Available online at www.sciencedirect.com

SCIENCE DIRECT®

Talanta 65 (2005) 1097–1101

Talanta

www.elsevier.com/locate/talanta

A sub-second, time-resolved, linear dichroism measurement system for visible attenuated total reflection spectroscopy with a slab optical waveguide

Kin-Ichi Tsunoda*, Yuichi Kasuya, Tomonari Umemura, Tamao Odake

Department of Chemistry, Faculty of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu 376-8515, Japan

Received 11 November 2003; received in revised form 29 March 2004; accepted 7 June 2004

Abstract

A sub-second, time-resolved, linear dichroism (LD) measurement system was constructed, fitted with a slab optical waveguide (SOWG), and utilized to observe the adsorption process of methylene blue (MB) onto silica surfaces. In the system, a semiconductor laser (670 nm) was used as the light source and the out-coupled beam from the SOWG was split by a polarizing beam splitter into two polarized beams (TE and TM modes) to allow sequential linear dichroic ratio data to be obtained; the acquisition rate was 11 data sets per second. For an MB solution that contained no sodium dodecylbenzenesulfonate (DBS), in contact with a bare silica surface, a clear decrease occurred in the average orientation angle of adsorbed MB in the initial stages of the adsorption process. This result may correspond to a change in the chemical form of MB from monomer to dimer.

Keywords: Slab optical waveguide; Linear dichroism; Visible attenuated total reflection spectroscopy; Methylene blue

---

1. Introduction

Visible attenuated total reflection (ATR) spectrometry using a slab optical waveguide (SOWG) is a surface-selective and highly sensitive technique that has been used successfully in the study of interfacial phenomena [1–6]. When linear dichroism (LD) measurements are used, this technique provides not only spectral information of substances occurring at interfaces, but also evidence of their orientation [7–10].

We have examined the application of glass SOWGs in the chemical sensing of various trace substances [11–16]. In the development of new sensing systems, it is essential to understand the dynamics of the molecules that reside at an interface. To this end, we have undertaken specific studies of the adsorption behavior of methylene blue (MB) on glass surfaces [9,16–18], as the MB molecule has been found to be particularly useful as a probe to study interfaces [19–23]. In the previous studies, we examined the behavior of MB molecules at silica/water and silylated-silica/water interfaces using visible attenuated total reflection spectra and LD with an SOWG [9,18]. LD measurements revealed that the orientation of the MB molecules depended not only on the surface nature of the SOWG, but also on the presence of an additive, sodium dodecylbenzenesulfonate (DBS), in the MB sample solution [9]. In that study, a linear dichroic ratio was determined by measuring the absorbance of the TE and TM polarization modes independently. Consequently, only values pertaining to equilibrium conditions were obtained, and dynamic changes could not be observed [9].

In this study, we constructed a sub-second, time-resolved, LD measurement system, fitted with an SOWG, which allowed us to observe the dynamic adsorption process of MB onto silica surfaces.

---

* Corresponding author. Tel.: +81 277 30 1250; fax: +81 277 30 1251.
E-mail address: tsunoda@chem.gunma-u.ac.jp (K.-I. Tsunoda).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.06.046

2. Experimental

2.1. Materials

Methylene blue (Junseikagaku, Japan) and sodium dodecylbenzenesulfonate (DBS, Kanto Chemicals, Japan) were used without further purification. The silylation reagent, octadecyltrichlorosilane (ODTCS), was purchased from Shinetsu Chemical Co. Ltd., Japan. Toluene and other organic solvents, which were used for the surface modification of silica sheet with ODTCS, were supplied by Wako Pure Chemicals, Japan. These reagents were of analytical reagent grade and used without further purification. Water was purified with a Milli-QII system (Millipore, U.S.A.).

2.2. Measurement system

Fig. 1a shows a schematic diagram of the SOWG used in this study, which was the same as that used in our previous work [9]. A thin fused silica sheet (50 μm thick, $n_D = 1.459$) was employed as the guiding layer. Fig. 1b is a schematic diagram of the measurement system. A flow cell was constructed on the SOWG using a 3-mm thick PTFE spacer and a glass window. The physical cell length was 10 mm. A semiconductor laser (Sakai Glass Engineering Co. Ltd., Japan, 670 nm, 1 mW) provided the light source. The source light was depolarized and collimated with an optical fiber collimator and was then coupled with the SOWG through a coupler prism (La-SF08, $n_D = 1.8785$, Kogakugiken, Japan). The incident angle (θ_i) of the source light (Fig. 1a) was set at 35°. The guided light was out-coupled through another coupler prism and passed through a lens and a polarizing beam splitter. The resultant two polarized beams (TE and TM modes) were detected by photodiodes and the current signals amplified by digital electrometers (TR8652 and R8240, Advantest Co., Japan). The signals were processed alternately by a personal computer through a general-purpose interface bus to obtain successive absorbance data for the TE and TM modes (A_{TM} and A_{TE}). The acquisition rate of the system was 11 data sets per second for A_{TM} and A_{TE}. Upon completion of the measurements, the linear dichroic ratio of each sampling point (the absorbance ratio of the TM mode to the TE mode, A_{TM}/A_{TE}) was calculated by dividing each A_{TM} value by the corresponding A_{TE} value using an Excel spreadsheet program.

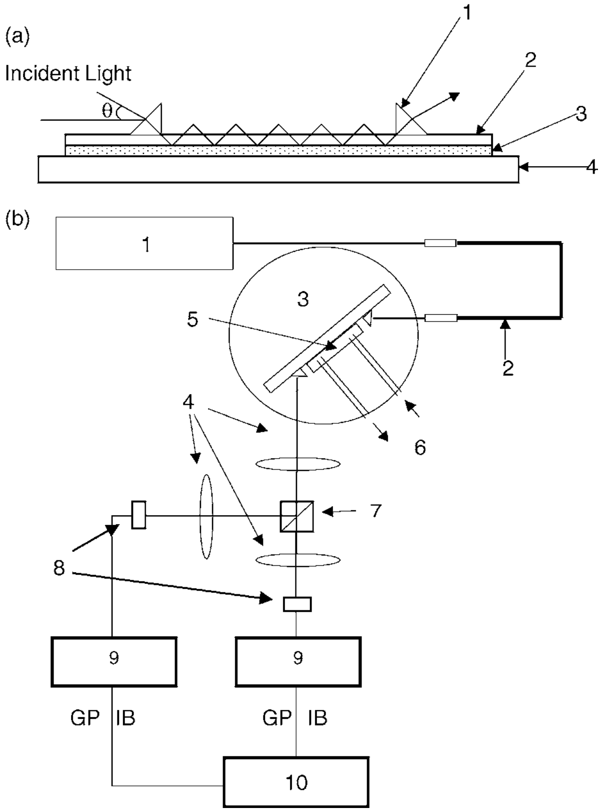

Fig. 1. (a) Schematic diagram of a slab optical waveguide: (1) coupling prism; (2) guiding layer (fused silica sheet, 50 μm thick, $n_D = 1.459$); (3) poly(tetrafluoroethylene-co-hexafluoro-propylene (FEP) film (25 μm thick, $n_D = 1.338$); (4) slide glass; θ, incident angle of source light. (b) Schematic diagram of the measurement system: (1) semiconductor laser (670 nm); (2) optical fiber; (3) rotation stage; (4) convex lens; (5) flow cell; (6) sample solution; (7) polarizing beam splitter; (8) photodiode; (9) digital electrometer; (10) personal computer.

2.3. Silylation procedure of silica surface

An octadecylsilane-coated (ODS) SOWG was prepared by a self-assembly procedure [24], as described previously [9]. The contact angle of water was 95° for the ODS-SOWG.

2.4. Measurement procedures

MB solutions (0.1 mmol/dm^3) with and without DBS (1.0 mmol/dm^3) were used as the sample solutions. For each measurement, the flow cell was initially filled with distilled water and the baseline intensity of the guided light was monitored. The sample solution was then added via an HPLC pump at 0.22 cm^3/s and measurements of A_{TM} and A_{TE} were initiated. Before each measurement, the bare silica SOWG was washed with 1 mol/dm^3 hydrochloric acid, distilled water, 1 mol/dm^3 sodium hydroxide, and finally with distilled water again. In the case of the ODS-SOWG, it was washed with 0.1 mol/dm^3 hydrochloric acid, distilled water, 99.5% ethanol, and a final rinse of distilled water.

3. Results and discussion

Results of time-resolved LD measurements for the MB solution containing no DBS and with a bare silica SOWG are shown in Fig. 2, and for the MB solution containing DBS with an ODS-SOWG in Fig. 3. As the A_{TM}/A_{TE} values were close to zero/zero just after the measurement started, the random values for the LD were obtained, typically as shown in the range before the time zero point of Fig. 3. Consequently, we

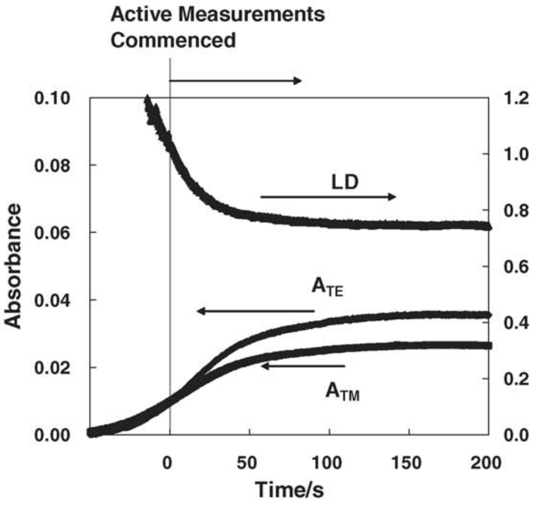

Fig. 2. Time-resolved linear dichroic ratio measurements for MB with a bare silica SOWG. LD, linear dichroic ratio; A_{TE}, absorbance value of TE mode; A_{TM}, absorbance value of TM mode; (▲) each measurement point of LD. A 0.1 mmol/dm^3 MB without DBS was used as the sample solution.

undertook active measurements only after the value of A_{TE} had reached 0.01. Throughout the regions in which active measurements were made, reproducibility of measurements proved to be good. Furthermore, a check on the response of the measurement system was made by evaluation and comparison of the following parameters:

$$\frac{A_{\mathrm{TM},n_i}}{A_{\mathrm{TE},n_i}}, \qquad (1)$$

$$\frac{A_{\mathrm{TM},n_i}}{A_{\mathrm{TE},n_{i-1}}}, \qquad (2)$$

$$\frac{2A_{\mathrm{TM},n_i}}{A_{\mathrm{TE},n_{i-1}} + A_{\mathrm{TE},n_i}}, \qquad (3)$$

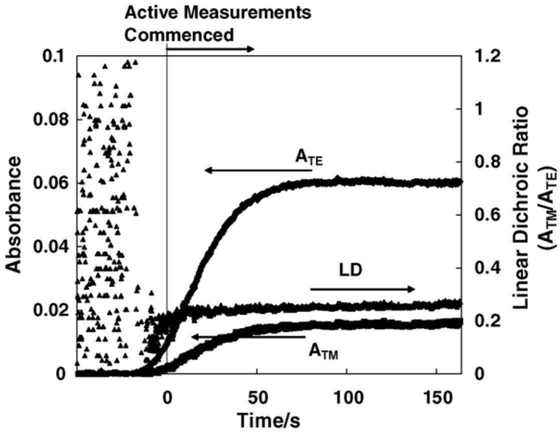

Fig. 3. Time-resolved linear dichroic ratio measurements for MB with an ODS-SOWG. LD, linear dichroic ratio; A_{TE}, absorbance value of TE mode; A_{TM}, absorbance value of TM mode; (▲) each measurement point of LD. A 0.1 mmol/dm^3 MB with 1.0 mmol/dm^3 DBS was used as the sample solution.

Table 1
The average orientation angle (θ) of methylene blue adsorbed onto silica surfaces[a]

Silica surface	Average orientation angle, θ (°)	
	Present study[b]	Previous study[c]
Without the addition of 1.0 mmol/dm^3 DBS[d]		
Bare silica	28.2 ± 0.4	28.9 ± 5.3
ODS silica	17.6 ± 0.2	24.7 ± 1.2
With the addition of 1.0 mmol/dm^3 DBS		
Bare silica	28.2 ± 0.3	26.8 ± 5.3
ODS silica	12.8 ± 0.5	16.0 ± 0.3[e]

[a] The average orientation angle (θ) of MB was calculated using a reported method [8] in which the following equation gives θ: $\frac{A_{\mathrm{TM}}}{A_{\mathrm{TE}}} = \frac{|E_x|^2+2|E_z|^2\cot^2\theta}{|E_y|^2}$ where E_x, E_y and E_z denote electric field amplitudes in the three Cartesian directions at the surface. To calculate these values, the propagation angle of 72.2° in the waveguide and the refractive indices of 1.459 and 1.333 for the guiding layer and the water phase, respectively, were used. Randomly orientated molecules have an average orientation angle of 35.3°.

[b] A 0.1 mmol/dm^3 MB solution was used for the measurements. The average of three measurements: the average of the linear dichroic ratio values measured for 30 s, 60 s after active measurement commenced.

[c] Ref. [9].

[d] Sodium dodecylbenzenesulfonate.

[e] The average orientation angle of the monomer fraction of MB.

where A_{TM,n_i} and A_{TE,n_i} are the n_ith values of A_{TM} and A_{TE}, respectively, following the commencement of measurement (A_{TM,n_i} was always acquired before A_{TE,n_i}). There was no substantial difference among the values, which implies that the response time of the system was sufficient to undertake these experiments.

In Fig. 2, the linear dichroic ratio decreases steeply in the initial region and then becomes constant. An almost constant linear dichroic ratio was obtained with the ODS-SOWG from MB solution with DBS, as shown in Fig. 3, with the ODS-SOWG from MB solution without DBS, and with the bare silica SOWG from MB solution containing DBS. The results of the latter experiments are not shown.

Table 1 summarizes the average orientation angles of MB (Fig. 4) found in this study. These were calculated from the average values of the linear dichroic ratio obtained over a 30 s interval, 60 s after the active measurements commenced. In the table, previous results are also shown from experiments in which the sample solutions were manually introduced to the flow cell more quickly by using a syringe [9]. As is shown in the table, better reproducibility in the measurement of the average orientation angle was obtained in this study. Moreover, the average orientation angles obtained with the bare silica SOWG were in good agreement with those of the previous study. As discussed in the previous paper, when DBS is not added, MB is adsorbed as dimer onto the bare silica surface and as monomer onto the ODS-SOWG surface under equilibrium conditions [9,18], whereas when DBS is added, MB is adsorbed onto bare silica as the ion-pair MB + DBS, which exhibits the same spectrum as the dimer, while the monomer fraction continues to be observed upon ODS-SOWG [9,18]. The average orientation angle of MB

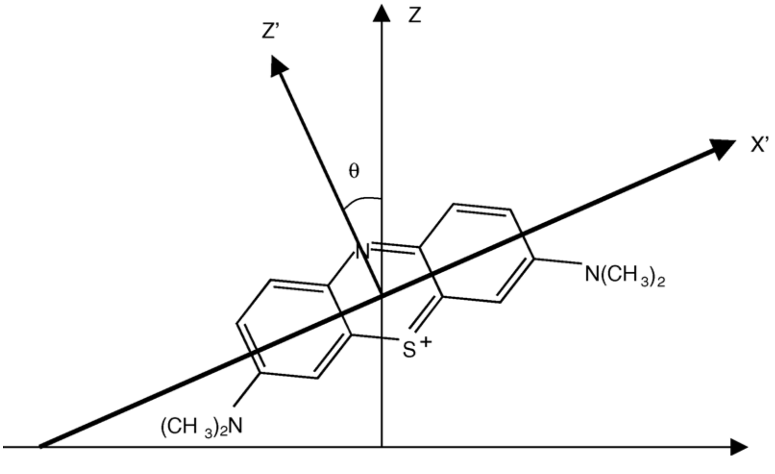

Fig. 4. Structure and orientation angle (θ) of the transition moment of methylene blue.

in the ion-pair was 33–35°, which is close to that of randomly oriented molecules (35.3°). The average angle of the monomer was much smaller, 16.0°, as shown in Table 1 [9]. As absorbance detection is more sensitive for the monomer ($\lambda_{max} = 670$ nm) than for the dimer ($\lambda_{max} = 600$ nm) at the wavelength of 670 nm used in this study, the present result of 12.8° mainly reflects the average orientation angle of the monomer fraction.

As mentioned above, a clear decrease in the linear dichroic ratio was observed in the initial region for the MB solution lacking DBS with the bare silica SOWG, as shown in Fig. 2. The data were converted to give the average of three orientation angle measurements as shown in Fig. 5. In Fig. 5 the orientation angle of MB in the initial region is close to that of randomly oriented molecules, but subsequently it decreases with an increase in the absorbance. We have previously reported, on the basis of simultaneous, dual-wavelength measurements with a soda-lime glass SOWG, that MB adsorbed onto a glass surface as a monomer during the initial stages of the adsorption process may subsequently transform into a dimer [18]. The change in the average orientation angle of MB observed in the present study may correspond to a similar process that involves conversion from the monomer to the dimer. Tentatively, we do not have any idea for why the dimer formation may cause the change in the orientation angle, in other words, why the orientation angle of the monomer on the bare silica surface is so great. Further careful spectroscopic studies may be necessary to answer the question.

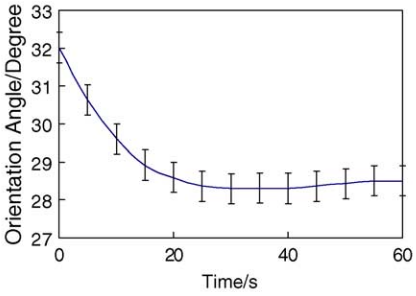

Fig. 5. The change in the average orientation angle of MB with a bare silica SOWG. Experimental conditions are those of Fig. 2. The time zero in this figure was set at the point of the active measurement commenced in Fig. 2. The average of three measurements was plotted, and the error bar shows the standard deviation of the three measurements.

In conclusion, a sub-second, time-resolved, LD measurement system was constructed with an SOWG and used to observe the adsorption process of MB onto silica surfaces. In the case of MB solution lacking DBS on a bare silica surface, a clear decrease in the average orientation angle occurred in the initial stages of the adsorption process. This may reflect a change in the chemical form of MB from the monomer to the dimer. Consequently, the new system offers a practical method for examining dynamic changes in the orientation of adsorbed molecules on various surfaces, such as silica, transparent electrodes (ITO) and polymers.

Acknowledgement

This work was supported, in part by a Grant-in-Aid for Scientific Research (No. 11450320) from the Japan Society for the Promotion of Science.

References

[1] J.D. Swalen, M. Tacke, R. Santo, K.E. Rieckhoff, J.F. Fischer, Helv. Chim. Acta 61 (1978) 960.
[2] D.A. Stephens, P.W. Bohn, Anal. Chem. 61 (1989) 386.
[3] S.S. Saavedra, W.M. Reichert, Langmuir 7 (1991) 995.
[4] K. Itoh, M. Murabayashi, J. Phys. Chem. 96 (1992) 8813.
[5] N. Matsuda, A. Takatsu, K. Kato, Chem. Lett. (1996) 105.
[6] H. Ohno, K. Fukuda, F. Kurusu, Langmuir 18 (2002) 1661.
[7] P.L. Edmiston, J.E. Lee, L.L. Wood, S.S. Saavedra, J. Phys. Chem. 100 (1996) 775.
[8] P.L. Edmiston, J.E. Lee, S. Cheng, S.S. Saavedra, J. Am. Chem. Soc. 119 (1997) 560.
[9] K.-I. Tsunoda, T. Umemura, H. Ueno, E. Okuno, H. Akaiwa, Appl. Spectrosc. 57 (2003) 1273.

[10] Z.-M. Qi, N. Matsuda, A. Takatsu, K. Kato, H. Isago, Appl. Spectrosc. 57 (2003) 871.
[11] K.-I. Tsunoda, H. Itabashi, H. Akaiwa, Bull. Chem. Soc. Jpn. 65 (1992) 1581.
[12] K.-I. Tsunoda, H. Itabashi, H. Akaiwa, Anal. Chim. Acta 276 (1993) 133.
[13] K.-I. Tsunoda, E. Yamamoto, H. Akaiwa, Chem. Lett. (1996) 919.
[14] K.-I. Tsunoda, S. Kikuchi, K. Nomura, K. Aizawa, K. Okamoto, H. Akaiwa, Anal. Sci. 15 (1999) 241.
[15] K.-I. Tsunoda, T. Umemura, K. Aizawa, Y. Takahashi, T. Odake, Anal. Sci. 16 (2000) 771.
[16] T. Umemura, Y. Kasuya, T. Odake, K.-I. Tsunoda, Analyst 127 (2002) 149.
[17] K.-I. Tsunoda, H. Itabashi, H. Akaiwa, Anal. Chim. Acta 299 (1994) 327.
[18] K.-I. Tsunoda, E. Yamamoto, H. Itabashi, H. Akaiwa, Anal. Sci. 11 (1995) 161.
[19] T. Hinoue, Y. Yokoyama, T. Ozeki, Bunseki Kagaku 43 (1994) 443.
[20] T. Hinoue, G. Imamura, Y. Yokoyama, Bull. Chem. Soc. Jpn. 66 (1993) 3680.
[21] D.R. Dunphy, S.B. Mendes, S.S. Saavedra, N.R. Armstrong, Anal. Chem. 69 (1997) 3086.
[22] N. Matsuda, J. Zheng, D.-K. Qing, A. Takatsu, K. Kato, Appl. Spectrosc. 57 (2003) 100.
[23] L.-X. Sun, A.M. Reddy, N. Matsuda, A. Takatsu, K. Kato, T. Okada, Anal. Chim. Acta 487 (2003) 109.
[24] D.G.I. Kingston, B.B. Gerhart, J. Chromatogr. 116 (1976) 182.