Related concepts

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.

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.

Tasks

Experimentally determine the extinction (absorbance) of an aqueous solution of thymol blue (thymolsulphonephthalein) 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.

Equipment

Spectrophotometer 190 - 1100 nm	35655.97	1
Cells for spectrophotometer	35664.02	1
Precision balance, 620 g	48852.93	1
Weighing dishes, 80 x 50 x 14 mm	45019.05	1
Microspoon	33393.00	1
Volumetric flask, 50 ml, IGJ 12/21	36547.00	3
Volumetric flask, 1000 ml, IGJ 24/29	36552.00	3
Funnel, glass, d_o = 55 mm	34457.00	1
Volumetric pipette, 1 ml	36575.00	1
Volumetric pipette, 5 ml	36577.00	1
Volumetric pipette, 10 ml	36578.00	1
Pipette dish	36589.00	1
Pipettor	36592.00	1
Graduated cylinder, 250 ml	36630.00	1
Glass beaker, 150 ml, tall	36003.00	3
Pasteur pipettes	36590.00	1
Rubber bulbs	39275.03	1
Laboratory thermometer	38034.00	1
Wash bottle, 500 ml	33931.00	1
Buffer solution pH 9.00, 1000 ml	30289.70	1
Thymol blue, indicator, powder, 5 g	31896.02	1
Hydrochloric acid, 0.1 M, 1000 ml	48452.70	1
Sodium hydroxide, 0.1 M, 1000 ml	48328.70	1
Ethanol, absolute, 500 ml	30008.50	1
Water, distilled, 5 l	31246.81	1

Set-up and Procedure

The spectrophotometer that is required for this experiment is shown in Fig. 1.

Fig. 1. Experimental set-up.

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 (thymolsulphonephthalein, $C_{27}H_{30}O_5S \cdot H_2O$) 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 ($c = 1 \cdot 10^{-3}$ mol $\cdot$ l^{-1}), the second one with HCl ($c = 1 \cdot 10^{-4}$ mol $\cdot$ l^{-1}), and the third flask with buffer solution of pH 9.
After correcting the zero line of the photometer using a water-filled 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.

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

$$HA \rightleftharpoons H^+ + A^-$$

where $A^- = [C_{27}H_{29}O_5S]^-$

The position of the dissociation equilibrium is quantitatively characterized by the acid or indicator constant K_a or the pK_a value derived from it:

$$K_a = \frac{a_{A^-}\, a_{H^+}}{a_{HA}} \approx \frac{c_{A^-}\, c_{H^+}}{c_{HA}} \qquad (1)$$

where:
a_i Activity of ion i

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

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

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

$$pK_a = pH + \lg \frac{c_{HA}}{c_{A^-}} \qquad (3)$$

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

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

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

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

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

In buffered solutions of pH 9 ≈ pK_a the ionized and non-ionized forms are present in practically the same concentration. These equilibrium concentrations, and so the constants K_a and pK_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 isosbestic point (Fig. 2).
The HA form that exists alone in acidic solutions absorbs in the blue spectral range ($\lambda_{max} \approx 430$ 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 ($\lambda_{max} \approx 595$ 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):

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

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:

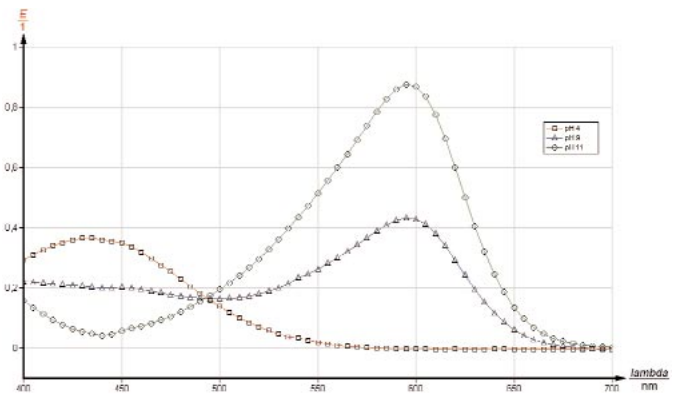
$$E_\lambda = \varepsilon_i\, c_i\, d \qquad (6)$$

where
E_λ Extinction at wavelength λ
ε_i Decadic molar extinction coefficient of the substance i at wavelength l
c_i Concentration of the substance i
d Layer thickness in the cell

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

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

Fig. 2: Absorption spectra of thymol blue ($c_0 = 2 \cdot 10^{-5}$ mol $\cdot$ l^{-1}) in $1 \cdot 10^{-4}$ molar HCl (□) $1 \cdot 10^{-3}$ molar NaOH (O) and a buffer solution of pH = 9.00 (△) at T = 299K.



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).

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

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

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

$$c_{A^-} = \frac{E_\lambda - E_{HA}\, c_0\, d}{d\,(E_{A^-} - E_{HA})} \qquad (7)$$

Equation (7) is one possibility for calculating the concentration of the ionized form A^-. In this equation, E_λ 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 isosbestic point. The extinction coefficients ε_{HA} and ε_{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:

$$E_\lambda = e_{A^-}\, c_{A^-}\, d \qquad (6.1.3)$$

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

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

This can be calculated from the extinctions E_λ and E_{λ,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):

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

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 λ = 460 nm for the acid solution ($E_{\lambda,HA}$ = 0.319), the basic solution (E_{λ,A^-} = 0.073) and the buffered solution (E_λ = 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_{λ,A^-} = 0.600 and E_λ = 0.300 can be taken from the spectra at λ = 460 nm. From these and acc. to (8), a degree of dissociation of α = 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).

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.