous measurements of liquid velocity and pH around single rising ellipsoidal CO₂ bubbles in a round column using PIV and 2-Tracer LIF. The zigzagging bubbles of 2-3 mm diameter are examined using uranine as fluorescent pH-tracer.

2. Experimental Set-ups and procedures

All experiments have been carried out in the same bubble column. A full description of the bubble column reactor has been published before [16, 17]. Therefore only the main information concerning the geometry, process parameters and measurement techniques are given here.

The bubble column has an inner diameter of 0.142 m (Fig.1) and is made from acrylic glass. In the bottom, one stainless steel nozzle with an inner diameter of 0.25 mm is placed for the generation of gas bubbles with a diameter of 2.3-3 mm, de-ionized water was used as liquid phase in the experiments. CO₂-gas with a purity of 99.5% was supplied from a pressurized bottle to form the bubbles. They rise in a stagnant fluid.

To investigate the flow and visualize the mass transfer around single CO₂ bubbles, three different measurement set-ups were applied.
2.1. LIF measurement with intensified high speed camera
Mass transfer in the bubble wake has been imaged by an Imager pro HS 4M CCD high speed camera. It was equipped with an image intensifier and a Nikon AF Micro Nikkor 105mm lens and had a resolution of 2016x2016 pixels. A 555nm longpass filter was mounted to suppress the laser light reflections on the bubble surface. As tracer, the pH sensitive fluorescent dye uranine was added into the water. To excite the dye, a high speed Nd:YLF laser (Litron) with a wavelength of 527 nm and an energy of 12.7 mJ/P was used at 450 Hz. The laser beam has been expanded by a light sheet optics and images were taken with a frame rate of 450 Hz just in the region above the nozzle exit.

2.2. PIV measurement with high speed camera
To get time-resolved velocity measurements in the flow around the bubble, the above mentioned high speed camera and laser combination was used for PIV measurements without the image intensifier. As tracer particles, polymethyl methacrylate (PMMA) Rhodamin B particles with a mean diameter of 10 µm were added to the fluid. Therefore, the optical filter was changed to a 537nm longpass filter. The images were taken as a time series with a frame rate of 1 kHz. Images were taken just 23mm over the bubble outlet. The geometrical calibration has been done with a 3D calibration target.

2.3. Combined LIF-PIV measurements
For the simultaneous characterization of the flow field and mass transfer around a single bubble PIV and Two-Tracer-LIF (2T-LIF) have been used. On one side of the bubble column an Imager Intense CCD camera with a 1376x1040 pixel² resolution recorded the double-frame PIV images. On the other side of the bubble column an Imager LX 8M CCD camera with 3312x2488 pixel² was mounted to record the LIF images from the pH sensitive fluorescent uranine dye. This tracer is dissolved in the de-ionized water, together with another tracer, that stays passive (pyridine 2). This tracer will enhance the live background for the LIF images. With the help of the live background, reflections on the bubble surface, bubble shadows and the laser sheet inhomogeneity can be reduced (see Fig. 2, for an example of a bubble curtain).

Fig. 2 2T-LIF technique; left: raw image from 1st camera (uranine); middle: raw image from 2nd camera (pyridine 2); right: resulting image

Ethidium bromide doped melamine resin particles with a diameter of 6.72μm were added to the liquid for the PIV measurements. The fluorescent dyes and particles were excited by a double-pulsed Nd:YAG laser (Spectra Physics) at 532nm. The laser beam has been expanded by a light sheet optics to a 15x20 mm² region of interest and a thickness of less than 0.5mm. All cameras were equipped with a Nikon AF Micro Nikkor 105mm lens. Optical filters were mounted according to the wavelength of the emitted light (Table 1).

<table>
<thead>
<tr>
<th></th>
<th>Excitation</th>
<th>Emission peak</th>
<th>Applied optical filter</th>
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<tbody>
<tr>
<td>Uranine dye</td>
<td>532nm</td>
<td>550nm</td>
<td>550nm bandpass</td>
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<tr>
<td>Pyridine 2 dye</td>
<td>532nm</td>
<td>705nm</td>
<td>555nm longpass</td>
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<tr>
<td>Ethidium bromide particles</td>
<td>532nm</td>
<td>600nm</td>
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Table 1 Emission peaks and selected filters

The geometrical positions were calibrated with a self-designed calibration target. On this target 20x20 dots were printed with a diameter of 0.8mm and a distance of 1.5mm. The cameras were triggered simultaneously with a frame rate of 3.3 Hz; single frame for the LIF camera; double-frame with a 750ns delay for the PIV camera.

The flow rate of CO₂ was set with a mass flow controller (Bronkhorst) to 4.8 ml/h. At this gas volume flow the single bubble generation through the steel capillary was almost constant with a 2.5-2.77 Hz bubble formation frequency. A light gate sensor was mounted just above the nozzle. When the bubble leaves the nozzle, it passes through the light gate and a trigger signal is sent to the computer to start the recording. The investigation window started 33mm above the nozzle outlet. The average vertical velocity of the bubbles was 0.3 m/s and they need about 110 ms to reach the recording area. In an ideal case, each recorded bubble would be at the same location on the images and this location could be modified with an additional recording delay. But in reality the exact bubble locations on the image is hard to predict, since the generated bubbles do not have exactly the same diameter, form and path. As we chose to generate technically relevant bubble diameters between 2.2 and 2.6 mm, the bubbles are not following a straight vertical path and they are no more spherical. They will only follow a straight path very near to the outlet, then a two dimensional zig-zag path, which broadens into a three dimensional helical path (Fig. 3). If the generated bubbles have a slight diameter difference, the bubble path would also change slightly. The challenging task was now to find the optimal location, where the bubbles already are wobbling, but still have a more or less two dimensional path to stay in the laser light sheet for a short while. High speed recordings were used to define this location (Fig. 3) up to 42 mm above the nozzle.
3. Post-processing of raw images and results

3.1. LIF measurements with intensified high speed camera

Mass transfer from single CO₂ bubbles into water is visualized by high speed LIF measurements with uranine as fluorescent tracer of the pH change. To enhance detection of the emitted fluorescence light, an image intensifier was mounted onto the high speed camera (Fig. 4). The images were recorded near to the nozzle output, to be sure, that the rising bubbles are staying in the light sheet.

On the images mass transfer from the CO₂ bubbles into water is clearly visible through the darker wake behind the bubbles. When the bubble just leaves the nozzle, this wake has a horseshoe like form (Fig. 5). When further rising in the liquid, the flow velocity around the bubble will be faster and the liquid renewal around the bubble is faster too. Thus less CO₂-concentrated solution will be transported to the bottom of the bubble and dissolve the wake. Then a new bubble arrives, and
thus the wake is also split through the vortex structures of this bubble. A series of such high speed images for one bubble cycle is shown in Fig. 5.

![High speed LIF image series with 4.4ms time step](image)

**Fig. 5** High speed LIF image series with 4.4ms time step

### 3.2. PIV measurements with high speed camera

Postprocessing of the raw PIV images started with masking out of bubbles and their shadows (Fig. 6), to avoid false vectors in these regions.

![Raw PIV image – left, and masked image – right](image)

**Fig. 6** Raw PIV image – left, and masked image – right

For the vector calculation a cross-correlation (multi-pass, decreasing size) PIV algorithm was used, with an interrogation window size from 64x64 pixels to 32x32 pixels. Then, with the help of a median filter, the vectors have been refined. For this, the median vector from the 8 neighbouring interrogation areas is computed and then compared to the vector in the centre. Its deviation from the neighbouring vectors, is evaluated and the highest (but in some cases wrong) correlation peak
was replaced by the second, third or fourth highest correlation peak, until a sufficient agreement is obtained within the neighbourhood. The current vector position was disabled if none of the four peaks were in the allowed range of the median vector. These few disabled areas were afterwards replaced with an interpolated value from the 8 neighbours.

The PIV series of a rising single bubble (Fig. 7), shows higher liquid velocity, with a maximal velocity magnitude of about 25 cm/s before and behind the bubble, whereas further away from the bubbles velocity is nearly zero. On both sides of the bubble, characteristic recirculation zones are recognizable, which show the displacement of the liquid as the bubble rises. These vortices cause some turbulent structures in the wake of the bubble.
Fig. 7 Vertical (left) and horizontal (right) velocity component (m/s) around a rising bubble (bubble and its shadow masked out); time step 6ms

3.3. Combined LIF-PIV measurement

As mentioned before, the generated bubbles had slightly different diameters and aspect ratios. They therefore had always slightly different rising paths and velocities. Fig. 8, left shows the summarized contour image of 60 single bubbles. It is clearly recognizable, that they follow almost the same path, but they overlap each other just rarely. For this reason, the evaluated liquid velocity fields at each position could not be averaged.

The PIV raw images have also been used to determine the bubble velocity. Since the time between two double images is known, the displacement of the bubble centroid and its velocity could be determined. This is depicted in Fig. 8 right for the case of six single bubbles, which are summarized at different positions to one image. It can be recognized, that the bubble velocity lies between 30 and 37 cm/s with a mean value of 34 cm/s for all evaluated bubbles.
Fig. 8 Bubble path in the investigation area: sum of 60 single bubbles (left); trajectories and velocity magnitudes for 6 single bubbles (right)

For the liquid velocity calculation the same evaluation procedure was applied as for the high speed images. Bubbles and shadows were masked out by the help of an algorithmic mask function. Before and behind the bubble a higher liquid velocity was noticeable, just as on the high speed images. Moreover the recirculation on both sides was also clearly visible. This flow generates small turbulent structures in the wake of each bubble (Fig. 9).
Fig. 9 Vertical (left) and horizontal (right) velocity components (m/s) for six bubble snapshots (not the same bubble)
Due to the three-dimensional bubble movement, as expected, a long wake could be recognized behind the bubble, if its trajectory stayed in the laser light sheet for a longer time (Fig. 10, left). But, if the bubble just passed through the light sheet in the third dimension, the wake seems smaller, as it follows the direction of the bubble trajectory (Fig. 10, right). The comparison of the maximal velocity magnitudes sustains this three-dimensional explication. A bubble, which stayed longer in the light sheet, has maximal 2d-velocity magnitudes of about 25 cm/s, while it is 20 cm/s for bubbles, which just passed through the light sheet in the third dimension.

![Fig. 10 Vertical velocity components of two bubbles: bubble which stays longer in the light sheet plane (left) and bubble that crosses the light sheet plane (right)](image)

Mass transfer has been recorded at different pH values between 9 and 5. The concentration of the pH sensitive fluorescent dye (uranine) was 20mg/l. During the LIF image evaluation process an active background is used to reduce light inhomogeneities due to the bubbles (reflection, shadows). In this study, the PIV-images served as an active background together with a small amount of pyridine 2 (1mg/l), added into the water. Pyridine 2 has an emission peak at 705 nm, therefore it is not visible on the uranine images, where a 550nm bandpass filter with 10nm bandwidth was applied, but it’s fluorescence is visible on the PIV images, where a 555nm longpass filter was mounted on the camera lens. Thus, the inert dye pyridine 2 represents the actual lighting situation at each image taken simultaneously with the pH-sensitive uranine.

All post processing steps for the LIF images are summarized on Fig. 11. For the background images, the raw PIV images were treated with a 9x9 pixel gaussian smoothing filter. With the help of this filter, the tracer particles were filtered out, but the reflections and shadows remained. Thus, this image could then be used as a simultaneous background for the uranine images.
Camera noise removal - **dark image subtraction**
Laser light absorption - **laser sheet correction**
Set the image from raw to world coordinates - **geometrical calibration**
Suppress reflections and shadows - **active background from PIV/pyridine image - 2T-LIF**
Convert intensity values to pH values - **pH calibration**

**Fig. 11** 2T-LIF processing steps

For the pH calibration, image sets were taken at different pH values without bubbles, to record the typical fluorescence intensity for each pH value in the water bulk. These images were treated in the same way, as the bubble images afterwards. Then, a pH calibration curve was fitted to the thus obtained intensity values (Fig.12) and with the help of the generated equation, every pixel on the LIF images could be calibrated to get the pH from the intensity values.

![Graph showing the pH calibration curve](image)

\[ y = 9.1923e^{-0.6}x^3 - 0.0015909x^2 + 0.10096x + 3.5781 \]

**Fig. 12** pH calibration curve for LIF processing

To compare the above mentioned 2T-LIF processing method with a standard evaluation without simultaneous background, the same image has been treated in both ways in Fig. 13. It can be recognized, that the inhomogeneities due to the bubble influence are reduced very strongly. On the left image, with conventional static background, the bulk fluid pH seems to vary from 9 (due to a reflection) to 6 (in the shadow). On the right, with simultaneous live background the actual pH of 7 from the initial solution can be found. Unfortunately it is not possible to remove completely the shadow and reflection influence with this method. This is also due to the very small pH difference (about 0.3) in the bubble wake and thus the dynamic range in the image representation is rather small.
As for the PIV images, the thin mass transfer wake with slightly lower pH is visible on the LIF images, behind the bubbles as a thin, long trail, if the bubble trajectory was in the light sheet for a longer while (Fig 14.). If the bubble trajectory crossed the light sheet in the investigated area, the visible wake is short. In this trail, the pH value is around 0.25-0.35 lower than in the surrounding liquid, because of the dissolved CO$_2$ gas. Due to the stronger sensitivity of uranine in the pH rage from 6 to 7, this trail is most visible at these pH values.
4. Conclusions
In the present study the flow and mass transfer around ascending CO₂ bubbles in a stagnant fluid has been examined. The experiments were carried out in a bubble column with an inner diameter of 142mm, to avoid wall effects to the bubble motion. The final aim was to investigate the flow and the mass transfer at the same time around a single bubble. The combined PIV-LIF experiment was based on experiences gained through high speed PIV and LIF experiments. The simultaneous images of zigzagging bubbles were taken at 33mm above the nozzle, just before the first inflection point of the ascending bubbles. At this location, the bubbles still have an almost two-dimensional movement. Therefore it was possible to measure velocity and pH in the wake of the bubbles. Dissolved CO₂ is transported to the sides and mainly the bottom of the bubbles, where it lowers the pH of the liquid and forms a long wake behind the bubble. In this wake, the pH is around 0.3
points less than in the bulk liquid. This small pH change can best be followed in the range of pH=6...7, where the applied fluorescent dye (uranine) fluorescence intensity changes the most dynamically. The acquired live background image with an inert second dye (2T-LIF) allowed for a much more exact calibration of the surrounding liquid pH.

In the light of these results can be concluded, that three dimensional measurements of the process, like e.g. tomographic PIV would allow to get more information about the flow around an ellipsoidal, zigzagging single rising bubble. These measurements are planned in the near future.

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**5. Literature**


