

A Photochromic Dye Activation Method for Measuring the Thickness of Liquid Films

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To measure the thickness of liquid films from 10 to 60 μm , we used photochromic dye activation. And we used silicone oil with 10 centi-Stokes and commercial photochromic dyes. To make films with exact and known thicknesses, we used two glass wafers. A film formed between two wafers after placing a drop of liquid of known volume on one wafer and covering the other. The film thickness could be estimated from the diameter of wafer and the dropped liquid volume. To quantitatively evaluate the result, captured the images using digital camera then analyzed the images using the image tool. The gray scale intensity using the captured images of activated dye with these thicknesses showed the repeatability below $\pm 1.0\%$ when measured with a silicone oil solution containing 0.1% SO and SO-ANTH dyes. And we showed that photochromic dye activation method could be used to measure our liquid film thickness ranges.

Key Words : Liquid film thickness, Photochromic dye activation

Introduction

Liquid films form during two-phase flow, lubrication, and coating phenomena. Measuring a film's thickness is essential in the analysis of its physical characteristics. With two-phase flow, including slug, annular, and stratified flows, liquid films occur in experiments using tubes or channels. Liquid films are also encountered in experiments using miniature to microscopic test systems, and a non-intrusive method of measuring thin films is needed.

Over the last thirty years, many studies have examined the measurement of liquid film thickness. The method of measurement can usually be categorized into one of two groups: contact (intrusive) and non-contact methods. One of the contact methods is conductance method, which uses the conductivity of the liquid; it was developed by Jayanti *et al.*,¹ Kang *et al.*,² and Fukano.³ Unfortunately, it cannot be applied to non-conducting liquids and contact with the liquid layer is required. Non-contact methods include capacitance, optical, ultrasonic transmission, and fluorescence methods. For the capacitance method, Klausner *et al.*⁴ developed a probe that can be applied to dielectric or conductive liquids and made a calibration curve up to 2 mm thick. Thorncroft *et al.*⁵ calibrated the thickness using other refrigerants. McAdam *et al.*⁶ devised the first optical method for measuring liquid film thickness using the Schlieren system. Other methods use laser scattering and reflection properties (*e.g.*, Salazar *et al.*⁷; Hurlburt *et al.*⁸; Evseev⁹; Shedd *et al.*¹⁰; Zhang *et al.*¹¹; Mouza *et al.*¹²). Most optical methods require a probe and a complicated system of optical and signal processing components. Kamei *et al.*¹³ compared methods with films on water up to 300 μm thick, using a needle probe. A number of researchers have developed fluorescence methods for measuring liquid film thickness (*e.g.*, Smart *et al.*¹⁴; Driscoll *et al.*¹⁵; Johnson *et al.*¹⁶; Makarytchev *et al.*¹⁷). Fluorescence methods usually have to need a

detector synchronized to measure the photon intensity for detection of steady-state fluorescence. And fluorescence dyes have the decrease characteristics of quantum efficiency to the time.

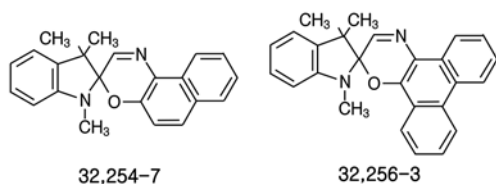
Here, we propose a method to measure the liquid film thickness from 10 to 60 μm using photochromic dye activation. It doesn't have the decrease of the quantum efficiency and the hysteresis to the temperature. Photochromic dye activation was usually used for measurement of velocity distribution or profile in the flow fields.¹⁹⁻²¹ But in this research, our method uses chemical characteristics of the photochromic dye. The number of photochromic dye molecules within the liquid layer is proportionate to the liquid film thickness under the same mass fraction. When irradiated with a laser, we can measure the different color intensities at different film thickness. We used one of spironaphthoxazine series and one of spiroanthraoxazine series. As working fluid, we chose silicone oil with viscosity of 10 centi Stokes. Silicone oil is one of the liquids that can dissolve the dyes.

Photochromic Dye Activation Method

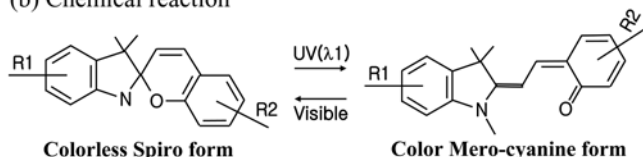
Photochromic dye. Photochromic dyes show a reversible color change when exposed to a certain wavelength of light. The reverse reaction either occurs instantly or requires energy input of some sort. This reaction is distinct from photochemical reactions, which are considered virtually irreversible.¹⁸ Photochromic dye activation methods are used to measure the velocity of various flow fields because they do not disturb the flow field of interest. Moreover, they have the advantage of co-existing with liquids and have been applied to study flow structures and flow fields in the liquid region of two-phase flows, such as slug, stratified, and wavy flows (Kawaji *et al.*¹⁹; Kawaji²⁰; Lorencez *et al.*²¹).

As shown in Figure 1, the general reaction of photo-

(a) Chemical structures

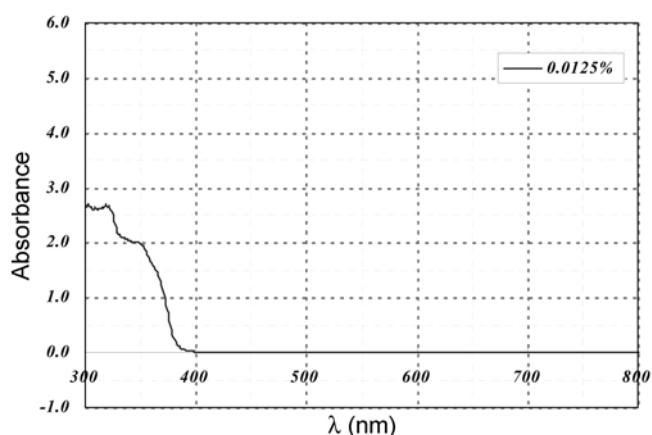


(b) Chemical reaction

**Figure 1.** Characteristics of photochromic dyes.

chromic dyes involves a change from a colorless form to a colored form on irradiation with UV and reversion to the colorless form within a short time after removing the UV source. We used two commercial photochromic dyes from Sigma-Aldrich Inc.: SO (spironaphthoxazine) and of SO-ANTH (spiroanthraoxazine) series, respectively. Two dyes used in our study turned violet under UV irradiation. SO (32254-7) is normally transparent, even at high mass fraction, while concentrated SO-ANTH (32256-3) solutions are a light pink. Both have similar chemical structures, as shown in Figure 1. Two dyes could be solved in the silicone oil used as our working fluid and refrigerants. For water, detailed explanations of the dye species and their mechanism have been published elsewhere (Fogwell *et al.*¹⁸).

Photochromic dye activation wavelength. To use these dyes, we needed to measure their spectra to determine the optimum activation wavelength for the photochromic reaction and a suitable laser light source. The spectra of 10 centi-Stokes silicone oil solution with 0.0125% mass fraction of SO dye was measured using a UV-2501PC spectrophotometer (Shimadzu Inc.) at wavelengths from 200 to 800 nm. The absorbance, A , was calculated from the ratio

**Figure 2.** Spectra using silicone oil with SO dye.

of the transmitted light intensity of the pure compound, I_0 , to that of a solution at concentration c , I_c , using the equation:

$$A = \text{Log}\left(\frac{I_0}{I_c}\right) \quad (1)$$

Figure 2 shows that SO has maximum absorbance at about 310 nm. And we also found that these spectral characteristics depend only on the dye species and are unaffected by mass fraction. Given these peaks, we used a 337-nm nitrogen laser as the excitation source. Based on results of previous studies, it is well known that the excitation wavelength does not change much for solvents of similar polarity (Kim *et al.*²²; Lee *et al.*²³). And we could obtain the same results with both dyes. All the measurements were performed at ambient temperature and atmospheric pressure.

Calibration Experiments

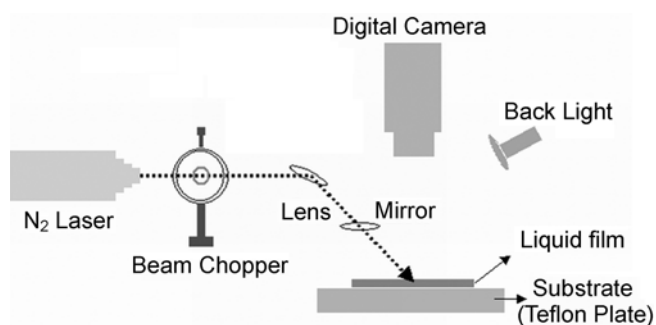
Experimental apparatus. The apparatus used to calibrate liquid film thickness consists a nitrogen laser and other optical components, an image-capturing system to obtain images of the color-change, and a device to make liquid films of constant, uniform thickness (Figure 3).

The optical system consisted of a 337-nm nitrogen laser (VSL-337, Laser Science Inc.), a beam chopper to chop the original laser beam, one mirror, and one lens. Using the chopper, lens, and mirror, we could reduce the area of irradiation from 3×8 mm at about $130 \mu\text{J}$, to an ellipse with major and minor axes of 2 and 1 mm, respectively, at $45 \mu\text{J}$. The intensities were measured with a PE25-SH and NOVA Display (OPHIR Inc.).

To capture color images of the dye solution, we used a DSC-F707 digital camera (Sony Inc.) with a maximum field of 2560×1920 pixels and two commercial desk lamps for back lighting. We captured 2048×1536 -pixel images using a focal length of 11 cm.

Experimental method. In the experiments, we needed to make a liquid film of exact known thickness using a silicone oil solution of the photochromic dyes and to use an image-processing tool to quantify each image of the liquid film irradiated by the laser.

To make liquid films with exact and known thicknesses from 10 to $60 \mu\text{m}$, we used two 4"-diameter soda-lime glass

**Figure 3.** Experimental apparatus diagram for calibration.

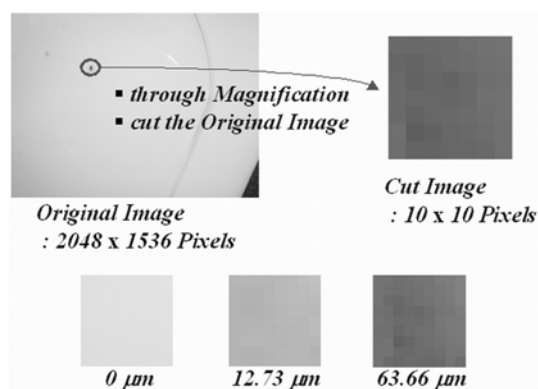


Figure 4. Image processing.

wafers with 1-nm roughness. A film formed between the two wafers within a few seconds after placing a drop of the liquid of known volume using a micropipette on one wafer and covering it with the other. The film thickness could be estimated from the diameter of the wafer and the volume of liquid by using the equation:

$$\delta = \frac{A_w}{V_s} \quad (2)$$

where δ is the liquid film thickness [m], A_w is the wafer area [m²], and V_s is the liquid volume [m³]. Both parameters could be determined with sufficient accuracy as following.

The minimum volume of liquid that could be spread uniformly on a 4"-wafer was 100 μ -liter, and the calculated liquid film thickness was 12.73 μ m. We could not make a liquid film between the two wafers using more than 700 μ -liter of liquid, because liquid spilled from between the wafers. The maximum thickness of 63.66 μ m was obtained for 600 μ -liter. The liquid volume was measured and dropped using the micropipette with 0.4%/0.1cc high accuracy; which 0.4%/0.1cc corresponds to 0.6 μ m.

Images of the photochromic dye solution were obtained using a digital camera on irradiation with the laser. And to check the uniformity of liquid film, we captured minimum 4 images for each thickness. Then, a 10 \times 10-pixel area of the original image of each thickness was obtained using Animation Shop from Jasc Software (Figure 4); the final images of each thickness were converted to gray-scale images and quantified using Paint Shop Pro. The rate at which the photochromic dyes fade is usually known as a function of concentration. For our dyes, the total fading time was about 3 s. Within 1 s, we found that the color maintained as the initial gray intensity.

To calibrate the system, we varied the liquid film thickness and dye species under 0.1% mass fraction at fixed laser intensity.

Results and Discussion

Calibration results. We calibrated our apparatus using 10 centi-Stokes silicone oil with a fixed 0.1% mass fraction of

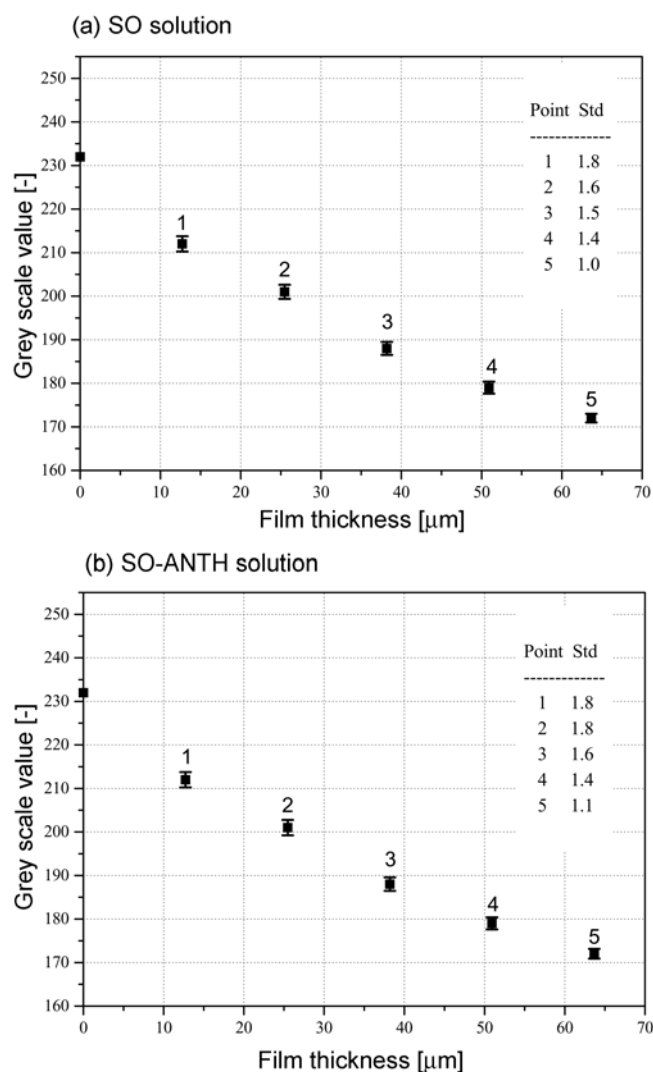


Figure 5. Standard deviation of liquid film thickness.

dye. 0.1% is the mass fraction that has been usually used to measure flow velocity and to reveal the flow structure of general flow fields or two-phase flow as like Kawaji *et al.*,¹⁹ Kawaji²⁰ and Lorencez *et al.*²¹ Solutions of two dyes were measured using films from 12.73 to 63.66 μ m thick and the gray-scale values are plotted and added the standard deviations for each thickness as gray-scale value in Figure 5. Gray-scale values of 255 and 0 represent absolute white and black, respectively. Each symbol in the figure is the average of at least nine measurements of each thickness. The standard deviation in measuring the liquid film thickness was ± 1.8 as the gray-scale value in case of 12.73 μ m and below $\pm 1.0\%$ over the full calibration range. For 63.66 μ m liquid film, the standard deviations decrease into about ± 1.0 . The gray-scale value of 1.8 and 1.0 is corresponding to 1.95 μ m and 1.09 μ m, respectively.

Results for various test conditions. Based on the calibration results using our methodology, we performed the tests to decide the optimum dye mass fraction for measuring film thickness of silicone oil. To do so, we measured the image intensities for 1.0, 0.5, 0.3, 0.1, 0.05, and 0.01%

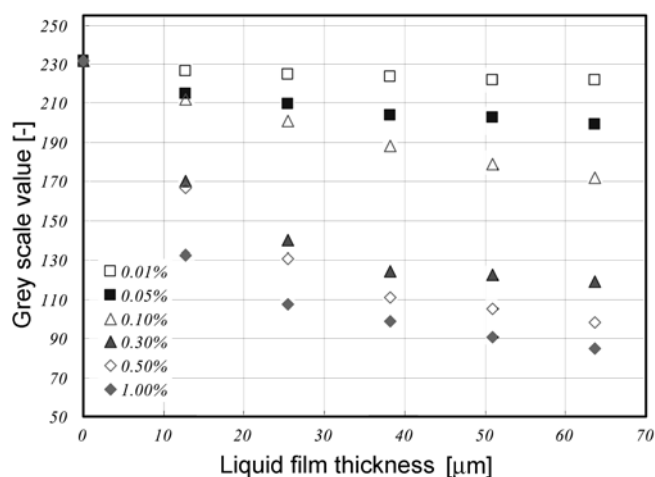


Figure 6. Thickness of liquid films using SO solution.

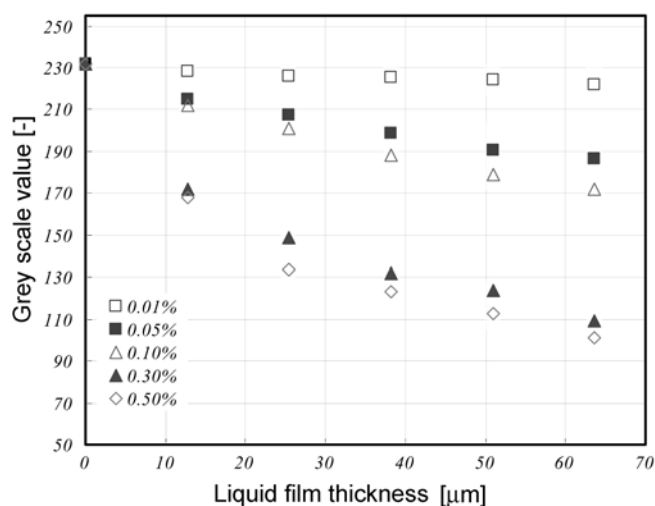


Figure 7. Thickness of liquid films using SO-ANTH solution.

solutions of SO and SO-ANTH dyes. As shown in Figures 6 and 7, the gray color intensity of the dyes decreased with mass fraction. Over all mass fractions, we obtained darker images for a thicker film at the same mass fraction. These results are reasonable, as at a constant mass fraction there are more dye molecules in a thicker film. And especially for 0.1% mass fraction of two dyes, the color intensities are almost linearly changed with liquid film thickness. The coefficients of determination of linearly fitted curve are 0.97 and 0.94 for SO and SO-ANTH dyes, respectively.

The relationship was not linear except thinner liquid thickness over 0.1%. For SO dye, the gray scale changed almost linearly at mass fractions up to 0.1%, while at mass fractions over 0.3%, the relative color intensity changed almost linearly for films less than 20 μm thick and then quickly became saturated. Similar results were seen for SO-ANTH. This can be explained using Lambert-Beer's Law.

$$\frac{I_i - I_a}{I_i} = \exp(-\varepsilon \cdot c \cdot \delta) \quad (3)$$

With assumption that $-\varepsilon \cdot c \cdot \delta$ term is small, equation (3) can be represented into equation (4).

$$\frac{I_i - I_a}{I_i} = -\varepsilon \cdot c \cdot \delta \quad (4)$$

And I_a can be arranged as following equation.

$$I_a = I_i \times (1.0 + \varepsilon \cdot c \cdot \delta) \quad (5)$$

Here, I_i is the intensity of the beam irradiating the liquid film, I_a is the intensity of the beam absorbed by the photochromic dye, ε is the molar absorptivity [$1/\text{M}\cdot\text{cm}$], c is the molar concentration of photochromic dye [mol/L], and δ is the liquid film thickness [m].

At higher mass fractions and thicker liquid films, the color intensity decreases exponentially, as in Equation (3). At lower mass fractions and thinner liquid films, the dye absorption intensity, I_a , can change almost linearly with liquid film thickness, as in Equation (5), which is derived from equation (3) via (4). Therefore, the measured color intensities showed the same trend.

SO-ANTH dye coagulated in silicone oil solution at mass fractions as low as 0.3%, and coagulation increased with mass fraction. Consequently, we could not obtain data for 1.0%.

Conclusions

We reached the following conclusions in this study.

1) Spectrometry determined that the optimum excitation wavelength for the maximum absorbance of the SO (spironaphthoxazine) and SO-ANTH (spiro-anthraoxazine) photochromic dyes dissolved in silicone oil was about 340 nm. The dyes turned violet on being irradiated.

2) We proposed a method for measuring liquid film thickness that uses a simple optical system, unlike the complicated systems in previous studies, and photochromic dye activation, which results in increased color intensity with increasing film thickness on irradiation at a fixed beam intensity. Our proposed method had the repeatability below $\pm 1.0\%$ over the full range from 10 to 65 μm .

3) Experiments showed that the color intensity of two dyes changed almost linearly within acceptable error range of this research over the full range from 10 to 65 μm at 0.1% by mass fraction. For lower than 0.1%, the image intensities had the lower coefficients of determination of linearly fitted curve than that of 0.1%. And for higher than 0.1% and thicker film thicknesses, the image intensities changed as logarithmic to the liquid film thickness. From these results, we can conclude that the optimum dye mass fraction in silicone oil is about 0.1% of our measuring mass fractions to apply to the measurement of the liquid film thickness from 10 to 65 μm .

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