1.a. Spectrophotometric determination of the dissociation constant of an acid-base indicator

The 3′,3″,5′,5″-Tetrabromo-m-cresolsulfonephthalein (bromocresol green) acid-base indicator behaves as a reversible system whose acidic form (yellow, HB^-) changes into a basic form (blue, B^{2-}) over the pH range 3.8–5.4. The concentration of both forms of the indicator can be determined using photometry.

The univalent anion of the indicator dissociates according to the chemical equation:

$$B^- + H_2O \leftrightarrow B^{2-} + H_3O^+ \quad (1.)$$

yellow solution blue solution

The thermodynamic equilibrium constant of dissociation to the second degree is given by:

$$K_A = \frac{a_{H_3O^+}\ a_{B^{2-}}}{a_{HB^-}} \quad (2.)$$

where a_i ($i = H_3O^+, B^{2-}, HB^-$) are the activities of the ions. The relationship between the true thermodynamic dissociation constant K_A and the approximate dissociation constant $K_A^{'}$ is:

$$K_A^{'} = \frac{[H_3O^+]\,[B^{2-}]}{[HB^-]} = K_A \frac{\gamma_{HB^-}}{\gamma_{H_3O^+}\ \gamma_{B^{2-}}} \quad (3.)$$

where γ_i are the activity coefficients of the ions. After mathematical rearrangement, we get:

$$K_A^{'} = pH - log\frac{[B^{2-}]}{[HB^-]} \quad (4.)$$

The ionic activity coefficients can be obtained from the extended Debye-Hückel law (DHL). The activity $\gamma_{B^{2-}}$ is given in aqueous solution at *25°C* as the following:

$$log(\ \gamma_{B^{2-}}) = -\frac{A\,(z_{B^{2-}})^2\sqrt{I}}{1+B\,(r_{B^{2-}})\sqrt{I}} = -\frac{2.034\sqrt{I}}{1+2.30\sqrt{I}} \quad (5.)$$

Where $A = 0.5085$, $B = 0.3281$, and $r_{B^{2-}} = 0.7$Å Å, which is the effective diameter of the ion B^{2-} in Ångström. The ionic strength I (at low concentrations) is given by:

$$I = \frac{1}{2}\sum_{i=1}^{k} c_i z_i^2 \quad (6.)$$

where z_i are charge numbers of all ions i in the solution, and c_i are their molarities.

The activity coefficients $\gamma_{H_3O^+}$ and γ_{HB^-} are equal according to the DHL; thus, the relationship between constants K_A and $K_A^{'}$ can be simplified to:

$$K_A = K_A^{'}\gamma_{B^{2-}} \qquad \text{ie: } pK^A = pK_A^{'} - log\left(\gamma_{B^{2-}}\right) \quad (7.)$$

and together with eqn (5.), results in the following:

$$pK^A = pK_A^{'}\ \frac{2.034\sqrt{I}}{1+2.30\sqrt{I}} \quad (8.)$$

The thermodynamic equilibrium dissociation constant K_A can be calculated using eqn (8.) or it can be more precisely graphically evaluated from an experiment at different ionic strengths.

TASK: Evaluate the thermodynamic equilibrium dissociation constant K_A of bromocresol green to the second degree at *0.1M* ionic strength.

LABORATORY AIDS AND CHEMICALS: UV/VIS spectrophotometer (minimum range *350-720 nm*), *2* cuvettes, *2* volumetric flasks *(50 cm³)*, *1* volumetric flask *(250 cm³)*, *3* volumetric pipettes *(1, 5, 25 cm³)*, *1* scale pipette *(10 cm³)*, $1.5 \times 10^{-4} M$ stock solution of bromocresol green (CAS No: 76-60-8), *0.2M* CH_3COONa, *1M* CH_3COOH, *1M KCl*, and *3M HCl*.

INSTRUCTIONS:

Preparation of solutions I and II. Using a 50 cm^3 flask, prepare *50* cm^3 of solution I: 1.5×10^{-5} *M* bromocresol green (BG) inside *0.01 M* CH_3COONa at ionic strength *I=0.1M* using stock solutions. Set the ionic strength to the desired value with a pre-calculated volume of *1M KCl*. Similarly, prepare *50* cm^3 of **solution II:** 1.5×10^{-5} *M* bromocresol green (BG) inside *0.25 M* CH_3COOH at ionic strength *I=0.1M* using *KCl* stock solution.

Measuring spectra of indicator at different pH. Pour all of solution I into a larger flask (250 cm^3). Take a sample of solution I, place it in a quartz cuvette and measure the entire UV / Vis spectrum. Determine the wavelength at which the solution has a maximum absorbance A_2 (see **FIG. 1**). Return the content of the cuvette to the flask with the original solution I. Add *1* cm^3 of solution II to the flask and mix. The pH of the solution is changed. Repeat sampling, spectrum measurement, sample return and addition of 1 cm^3 of solution II a total of 6 times. For the last addition, use *1* cm^3 of *3M* HCl.

The solution containing an equimolar ratio of CH_3COONa and CH_3COOH is green in colour and has two maxima (see **FIG. 1**).

DATA ANALYSIS: The ratio of the concentrations of the basic and acidic forms of the indicator is equal to the absorbance ratio at the adsorption maximum (compare **FIG. 1**):

$$\frac{\left[B^{2-}\right]}{\left[HB^{-}\right]} = \frac{A_i - A_1}{A_2 - A_i} \qquad (9.)$$

where A_2 is the absorbance of the B^{2-} anion if the HB^-anion is not present (i.e., in a very basic environment). A_1 is the absorbance of the HB^- anion if the B^{2-}anion is not present (i.e., in a very acidic environment). A_i is the absorbance of the B^{2-} anion at a general *pH* when both anions B^{2-} and HB^- coexist in the solution.

The pH of the solutions to be monitored is determined by the concentration of the majority of the solution components, which are acetic acid and sodium acetate. They form a conjugated acid-base buffer. The pH is given by the Henderson-Hasselbalch eqn:

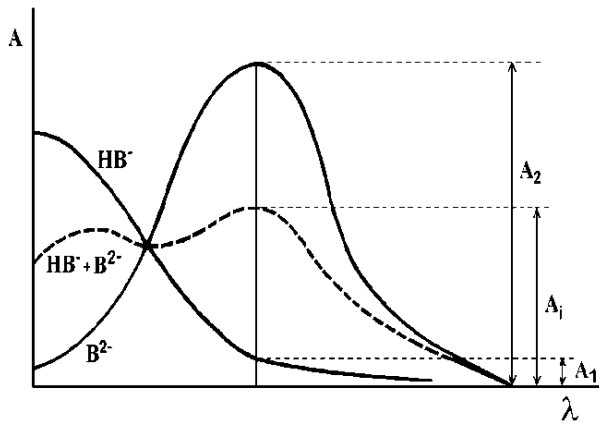

FIG. 1: Evaluation of spectra of acid-base indicator of bromocresol green obtained at different pH.

$$pH = pK^{HAc} + log\frac{c^{NaAc}}{c^{HAc}} \quad (10.)$$

where $pK^{HAc} = 4.76$ is the negative logarithm of the dissociation constant of acetic acid. c^{NaAc} and c^{HAc} are analytical concentrations of sodium acetate and acetic acid.

REPORT: TABLE 1: The volumes of the stock solutions used to prepare solutions I and II. A detailed calculation of the ionic strength. **Common graph 1:** UV/Vis spectra for all sample solutions. **Also include:** wavelength of absorption maxima of B^{2-} and HB^{-}, values A_2 and A_1 (**FIG. 1**). **Table 2:** for each sampling: addition of solution II, experimental absorbance A_i, calculated ratio $(A_i - A_1)/(A_2 - A_i)$ (use eqn (9.)), $\log[(A_i - A_1)/(A_2 - A_i)]$, c^{NaAc} and c^{HAc} , *pH* value calculated using eqn (10.) and pK^{HAc} from literature. $pK_A^{'}$ (eqn (4.)), pK_A (eqn (8.)). **Also include:** The mean value pK_A and its confidence interval according to the Student's t-distribution.