ผลของอุณหภูมิที่มีต่อสเปกตรัมของการวาวแสงในสีย้อม

Temperature dependence of the luminescence decay in the fluorescent dyes

ศักดิ์สิทธิ์ สุขประสงค์[1,2], ธนบัตร พรมจันทร์[2] และ อธิพงศ์ งามจารุโรจน์[1]*

[1]*ภาควิชาฟิสิกส์และวัสดุศาสตร์ คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่*

[2]*คณะวิทยาศาสตร์ ศรีราชา มหาลัยเกษตรศาสตร์ วิทยาเขตศรีราชา*

Saksit Sukprasong[1], Tanabat promjun[2] and Athipong Ngamjarurojana[1]*

[1]*Department of Physics and Materials Science, Faculty of Science, Chiang Mai University*

[2]*Faculty of Science at Si Racha, Kasetsart University Si Racha Campus*

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

***Corresponding author.** E-mail: wisatre@buu.ac.th

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; Mitsuishi *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 inFigure1 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).

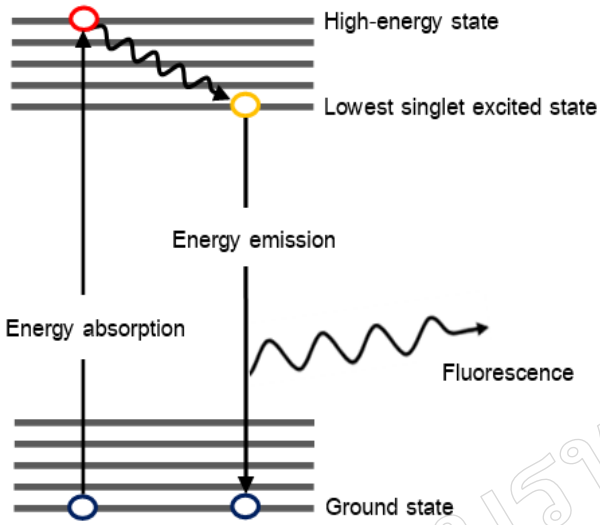

Figure 1 The Jablonski's energy level diagram describes the fluorescence phenomenon.

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 dyeswas 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 ethanolin a ratio of 50% of the total volume. The solutions were allowed to cureunder ambient conditions for 1 h before measurements.

Luminescence spectra of fluorescence dye solutions were recordedusing fiber optic spectrometer, model BTC-110S. The experimental setup consists of the blue laser 470 nm and a temperature control chamberas shown in Figure 2. Effect oftemperature 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 normalizedintensity was plotted versus temperature. The temperaturesensitivity of the intensity offluorescence dye solutions was interpreted from the slope of the spectra and then compared between the different dyes.

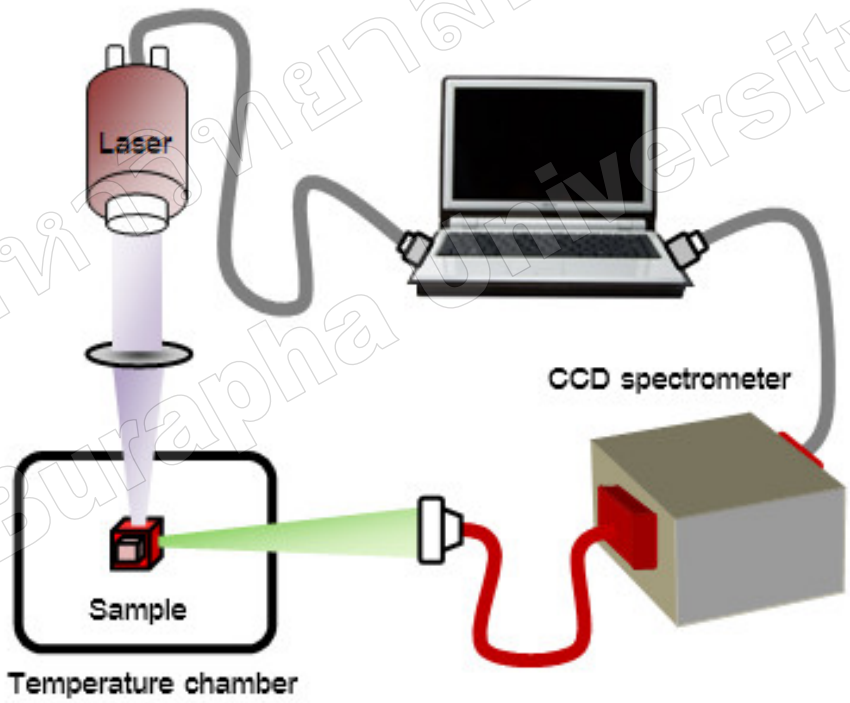

Figure 2 Schematic diagram of the experimental set-up. The laser and the spectrometer system were controlled by a computer.

3. Results

When fluorescence dye solutionswere 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 wererecorded at different temperatures from room temperature (25°C) to 55°C.

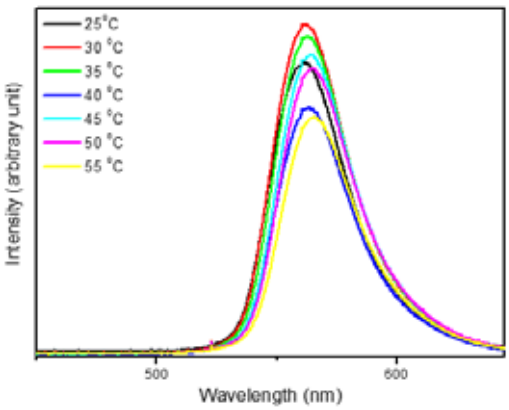

Figure 3 Effect of temperature on the luminescence emissionspectraof the green dye

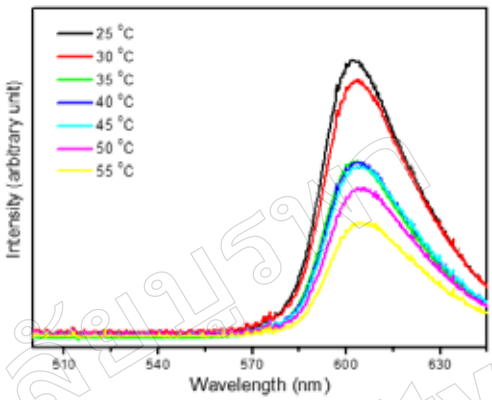

Figure 4 Effect of temperature on the luminescence emission spectra of the orange dye

Fluorescence spectra of the green dye, the orange dye, andthe red dye at different temperatures are shown in Figures 3-5.The emission peak was observed at the wavelength around 500-650nm andemission 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 temperaturesensitivity of the fluorescence dye solutions is basedon 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 practicallyno 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.

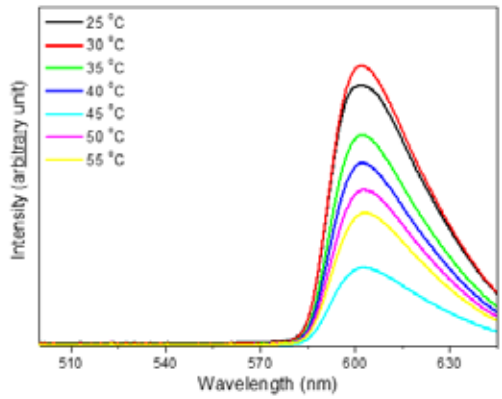

Figure 5 Effect of temperature on the luminescence emission spectra of the red dye

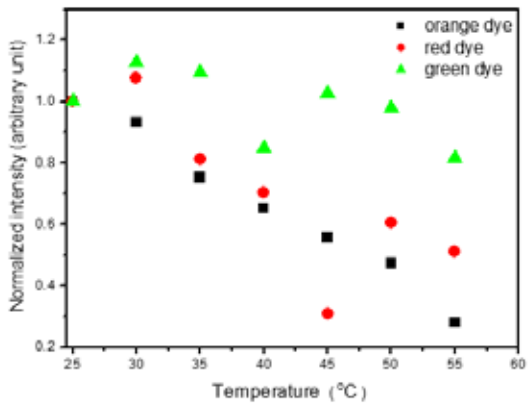

Figure 6 Temperature dependence of spectraof the three fluorescence dyes at the same concentration (50 vol%)

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 thevariation in the normalized intensity ratio from 25 to 55°C of the threefluorescence dyesto compare the intensity to explain the effect of temperature to the fluorescence spectra. Eventhough all the fluorescence dyesshow a decrease in intensity with an increase in temperature,the rate of decrease in intensity of each fluorescence dye is varied. The plots ofnormalized intensity versus temperature were linear or nearly linear for the orange dye whereas plot of the red dye and the green dyewere nonlinear or linear with lower correlation.

4. Conclusions

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

5. Acknowledgment

This work was supported byLaser and Applied Optics Research Laboratory, Department of Physics and Materials Science, Faculty of Science, CMU. We also acknowledge Assist. Prof. Dr. Samran Lacharojana for discussion and technical support.

6. References

Burt, M.C. and Dave, B.C. (2005). An optical temperature sensing system based on encapsulation of a dye molecule in organosilica. sol–gels. *B.C. Sensor. Actuator. B, 107*, 552-566.

Campbell, B., Liu, T., Burns, S.P. and Sullivan, J.P. (1997). Rotor blade pressure measurement in a high speed axial compressor using pressure and temperature sensitive plants.*AIAA Paper. 94,* 6-9.

Gallery, J.,Gouterman, M., Callis, J. and Khalil, G.(1994).Luminescent thermometry for aerodynamic measurements. *Rev. Sci. Instrum. 65*, 712-720.

Guilbault, G. G. (1990). Practical Fluorescence(2th ed.).New York: Marcel Dekker. Kolodner, P. and Tyson,J.A. (1983).Remote thermal imaging with 0.7-μm spatial resolution using temperature-thin flims.*Appl. Phys. Lett. 42,* 117-119.

Khalil, G.E., Lau, K., Phelan, G.D., Carlson, B., Gouterman, M., Callis, J.B., et al.(2004). Europium beta-diketonate temperature sensors: Effects of ligands, matrix, and concentration.*Rev. Sci. Instrum. 75,* 192-206.

Liu, T., Campbell, B., Burns, S.P. and Sullivan, J.P.(1997). Temperature- and pressure-sensitive luminescent paints in aerodynamics.*Appl. Mech. Rev. 50*, 227-246.

Mills, A. andLepre, A.(1999). Development of novel thermochromic plastic films for optical temperature sensing. *Analyst, 124*, 685-689.

Mills, A.,Tommons, C., Bailey, R.T., Tedford, M.C. and Crilly, P.J.(2006).Luminescence temperature sensing using poly(vinyl alcohol)-encapsulated $Ru(bpy)_3^{2+}$ films. *Analyst. 131,* 495-500.

Mitsuishi, M., Kikuchi, S., Miyashita, T., Amao, Y. and Mater,(2003).Characterization of an ultrathin polymer optode and its application to temperature sensors based on luminescent europium complexes. *J. Chem. 13*, 2875-2879.

Pantke, E.R. and Labhart, H. (1972). On the temperature dependence of non-radiative deactivation processes. Chemical Physics Letters.16, 255-259.