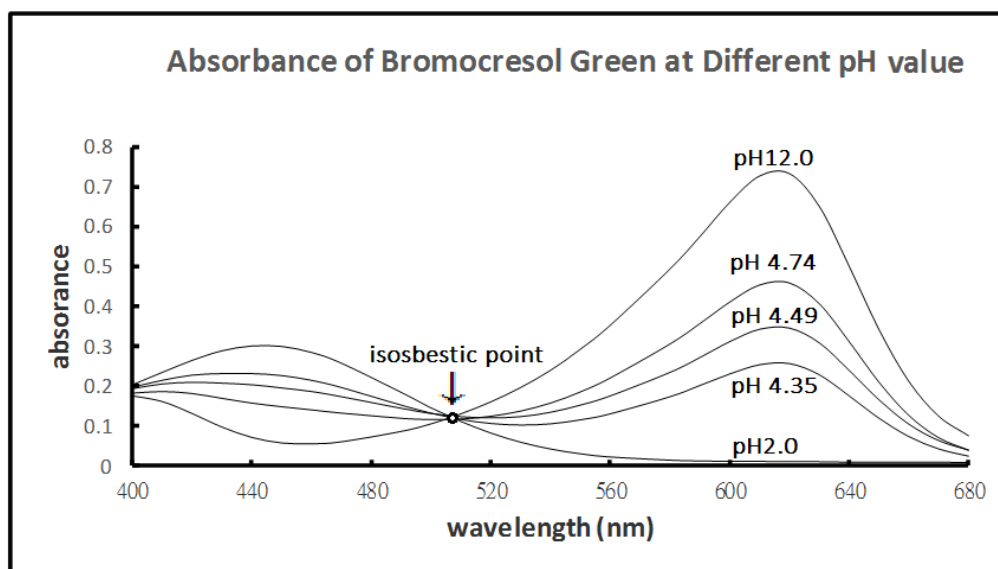


Experiment 4 Determination of the Ionization Constant of an Indicator

Introduction

This experiment combines the acid-base equilibria and pH measurement with spectrophotometer.



Often one absorbing species, X, is converted to another absorbing species, Y, during the course of a chemical reaction. This sort of transformation leads to a very obvious and characteristic behavior as shown in figure. If the spectra of pure X and pure Y cross each other at any wavelength, then every spectrum recorded during this chemical reaction will cross at that same point, called an **isosbestic point**.

Procedure

1. Prepare five solutions in five 25ml volumetric flasks as follow:

- (1) 2.50 ml of 0.10 M NaOH
- (2) 2.50 ml of 0.10 M NaOH + 3.80 ml of 0.10 M HOAC
- (3) 2.50 ml of 0.10 M NaOH + 5.00 ml of 0.10 M HOAC
- (4) 2.50 ml of 0.10 M NaOH + 6.30 ml of 0.10 M HOAC
- (5) 2.50 ml of 0.10 M HCl

To each of five solutions, add **exactly 1.00 ml** of 0.03% bromocresol green indicator solution. Dilute each flask with distilled water to the mark and mix well.

2. Measure the absorbance of each one of five solutions from 400 ~ 680 nm using UV-Vis.

Notes A series of curves will be obtained which ideally should all intersect at a point called the isosbestic point. For a family of curves like these to show an isosbestic point, two conditions are necessary:

1. The total indicator concentration must be the **same** in every case.
2. The indicator must exist in **two**, and two forms whose proportion changes as the conditions are changed (in this case as the pH is changed). A good isosbestic point is also an indication of good experimental technique.
3. Measure the pH of each of the solution 2, 3, and 4 by using a pH meter. Be sure to standardize the meter with a known buffer prior to use.

Calculation

To calculate the ionization constant of bromocresol green from pH measurements and absorbance curved, **two methods** can be used:

1. Let λ_1 be the wavelength of maximum absorbance of the **acid** form of the indicator

P be the absorbance at λ_1 for the acidic form of the indicator

R be the absorbance at λ_1 for the basic form of the indicator

Q be the absorbance at λ_1 for the buffer

In the buffer the concentrations of basic and acid forms of the indicator are in the ratio of (P – Q) to (Q – R). The ionization constant of the indicator is therefore:

$$K_a = \frac{[H^+][In^-]}{[HIn]} = \frac{[H^+](P - Q)}{(Q - R)}$$

where $[H^+]$ is known from the pH reading of the buffer solution, hence K_a can be calculated.

2. If more than three data points are used, the ionization constant of the indicator can be calculated as follows:

$$\text{Let } C_a + C_b = C_t \dots\dots\dots (1)$$

where C_a and C_b are concentrations of indicator in its acidic form and basic form, respectively; C_t is the total analytical concentration of an indicator.

Assuming that the solutions of the indicator follow the Beer's law at a specified wavelength, the absorbance of the indicator in a mixture, A, can be expressed as follows:

$$A_m = \epsilon_m b C_t = \epsilon_m b (C_a + C_b) \dots\dots\dots (2)$$

$$\text{or, } A_m = \epsilon_a b C_a + \epsilon_b b C_b \dots\dots\dots (3)$$

where ϵ_m , ϵ_a , and ϵ_b are molar absorptivities for the mixture, acid and base of the indicator at λ_1 , respectively; b is the cell thickness and usually 1 cm is used.

Comparing eq.(2) with eq.(3) obtains

$$\epsilon_m b (C_a + C_b) = \epsilon_a b C_a + \epsilon_b b C_b \dots\dots\dots (4)$$

Dividing eq.(4) by C_a and rearranging it becomes

$$\epsilon_m = \epsilon_a + (\epsilon_b - \epsilon_m) C_b / C_a \dots\dots\dots (5)$$

Since the ionization constant for the indicator, K_a , can be expressed as

$$K_a = \frac{[H^+][In^-]}{[HIn]} = \frac{[H^+]}{C_b} \cdot C_a \dots\dots\dots (6)$$

or, $C_b / C_a = K_a / [H^+] \dots\dots\dots (7)$

Incorporating eq.(7) into eq.(5) yield

$$\epsilon_m = \epsilon_a + (\epsilon_b - \epsilon_m) K_a / [H^+] \dots\dots\dots (8)$$

Multiplying eq.(8) by bC_t becomes

$$A_m = A_a + \{(A_b - A_m) / [H^+]\} K_a \dots\dots\dots (9)$$

where A_a and A_b are absorbance of indicator in a pure acidic form and in a pure basic form at λ_1 , respectively; $[H^+]$ can be obtained from the pH meter.

A plot of A_m versus $(A_b - A_m) / [H^+]$ as shown in eq.(8) will yield a straight line with the **slope** of K_a and the intercept of A_a .

(If the least squares method is used, the best straight line can be approached.)

Example

Three solutions of an indicator having the same total concentration of indicator have absorbance at a certain wavelength that are 0.90, 0.64, and 0.10 in solutions of pH 2.00, 7.40, 12.00, respectively. What is the ionization constant of the indicator?

In the solution of pH 7.40 the proportion of In^- to HIn is $(0.90 - 0.64)$ to $(0.64 - 0.10)$ that is, 0.26 : 0.54. The hydrogen ion concentration is 3.98×10^{-8} . The ionization constant is, therefore, $0.26 \times 3.98 \times 10^{-8} / 0.54 = 1.91 \times 10^{-8}$.

儀器設定：

λ :

blank :

結果：

(1)完成下表

樣品溶液	1	2	3	4	5
pH					
$[\text{H}^+](\text{M})$					
$\lambda_{\text{max}}(\text{in acidic}) :$ (A)					
$\lambda_{\text{max}}(\text{in basic}) :$ (A)					

(2)利用實驗原理中所敘述的兩種方法，分別求出 K_a 。

(a) 理論計算：

Let λ_1 be the wavelength of maximum absorbance of the **acid form** of the indicator

P be the absorbance at λ_1 for the acidic form of the indicator

R be the absorbance at λ_1 for the basic form of the indicator

Q be the absorbance at λ_1 for the buffer

In the buffer the concentrations of base and acid forms of the indicator

are in the ratio of (P - Q) to (Q - R). The ionization constant of the indicator is therefore:

$$K_a = [\text{H}^+][\text{In}^-] / [\text{HIn}] = [\text{H}^+](\text{P} - \text{Q}) / (\text{Q} - \text{R})$$

(b) 作圖法：

$$A_m = A_a + \{(A_b - A_m)/[H^+]\}K_a$$

where A_a and A_b are absorbance of indicator in a pure acidic form and in a pure basic form at λ_1 , respectively.

A plot of A_m versus $(A_b - A_m)/[H^+]$ will yield a straight line with the **slope of K_a** and the intercept of A_a .