

Articles

Determination of the Dissociation Constant of Thymol Blue with Diode-Laser/Fiber-Optic Thermal Lensing Spectroscopy

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The simple and convenient measurement of the dissociation constant of an indicator, thymol blue, was achieved by using a portable diode-laser/fiber-optic thermal lensing spectroscopy, which consisted of a visible diode laser, a photodiode, and an optical fiber. It gives comparable results to the cited value obtained from a conventional UV/VIS spectroscopy.

Introduction

Various instrumental methods such as NMR,¹ chromatography,² potentiometry,³ etc. are used for the determination of a dissociation constant, K_a , of weak acids. Among them, UV/VIS spectrometry,^{4,5} which measures the absorbance of a sample, has been used for a long time⁶ because of its easiness and simplicity of experiments.

On the other hand, one of the accurate and alternative technique to measure the absorbance is thermal lensing spectroscopy (TLS), reported by Gordon in 1965.⁷ Using the TLS, Erskine measured the pK_a of the weak acid, bromocresol green, for the first time in 1989.⁸

But because the system requires a large dimension, complexity in operation, and sophisticated experimental alignment skill, it still has a restriction to be a popular measurement method for pK_a .

Recently, we developed a simple, compact, and portable TLS system, which consisted of inexpensive red color diode laser, a photodiode, and an optical fiber.⁹⁻¹⁰ Its application to measure the concentration of a blue colored indicator was reported in previous study.¹⁰ In this paper, the measurement of pK_a of the indicator was performed in order to make the use of the fiber-optic/diode-laser TLS system. The thymol blue was selected as a sample for this system because it shows high sensitivity at the 635 nm that is a wavelength of the diode laser source used in this study.

Principle and Measurement

A color indicator, thymol blue(thymolsulfophtalein), which is used in the analytical practice, exists as a weak acid HA in aqueous solution



where A^- is a conjugate base. The correlation between the pH and the composition ($[\text{A}^-]/[\text{HA}]$) of buffer systems for a given acid strength (pK_a) is expressed by Henderson-Hasselbach equation¹¹

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (2)$$

A plot of pH versus the logarithmic ratio of the concentrations between anion and weak acid, $\log([\text{A}^-]/[\text{HA}])$, will yield a straight line with an intercept equal to the pK_a . For thymol blue, the HA absorbs light in the blue spectral region ($\lambda_{\text{max}}=430$ nm), while the A^- has an absorption maximum in the red spectral region ($\lambda_{\text{max}}=595$ nm). In a buffered solution, a mixed colour is observed due to the coexistence of HA and A^- . At 635 nm which is a wavelength of the diode laser source used in this study, only A^- absorbs the laser light because its λ_{max} is quite close together, while HA could not absorb. If the absorbance of a solution at 635 nm with a certain pH is a , and the absorbance of the most basic solution at high pH is b , the Eq. (2) can be changed as follows;

$$\text{pH} = \text{p}K_a + \log \left(\frac{a}{b-a} \right) \quad (3)$$

According to the theory of the TLS,^{12,13} thermal lensing signal TS , which is defined by Eq. (4), is proportional to the concentration of an analyte and then is expressed as

$$TS = \frac{I_0 - I_f}{I_0} \quad (4)$$

where I_0 and I_f are the probe beam intensities at the beam center before and after thermal lensing effect occurs, respectively. Because the absorbance of a and b in the Eq. (3) can be replaced with TS_a and TS_b , respectively, the Eq. (3) is rewritten as follows;

$$\text{pH} = \text{p}K_a + \log \left(\frac{TS_b}{TS_b - TS_a} \right) \quad (5)$$

where TS_a is the TL signal of a solution at certain pH and TS_b is that of the most basic solution. Because pK_a is not dependent on the magnitude of the TL signal, one can determine pK_a from the ratio of thermal lensing signal of the acidic and basic forms of the indicator.

Experimental

Apparatus. Figure 1 shows the block diagram of the

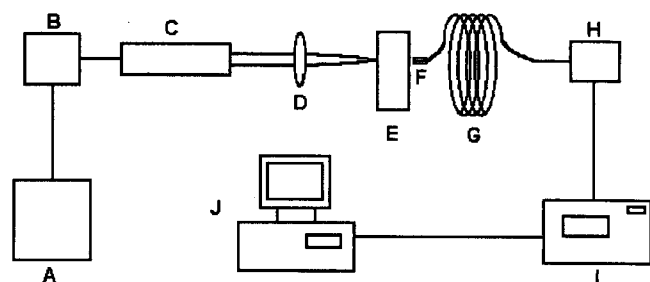


Figure 1. Experimental setup for the portable diode-laser/fiber-optic thermal lensing spectroscopy system; A) power supply, B) current controller, C) diode laser, D) focusing lens, E) sample cell, F) fiber holder, G) optical fiber, H) photo diode, I) oscilloscope, J) PC.

system used in this study. Since the detailed configuration has been reported elsewhere,⁹⁻¹⁰ the system is briefly described here. A light source of a diode laser (LDM 145, Immatronics, UK) emitting at 635 nm (output power < 5 mW) was modulated at the frequency of 14 Hz and was focused by a convex lens (F.L.=7 cm). A 1 cm UV cuvette was used as a sample cell. The transmitted light was sent through a 30 cm long single mode optical fiber (F-SV, Newport Co., USA), which was connected with a photodiode detector (Pin-6DP, UDT Sensors Inc., USA). The TL signal was monitored by an oscilloscope (5802, Hung Chang Co., Korea) and aquisitioned by a PC (IBM 386 compatible) through an A/D converter (PCL-711S, Advantech Co. Ltd., Taiwan).

Reagents and Procedure. Thymol blue, NaHCO₃, NaOH, and HCl were obtained from Aldrich Chemical Co. The stock solution of thymol blue was prepared at the concentration of 3×10^{-4} M by dissolving the 0.145 g thymol blue (C₂₇H₃₀O₅SH₂O) to 200 mL ethanol and 800 mL distilled water. A series of buffer solutions from pH 9.0 to pH 10.8 with 0.2 pH intervals were prepared by using 0.2 M NaHCO₃ and 0.2 M NaOH. The pH 9.0 buffer solution was prepared by mixing 50 mL of NaHCO₃ and 3.0 mL of 0.2 M NaOH, and diluted with distilled water in a total volume of 100 mL. All of the 10 buffer solutions were made by increasing the volume of 0.2 M NaOH appropriately. Each of the solutions to be used should be carefully filtered to insure the removal of particulates that may cause the scattering of laser beam. The 0.05 M HCl and 0.05 M NaOH solutions were used to measure the TL signals for the pure acidic and basic forms of thymol blue, respectively. For the case of 10 sample solutions, 1 mL of thymol blue stock solution, 4 mL buffer solution at the given pH, and 5 mL of methanol were mixed and then left for 30 minute in order to mix completely.

Results and Discussion

The thermal lensing signal of 3×10^{-5} M buffer solutions of thymol blue at pH between 9.2 to 10.6 with 0.2 intervals is depicted in Figure 2. Below the pH 9.2, the concentration of A⁻ was so low that the TL signal could not be detected. Over the pH 10.6, the signal remained all the way same. For the case of signal at pH 9.2, the initial relative intensity ($I_0=508.562$) decreased along the exponential decay curve

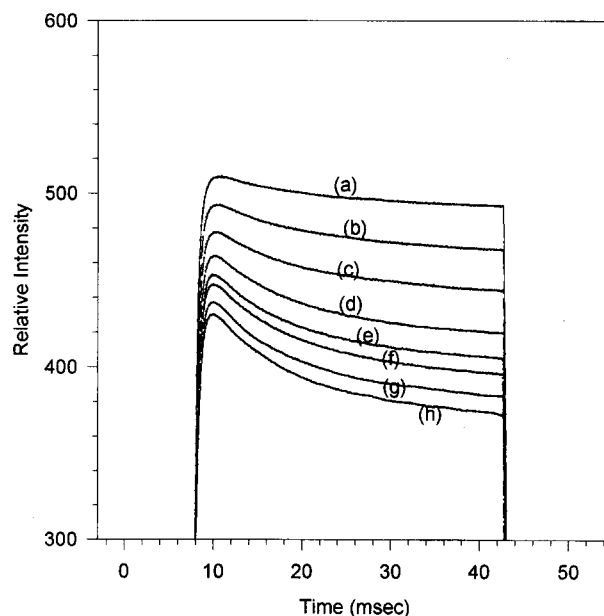


Figure 2. Transient signal of thymol blue by the diode-laser/fiber-optic thermal lensing spectroscopy at the pH of a) 9.2 b) 9.4 c) 9.6 d) 9.8 e) 10.0 f) 10.2 g) 10.4 h) 10.6.

to asymptotic limit ($I_f=488.699$) during 35 msec. This means that the relative intensity loss, I_0-I_f , is 19.863. Along this procedure, the thermal lensing signal (TS) was calculated according to Eq. (4). The calculated values are listed in Table 1. When the pH of thymol blue increases from 9.2 to 10.6, the thermal lensing signal increases from 0.0391 to 0.1491. The fact can be easily explained by the increment of the concentration of basic form A⁻, with increasing pH. From these values, the ratio of $\log(TS_a/TS_b-TS_a)$ could be calculated according to the Eq. (5).

Figure 3 shows the plot of pH versus $\log([A^-]/[HA])$ for thymol blue. It represents a linearity with the regression coefficient of 0.9938 in the given pH range between 9.2 to 10.6. In the figure, the intercept of pH axis, which determines the pK_a of thymol blue, is calculated as 9.5 ± 0.02 . The standard deviations are calculated on the basis of 5 measurements. The pK_a value is comparable to that of reference value of 9.0.¹¹ The difference can be easily attributed to the solvent system with contained 50% methanol. In principle, the thermal lensing signal is proportional to the change of refractive index versus temperature (dn/dT). Because the magnitude of the TL signal of methanol is about 5 times higher than that of water, the methanol was added to

Table 1. The thermal lensing signal of thymol blue depending on the pH

pH	I_0	I_0-I_f	TS	$\log([A^-]/[HA])$
9.2	508.562	19.863	.0391	-.450
9.4	491.633	29.871	.0608	-.162
9.6	475.468	38.349	.0807	.071
9.8	460.266	50.215	.1091	.435
10.0	449.928	54.083	.1202	.618
10.2	443.309	57.494	.1297	.824
10.4	433.307	59.714	.1378	1.085
10.6	426.026	63.536	.1491	-

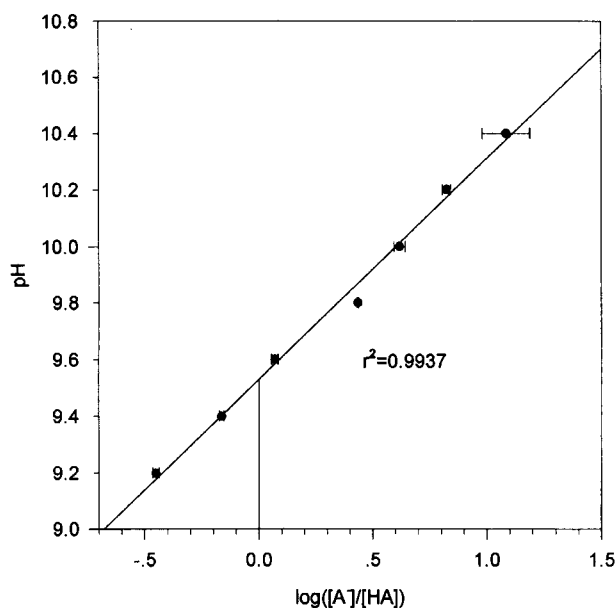


Figure 3. Plot of pH versus $\log([A^-]/[HA])$.

the buffer in order to increase the TL signal. However, at higher concentration of methanol up to 90%, the concentration of thymol blue decreases depending on time, which diminished the thermal lensing signal completely within 30 minute. It seems that the dissociation reaction of thymol blue would occur at the high concentration of methanol in basic condition. In contrast, at lower concentration of methanol upto 10%, the TL signal of A^- form of thymol blue is so weak, which the sensitivity is lower than detection limit. When 50% of methanol was added to the buffer solution in the pH between 9.2 and 10.6 in this experiment, the TL signal showed the largest value. The signal slightly changed within few minutes, but reached to the steady state for several hours. This process seems to cause a discrepancy between the experiment and cited value. The added methanol perturbates the activity of A^- in the indicator solution. As a results, the equilibrium shifts. Another possibility for the difference of pK_a is the increments of local temperature due to the radiation through the sample

solution. Since the pK_a was affected by the temperature, the change of local temperature could shift the equilibrium, too. In order to study these in detail, a thermodynamic investigation is needed in further study for the temperature dependence of pK_a .

Summary

In this study, the pK_a of a thymol blue is determined to be 9.5 by the relatively simple and inexpensive fiber-optic/diode-laser TLS system. The measured pK_a is comparable to the cited value of 9.0 obtained from a conventional UV/VIS spectroscopy.¹² In principle, the thermal lensing effect occurs in any sample solution which absorbs the laser radiation. The application could be expanded to the determination of equilibrium constants for various indicators, of which λ_{max} is close to the wavelength of laser light source.

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