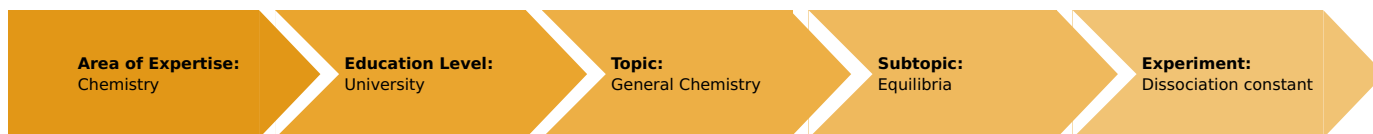


# Dissociation constant (Item No.: P3031101)

## Curricular Relevance



### Difficulty



Intermediate

### Preparation Time



10 Minutes

### Execution Time



10 Minutes

### Recommended Group Size



2 Students

### Additional Requirements:

- Precision balance, 620 g / 0.001 g

### Experiment Variations:

### Keywords:

True and potential electrolytes, Strong and weak acids, Law of mass action, Dissociation constants and  $pK_a$  values, Henderson-Hasselbach equation, UV-visible spectrometry, Lambert-Beer's Law, Photometry

## Introduction

### Short description

#### Principle

The coloured indicator thymol blue is a weak acid that is partially dissociated in aqueous solution, whereby non-ionized and ionized forms show absorption maximums at different wavelengths in the visible range. Photometric measurements in the visible spectral range can therefore be used to advantage to determine the position of the  $K_a$  and  $pK_a$  values of the indicator which characterize dissociation equilibrium.



## Equipment

Position No.	Material	Order No.	Quantity
1	Spectrophotometer 190-1100 nm	35655-99	1
2	Cell for spectrophotometer, optical glass	35664-00	2
3	Weighing dishes, square shape, 84 x 84 x 24 mm, 25 pcs.	45019-25	1
4	Volumetric flask 50 ml, IGJ12/21	36547-00	3
5	Volumetric flask 1000ml, IGJ24/29	36552-00	3
6	Volumetric pipette, 1 ml	36575-00	1
7	Volumetric pipette, 5 ml	36577-00	1
8	Volumetric pipette, 10 ml	36578-00	1
9	Pipettor	36592-00	1
10	Pipette dish	36589-00	1
11	Graduated cylinder 250 ml	36630-00	1
12	Beaker, high, BORO 3.3, 150 ml	46032-00	3
13	Pasteur pipettes, 250 pcs	36590-00	1
14	Rubber caps, 10 pcs	39275-03	1
15	Microspoon, steel	33393-00	1
16	Funnel, glass, top dia. 55 mm	34457-00	1
17	Wash bottle, plastic, 500 ml	33931-00	1
18	Thermometer -10...+50 °C	38034-00	1
19	Buffer solution, pH 9 1000 ml	30289-70	1
20	Thymol blue indicator 5 g	31896-02	1
21	Hydrochloric acid, 0.1M 1000 ml	48452-70	1
22	Caustic soda sol., 0.1M 1000 ml	48328-70	1
23	Ethyl alcohol, absolute 500 ml	30008-50	1
24	Water, distilled 5 l	31246-81	1

## Tasks

Experimentally determine the extinction (absorbance) of an aqueous solution of thymol blue (thymolsulphonophthalein) in dilute HCl, NaOH and a buffer of known pH value as a function of wavelength between 400 and 700 nm at constant concentration and constant temperature. Calculate the dissociation constant (indicator constant)  $K_a$  from the measurement results.



## Set-up and procedure



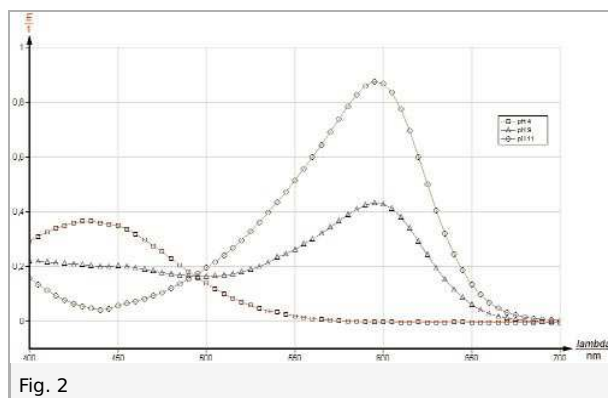
- The spectrophotometer that is required for this experiment is shown in Fig. 1.
- Pipette 10 ml of 0.1 molar sodium hydroxide and 1 ml of 0.1 molar hydrochloric acid into a 1000 ml volumetric flask and fill up to the mark with distilled water.
- Completely dissolve 0.145 g ( $3 \cdot 10^{-4}$  mol) of thymol blue (thymolsulphonophthalein,  $C_{27}H_{30}O_5S \cdot H_2O$ ) in 200 ml of ethanol in a 1000 ml volumetric flask and dilute up to the mark with distilled water.
- Pipette 5 ml of this  $3 \cdot 10^{-4}$  molar stock solution into each of three 50 ml volumetric flasks: Fill the first flask up to the mark with sodium hydroxide ( $c = 1 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ ), the second one with HCl ( $c = 1 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ ), and the third flask with buffer solution of pH 9.
- After correcting the zero line of the photometer using a waterfilled cell, record the absorption spectra of the three  $3 \cdot 10^{-5}$  molar thymol blue solutions in the visible spectral range between 700 and 400 nm at a slow recording speed.
- Read off the extinction values from the spectra displayed by the monitor in 5 nm steps and plot a graph of them as a function of wavelength.



## Results and evaluation

### Results

The absorption spectra recorded at  $T = 299 \text{ K}$  are shown in Fig. 2. Absorption spectra of thymol blue ( $c_0 = 2 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ ) in  $1 \cdot 10^{-4}$  molar HCl ( $\square$ )  $1 \cdot 10^{-3}$  molar NaOH ( $\circ$ ) and a buffer solution of  $\text{pH} = 9.00$  ( $\triangle$ ) at  $T = 299 \text{ K}$ .

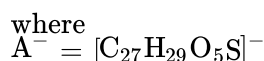
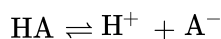


### Note

The graphical evaluation of the measured values can be very easily carried out by means of 'Measure' software. A downloadfile of this software is available as freeware for use in evaluating and graphically representing measured values under URL "www.phywe.com". Fig. 2 was created by this software.

### Evaluation

The coloured indicator thymol blue, which is used in analytical practice, is present in aqueous solutions in the partly dissociated weak acid form:



The position of the dissociation equilibrium is quantitatively characterized by the acid or indicator constant  $K_a$  or the  $\text{p}K_a$  value derived from it:

$$K_a = \frac{a_{\text{A}^-} \cdot a_{\text{H}^+}}{a_{\text{HA}}} \approx \frac{c_{\text{A}^-} \cdot c_{\text{H}^+}}{c_{\text{HA}}} \quad (1)$$

where:  
 $a_i$  Activity of ion  $i$

At ideal dilution, the activity  $a_i$  is identical to the concentration  $c_i$ .

$$\text{p}K_a = -\lg \frac{K_a}{\text{mol} \cdot \text{l}^{-1}} \quad (2)$$

From (1), considering formulation (2) and the analogue definition of the  $\text{pH}$  value and taking logarithms, we obtain the Henderson-Hasselbach equation (3). This describes, at a given acid strength, the connection between the  $\text{pH}$  value and the composition ( $c_{\text{HA}} / c_{\text{A}^-}$ ) of the buffer system, and so the share of the two forms in the total concentration  $c_0$  of the weak acid.

$$\text{p}K_a = \text{pH} + \lg \frac{c_{\text{HA}}}{c_{\text{A}^-}} \quad (3)$$

$$c_0 = c_{\text{HA}} + c_{\text{A}^-} \quad (4)$$

We so have, in the acid form ( $1 \cdot 10^{-4}$  molar HCl,  $\text{pH} = 4 \ll \text{p}K_a$ ), practically only the non-ionized acidic form HA, so that (4) becomes (4.1).

$$c_0 = c_{HA} \quad (4.1)$$

In contrast to this, in basic milieu ( $1 \cdot 10^{-3}$  molar NaOH,  $\text{pH} = 11 \gg \text{p}K_a$ ), equilibrium is shifted almost completely in the direction of the ionized salt form  $A^-$ , and we have

$$c_0 = c_{A^-} \quad (4.2)$$

In buffered solutions of  $\text{pH} 9 \approx \text{p}K_a$  the ionized and non-ionized forms are present in practically the same concentration. These equilibrium concentrations, and so the constants  $K_a$  and  $\text{p}K_a$ , for thymol blue, can be advantageously measured via photometric measurements as, because of their different atomic structures, the acid and salt forms give different absorption spectra which cross each other at an isobestic point (Fig. 2).

The HA form that exists alone in acidic solutions absorbs in the blue spectral range ( $\lambda_{\text{max}} \approx 430 \text{ nm}$ ) and appears as the complementary colour, yellow. On the other hand, the blue salt form  $A^-$  that exists alone in basic solutions absorbs in the yellow spectral range ( $\lambda_{\text{max}} \approx 595 \text{ nm}$ ). In buffered solutions a mixed colour is observed because of the existence of HA and  $A^-$ , both of which absorb in the visible spectral range.

In analytical practice, the intensity of absorption is usually quantified by the extinction that is defined in equation (5):

$$E_\lambda = \lg \frac{I_0}{I} \quad (5)$$

where:

$I_0, I$  Intensity of the radiation used before and after passage through an absorbing medium

Its dependence on the concentration  $c_i$  of an absorbing substance  $i$  and the layer thickness  $d$  at constant wavelength is given by the Lambert-Beer law:

$$E_\lambda = \varepsilon_i c_i d \quad (6)$$

where:

$E_\lambda$  Extinction at wavelength  $\lambda$

$\varepsilon_i$  Decadic molar extinction coefficient of the substance at wavelength  $\lambda$

$c_i$  Concentration of the substance  $i$

$d$  Layer thickness in the cell

which, with the simultaneous presence of two absorbing substances (here HA and  $A^-$ ), takes on the form:

$$E_\lambda = \varepsilon_{HA} \cdot c_{HA} \cdot d + \varepsilon_{A^-} \cdot c_{A^-} \cdot d \quad (6.1)$$

In acidic solution ( $c_{A^-} = 0, c_{HA} = c_0$ ) or basic solution ( $c_{HA} = 0, c_{A^-} = c_0$ ), equation (6.1) can be simplified to (6.1.1) and (6.1.2).

$$E_\lambda = \varepsilon_{HA} \cdot c_0 \cdot d = E_{\lambda, HA} \quad (6.1.1)$$

$$E_\lambda = \varepsilon_{A^-} \cdot c_0 \cdot d = E_{\lambda, A^-} \quad (6.1.2)$$

Insertion of  $c_{HA} = c_0 - c_{A^-}$  (4) in (6.1) gives:

$$c_{A^-} = \frac{E_\lambda - E_{HA} \cdot c_0 \cdot d}{d(\varepsilon_{A^-} - \varepsilon_{HA})} \quad (7)$$

Equation (7) is one possibility for calculating the concentration of the ionized form  $A^-$ . In this equation,  $E_\lambda$  represents the extinction of the buffered solution that should be measured at a wavelength ( $\varepsilon_{HA} \neq \varepsilon_{A^-}$ ) that is sufficiently well away from the isobestic point. The extinction coefficients  $\varepsilon_{HA}$  and  $\varepsilon_{A^-}$  can be calculated from equations (6.1.1) and (6.1.2) from the extinctions of the acid and basic thymol blue solutions of  $c_0 = 3 \cdot 10^{-5}$  molar at the same wavelength. With  $c_{A^-}$  known, then  $c_{HA}$  is accessible via equation (4). Insertion of the values for  $c_{A^-}$  and  $c_{HA}$  the concentration determined by the buffer of  $c = 1 \cdot 10^{-9}$  mol  $\cdot$  l $^{-1}$  in the law of mass action (1) gives the indicator constant  $K_a$ .

For the compound examined here, an alternative evaluation procedure can be used. As at wavelengths above 625 nm (Fig. 2) practically only the conjugated base  $A^-$  absorbs ( $\varepsilon_{HA} = 0$ ), equation (6.1) changes to:

$$E_\lambda = \varepsilon_{A^-} \cdot c_{A^-} \cdot d \quad (6.1.3)$$

The quotient from the relationships (6.1.3) and (6.1.2) is, according to definition, equal to the degree of dissociation  $\alpha$ ,

$$\alpha = \frac{c_{A^-}}{c_0} = \frac{E_\lambda}{E_{\lambda, A^-}} \quad (8)$$

This can be calculated from the extinctions  $E_\lambda$  and  $E_{\lambda, A^-}$  measured in buffered solution or NaOH at constant wavelength. The indicator constant  $K_a$  is then accessible from the relationship derived from the law of mass action (1) and the relationships (4) and (8):

$$K_a = \frac{c_{H^+} \cdot \alpha}{1 - \alpha} \quad (9)$$

The negative decadic logarithm of its numerical value is, according to definition (2), equal to the  $pK_a$  value.

#### Data and Results

The absorption spectra recorded at  $T = 299$  K are shown in Fig. 2. From the extinctions measured at  $\lambda = 460$  nm for the acid solution ( $E_{\lambda, HA} = 0.319$ ), the basic solution ( $E_{\lambda, A^-} = 0.073$ ) and the buffered solution ( $E_\lambda = 0.195$ ), the acid constant can be obtained from the relationships (6.1.1), (6.1.2), (7), (4) and (1) given in the text above, and we obtain  $K_a = 1.02 \cdot 10^{-9}$  mol  $\cdot$  l $^{-1}$ , from which, using (2), it follows that  $pK_a = 8.99$  (evaluation procedure 1).

The extinctions  $E_{\lambda, A^-} = 0.600$  and  $E_\lambda = 0.300$  can be taken from the spectra at  $\lambda = 460$  nm. From these and acc. to (8), a degree of dissociation of  $\alpha = 0.50$  is given, which can be inserted in (9) to give  $K_a = 1.00 \cdot 10^{-9}$  ( $pK_a = 9.00$ ) (evaluation procedure 2).

The average value of several calculations at various wavelengths is  $pK_a = 9.01$ . This lies in the region of values given in the literature, that fluctuate around  $pK_a = 9.00$  ( $T = 293$  K).