

ผลของอุณหภูมิที่มีต่อสเปกตรัมของการวาวแสงในสีย้อม

Temperature dependence of the luminescence decay in the fluorescent dyes

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Abstract

The main aim of this study is to use laser induced fluorescence (LIF) technique to study and compare the temperature dependence of the luminescence decay curves of the fluorescent dyes (the green dye, the orange dye, and the red dye). The 470 nm blue laser was used as an excitation light source to induce fluorescence. The LIF spectra were detected by a compact fiber coupled BTC-110S CCD spectrometer. All the controls and data acquisition were performed under a computer interfacing software. It was found that temperature affected the fluorescence spectra of fluorescence dyes in terms of both peak intensity and peak position at maximum intensity. The fluorescent intensity decreased at higher temperature for all the samples under the range of 25–55°C and the orange dye was found to be the most temperature sensitive in this temperature range.

Keyword: Laser- induce fluorescence; Fluorescence dyes; Fiber optic spectrometer

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1. Introduction

Optical methods for the measurement of temperature are based on the temperature dependence of absorption, reflectance or luminescence of certain materials. Luminescent temperature sensors have some advantages as they are more suitable for measuring temperature in remote environments (Burt et al., 2005; Campbell et al., Gallery et al., 1994; 1997; Kolodner et al., 1983; Liu et al., 1997; Mills et al., 1999; Mills et al., 2006). Temperature-sensitive paint, known as TSP, is used to create the surface temperature profile of an aerodynamic body. TSP is based on thermal quenching of the luminescence and consists of luminescent dye molecules embedded in an oxygen-impermeable binder. TSP has a much higher spatial resolution compared to the conventional method of thermocouples. The applications of TSP include studying the surface temperature distribution of hypersonic vehicle models, shock boundary layer interactions and boundary layer transition detection. The luminescent sensors are based on the changes in intensity or decay lifetime with temperature. Different types of materials such as inorganic phosphors or organic dye molecules are commonly employed for luminescence based temperature sensing (Khalil et al., 2004; Mills et al., 2006; Mitsubishi et al., 2003).

Fluorescence is an optical phenomenon that involves the illumination of a fluorescent compound with a particular wavelength of light absorbed by the fluorescent compound. As a result, the emission of light with a longer wavelength from the sample is observed. The energy diagram in Figure 1 shows the process of the absorption of a photon at the ground state of fluorescent molecule. The photon absorption excites the fluorescent molecule, which enters a high-energy state. This state is not favorable for the fluorescent molecule for a long period of time. Therefore, in order to re-enter the ground state again the additional energy gained from the photon absorption has to be removed. This can happen in several ways, for instance, by bond cleavage or heat formation. The most common way to release the excess energy in fluorescent molecule is to emit a photon with an energy equivalent of the energy difference between the lowest excited state and the ground state. Hence the emitted photon loses some energy compared with the absorbed energy thus is less energetic and has a longer wavelength than the absorbed photon (Guilbault et al., 1990).

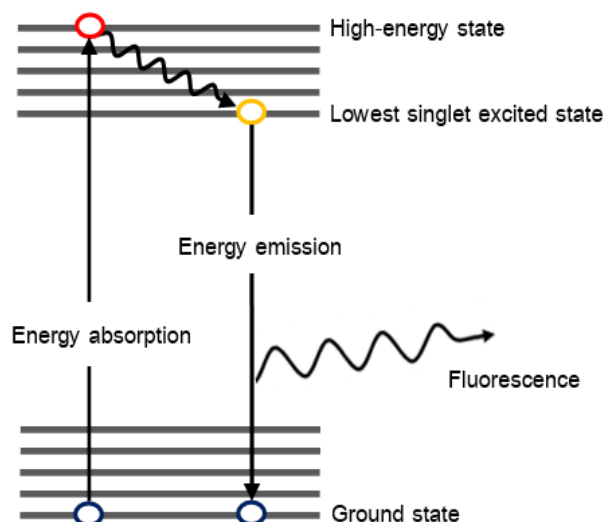


Figure 1. The Jablonski's energy level diagram describes the fluorescence phenomenon.

The effect of temperature illustrates a general tendency for fluorescence quantum yields of solute molecules in liquid solutions to decrease slightly with increasing temperature, presumably because non-radiative decay rate (intersystem crossing and/or internal conversion) increases with increasing temperature (Pantke et al., 1972). Generally, this effect is not large enough to be analytically important unless (a) the luminescence behavior or the solute in question is perturbed by a temperature-dependent chemical and physical phenomenon (such as ground state complex formation, hydrogen bond, or collisional quenching) or (b) two electronically excited states of the solute are very similar in energy, such that thermal energies are sufficient to induce promotion of the molecule from the lower to the upper state (Guilbault et al., 1990).

In this study, the temperature dependence of luminescence decays of fluorescence dyes in different type (the green dye, the orange dye, and the red dye) was investigated. The relationship between the temperature and the intensity of the fluorescence dyes was investigated and compared between the three different dyes to see the temperature sensitivity by luminescence decays of fluorescence dyes.

2. Experimental Procedure

Solutions of fluorescence dyes were prepared by diluting with ethanol in a ratio of 50% of the total volume. The solutions were allowed to cure under ambient conditions for 1 h before measurements.

Luminescence spectra of fluorescence dye solutions were recorded using fiber optic spectrometer, model BTC-110S. The experimental setup consists of the blue laser 470 nm and a temperature control chamber as shown in Figure 2. Effect of temperature on the luminescent intensity of the fluorescence dye solutions was studied using Spectrum Studio software program. The fluorescence dye solutions were illuminated with a radiation of 470 nm using a blue laser excitation source. To study the effect of temperature, the temperature was increased from 25 to 55°C with the step of 5°C. The emission intensities were normalized with the intensity at a reference temperature of 25°C and the normalized intensity was plotted versus temperature. The temperature sensitivity of the intensity of fluorescence dye solutions was interpreted from the slope of the spectra and then compared between the different dyes.

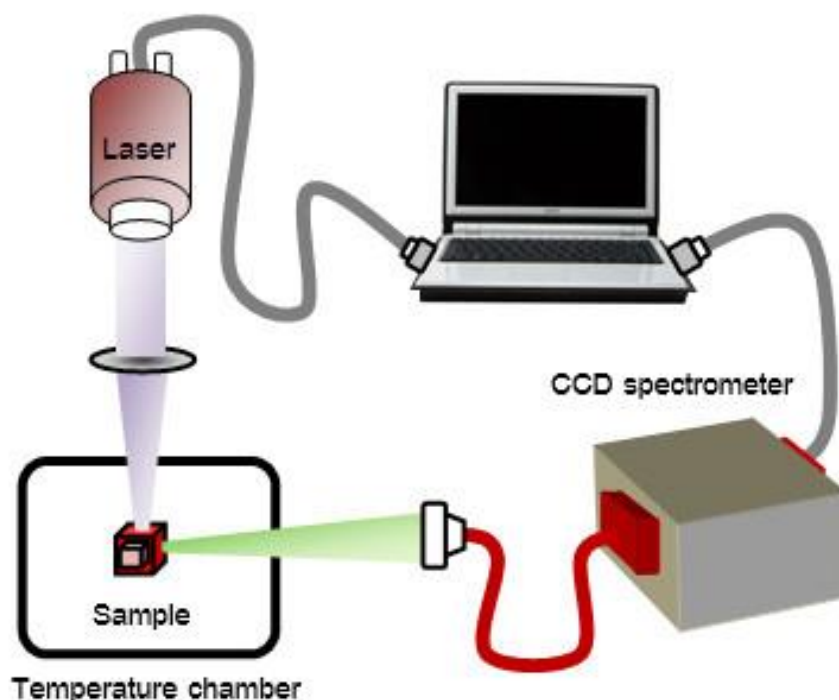


Figure 2. Schematic diagram of the experimental set-up. The laser and the spectrometer system were controlled by a computer.

3. Results

When fluorescence dye solutions were excited by the blue laser in the wavelength range of 470 nm, the energy was absorbed by the molecule dye. This molecule was excited to exciting state energy level and this energy was transferred to the ground state by the fluorescence emission. The fluorescence emission spectra of these solutions were recorded at different temperatures from room temperature (25°C) to 55°C.

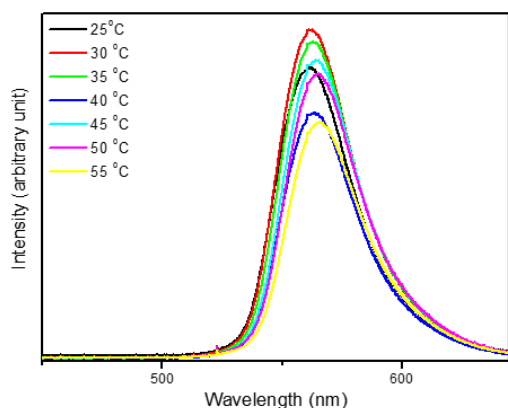


Figure 3. Effect of temperature on the luminescence emission spectra of the green dye

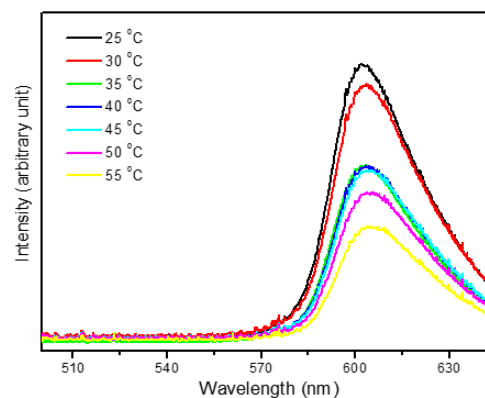


Figure 4. Effect of temperature on the luminescence emission spectra of the orange dye

Fluorescence spectra of the green dye, the orange dye, and the red dye at different temperatures are shown in Figures 3-5. The emission peak was observed at the wavelength around 500-650 nm and emission intensity decreased with an increase in temperature in most cases. The luminescence decays of fluorescence dye, which can be seen from the decrease after the maximum intensity, decrease as the temperature increased. The mechanism of the temperature sensitivity of the fluorescence dye solutions is based on thermal quenching. The effect shows a general tendency for fluorescence quantum yields of solute molecules in liquid solutions to slightly decrease with increasing in temperature because non-radiative decay rate increases with increasing temperature (Guilbault et al., 1990; Pantke et al., 1972). In this case, the luminescence of fluorescence dyes shows practically no quenching by oxygen. It can be seen that the wavelength of the maximum intensity of the green dye spectra is shifted to the higher wavelength at the higher temperatures (Figure 3) and the spectra of the other two dyes show lower sensitivity to the higher temperatures as there is no significant peak shift observed (Figures 4-5) but only the change of the intensity.

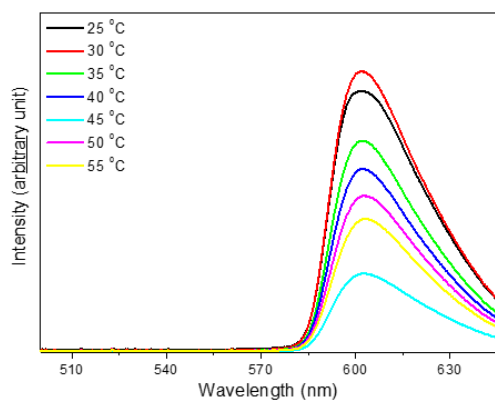


Figure 5. Effect of temperature on the luminescence emission spectra of the red dye

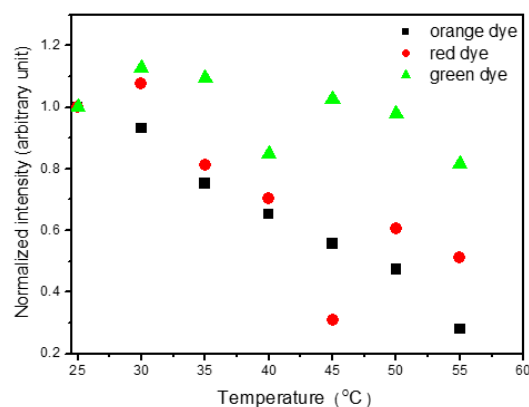


Figure 6. Temperature dependence of spectra of the three fluorescence dyes at the same concentration (50 vol%)

From Figures 3-5, it can also be seen that the intensity of the spectra obtained the green dye is the least sensitive to the change of temperature whereas the spectra of the other two dyes show the greater temperature sensitivity. Figure 6 shows a graph of the variation in the normalized intensity ratio from 25 to 55°C of the three fluorescence dyes to compare the intensity to explain the effect of temperature to the fluorescence spectra. Even though all the fluorescence dyes show a decrease in intensity with an increase in temperature, the rate of decrease in intensity of each fluorescence dye is varied. The plots of normalized intensity versus temperature were linear or nearly linear for the orange dye whereas plot of the red dye and the green dye were nonlinear or linear with lower correlation.

4. Conclusions

The luminescence decays of fluorescence dye decreased as temperature increased and there was no tendency that quenching by oxygen was responsible for the decay. The temperature sensitivity of luminescence intensity of fluorescence dye was found to be dependent on the type of fluorescence dye and temperature sensitivity was maximum for the orange dye and minimum for the green dye in the temperature range of 25–55°C.

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