Laser-induced Fluorescence of Rhodamine B in Ethylene Glycol Solution

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Abstract

This paper presents the temperature effects on the emission spectra of Rhodamine B in ethylene glycol solution mixed with 50% pure water. The emission spectra at different Rhodamine B dye concentration were studied in a temperature range of -34°C through 64°C. Results show that growing solution temperature reduces the fluorescent emission intensity, and no obvious discrepancy between fluorescent characteristics of RhB in ethylene glycol and in pure water was observed. A dual normalization method was developed to process the experimental data and to correlate the relative intensity with solution temperature, this method effectively eliminates the influence of signal fluctuations during fluorescence detection. Tests of droplets temperature measurements were also carried out to demonstrate the feasibility of the current non-intrusive method in applications concerning droplets temperature monitoring.

Keywords: Rhodamine B; ethylene glycol; fluorescence; droplets; temperature measurement

1. Introduction

Slurry ice making technique is an essential aspect in the development of Ice Storage Air Conditioning. According to the open literatures, the dynamic ice-making technique using super-cooled water is one that gains much focus of researchers [1, 2]. Satoh and his co-workers [3] experimentally studied the freezing of water droplet due to
evaporation, which gives rise to the development of a new slurry ice-making technique. During their experiments, liquid water was firstly atomized into very small droplets, and then forced into an environment with low pressure and humidity to evaporate and to reach a super-cooled state. Yan and his co-workers [4] established a simulation model to examine the effects of super-cooled droplet temperature, speed, and droplet diameter on the ice-making efficiency during the evaporation process, the results were compared with their experiments. Among such researches, temperatures of the super-cooled water [5] or water droplets [3, 4] were measured intrusively by means of very tiny thermal couples. However, in case of super-cooled water or water droplets temperature measurements, the thermal couples themselves may become freezing nuclei and may introduce extra perturbation to the liquid temperature change. This problem can be circumvented by using non-intrusive temperature measurement technique such as Laser-Induced Fluorescence (LIF).

The LIF technique has been carried since the 1990s [6~8], and as a non-intrusive measurement method, a number of researches had been carried out since then, such as applications in fluid flow temperature measurement [9~11] and droplets temperature measurement [12~17], thermal properties in microfluidic devices [18], and heat flux in mixed convective flow over solid waves [19]. The most commonly used fluorescent dyes are Rhodamine B (RhB), Fluorescein and Kiton Red [20] for their high temperature sensitivities, separable absorption and emission spectra and can be easily induced by commercial lasers, such as Argon-ion laser (488nm and 514.5nm) and Nd: YAG laser (532nm). However, published literatures mainly focus on liquid or droplets temperature measurement which are above standard temperature (>20°C), few of them concern the temperature range below 20°C. Ali and his co-workers [21] once studied the performance of continuous-wave Rhodamine B dye laser, and briefly examined the temperature effects in RhB dyes at four temperatures (23°C, -5°C, -20°C, -60°C). The authors primarily concentrated on the lasing characteristics of RhB dye while the temperature dependence of fluorescent intensity were merely qualitatively presented without further investigation. However, the work of Ali et al. introduced a possible application for the laser-induced fluorescence technique in the temperature measurement of super-cooled water/droplets. To this end, the fluorescent characteristics of Rhodamine B dye in ethylene glycol solution against temperature variation must be known in detail, which also forms the target of this paper. The current research studied the fluorescent characteristics of RhB in ethylene glycol in a wide temperature range (expanded even below 0°C), a dual-normalization data reduction method was presented to describe the temperature dependence, in order to examine the feasibility of the method in super-cooled liquid or droplets temperature measurement, a test bench was designed and established to create liquid droplets, some preliminary results were presented in the paper as well.

2. Experiments

2.1. Principles

RhB is widely used as fluorescent tracer in many applications due to its high water solubility, low cost, non-toxicity and its emission spectra, located in the visible region, can be easily induced by common commercial lasers. As shown in Fig. 1, the temperature sensitivity of RhB in water is -1.43% C⁻¹ in average over a temperature range of 20-90°C, which is a bit smaller than that reported by Sutton et al. [22], who obtained a temperature sensitivity of -1.59% C⁻¹ over the temperature range of 20-60°C. When the dye concentration is low enough and the optical path is very short so that Beer’s attenuation and fluorescence re-absorption along the laser beam can be neglected, dependence of fluorescence intensity upon temperature can be found mainly in the changing quantum yield of the tracer itself [23]. For RhB in aqueous flow, its quantum yield falls to a lower level which results in weak signal intensity when solution temperature increases.

In general, fluorescence intensity at certain wavelength and temperature can be written as [13, 23, 24]:

\[
I(\lambda, T) = I_0 \cdot e \cdot C \cdot K_{opt} (\lambda) \cdot K_{specific} (\lambda) \cdot B(\lambda, T)
\]  

(1)
Where, $I_F$ is the fluorescence intensity, $I_0$ the incident laser intensity, $\varepsilon$ the molar absorption coefficient, $C$ the solution concentration, $K_{OPT}$ is a constant which only depends on the optical system structure, and $K_{SPEC}$ a spectroscopic constant depending on the chosen fluorescent indicator. $B(\lambda, T)$ can be interpreted as a temperature characteristic parameter and be remained in data reduction while the others should be dropped from equation (1) by introducing a reference temperature $T_{ref}$. A reference measurement at this certain temperature $T_{ref}$ used to calibrate the temperature response had been developed by many authors [10, 11, 23, 25, 26]. The fluorescence intensity at an arbitrary temperature $T$ and a chosen $T_{ref}$ over a certain spectral band $(\lambda_1, \lambda_2)$ are,

$$I_F(\lambda_1, T) = I_0 \cdot \varepsilon \cdot C \cdot K_{OPT} (\lambda_1) \cdot K_{SPEC} (\lambda_2) \cdot B(\lambda_1, T)$$  

(2)

$$I_F(\lambda_1, T_{ref}) = I_0 \cdot \varepsilon \cdot C \cdot K_{OPT} (\lambda_1) \cdot K_{SPEC} (\lambda_2) \cdot B(\lambda_1, T_{ref})$$  

(3)

Compare equation (2) and (3), the relative intensity at temperature $T$ can be obtained,

$$I_{ref} = \frac{I_F}{I_{F,ref}} = \frac{B(T)}{B(T_{ref})}$$  

(4)

Before the application of the reference temperature, we introduce a pre-normalization of the emission spectrum using the peak intensity. During the fluorescence detection process, usually several scans are collected continuously and averaged as the fluorescent spectrum at a specific temperature, this requires the emission spectra behave stably over the entire duration of these scans. However, in case that the incident laser power fluctuates during these scans, or the number of droplets passing through the probe volume varies, the detected raw fluorescence intensities do not remain stable at the specific temperature, thus make the averaging process not feasible. This problem can be eliminated by normalizing the raw spectrum with its peak intensity in every scan. The normalized relative spectra of all the scans at the same temperature are the same despite of the incident laser fluctuation or the droplets number variation. The intensity integration over a selected spectral band and a second normalization by reference measurement should be performed afterwards. This data reduction process is called Dual-Normalization Method.

Investigation of fluorescent characteristics of RhB at temperatures lower than 0 °C was made available by introducing ethylene glycol into the dye solution. Thus, the effects of ethylene glycol on the emission characteristics of RhB must be examined beforehand.

2.2. Experimental Setups

This section presents two experimental systems, one for the investigation on the fluorescent characteristics of RhB in ethylene glycol solution, the other for the droplets formation and their temperature measurements.
2.2.1. Test bench for fluorescence characteristics examination

The optical system used in this investigation is simply shown in Fig. 2, the incident laser (532nm, LASERWAVE) directly passes through a sample tube (quartz, inner/outer diameter: 26/32mm, length: 126mm) holding the aqueous solution. The laser intensity is not monitored because the effect of incident laser fluctuation upon emitted fluorescence can be reduced by spectra processing. Fluorescent signals were detected by a collector (84UV, Ocean Optics) placed at the same side of the incident laser and were sent into a spectrometer (MAYA2000PRO, Ocean Optics) specifically customized to cover the entire emission spectrum of RhB. The fluorescence spectrum at a given temperature is the average of 20 scans. The temperature of the RhB-Water solution and the RhB-Ethylene Glycol solution were controlled by a Constant Temperature Bath (CTB, DC4006, Shanghai Sunny Hengping) and circulated through the measurement system. In order to measure the fluorescence characteristics of RhB at temperatures below 0℃, the solvent was prepared with 50% ethylene glycol and 50% pure water, this volume ratio can lower the freezing point of the solution to -38℃ at standard pressure.

To reduce the heat loss of the solution to minimum, the test section was designed to be an annular quartz tube with the space between the outer and inner walls vacuumed, see Fig 3. The two ends of the sample tube were connected to the outlet/inlet of the constant temperature bath by rubber pipes coated with foam heat-insulation layers (thickness: 2mm). The most part of the sample tube itself was also covered by foam heat-insulation layers in order to keep the solution temperature inside the tube consistent with that in the bath, only small enough area in the middle allowing the solution to be induced and the fluorescent signals to be collected left. Temperature of the solution was monitored and controlled respectively by platinum resistance (Pt100) and the heating device installed in the bath after setting the expected temperature. The fluctuation of the constant temperature bath is ±0.05℃ with a display resolution of 0.1℃. Two extra K-type thermal couples were installed in the inlet and outlet of the sample tube to read the actual temperatures of the fluid flowing through the tube, the average value of these two readings were considered as the fluid temperature at the excitation point.
Comparison of the fluorescence characteristics of RhB in pure water and ethylene glycol solution were first carried out, then the temperature effects on the fluorescence of RhB in ethylene glycol were examined at several different dye concentrations ranging from 1.6E-4g/L to 0.25g/L. Such high concentration provides adequate fluorescence emission intensity during droplets measurement. For flowing fluid experiments, high concentration substantially increases the Beer’s attenuation so that the incident laser cannot pass through the whole flow field and the probe volume shrinks to a very small area at the touch point of the incident laser. However, placing the fluorescence detector at the same side of the laser source (see Fig. 2) could collect enough emission signals with the reflection of the incident laser cut by means of a 532nm filter (BLP01-532R-25, Semrock).

Photo bleaching effects [27] were not considered as the solution was continuously circulated through the system. PH value of the solution does not affect the fluorescent characteristics as long as the PH > 6 [20]. The solution of the current experiments were all made with pure water, thus the PH effects were not considered.

2.2.2. Test bench for droplets temperature measurement

In order to apply the fluorescent characteristics of RhB to the temperature measurement of droplets, a droplets atomizer needs to be designed beforehand. Fig. 4 shows the schematic of our designed droplets atomizer which based on the principle of ultrasonic atomizing. The whole atomizer was based on a stainless steel chamber. Two ultrasonic transducers were installed at the bottom of the chamber to atomize the RhB solution into droplets. Ambient air was used as driving flow to lead the droplets out of the chamber from a rectangular exit at the top. The droplets were excited by the incident laser closely above the exit of the chamber, as shown in Fig. 5.

The RhB solution was first heated by an electrical heater to 60~80°C and then allowed to cool down naturally. During the cooling process, the atomizers were turned on to produce droplets at certain temperatures. Three Pt100 thermal resistances were used to monitor the temperatures of RhB solution, the driving air flow and air-droplets mixture. It was assumed that the heat transfer between droplets and the driving air flow was quick and uniform so that the readings of Pt100-2 could represent the temperatures of the mixture closely enough. This assumption is possible because the diameters of the droplets are small (≈5 um), which indicates small amount of heat capacity in the droplet itself and quick temperature response to the ambient condition. Before each test, a reference measurement at room temperature was carried out as required in the principle of data reduction in aforementioned
section.

3. Results

3.1. Tests of dual-normalization method

In order to validate the dual-normalization method, two tests were carried out:
- Incident laser power agitated in each spectrum scan;
- Incident laser power kept stable during all the scans at a certain temperature, and changed at another temperature.

For a certain temperature, 20 scans were taken and averaged as the mean spectrum at this temperature, each scan takes 20ms. During test (1), the exciting laser was agitated by moving a scratched transparent plastic sheet continuously, thus the incident laser intensities of all the 20 scans differed from each other. The raw signal intensity over a selected spectral band would behave randomly as the plastic sheet moving, which is shown as the empty circle in Fig. 6. By peak-normalizing the raw spectrum of each scan, the relative intensities over the same spectral band behaved nearly the same, as is shown in Fig. 6 as empty triangular.

![Fig. 6 Comparison between raw signals and peak-normalized signals](image)

During test (2), the 20 scans at a certain temperature were taken at stable exciting laser power with the scratched plastic sheet kept still at a fixed position. When the solution temperature was changed, the plastic sheet was moved a bit to a different position so that the incident laser power varied to a new value. Test (2) was conducted at several different temperatures, the variations of the raw signal intensities over a selected band were shown in Fig. 7. As can be seen, the signal intensities distributes somewhat randomly without a manifest relation to the temperature changes.

![Fig. 7 Raw signal intensities against temperatures in TEST2](image)
Fig. 8 shows the relative intensities of TEST (2) after dual-normalization (reference temperature at 42°C), together with the results of TEST (1) at different temperatures. It is obviously shown that the effects of incident laser fluctuation were sufficiently eliminated, and the relative intensities increase as the solution temperature increasing. Results of both tests are in good accordance.

![Fig. 8 Relative intensities against solution temperatures in TEST1 and TEST2](image)

**Fig. 8 Relative intensities against solution temperatures in TEST1 and TEST2 (reference temperature at 42°C)**

### 3.2. Comparison of fluorescence characteristics of RhB in water and ethylene glycol

In order to measure the temperature of super-cooled liquid or droplets using laser-induced fluorescence technique, the fluorescence characteristics below standard temperature (even below 0°C) must be studied. However, liquid water freezes at temperatures below 0°C under standard pressure, thus makes the experiments not applicable. To keep the solution in liquid state below 0°C, ethylene glycol were added into pure water with a 50% volume fraction, which makes the freezing point of the mixed solution as low as -38°C under standard pressure.

Comparison of fluorescence characteristics of RhB in both pure water and ethylene glycol solution were carried out to examine if there is any unknown effects aroused by the addition of ethylene glycol. Experiments on RhB in pure water were performed with a concentration 3.0e-3g/L, and 3.2e-3g/L for ethylene glycol solution. There was no specific reason for the concentration difference between the two solutions and no needs to keep them exactly the same, as the concentration effects could be well eliminated by data reduction. Tests of the ethylene glycol solution were repeated 3 times to check the repeatability of the experiments.

![Comparison of fluorescence characteristics of RhB in water and ethylene glycol](image)
As shown in Fig. 9, the temperature dependence of relative intensities of RhB in pure water and ethylene glycol solution (EG) are in good accordance, both follow a linear increasing tendency, which further validates the test results in Fig. 8. The three repeated tests of RhB in ethylene glycol present a solid repeatability of the temperature dependency. According to these findings, it can be concluded that ethylene glycol does not affect the fluorescence characteristics of RhB, so that the fluorescent temperature dependence of RhB in ethylene glycol solution is applicable to the super-cooled liquid or droplets temperature measurements.

3.3. Temperature effects on the fluorescence characteristics of RhB in ethylene glycol

The fluorescence characteristics of RhB in ethylene glycol were briefly reported by Ali and his co-workers [21]. The raw fluorescent signal intensities sharply increase as the solution temperature lowering. With the application of our dual-normalization method, the relative fluorescent intensities present a positive dependence upon the solution temperature. In this section, several concentrations of RhB in ethylene glycol solution were carefully tested to examine its fluorescence characteristics in low temperature. Dye concentration ranges from $1.6e^{-4}$g/L through $0.25g/L$, and solution temperature was controlled between $-34^\circ C$ and $64^\circ C$. The highest concentration is about 1500 times denser than the lowest value. Such a wide range of concentration would make obvious the concentration effects and fluorescent self-absorption effects. In addition, high concentration is necessary during droplets measurement where the probe volume is usually very small compared to flowing liquid experiments.

Results are shown in Fig. 10, the reference temperature was chosen at $20^\circ C$. As is shown, the temperature dependences at all the concentrations present a positive increasing tendency. The wide range of concentration used in the experiments does not affect the fluorescent characteristics significantly although small deviations exist among the intensity-temperature relations of various concentrations. Careful examination of Fig. 10 reveals that the dual-normalized intensity-temperature relations at lower concentrations ($1.6e^{-4}$ $- 1.74e^{-3}g/L$) accord with each other closely, while those at higher concentrations present obvious deviation especially at temperatures less than $0^\circ C$.

The dual-normalized intensity-temperature relations presented in Fig. 10 approximately follow a linear regression, with their slopes representing the temperature sensitivities at various concentrations. Fig. 10 also indicates that the temperature sensitivity weakens as the dye concentration increases. This may be attributed to the fluorescent self-absorption effect, which becomes stronger at higher concentration.
As the solution cooled to lower temperature, the fluorescent quantum yield increases [28] and produce much stronger emission signal. Meanwhile, the incident laser absorption is also substantially enhanced, thus gives rise to a stronger self-absorption effect due to the large overlapping between the absorption and emission spectrum of RhB, as shown in Fig. 11. The deviation of the intensity-temperature relations at higher concentrations from those at lower concentrations could be explained as the result of a combined effect caused by high concentration and self-absorption.

![Absorption and Emission spectrum of RhB](image)

Fig. 11 Absorption and Emission spectrum of RhB [29]

Results in Fig. 10 provide a feasible method for super-cooled water or water droplets temperature measurement. As long as the dual-normalized fluorescence intensities are measured, the corresponding temperature of the tested liquid could be obtained inversely using the fluorescent characteristics presented. When in engineering applications, a reference measurement should be performed previously. Note that the reference temperature in Fig. 10 can be changed according to the practical measuring convenience.

### 3.4. Droplets temperature measurements

In order to validate the feasibility of the proposed droplets temperature measurement method, preliminary experiments were carried out using the fluorescent characteristics in Fig. 10. RhB solution was first poured into the chamber of the ultrasonic atomizer (see Fig. 4) and then left still for a period of time so that the solution temperature is closing to the room temperature (15~20°C). When the atomizer was turned on, liquid droplets began to spread out from the solution surface, and driving air flow at room temperature leads the droplets out from the top exit of the atomizer. The reference measurement was taken at this stage of the experiments, for the temperatures of the driving air, liquid solution and the droplets are considered to reach a balance state.

Droplets temperature measurement had been carried out four times to examine the performance of the atomizer and repeatability. The RhB solution was first heated to a temperature above 60°C, and then allowed to cool naturally. During the cooling process, the atomizer was turned on and droplets at the exit of the chamber were excited by the laser source. Fluorescence detection and data analysis were performed immediately by a self-designed computer program which outputs the droplets temperature calculated by the method proposed at the end of section 3.3.
Fig. 12 shows the droplets temperature results obtained by LIF method comparing to that measured by thermal resistance Pt100-2 (see Fig. 4). It can be seen that the calculated droplet temperatures are lower than the values measured by Pt100-2. This phenomenon is understandable for the thermal resistance was installed upstream from the excited probe volume. The temperatures of the atomized droplets were initially equal to that of the solution. When the droplets were mixed with the driving air and flew out from the chamber, the heat transfer between the droplets and the air decreases the temperatures of the droplets. Therefore, the temperatures of the droplets at the location of Pt100-2 must be higher than that of the droplets at the probe volume.

However, the current explanation is based on the assumption that the heat transfer between droplets and the surrounding air reaches a balance state so that the temperatures of the two are almost equal, in addition, the temperature readings of the Pt100-2 can approximately represent the exact temperatures of the droplets leaving the exit of the chamber. In order to validate the temperature measurement results by LIF method, a more precise examination of the flow field and transient temperature monitoring are necessary to improve the performance of the current test bench.

4. Conclusions

Fluorescence characteristics of RhB in ethylene glycol solution were studied in this work, the tested RhB dye concentrations range from 1.6e-4g/L to 0.25g/L, solution temperatures range from -34°C to 64°C. Results can be summarized as follows:

(1) The developed dual-normalization method can effectively eliminate the influence caused by fluorescent emission intensity fluctuations. This method is particularly effective in polydisperse droplets temperature measurements where the number of droplets passing the probe volume varies continuously so that the emission signal intensities are unstable.

(2) There is no obvious difference between the fluorescence characteristics of RhB in water and in ethylene glycol solution. Thus the temperature dependence of relative fluorescent intensity of RhB in ethylene glycol can be used to measure the temperature behavior of water solution or water droplets.

(3) The dual-normalization method results in a linear relation between relative fluorescent intensity and solution temperature, which can be applied inversely to measure the temperature of water or water droplets in a range from -34°C to 64°C.

(4) Preliminary droplets temperature measurements reveal that the LIF technique is capable of predicting the droplets temperature variation. However, a convincing validation method needs to be developed to improve the measurement accuracy and justify the results obtained by LIF method.

Further research work will be focused on the recommended improvements and apply the proposed LIF technique into super-cooled droplets temperature measurements.

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