Exercise 26

SPECTROFOTOMETRIC DETERMINATION OF THE p*K* INDICATOR (OF BROMOCRESOL GREEN)

Key concepts: Electrolytes. Electrolytic dissociation and the dissociation constant. Determination of pK_a of acids and bases. pH. Buffer solution and pH of a buffer solution. pH indicators. Lambert-Beer law. Spectrophotometry.

The exercise involves the spectrophotometric determination of the effect of pH on the concentration of the dissociated $[In^-]$ and undissociated [HIn] forms of the indicator and determining, based on the obtained results, the dissociation constant K_{In} of this indicator. The indicator under study is bromocresol green. It is a weak, monoprotic acid. In aqueous solution it dissociates:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq) \tag{1}$$

Its undissociated form, which predominates in acidic environments, is yellow, while the dissociated form, present in an alkaline environment, is blue. The equilibrium constant K_{In} of the above reaction described by the formula:

$$K_{\mathrm{In}} = \frac{a_{\mathrm{In}^-} \cdot a_{\mathrm{H_3O^+}}}{a_{\mathrm{HIn}} \cdot a_{\mathrm{H_2O}}} \tag{2}$$

Where a_J is the activity of reactant J.

If the concentration of the indicator is low, then it can be assumed that the activity of water is equal 1. After applying logarithm to the above equation and using the substitutions:

$pK_{In} = -\log K_{In}$

$pH = -\log a_{H_3O^+}$,

and replacing the activity of the two forms of the of the indicator with the corresponding concentrations, we obtain:

$$\mathrm{p}K_{\mathrm{In}} \approx \mathrm{pH} + \log \frac{[\mathrm{HIn}]}{[\mathrm{In}^-]} \tag{3}$$

It follows from this equation that the pH value at which the concentrations of the two forms of the indicator are equal to each other ($[In] = [HIn^-]$) corresponds to its pK_{In} value. Required pH values can be obtained by using a buffer solution of acetic acid and sodium acetate.

Experiment method and procedure

First part:

In the first part of the exercise, we measure the absorption spectra of the dissociated (**D**) and undissociated (**UD**) form of the indicator (bromocresol green). For this purpose, we prepare the following two solutions:

UD: into a 50 cm^3 volumetric flask, add 5 cm^3 of a 0.0001 M solution of bromocresol green, 5 cm^3 of 0.1 M HCl, fill the remaining volume with distilled water and stir;

D: into a 50 cm^3 volumetric flask, add 5 cm^3 of 0.0001 M solution of bromocresol green, 5 cm^3 of 0.1 M NaOH, fill the remaining volume with distilled water and stir.

When preparing solutions, use separate pipettes for the indicator, HCl acid and NaOH. The presence of hydrochloric acid or sodium hydroxide at the concentrations used in the exercise causes solution **UD** to contain only the undissociated form of the indicator, while solution **D** contains the dissociated form.

(a) Perform absorbance measurements (A) for solutions **UD** and **D** in the visible light range. The wavelengths λ at which measurements should be made are given in Table 1.The measurements are performed on a spectrophotometer CECIL CE 2020.

(b) Place the results in Table 1.

(c) Create a graph of the **UD** and **D** absorbance dependence on the wavelength.

(d) Find the wavelength at which the difference in absorbance of solutions **D** and **UD**, ΔA, is the biggest – and apply it further as the analytical wavelength $\lambda_{\text{analytical}}$.
The absorbance of solution **UD** at analytical wavelength will be denoted by the symbol A_{HIn}, while that of solution **D** will be denoted by the symbol A_{In^-}.

Second part:

In the second part of the exercise, the effect of pH on the absorbance of the indicator solution will be measured using the analytical wavelength.

(a) Prepare 9 solutions of bromocresol green in environments of different pH. To do this, into each of 9 dry and clean 50 cm^3 volumetric flasks, add 5 cm^3 of 0.0001 M bromocresol green solution, 20 cm^3 of 0.1 M acetic acid and 2, 4, 6, ... , 18 cm^3 of 0.1 M NaOH, respectively. Fill the remaining volume of each flask with distilled water and stir.

Use separate pipettes for particular reactants.

(b) As a result of the reaction between acetic acid and sodium hydroxide, sodium acetate is formed. Acetic acid and sodium acetate form a buffer solution. The pH value of the buffer composed of a weak acid and its salt can be calculated from the formula:

$$\text{pH} \approx \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} \tag{4}$$

where [salt] and [acid] are the concentrations of weak acid and its salt in buffer solution, respectively and pK_a is acidity constant (pK_a = -log K_a).

Since in the exercise the buffer is made from solutions of the same molar concentrations (0.1 M), and the volume of the CH_3COOH solution is always the same (20 cm^3), you we write:

$$[\text{salt}] \backsim V_{\text{NaOH}} \qquad\qquad [\text{acid}] \backsim 20 - V_{\text{NaOH}}$$

And by applying the pK_a value of acetic acid (4.76) we can write:

$$\text{pH} = 4.76 + \log \frac{V_{\text{NaOH}}}{20 - V_{\text{NaOH}}} \tag{5}$$

The equation above is correct only when $V_{\text{NaOH}} < 20$ cm^3 (if the bigger volume is applied the solution is not a buffer solution).

(c) Calculate pH of each of 9 prepared solutions and write them in Table 2.

(d) Measure the absorbance, A, of each solution, using the analytical wavelength determined in the first part.

These results will be used for calculating both forms, [HIn] and [In$^-$], of the indicator. Note that the absorbance of the solution containing both forms of the indicator can be written as:

$$A = A_{\text{HIn}} \left(\frac{[\text{HIn}]}{[\text{HIn}]_0}\right) + A_{\text{In}^-} \left(\frac{[\text{In}^-]}{[\text{HIn}]_0}\right) \tag{6}$$

Where

A_{HIn} is the absorbance of the solution containing only the undissociated form of indicator,
A_{In^-} is the absorbance of the solution containing only the dissociated form of indicator,
$[\text{HIn}]_0$ is the total concentration of the indicator:

$$[\text{HIn}]_0 = [\text{HIn}] + [\text{In}^-] \tag{7}$$

By solving the set of equations (6) and (7) we obtain:

$$[\text{HIn}] = [\text{HIn}]_0 \frac{A - A_{\text{In}^-}}{A_{\text{HIn}} - A_{\text{In}^-}} \tag{8}$$

$$[\text{In}^-] = [\text{HIn}]_0 - [\text{HIn}]$$

(e) Calculate the concentrations of [HIn] and [In$^-$] and write the results in Table 2.

(f) Draw a graph of the dependence of the concentrations of the dissociated and undissociated form of the indicator on the pH of the solution.

(g) Read the pH value at which the concentrations of the two forms are equal (the point of intersection of the curves) from the graph. This pH value is equal to the searched pK_{In} of the indicator.

Table 1. Absorbance of **D** and **UD** solutions.

Wavelength, λ [nm]	Absorbance, *A*	
	D solution	**UD** solution
400		
420		
440		
460		
480		
500		
520		
540		
560		
580		
600		
620		
640		
660		
680		
700		

$\lambda_{\text{analytical}}$ =

A_{HIn} =

A_{In^-} =

Table 2. Data for solutions of bromocresol green.

V_{NaOH}[cm^3]	pH	*A*	[HIn]	[In$^-$]
2				
4				
6				
8				
10				
12				
14				
16				
18				