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Quantitative Measurements of Micro- and Macromixing in a Stirred Vessel using Planar Laser-Induced Fluorescence

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Abstract : The Planar Laser-Induced Fluorescence (PLIF) technique enables measurement of the local degree of deviation in an arbitrary plane inside the mixing vessel. This is achieved by injecting a mixture of an inert dye and a reacting fluorescent into the vessel. The inert dye serves as a tracer for the macromixing. The fluorescent characteristics of the reacting dye change while undergoing a fast chemical reaction with the vessel content and it therefore shows the micromixing indirectly. The concentration fields of the dyes are measured simultaneously. For that a laser beam is expanded into a thin light sheet which illuminates an arbitrary plane in the mixing vessel, exciting the fluorescent dye in this area. The emitted light is detected by a CCD-camera which is positioned vertical to the measurement plane. The fluorescent light passes through two optical filters which are suitable for separating the fluorescent light of the two dyes. The light is then projected on half of the camera chip each so that the same display window is detected twice, and thus the local concentration of the two dyes can be measured simultaneously. Low Reynolds number measurements are performed in a mixing vessel equipped with a Rushton turbine. The lamellar structure is clearly resolved. Areas of micromixing are detected by calculating the local degree of deviation from the concentration fields. These areas are mainly found in the boundary layer of the lamellas.

Keywords : Micro- and macromixing, LIF, Stirred vessel, Concentration field.

1. Introduction

The blending of various liquids is a fundamental task in the chemical, pharmaceutical and food industries. During the mixing process transport phenomena with different characteristic length and time scales occur. At the beginning of the laminar mixing process the injected dye is transported convectively throughout the mixing vessel forming homogeneous lamellas with the vessel contents. Due to a deformation in the flow field the lamellas become thinner and longer with increasing mixing time. As the thickness of the lamellas decreases, the concentration gradient becomes steeper and diffusion becomes more important. Finally, a molecular-scale equilibrium state is reached. If the mixing process is accompanied by a fast chemical reaction, the selectivity of the mixing process depends on the quality of the mixing. Therefore, the composition at the molecular

scale of the compounds must be known in order to predict the processing of the chemical reaction. For the laminar mixing process, the local value may vary strongly because the molecular transport is not independent of the (relatively) slow convective transport.

Concentration differences on the molecular scale can not be measured directly. Small-scale measurements which allow structures smaller than 100μm to be resolved were performed by Bakker and van den Akker in 1996, but the molecular scale still can not be resolved. Hence, a variety of techniques for indirectly measuring the characteristic features of the micromixing have been developed. Several studies, mostly on turbulent mixing, have been conducted (Baldyga and Pohorecki, 1995; Bourne and Baldyga, 1983; Ottino, 1994). Most of these techniques lack the necessary spatial resolution and can only determine global, averaged values. As described above, for the laminar mixing process, spatially and/or temporally averaged data for the concentration field are of limited importance.

The laser-induced fluorescence technique is suitable for the measurement of small-scale structures, either point-by-point or on a two-dimensional plane. This technique is used primarily for the visualization of passive scalars (Distelhoff et al., 2000; Unger and Muzzio, 1999; Guillard, Träghard and Fuchs, 2000). Reactive tracers, mostly pH-sensitive dyes, are used to measure the micromixing indirectly (Bellerose and Rogers, 1994). Sakakibara and Adrian (1999) used two different dyes to measure temperature fields. The fluorescent characteristics of one of the dyes change with temperature; whereas those of the other dye are independent of temperature. The ratio of fluorescence intensities, measured at different wavelengths, is independent of concentration, laser power and absorption.

Buchmann and Mewes (1998) used the tomographic dual-wavelength photometry to measure the three-dimensional concentration fields of one inert dye and one reacting dye simultaneously. Zones of macro- and micromixing are detected in a mixing vessel equipped with various stirrers. However, the spatial resolution of the tomographic system was not sufficient to resolve the lamellar structures.

In the present paper, an experimental technique is presented that provides high spatial and temporal resolution for local measures of the macro- and micromixing simultaneously.

2. Experimental Technique

In order to distinguish between macro- and micromixing, a mixture of two dyes is injected into the mixing vessel. One of the dyes is an inert dye, and the other dye undergoes a fast chemical reaction with the contents of the vessel. The distribution of the inert dye serves as a tracer for the macromixing, but does not predicate the mixing quality on the nano scale. The chemical reaction requires mixing on the molecular scale. Therefore, the reacting dye indirectly visualizes the micromixing. In analogy to Danckwerts' intensity of segregation (Danckwerts, 1958), a local degree of deviation Δ is defined as a measure of the micromixing, and is obtained by comparing the local concentration of the reacting dye $c_{2,\mathrm{react}}$, which is produced during the reaction, with the concentration c_2 the reacting dye would have locally if the reaction would not have taken place:

$$\Delta = 1 - \frac{c_{2,\mathrm{react}}\left(\vec{x},t\right)}{c_2\left(\vec{x},t\right)}. \tag{1}$$

The latter is calculated from the local concentration of the inert dye c_1, considering also the initial concentration ratio:

$$c_2\left(\vec{x},t\right) = c_1\left(\vec{x},t\right)\frac{c_{2,0}}{c_{1,0}}. \tag{2}$$

The macromixing leads to an equal degree of dilution of both dyes; whereas the micromixing varies only the concentration of the reacting dye. For a completely segregated fluid, the local degree of deviation is one. During the micromixing, the local degree of deviation decreases to its minimum value of zero for a completely homogeneous fluid.

2.1 Fluorescent dyes

A system of two fluorescent dyes is used for the experiments. The following set of predetermined criteria, as well as other criteria, must be met. The dyes are required to be excitable at the same wavelength, and their emission characteristics must be distinguishable. Only one of the dyes should undergo a chemical reaction which alters its fluorescent behavior.

Two dyes purchased from Molecular Probes are used. The reacting dye, fluo-3, is an indicator for Calcium ions and is essentially non-fluorescent unless bound to Ca^{2+}. In this case, the fluorescence intensity is enhanced depending on the concentration of Calcium ions, as shown in Fig. 1 a). For a concentration of free Ca^{2+} of approximately 40 μM, a saturation condition is reached and the fluorescence intensity shows its maximum. Only this condition is used during the experiments since only the concentration of the dye which has already reacted with its environment (and therefore has been mixed on the molecular scale) is of interest. The absorption and the emission spectrum of fluo-3 in the saturated condition is shown in Fig. 1 b).

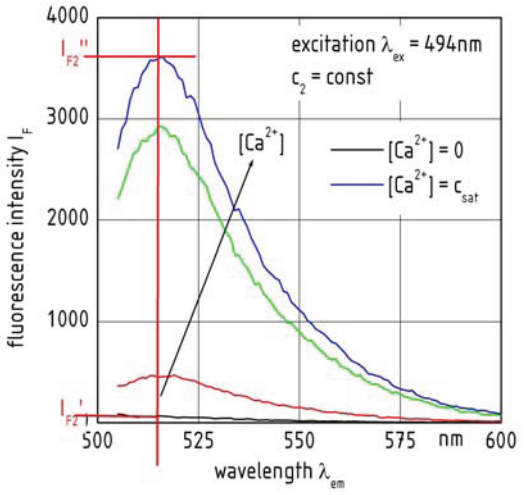


Fig. 1a. Fluorescence emission spectrum of fluo-3 for variable concentrations of Ca^{2+}.

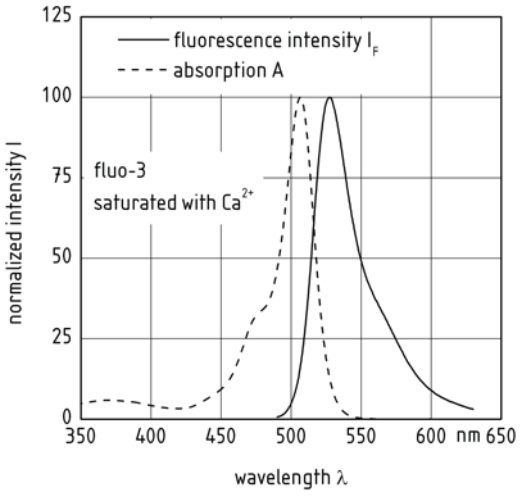


Fig. 1b. Normalized absorption and fluorescence emission spectrum of fluo-3, saturated with Ca^{2+}.

The second dye, carboxy-SNARF, does not react with Calcium ions and therefore serves as the inert dye. On the other hand, its absorption and emission spectrum varies greatly with pH, as shown in Fig. 2. Therefore, a buffer solution of constant pH must be used. During the experiments, a buffer solution of pH = 8 is used. As such, carboxy-SNARF is excitable at the same wavelength as fluo-3 but can be detected at much longer wavelengths, which allows separation of the fluorescent light by means of optical filters.

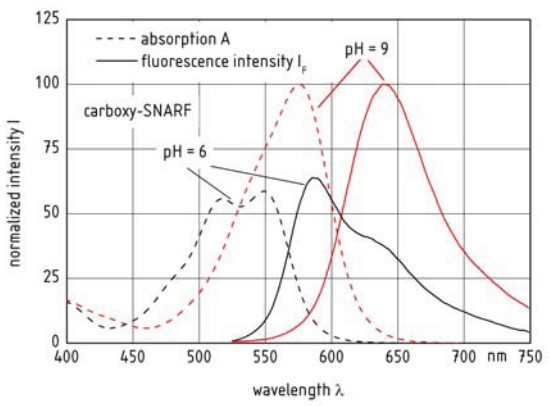


Fig. 2. Normalized absorption and fluorescence emission spectrum of carboxy-SNARF for pH = 6 and 9.

The fluorescence intensity emitted by a fluorescent dye I_F is proportional to the intensity of the light absorbed by the dye I, which is calculated by Lambert-Beer's Law. The quantum yield Φ describes the effectiveness of the fluorescent emission:

$$I_F = \Phi I = \Phi I_0 e^{-\varepsilon b c}. \tag{3}$$

where I_0 is the intensity of the exciting light, ε is the molar extinction coefficient and b is the length of the measurement volume. For small concentrations, Eq. (3) can be simplified by a series expansion so that I_F is linearly dependent on only the concentration c of the dye:

$$I_F = I_0 K \Phi \varepsilon b c \tag{4}$$

where K is a parameter that depends on the measurement system, considering for example the viewing angle of the detector. For constant parameters I_0, K, Φ, ε and b, which is valid under certain conditions, only a simple calibration procedure involving measurement of the fluorescence intensity for known dye concentrations is necessary in order to predict the concentration from measured intensities.

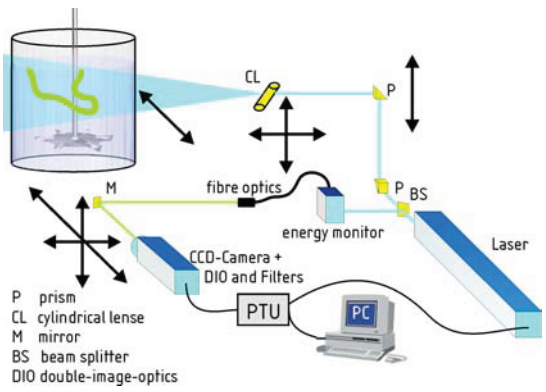
2.2 Optical Set-up for the Planar Laser-Induced Fluorescence (PLIF) Technique

The Planar Laser-Induced Fluorescence (PLIF) technique is used to measure the concentration fields of both dyes simultaneously in the mixing vessel. The optical set-up is schematically depicted in Fig. 3a, and a photograph of the experimental set-up is presented in Fig. 3b.

As a light source, a pulsed laser of wavelength λ = 510 nm (NewWave Nd : Yag, Tempest 30 and GWU OPO VisIr) is used. The laser beam is split at a ratio of approximately 9:1 by a beam splitter. The beam of higher energy is expanded to a thin light sheet using a system of spherical and cylindrical lenses. The divergent light sheet illuminates an arbitrary plane in the mixing vessel, exciting the fluorescent dye in this area. The emitted light is detected by a CCD-camera (LaVision, Imager 3L) which is positioned vertical to the measurement plane. At the same time, an energy monitor, powered by the second laser beam, is detected by the camera. The functionality of the energy monitor will be explained in detail later. The light sheet optics, the mixing vessel and the camera are mounted to a linear positioning system so as to allow reproducible adjustment. The exposure of the camera and the pulsation of the laser are controlled by a computer. The measurement frequency is 30 Hz and the resolution of the camera is 640 x 480 pixels. With the start of the camera exposure the injection of the dye is automatically begun. The position of the injection and the flow rate can be adjusted within wide limits. The fluorescent light is passing

through two optical filters (BP523/10 and RG645) which are suitable for the separation of the fluorescent light of the two dyes. The light is then projected on both halves of the camera chip using double-image optics (LaVision), the functionality of which will be explained later. Hence, the local concentrations of the two dyes can be measured simultaneously, which allows calculation of the local degree of deviation according to Eq. (1).

(a)



(b)

Fig. 3. Optical set-up for the Planar Laser-Induced Fluorescence (PLIF) Technique.
(a) schematic diagram, (b) photograph.

2.3 Calibration Procedures

Before experimental results are presented in the next section we describe the calibration procedures used in the present study, which are necessary in order to obtain not only qualitative but also quantitative results from the measured values.

2.3.1 Double-Image Optics

Double-image optics are used to simultaneously detect the same display window twice. The double-image optic consists of two apertures and a set of adjustable and fixed mirrors. The light emitted by the fluorescent dyes passes through the two apertures which can be equipped with optical filters so that only light of a certain wavelength can pass through. The light is then reflected by the mirrors onto the light-sensitive camera chip such that the same display window (AOI) is projected side-by-side on the camera chip with each half representing the fluorescent light emitted by one of the fluorescent dyes. The intensity of the light is measured in 12-bit gray values.

Since the AOI is imaged by two different apertures with a small space between, the angle of

detection is not the same. This effect of oblique viewing has to be considered by calibrating the system before measurement. Therefore, a calibration plate, i.e. a black plate with white marks of defined spacing, is placed at the same position as the laser light sheet. A mapping function is calculated by cross-correlating the marks on the plate. The images are corrected by applying the inverse of the mapping function on the images.

2.3.2 Correction of the Laser Profile

The intensity of the laser beam is not homogeneous over the radius, but rather is higher in the center and decreases towards the boundary. By expanding the laser beam into a light sheet the profile is flattened but remains. Therefore, the image $K(x,y)$ of a solution of fluorescent dye with constant concentration has varying intensities for pixels x_i, y_j, as shown in Fig. 4a. For small concentrations, absorption phenomena are negligible and this image $K(x,y)$, with the average value $\bar{k} = \frac{1}{mn}\sum_{i=1}^{n}\sum_{j=1}^{m} K(x_i, y_j)$, can be used to calculate a correction matrix by simply inverting the image:

$$M(x,y) = \frac{\bar{k}}{K(x,y)} \tag{5}$$

The corrected image $K_{korr}(x,y) = K(x,y) \cdot M(x,y)$ has a relatively smooth profile over the whole image, as shown in Fig. 4b. The intensity values vary with a standard deviation of 6.3 around the mean fluorescence intensity for a solution of constant concentration of I_F = 190.7. These variations cannot be corrected for, so that the measurement error of the method is 3.3%.

a)

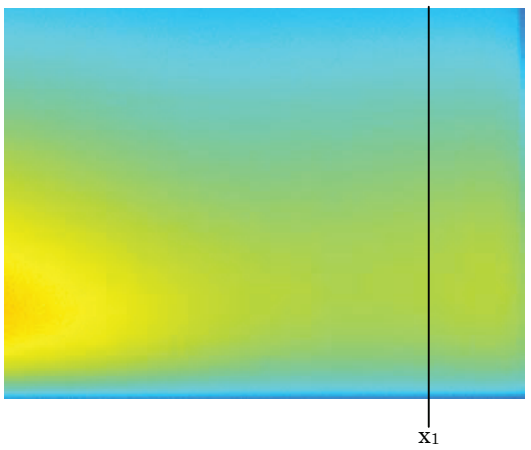


Fig. 4a. Image of a solution of fluorescent dye with constant concentration.

b)

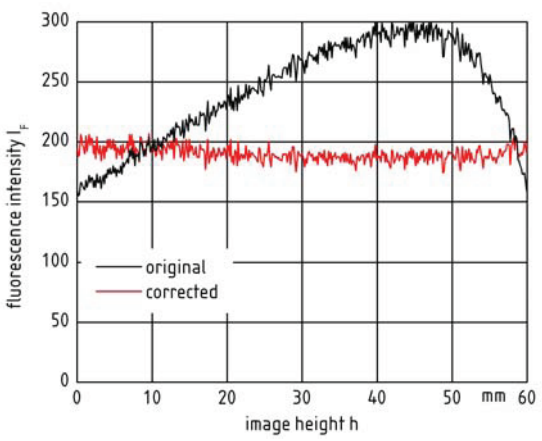


Fig. 4b. Original and corrected profile at position x_1 of the image in Fig. 4a.

2.3.3 Energy Monitor

A pulsed laser was used as the light source. Since the energy emitted by the laser varies from pulse to pulse, the energy must be measured online. If the intensity of the exciting light I_0 is unknown, the intensity of the fluorescent light I_F cannot be uniquely related to the concentration c of the dye according to Eq. (3). Variation in the measured intensity could be caused by either a difference in the concentration of the dye or by a different energy of the exciting light source.

Therefore, an energy monitor was installed, and the laser beam was split at the ratio of approximately 9:1 using a beam splitter. The laser beam of lower energy is used to illuminate a small cuvette filled with fluorescent dye. This cuvette is placed inside a small box in order to prevent reflections from being detected by the camera. The fluorescent light emitted by the dye is

detected by a fiber optic which is directed towards a small mirror. This mirror is placed such that the small light point of the fiber optics is focused on the camera chip. The average of the intensity measured over the area of the light point $e_{avg}(n)$ is calculated for each laser pulse n and is then averaged over the time $\overline{e}_{avg}$ to obtain a reference value. Both values are then used to correct the measured intensities I_F of the whole image:

$$I_{F,korr}(n) = I_F(n) \frac{\overline{e}_{avg}}{e_{avg}(n)}. \quad (6)$$

Due to the application of the energy monitor, the measurement errors caused by variations of the laser power can be reduced by at least 50%.

3. Experimental Results

Measurements are performed in a flat-bottomed, transparent vessel of diameter 100 mm placed inside a rectangular viewbox filled with water in order to minimize reflections and distortions. The vessel is filled to a height of 125 mm. The Rushton turbine is placed in the center of the vessel. The stirrer speed is 300 min^{-1}, which gives a Reynolds number in the laminar region.

In order to achieve low Reynolds number mixing, the viscosity of the liquid is increased. This is achieved by dissolving 1% (w/w) carboxy-methyl-cellulose (CRT 10000, Wolff Walsrode) in the liquid, which leads to a shear thinning behavior of the liquid. Viscosity measurements of the liquid are very well described with the Bird-Carreau model, with a zero shear rate viscosity of 1 Pas and a power law index of 0.55. The refraction index of the aqueous solution is nearly the same as that of water. A calcium salt ($CaCl_2$) is dissolved in the liquid and a constant value of pH = 8.0 is adjusted using a Tris-buffer (Tris(hydroxymethyl)aminomethane).

A mixture of the inert dye with $c_{1,0}$=5,5 10^{-5} mol/l and the reacting dye with $c_{2,0}$ = 3,9 10^{-5} mol/l is prepared, and a volume of 1 ml is injected into the vessel after the velocity field reached a steady state. Measurements are performed only for a short period of time, on the order of 1 minute, so that temperature variations are negligible. The injection position is located in the upper vortex close to the stirrer shaft. The distribution of the two dyes is measured in the symmetry plane of the vessel. The display window is of size 28 x 39 mm, and 1 pixel of the camera corresponds to approximately 0.11 mm in nature.

In Fig. 5, the upper vortex core is shown at 5 s, 13 s and 13.6 s after the injection. The concentration field of the inert dye is shown at the left of the figure, and that of the reacting dye is shown in the center. The stretching and folding of the fluid elements in the flow field of the mixing vessel are clearly visible. After 5 s, the initial droplet forms one lamella which coils up to several layers after 13 s. The thickness of the lamellas decreases with time. The chemical reaction can take place only in the boundary layers. This effect is distinct from the field of the local degree of deviation, which is presented at the right of Fig. 5. In those areas where the thickness of the lamellas has already decreased, the degree of deviation also decreases; whereas in regions of high concentration and thick lamellas, especially after 5 s, the degree of deviation remains at the initial value.

In addition, however, after 13 s the mixing quality in the circumferential direction continues to vary, which is obvious from the images for t = 13.6 s, that is, only 0.6 s later. Due to the main rotating flow, dye elements of different residence time leave and enter the plane of the light sheet. Therefore, varying dye concentrations and lamellar structures exist, particularly in the center of the vortex core.

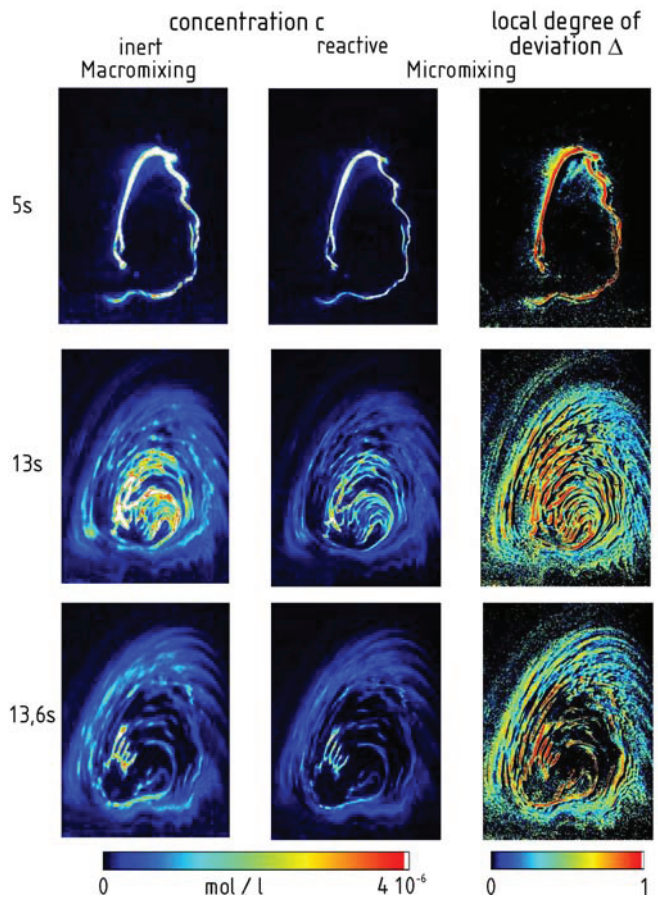


Fig. 5. Local concentration of (a) the inert dye (b) the reacting dye (c) and the degree of deviation.

4. Conclusion

The two-color laser-induced fluorescence technique provides new insight into the mixing process by enabling the local intensity of segregation at a multitude of points inside the stirred vessel to be measured. This is achieved by injecting a mixture of an inert and a reacting fluorescent dye into the vessel and then measuring the concentration fields of these dyes. The fluorescence intensity of the inert dye depends only on the concentration of the dye and therefore serves as a tracer for the macromixing. Instead, the fluorescence intensity of the reacting dye is enhanced by a chemical reaction which requires mixing on the molecular scale and therefore shows the micromixing. Low-Reynolds-number measurements are performed in a mixing vessel equipped with a Rushton turbine. The lamellar structure can clearly be resolved. Areas of micromixing are detected by calculating the local degree of deviation according to Eq. (1) from the concentration fields. These areas are mainly observed in the boundary layer of the lamellas.

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