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Notes

Multispectral Determination of Soap Film Thickness

Paul D. T. Huibers[*,†] and Dinesh O. Shah

Department of Chemical Engineering, Center for Surface
Science & Engineering, University of Florida,
P.O. Box 116005, Gainesville, Florida 32611-6005

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Introduction

Everyone has seen the colorful bands in a soap film, or in an oil slick on the surface of water. The brilliant bands that we see are the components of the spectrum, ranging from red to violet. We see these interference colors because the film is being illuminated with polychromatic light, and the thickness of the film is roughly of the order of a wavelength of light.[1] The light reflected from the top of this film travels a different distance to our eye than reflections from the bottom of the film, and light from these two paths interferes both constructively and destructively. This interference is strongly wavelength dependent, resulting in certain colors having a high intensity while other colors are absent, depending on the thickness of the film and the angle of observation.[2−4] Light passing *through* a transparent film undergoes similar interference, which can be taken advantage of for the measurement of film thickness. The interference caused by light transmitted through two partially reflecting surfaces was first used almost a century ago by Fabry and Perot,[5] who used their interferometer to accurately characterize monochromatic light sources.

The availability of fast diode-array UV−vis spectrophotometers in the last few years has brought about an interesting situation, where one can simultaneously measure the intensity of light transmitted through a sample at many wavelengths and repeat these measurements over relatively short time intervals. Typical capabilities of a modern instrument are the measurement of absorbance at over 900 different wavelengths, covering the range from 190 to 1100 nm in 1 nm steps, with measurements taken every 0.1 s of accuracy greater than 0.001 absorbance unit. Although traditionally a cuvette is placed in the beam path, allowing the absorbance of a liquid sample to be measured through a 1 cm liquid path, the cuvette holder can easily be replaced with a cell holder for a wire loop containing a soap film (Figure 1).

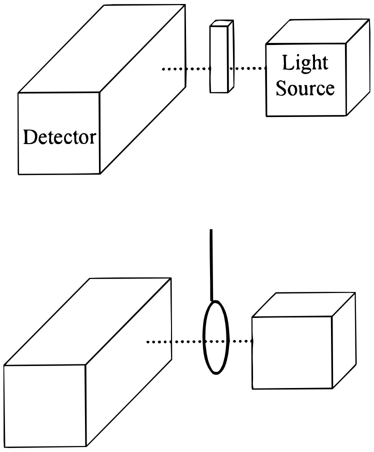

Figure 1. Application of a UV−vis spectrophotometer for measurement of solution absorbance (top) and soap film thickness (bottom).

As with the soap film or oil slick mentioned above, we take advantage of the difference in distance traveled by light reflected from the film interfaces. The measurement of film thickness from reflected light has been well-established.[3,6] The measurement of film thickness by transmitted light is well understood from a theoretical point of view but could not be taken advantage of until the development of fast and sensitive diode array spectrometers. By measurment of the transmitted light over a broad wavelength range, the film thickness can be determined from the peaks and valleys of the absorbance spectrum. Additionally, measurement of film thickness over time allows calculation of the rate of film drainage. The determination of film thickness and drainage rate can provide valuable insight into processes involving foamability and foam stability, allowing the study of the effect of different surface active materials or bulk solutes on these properties in a repeatable way. Detailed studies can be done on individual soap films that are not possible on the films present in foams.

Experimental Section

Soap films were made with 200 mM sodium dodecyl sulfate (SDS) solutions by dipping a 1.3 cm diameter loop made from 21 gauge wire into the solution and placing in the light path of the spectrophotometer. SDS (99%, Sigma, St. Louis, MO) was used as received. Absorbance measurements were taken at 25 °C using a Hewlett-Packard 8453 UV−visible diode array absorbance spectrometer. The kinetics mode available in the HP Biochemical Analysis Software (part no. G1117) was used to measure absorbance spectra at regular intervals.

Results and Discussion

A schematic diagram of the transmitted and reflected light through a transparent thin film can be seen in Figure 2. It is a fundamental property of optics that light passing through an interface between materials of different indices of refraction will be divided into transmitted and reflected components, assuming the incident angle is less than the Brewster angle. The relative proportions of the two components are determined by the angle of incidence (θ_i) and the indices of refraction (n_1, n_2) of the two materials.

The interference of light rays observed from reflections off of a film are different than the interference from transmitted light (Figure 2), as the reflected rays (I_1^r, I_2^r)

[†] Current address: Department of Chemical Engineering, Massachusetts Institute of Technology, #66-317, Cambridge, MA 02139-4307. E-mail: huibers@mit.edu.

(1) Perkampus, H.-H. *Encyclopedia of Spectroscopy*; VCH: New York, 1995; pp 283−288.

(2) Vasicek, A. *Optics of Thin Films*; North Holland: Amsterdam, 1960; Chapter 3.

(3) Heavens, O. S. *Optical Properties of Thin Solid Films*; Dover: New York, 1965.

(4) Princen, H. M.; Mason, S. G. *J. Colloid Sci.* **1965**, *20*, 453.

(5) Fabry, C.; Perot, A. *Ann. Chim. Phys.* **1899**, *16*, 115.

(6) Lyklema, J.; Scholten, P. C.; Mysels, K. *J. Phys. Chem.* **1965**, *69*, 116.

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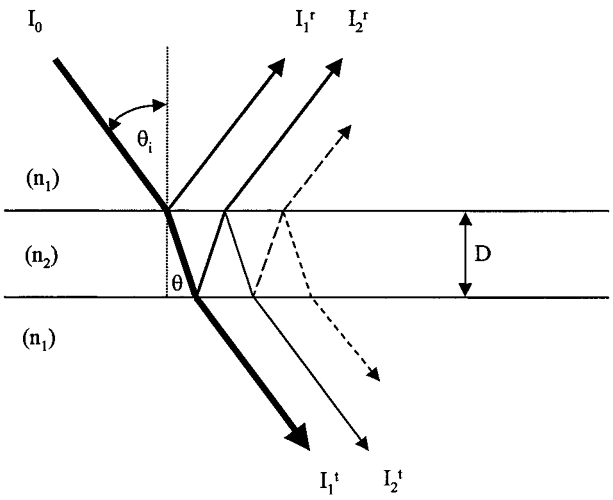

Figure 2. Interference caused by light traveling different paths through a film.

are approximately the same intensity, while the transmitted rays (I_1^t, I_2^t) are of much different intensities. Thus, bright color bands can be seen in the reflected light but not in the transmitted light, where the film generally appears transparent.[2,3] The interference caused by the twice reflected transmitted light (I_2^t) is detectable by a sensitive absorbance spectrophotometer, and the wavelength dependence of this absorbance is what we take advantage of for film thickness measurements.

Interference Maxima and Minima. Constructive interference between two rays of the same wavelength occurs when the light from one ray has traveled an integral multiple of the wavelength with respect to the other ray, and destructive interference occurs when the path difference is a half integral multiple of the wavelength. The phase shift introduced by the different light paths traveling through a thin film (Figure 2) must be treated separately for each wavelength (λ) of light. The path length of light through the film must be modified by the angle (θ) and the optical thickness (index of refraction, n_2) of the film material.[7] For light transmitted through a film, a maximum in intensity (minimum in absorbance) will occur when

$$2n_2D\cos\theta/(m+1) = \lambda \tag{1}$$

and a minimum (maximum in absorbance) will occur when

$$2n_2D\cos\theta/(m+1/2) = \lambda \tag{2}$$

where D is the film thickness and m is a nonnegative integer (m = 0, 1, 2, ...). Note that for all cases except normal incidence ($\theta = 0$), the reflected and transmitted rays must be considered as consisting of two polarized components, one normal and one perpendicular to the plane of incidence, with different coefficients for both components.

Wavelength Dependence of the Index of Refraction. The index of refraction data reported for most substances is measured at a wavelength of 589.3 nm (a sodium emission line), and in thickness calculations it is often assumed to be constant over the visible range. For water this assumption is accurate to within 1% over the range 400−700 nm, but the error becomes much larger in the ultraviolet region. Quan and Fry[8] have developed an empirical model for the index of refraction of water as a function of temperature, salinity, and wavelength (400−700 nm). Assuming 25 °C and 0% salinity, their equation reduces to

$$n(\lambda) = 1.31279 + 15.762\lambda^{-1} - 4382\lambda^{-2} + (1.1455\times10^{6})\lambda^{-3} \tag{3}$$

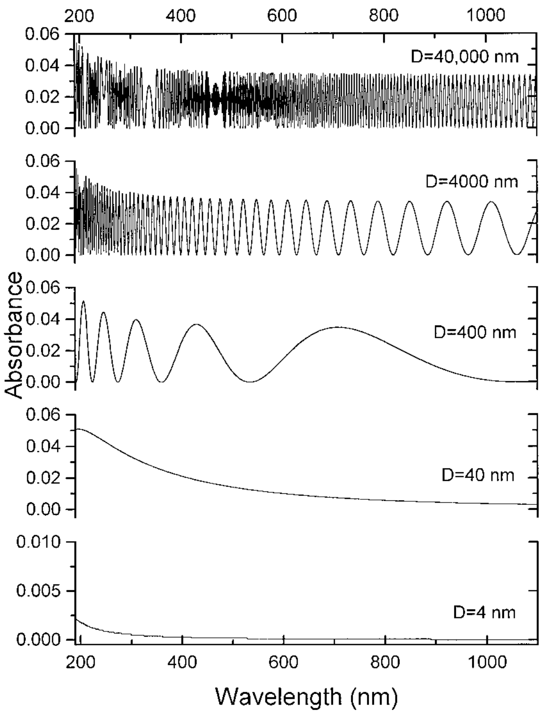

Figure 3. Predicted absorbance spectra for soap films of different thickness.

where λ is the wavelength in nanometers. On testing with additional data outside the 400−700 nm wavelength range, it can be demonstrated that the equation is valid over 200−1100 nm.[9] The error caused by assuming a constant index of refraction is over 10% for water at 190 nm. The calculation of film thickness can be corrected by using n calculated from eq 3.

Determination of Film Thickness. There are several possible regimes where different methods of calculating the film thickness are required. For the thickest films, many absorbance maxima and minima are observable (Figure 3, top). The period of one cycle may be so small that the lower end of the absorbance spectrum is useless, and complete cycles will only be resolved well at the higher end of the spectrum. The irregular envelope of the left part of the top spectrum (D = 40 000 nm) is due to the sampling of a sinusoidal waveform at less than twice its frequency. For regions where individual cycles can be clearly resolved in the spectrum, the film thickness can easily be determined by the formulas

$$\nu = [n_2(\lambda_1)/\lambda_1 - n_2(\lambda_2)/\lambda_2]/N_{\text{cyc}} \tag{4a}$$

$$D = (2\nu)^{-1} \tag{4b}$$

where D is the film thickness, N_{cyc} is the number of cycles observed from wavelength λ_1 to λ_2 ($\lambda_1 < \lambda_2$), and ν is the period of a single cycle, adjusted for the wavelength dependent index of refraction.

Once the film thickness is so small that one complete cycle is not observable, the thickness can be determined from a single maximum and a single minimum (half of a

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[7] Born, M.; Wolf, E. *Principles of Optics*, 6th ed.; Pergamon Press: New York, 1980; Section 7.6, 15b.

[8] Quan, X.; Fry, E. S. *Appl. Opt.* **1995**, *34*, 3477.

[9] Huibers, P. D. T. *Appl. Opt.* **1997**, *36*, 3785.

cycle) in the absorbance spectrum. Equation 4 can be used, with λ_1 for the maximum and λ_2 for the minimum, using $N_{cyc} = 0.5$. Given a single maximum, it is still possible to precisely determine film thickness. The theoretical minimum thickness that can be determined unambiguously from the absorbance maximum is $D = \lambda/(4n_2)$, which for 190 nm is a minimum measurable thickness of water ($n_2 = 1.441$) of 33.0 nm.[10] This formula can be derived by solving eq 2 for $m = 0$.

It is possible to estimate absorbance from thinner films, but one has only the slope to the right of the peak (Figure 3, bottom) to use in order to estimate the wavelength where the absorbance peak would occur. Although the peak will occur below 190 nm, the shape of the absorbance spectrum above 190 nm will be dependent on the thickness and can be predicted, using eq 5. For example, given only the absorbance spectrum above 400 nm in Figure 3 (for $D = 40$ nm), it should be possible to estimate that the absorbance peak will occur at 195 nm, from which the film thickness can be determined. The observed maximum and minimum absorbance values as predicted by eq 5 should be established with measurements on films of the same material that are sufficiently thick for multiple maxima and minima to be observed. This must be done in order to establish whether a baseline adjustment in the absorbance spectrum is necessary (due to the influence of solutes with UV absorption chromophores or other absorbance mechanisms), so that the minimum and maximum expected absorbance values can be correctly offset.

Estimation of Absorbance Spectra. The intensity as a function of wavelength for light transmitted through a transparent film at normal incidence may be calculated by[7]

$$I(\lambda) = I_0(1 - r)^2/[1 + r^2 - 2r\cos(4\pi n_2 D/\lambda)] \quad (5)$$

where I_0 is the incident intensity on the film, n_2 is the index of refraction of the film material, D is the thickness of the film, and r is the reflection coefficient at a single interface, which can be calculated by the following

$$r = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2 \quad (6)$$

At the air/water interface, where n_1 (air) is 1.000 and n_2 (water) is 1.333, the reflectivity (r) is 0.0204, so 98% of light entering at normal incidence is transmitted. Note that r is a function of wavelength because of the n dependence, with r increasing at shorter wavelengths. From eq 5, the maximum transmission coefficient ($T = I/I_0$) can be determined as well as the minimum, $T_{min} = (1 - r)^2/(1 + r)^2$. For any r the maximum transmission coefficient is 1.0, and for $r = 0.0204$ ($n = 1.333$) the minimum transmission coefficient is 0.922 ($A = 0.035$). Absorbance (A) is determined from transmitted intensity (I) by the following equation:

$$A = -\log\left(\frac{I}{I_0}\right) \quad (8)$$

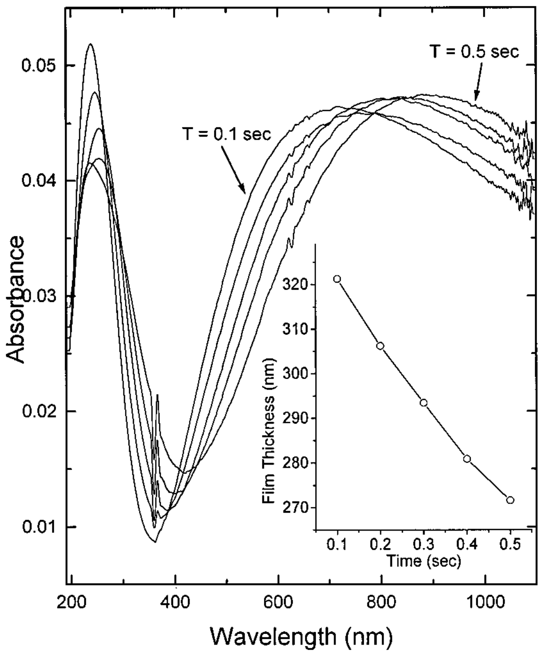

Figure 4. Absorbance spectra of light transmitted through a soap film, measured at 0.1 s intervals. Inset: Soap film thickness vs time.

Range of Thickness Measurements. The minimum and maximum observable thicknesses are determined by the capability of the UV–visible spectrophotometer. For a spectrometer with a detection capability of 190–1100 nm in 1 nm steps, this technique should allow measurement of a wide range of film thickness. The maximum thickness is determined by the detector spacing ($\Delta\lambda$) in the infrared. Assuming $\Delta\lambda = 1$ nm and observed peaks spaced every 2 nm (e.g., 1100, 1098, 1096 nm) the maximum observable thickness of aqueous films is 57 μm. The minimum thickness is determined by the ultraviolet capabilities of the instrument. For a minimum detectable wavelength of 190 nm, the thinnest possible film determined unambiguously from absorbance peaks (see above discussion) for water is 33.0 nm. It should be possible from accurate modeling of the absorbance spectrum using eq 5 to estimate film thickness below 5 nm. Sample absorbance spectra calculated for films of different thickness can be seen in Figure 3. It must be emphasized that the thickness measurement is derived entirely from reflections at the film/air interfaces and are not dependent on any absorption property of the film material (as in thickness measured by the Beer–Lambert law). Thus, the ability to measure the film thickness, and the accuracy of the measurement, is not diminishing as the film thickness decreases.

Measurement of Soap Film Thickness. For a demonstration of the optical method of film thickness determination, we measured soap film thickness for some SDS films. Five measurements were taken over a half second, immediately after the film loop was dipped into the solution. Absorbance measurements over the range 190–1100 nm were taken (0.1 s intervals) for a film made from 200 mM SDS. From the resulting absorbance spectra (Figure 4), the film thickness was calculated from the observed minima and maxima (Figure 4, inset) by applying eq 4. By measurment of film thickness over time, the rate of drainage of a film can be studied. Foam drainage occurs due to gravity and border channel edge effects.[11] Generally, the rate of thinning varies inversely with the width of the film.[12] The slope of the graph of film thickness vs time for this film (Figure 4, inset) establishes the initial drainage rate.

Validation with a Mica Sheet. In order to test the methods developed here, it would be ideal to have an

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(10) Bikerman, J. J. *Foams*; Springer-Verlag: New York, 1973, pp 214–222.

(11) Adamson, A. W. *Physical Chemistry of Surfaces*; Wiley: New York, 1990; pp 546–551.

(12) Mysels, K. J.; Shinoda, K.; Frankel, S. *Soap Films, Studies of Their Thinning and a Bibliography*; Pergamon: New York, 1959.

optically transparent film of known thickness. A test was done with a thin sheet of muscovite (mica). Mica was used because it cleaves perfectly along its {001} plane, providing a sufficiently large sheet of uniform thickness. The index of refraction of this material depends on direction, and normal to the {001} plane the index is reported to be $n_\alpha = 1.552-1.574$. To validate the optical technique, the thickness if a sample mica sheet was determined from the mass, area, and density of the sheet using $D = M/(\rho A)$. Given a mass of 8.0 mg (specific gravity[13] of 2.77−2.88), and a 0.801 cm^2 area, the resulting thickness was 35.0 μm. By comparison, the mica thickness is measured using the optical technique. The mica absorbance spectrum has 20 peaks in the 700−802 nm range, and using $n = 1.562$ for this wavelength range, the thickness can be calculated (eq 4) to be 35.2 μm. This compares favorably (±0.6%) to the thickness determined by the weighing technique, as terms such as the specific gravity are not known to greater accuracy.

Design of the Transmission Cell. For the measurements seen in Figure 4, a beam block was used to examine the film thickness at the center of the film. The beam block reduced the diameter of the light path from the spectrophotometer, normally 1 cm, to 1 mm. By modification of the design of the beam block or by addition of focusing elements, different points or areas on the film can be studied. The film thickness determined by this analysis will be an average thickness over the area considered. While the beam block is the simplest way to study a region of the film, focusing elements have several advantages in that they can examine a smaller area with more light delivered through the region of interest, for a higher signal to noise ratio. Other possible but more complicated detection arrangements can allow the simultaneous measurement of film thickness at different points of the film by using fiber optics on the detector side coupled to multiple spectrophotometers. Another possible method is the application of a CCD imaging spectrometer, where a two-dimensional detector is used, with one spatial dimension and one wavelength dimension.

Sources of Error. The major sources of error are expected to be due to the ability to determine the index of refraction. It is often assumed that n is a constant, but this is clearly not the case in the ultraviolet, where this assumption will lead to a 10% error. Another potential error comes from the assumption that the film has the n of water and that the film has the same n across its entire thickness. The surface of a soap film obviously will have more surfactant than the bulk liquid, although this surface layer is extremely thin. If the surface layer had a different n than the bulk, we would have a multiple layer film, requiring a much more complex mathematical model. Equations for interference in multiple layer films have been developed, a very important application being nonreflective coatings of optics.[7] Previous work on film thickness measurement by reflected light used a three-layer model, where film had an n of 1.33 and the surfactant monolayers were assigned[6] an n of 1.45. We assume that this source of error is negligible in film thickness studies. Another possible source of error is wavelength accuracy of the spectrophotometer, although this should also be insignificant with modern instruments.

Conclusion

The analysis presented here allows simple and rapid measurements of soap film thickness using a standard laboratory diode array UV−visible absorbance spectrophotometer. Film thickness measurements are possible over 4 orders of magnitude, from greater than 50 μm to less than 5 nm, depending on the spectral range and accuracy of the spectrophotometer. Periodic measurements may be taken at intervals as short as 0.1 s, allowing measurement of film drainage rate, again depending on the capabilities of the instrument.

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(13) Phillips, W. R.; Griffen, D. T. *Optical Mineralogy, The Nonopaque Minerals*; W. H. Freeman & Co.: San Francisco, CA, 1981.