Application of Two Dye Two-Color Laser-Induced Fluorescence Spectroscopy on Droplets of Green Solvent Mixtures containing Water and Ethanol

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ABSTRACT

In order to reach a higher sustainability, the utilization of green solvents is decisive in many technical applications. Water and ethanol substitute more complex solvents, showing advantages like ecological manufacturing, reusability or biodegradation. Both liquids are found in various industrial areas, ranging from a use as additives in biofuels, coolants or solvents for extraction in pharmaceutical, medical or food industries. Regarding these industrial processes, important variables are the liquid phase temperature and the composition in binary fluids. The focus of this work is two dye two-color laser induced fluorescence (2c-LIF) measurements in ethanol, water and their mixtures.

Liquid phase thermometry via 2c LIF requires a selection of suitable fluorescence dyes regarding solubility, temperature sensitivity and the interaction among the dyes themselves. A mixture of a temperature sensitive and a temperature insensitive dye is used in order to reach a large change in signal ratio for thermometry. In this work, two dyes – fluorescein disodium (FL) and sulforhodamine 101 (SRh), as proposed by Chaze et al. (Chaze et al. 2016) – are analyzed regarding their absorption and emission behavior in various ethanol/water mixtures, which are examples of "green solvents". The absorption spectra of the dissolved dye mixture are measured with a spectrophotometer at temperatures from 293 K to 343 K. Information on the temperature dependent absorption of the single dyes and reabsorption effects in ethanol/water mixtures is obtained. Additionally, the fluorescence of the mixtures is analyzed spectrally and by an imaging system. Therefore, a fiber coupled spectrometer and a system with two sCMOS cameras equipped with a long distance (LD) microscope are applied for simultaneous detection of the signal of tempered solutions a monodisperse droplet chain. A study of small droplets with sizes below 50 µm are evaluated and the limit of the spectral detection system is determined and discussed. The application of the measurement technique to several solvent mixtures is investigated.

1. Introduction

Higher sustainability in technical applications require utilization of green solvents such as water and ethanol. They are advantageous regarding ecological manufacturing, reusability, biodegradation, and lead to lower health and safety risks (Capello et al. 2007). Both liquids and their mixtures are applied in various industrial areas. For example, they are used for spray or film cooling (Bhatt et al. 2017), or as coolants in electrosprays for high power density devices (Taheri et al. 2024): Further application are regular adsorption coolers (Dzigbor and Chimphango 2019). Ethanol is applied in biofuel blends and both solvents are utilized for extraction in pharmaceutical, medical or food industries (Plaskova and Mlcek 2023). Especially, the liquid phase temperature and the mixture composition are relevant quantities for optimization of these processes. For this purpose, the present paper focusses on limitations and opportunities of two-dye 2c-LIF measurements in droplets for thermometry and mixture analysis. The basic thermometry concept was presented in our recent work (Ulrich et al. 2023). Investigations are extended to measurements in ethanol, water and their mixtures esp. for very small droplets and to determination of the mixture composition.

2c-LIF thermometry was applied in liquid or two-phase flows, like e sprays (Prenting et al. 2020) or liquid films (Collignon et al. 2021, 2022). By addition of a temperature-sensitive fluorescent dye to the liquid, a fluorescence signal ratio of two wavelength ranges is used to infer the temperature. Ideally the signal of one of these wavelength bands shows a temperature-sensitivity. The second band should provide an oppositely sensitive or temperature insensitive behaviour. The selection of these spectral bands by respective filters may lead to a higher temperature-sensitivity of the signal ratio. Approaching the 2c-LIF technique with two different dyes (two-dye two-color LIF) may show some advantages. In principle, it allows for a wider range of wavelength channels to produce a maximum temperature sensitivity of the signal ratio. Additionally, effects of signal reabsorption in certain wavelength areas and resulting temperature uncertainties can be reduced. Consequently, the selection of the dyes and the respective filter pair considers the overlap of absorption and fluorescence spectra.

Different fluorescent dyes were characterized for liquid thermometry in cuvettes (Mishra et al. 2020). Chaze et al. proposed the dye mixture fluorescein and sulforhodamin 101 in water for 2c-LIF thermometry. Temperature fields of a heated water jet were studied with this dye mixture (Chaze et al. 2016). Another application was thermometry in millimetre-sized water droplets interacting with a hot surface (Chaze et al. 2017). This dye mixture was adopted by Collignon et al. for thermometry in wavy liquid films (Collignon et al. 2021). Earlier works presented thermometry in relatively large single droplets in the range of 0.5 mm to 1 mm (Volkov and Strizhak 2020). Only few papers deal with thermometry in individual µm-sized droplets. For example, Palmer et al. studied temperature distributions in droplets with diameter of 67 µm (Palmer et al. 2016).

In our previous paper, the dye couple FL and SRh was taken for temperature calibration as well as droplet heating and cooling studies. 100 µm sized ethanol droplets were investigated in a monodisperse droplet chain (Ulrich et al. 2023). Planar LIF and a spectral detection system were used to record the fluorescence signals. Small µm-sized droplets are a focus of the present work in order to judge the detection limit of the technique. Because of the polydisperse nature of sprays, the smallest droplets may not be detectable at all since the LIF signal roughly depends on the volume of the droplet. Consequently, larger droplets in sprays dominate the signal intensity distribution. This means that contributions of small droplets in dense sprays may be lost (Storch et al. 2016). Other effects are bright LIF signals because of dye lasing. These "morphology dependent resonances" (MDR) occur at the surface inside the droplet. These effects may not be resolved in spray but will potentially bias the fluorescence signals and derived temperature or concentration.

Additionally, the application of 2c-LIF with the proposed dyes is considered for determination of the droplet composition in water/ethanol mixtures. So far, fluorophores were rarely applied for composition analyses in droplets. Koegl et al. utilized Nile Red for analysing isooctane/ethanol mixtures (for ethanol contents between 0 vol% and 100 vol%) with a 2c-LIF concept (Koegl et al. 2022). Maqua et al. applied 3c-LIF with Rhodamine B for thermometry in binary ethanol/acetone droplets with varying compositions (Maqua et al. 2006). However, there is no LIF technique available for studying binary ethanol/water mixtures until now. Other diagnostics based on light scattering (Raman, Rainbow refractometry etc.) for detection of droplet compositions are provided in the review of Lemoine and Castanet (Lemoine and Castanet 2013).

The present publication gives an overview of calibration data and spectroscopic LIF measurements in the droplet chain produced by a droplet generator, while a detailed description is given in [Ulrich et al. EXIF 2024, submitted]. The LIF imaging system with is utilized for the determination of droplet sizes in the droplet chain produced by the droplet generator. The main study is conducted with the spectrometric setup. It serves for identification of MDR and the avoidance of their detection in the chosen 2c-LIF filter bands. The spectral shifts depending on temperature and ethanol concentration are applied to develop 2c- and 3c-LIF techniques for thermometry and liquid mixture analysis. Due to fibre couplings and their flexible and compact sizing, spectral LIF measurements are more feasible for applications with reduced optical access.

2. Materials and Methods

The focus of the present measurements is a spectral setup, detecting the fluorescence emission of a dye/solvent mixture in a droplet chain. A mixture of the commonly used solvents water and ethanol, as well as different mixtures are studied. To simplify the description, all solvent mixtures are named by their ethanol fraction (EtOH0 for pure water, EtOH100 for pure ethanol). The solvents are doped with a dye mixture of two fluorescent dyes, 750 mgFL/l and 75 mgSRh/l. Using a two-dye LIF approach offers many advantages for spectral investigations. By selecting two dyes with contrary temperature dependent behavior, a higher temperature sensitivity of the intensity ratio can be achieved. The broad spectrum of the dye mixture offers more possibilities of selected color channels to form the intensity ratio. Disturbing lasing effects, occurring in relevant, sensitive wavelength areas, can be switched to other wavelength regions by combining the two dyes. The observed ring structures inside the droplet (see also figure 2 on the right) are MDR. They develop at the phase boundary of spherically shaped droplets, acting as optical cavity. Additionally, the influence of liquid evaporation and varied absorption on the intensity ratio is minimized, by the use of a dye couple. This is because the mass ratio of the dyes remaining inside the droplet is not affected by solvent evaporation.

In the experimental setup, a pulsed Nd:YAG laser (Q-SMART 850, Quantel) generates a 8 mm laser beam at 532 nm. With a frequency of 10 Hz the beam is led through a beam splitter to measure and regulate the laser power to 2.4 mJ/cm2. Subsequently, the beam passes the droplet chain, generated by a piezoelectrical droplet generator (FMAG 1520, TSI). For size calibration and monitoring of the droplets through both color channels, an imaging system is placed at 90° to the laser beam. Following a long-distance microscope, two sCMOS cameras (Imager, LaVision) are equipped with the respective bandpass filters. However, the investigations for this paper are conducted with the spectral detection system, located orthogonally to the laser beam. Fiber coupling optics enable detection of the low signal fluorescence emission with a VIS spectrometer (WP-VIS-A-S-50, Wasatch Photonics).

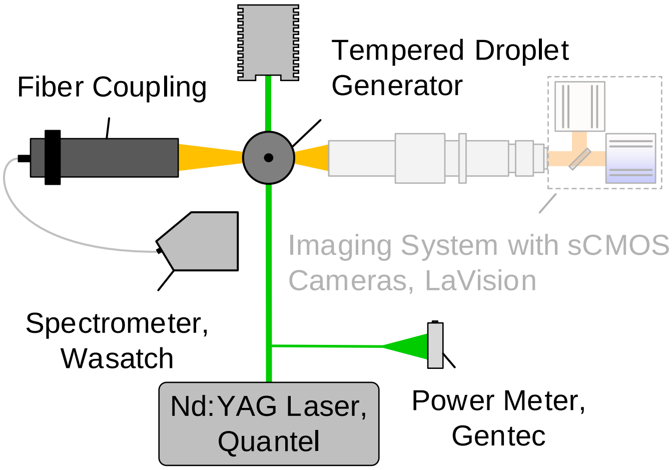

Figure. 1 Schematic Drawing of the setup around the heated droplet generator.

The obtained emission spectra offer similar results of the signal intensity ratio as the imaging system (Ulrich et al. 2023) and allow a simplified and time-efficient post-processing while requiring only little memory and also setup space. For each measurement, five spectra are recorded with an integration time of 50 ms each consisting of 100 temporally averaged single spectra. The data are processed with a background subtraction and baseline fit. Subsequently, the spectra are averaged and a ratio of the two-color channel signals is formed.

In addition to the emission measurements, investigations of the absorption behavior are conducted. Therefore, temperature dependent absorption measurements are recoded in a cuvette in an UV/VIS-spectrophotometer (V-750, Jasco). For the light to pass the path length of the cuvette, the investigated mixtures are diluted with solvent up to a concentration of 50 mg_{FL}/l and 5 mg_{SRh}/l.

3. Results

In this work, the measurements focus the lower droplet size limit for the proposed spectral detection setup. Furthermore, the application of the two-dye 2c-LIF technique to different ethanol/water mixtures is investigated and discussed.

By adjusting the liquid mass flow and the frequency of the droplet generator, droplet sizes from 30 µm to 120 µm can be generated. The fluorescence signal of variously sized droplets is recorded spectrally, to analyze the influence of the droplet size on MDR and also the signal ratio. Normalized fluorescence spectra are depicted in figure 2. Without normalization a strong size dependence of the signal intensity can be observed as expected due to the d^3 dependency. While the 120 µm sized droplets show a spectrum with maximum intensities of around 2150 counts, only little emission of around 25 counts are detected in the small droplets (30 µm). The spectra indicate three peaks at around 530 µm (blocked by a notch filter), at 595 µm and a third peak located around 650 µm. The first two peaks are based on the spectra of the two dyes - FL at lower wavelengths and SRh at higher wavelengths.

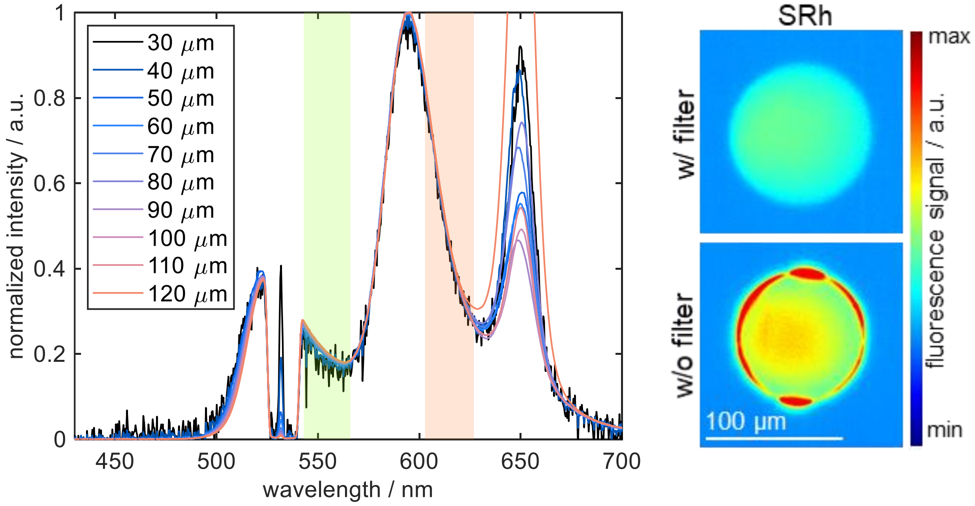

Figure. 2 Left: Normalized fluorescence signals of the dye mixture in differently sized ethanol droplets at 293 K measured at a distance of 4 mm below the nozzle exit. Right: Droplet images with fluorescence signal over 588 nm (dichroic mirror in front of cameras). The upper picture is with additional bandpass filter (shaded in red on the left).

The third maximum is due to MDR effects. These MDR effects are visible on the bottom image on the right side in figure 2. The bandpass filter is removed and all wavelengths above 588 nm, including the lasing signal, are detected. In the spectral post-processing no influence of the droplet size on the MDR peak position can be obtained. Calibration curves, resulting from temperature dependent signal ratios showed a very similar temperature sensitivity of 1.5 %/K for all studied droplet sizes. Thus, an applicabilty of the 2c-LIF approach is assumed for thermometry in processes with a polydisperse droplet distribution, like e.g. sprays. Furthermore, the low signal detected in droplets below 50 µm suffices for spectra processing without information loss.

Figure 2 shows the absorption spectra of the dye combination in ethanol and water at 283 K and 343 K. The spectra offer two peaks, each corresponding to one of the dyes. The first peak, visible at wavelengths from 410 nm to 540 nm, is mainly due to the absorption spectrum of FL. Additionally, SRh absorbs light in a wavelength area around 555 nm to 610 nm. At 283 K, the absorbance of FL is larger in water while the peak is blue-shifted, compared to ethanol. This is a possible explanation for lower emission signals in water. At higher temperatures, the absorbance of FL rises in both, ethanol and water. In ethanol a strong increase with higher temperature is visible with an absorbance larger than in water at 343 K. The absorption behaviour of the second dye, SRh, is differently to FL. A lower absorbance can be observed with a temperature increase. Contrary to the FL absorbance, the SRh spectrum in water shows a red-shift, compared to the spectrum in ethanol. Thus, less laser light is absorbed by SRh in water leading to a lower emission signal.

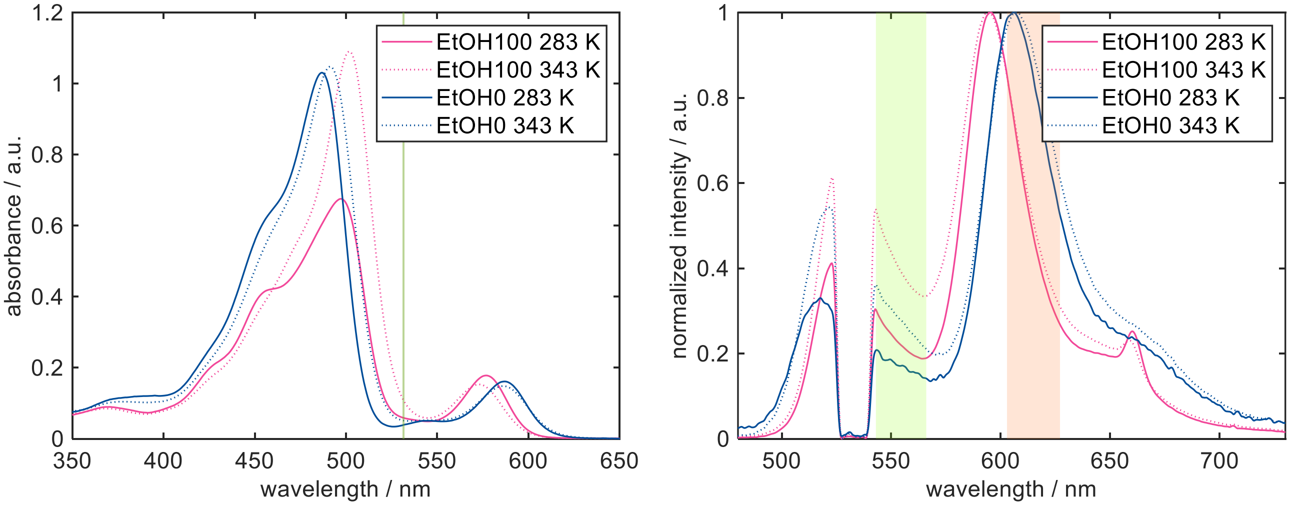

Figure. 3 Left: Absorption spectra of the dyes in ethanol and water at different temperatures. The laser line is indicated in green Right: Fluorescence spectra in 100 µm sized ethanol and water droplets at different temperatures. The shaded areas show the color channels for calculation of the intensity ratio.

The right graph in figure 3 depicts normalized fluorescence emission spectra, measured in the droplet chain at 100 µm droplet size. The measurement lcation was 4 mm below the nozzle of the droplet generator. Recordings of tempered ethanol and water droplets are shown at 283 K and 343 K. Similar to the absorption spectra, the FL peak in water indicates a blue shift and the SRh peak a red shift, when compared to ethanol droplets. For both heated solvents, a signal increase is visible in the first color channel. The temperature dependence in the second color channel is marginal. Therefore, a sufficient temperature sensitivity for 2c-LIF is observed in both solvents, as well as in binary ethanol/water mixtures.

With the additional solvent dependence visible in the spectra, the applicability of the 2c-LIF approach on determination of mixture compositions is investigated. Figure 4 shows the normalized fluorescence emission of six different solvent combination from pure ethanol (EtOH100) to pure water (EtOH0) in the left graph. All spectra are recorded from 50 µm sized droplets at 293 K and normalized to the maximum of the SRh spectrum. The lowest signal is detected in the dye combination in water. This can be explained by the lower absorption of the dyes in water at the laser wavelength of 532 nm, as mentioned above. To investigate the composition dependence of the 2c-LIF ratio, the same color channels are used as for the thermometry. The contrary peak shifts of FL and SRh with increase of ethanol content are favorable for this approach. In the right graph of figure 4 the resulting intensity ratio is depicted with the solid curve. For ethanol fractions above 20 vol% the ratio offer a reliable dependence on the mixture composition.

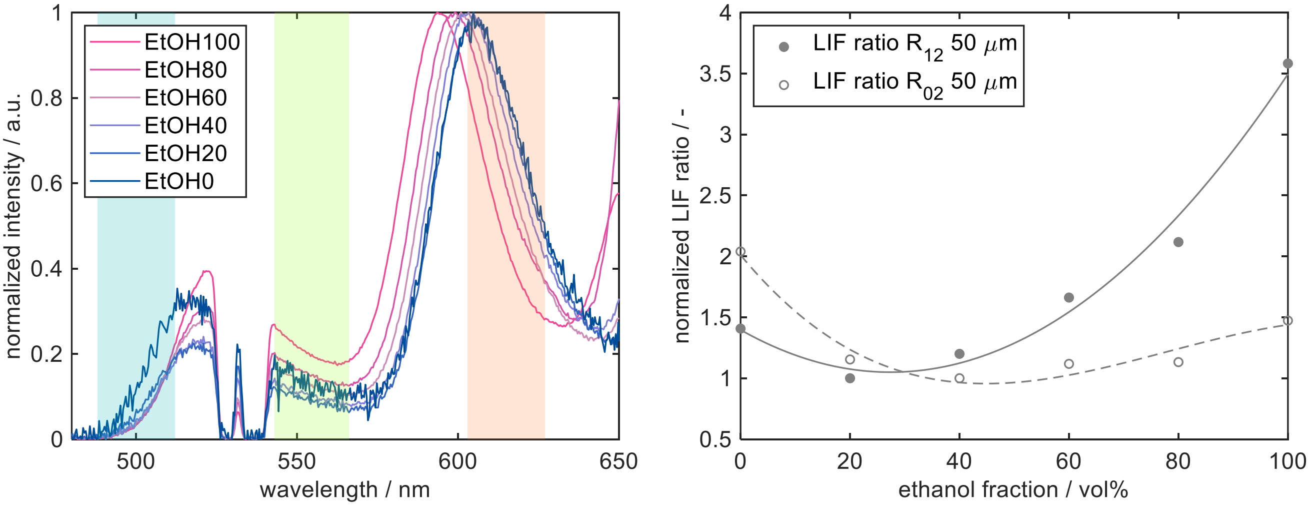

Figure. 4 Left: Fluorescence spectra in 50 µm sized droplets of different ethanol/water mixtures at 293 K. The shaded areas show the color channels for calculation of the intensity ratios (center wavelength at 500 nm (channel 0), 554 nm (channel 1) and 615 nm (channel 2)). Right: LIF ratios calculated with the intensities of two color channels, each with polynomial fit.

To also include lower ethanol fractions, a third color channel "channel 0" is determined, according to a commercially available bandpass filter (500/24 BrightLine HC). The method of 3c-LIF was also proposed by Maqua et al. for PMT measurements in ethanol/acetone mixtures (Maqua et al. 2006). In this third wavelength region the FL emission behaviour is very sensitive for low ethanol fractions and is shaded in blue in the left graph of figure 4. A second ratio R_{02} is formed with the second color channel (shaded in red). The additional ratio is depicted with a dashed curve in the right graph. For ethanol fractions between 0 vol% and 40 vol% a strong composition dependence of the ratio is obtained. To get a definite allocation of an ethanol fraction, both ratios have to be determined.

4. Conclusion and Outlook

This paper presents the application of a two-dye 2c-LIF approach for thermometry in a droplet chain with droplet sizes also below 50 µm. Additionally, an application for composition investigations of binary water/ethanol droplets via 3c-LIF was proposed. A spectrometric setup was used for detection of the dye couple FL and SRh in ethanol/water mixtures. An imaging system was setup for size calibration and further insights on droplet behaviour. Furthermore, the occurrence of interfering effects such as MDR was monitored while the respective wavelength regions can be investigated simultaneously with the spectrometer.

A droplet size study was conducted for ethanol droplets sized between 30 µm and 120 µm. The signal of the smallest droplets was at about 25 counts. Since fluorescence signals show a d^3 dependence, a detection limit of the 2c-LIF approach was expected. For thermometry, two intensity regions of the spectra are used to form a temperature sensitive ratio. These color channels cover each a part of the fluorescence spectrum of one dye. By comparing the signal ratios measured in differently sized droplets, no influence of droplet size and also the size-dependent MDR could be identified. Even the low signals of the small droplets led to a similar signal ratio and also temperature sensitivity of the ratio. The application of the 2c-LIF approach was further tested in different compositions of water and ethanol. Results were presented for both pure solvents at 283 K and 343 K. The absorbance spectra of the liquids offer explanations, on the lower signals in water droplets. Both dyes, FL and SRh, show a spectral shift away from the laser line at 532 nm, compared to ethanol. Despite an only small temperature sensitivity of FL in the absorption spectra (in water), FL offers a strong temperature dependence of the emission in all solvents.

Apart from the use for thermometry, 2c-LIF was considered for composition studies in ethanol/water mixtures. A composition dependent calibration curve was formed, using the same color channels as in the thermometry approach. The resulting ratio curve only showed a distinct progression for ethanol fractions above 20 vol%. Consequently, a third color channel was selected, to form a second signal ratio with sensitivity at lower ethanol fractions. With this 3c-LIF approach, the determination of both ratios enables a definite allocation of the mixture composition from the recorded spectrum.

The combination of both, the 2c-LIF thermometry approach and the 3c-LIF method to study mixture compositions, would give huge benefits for solvent mixture investigations. Further studies with variations in both, solvent composition and temperature are necessary for a diverse calibration data set. In addition, studies of the dye couple in other solvents (and their mixtures) such as propanol, butanol, and water with varied pH-value, would increase the application range.

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