1. Acid-base Equilibria

1.a. Photochemical determination of dissociation constant of 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*$^{2-}$) at pH range 3.8–5.4. The concentration of both forms of the indicator can be determined by the photometric method.

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

$$HB^- + H_2O \Leftrightarrow B^{2-} + H_3O^+ \qquad (1.1.)$$

yellow solution *blue solution*

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

$$K_A = \frac{a_{H_3O^+} . a_{B^{2-}}}{a_{HB^-}} \qquad (1.2.)$$

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

$$K'_A = \frac{\left[H_3O^+\right].\left[B^{2-}\right]}{\left[HB^-\right]} = K_A \frac{\gamma_{HB^-}}{\gamma_{H_3O^+} \cdot \gamma_{B^{2-}}} \qquad (1.3.)$$

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

$$pK'_A = pH - \log \frac{\left[B^{2-}\right]}{\left[HB^-\right]} \qquad (1.4.)$$

The activity coefficients of ions can be obtained by use extended Debye-Hückel law (DHL). The activity $\gamma_{B^{2-}}$ is given in aqueous solution at *25°C* by expression:

$$\log \gamma_{B^{2-}} = -\frac{A \cdot \left(z_{B^{2-}}\right)^2 \cdot \sqrt{I}}{1 + B \cdot r_{B^{2-}} \cdot \sqrt{I}} = -\frac{2{,}034\sqrt{I}}{1 + 2{,}30\sqrt{I}} \qquad (1.5.)$$

where $A = 0{,}5085$, $B = 0{,}3281$, $r_{B^{2-}} = 0{,}7$ Å is effective diameter of the ion B^{2-} in Ångström. The ionic strength I is (at low concentrations) given by:

$$I = \frac{1}{2} \sum_{i=1}^{k} c_i z_i^2 \qquad (1.6.)$$

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

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

$$K_A = K_A^{'} \gamma_{B^{2-}} \qquad \text{ie: } pK^A = pḰ^A \ - log\left(\gamma_{B^{2-}}\right) \qquad (1.7.)$$

and together with eqn (1.5.) it gives:

$$pK_A = pK_A^{'} + \frac{2{,}04\sqrt{I}}{1+2{,}3\sqrt{I}} \tag{1.8.}$$

The thermodynamic equilibrium constant of the dissociation K_A can be calculated using eqn (1.8.) or it can be graphically evaluated more precisely from an experiment at different ionic strength.

TASK: Evaluate thermodynamic equilibrium constant of dissociation K_A of bromocresol green to the second degree at ionic strength *0,1M.*

LABORATORY AIDS AND CHEMICALS: UV/VIS spectrophotometer (minimum range *350-720 nm*), *2* cuvettes, *2* volumetric flasks *(50ml)*, *1* volumetric flask *(250ml)*, *3* volumetric pipettes *(1, 5, 25ml)*, *1* scale pipette *(10ml)*, $1{,}5.10^{-4}M$ 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. Prepare *50 ml* (use flask of same volume) of solution I of concentration $1{,}5{\cdot}10^{-5}\ M$ bromocresol green (BG) inside $0{,}01\ M\ CH_3COONa$ at ionic strength $I=0{,}1M$ from stock solutions. Set the ionic strength to the desired value with a pre-calculated volume of *1M KCl*. Prepare *50 ml* of solution II of concentration $1{,}5{\cdot}10^{-5}\ M$ bromocresol green (BG) inside $0{,}01\ M\ CH_3COONa$ at ionic strength $I=0{,}1M$ from stock solutions.

Measuring spectra of indicator at different pH. Pour whole solution I into larger flask (250 ml). 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 **FIGURE 1**). Return the content of the cuvette to the flask with the original solution I. Add *1 ml* of solution II to the flask and mix. The pH of solution is changed. Repeat sampling, spectrum measurement, sample return and addition of 1 ml of solution II. Repeat this procedure 6 times. The last addition is done with *1ml* of *3M HCl*.

The solution containing the equimolar ratio CH_3COONa and CH_3COOH is green in color and has two maximas (see **FIGURE 1**).

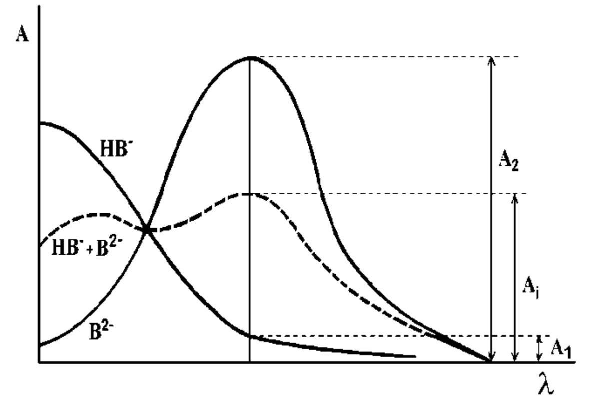

FIGURE 1: Evaluation of spectra of acid-base indicator of bromocresol green obtained at different pH.

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

$$\frac{\left[B^{2-}\right]}{\left[HB^{-}\right]} = \frac{A_i - A_1}{A_2 - A_i} \tag{1.9.}$$

where A_2 is absorbance of B^{2-} anion if the anion HB^- is not present (ie in a far basic environment). A_1 is absorbance of HB^- anion if the anion B^{2-} is not present (ie in a far acidic environment), A_i is absorbance of B^{2-} anion at a general *pH* when both anions B^{2-}, 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 conjugated acid-base buffer. The pH is given by Henderson-Hasselbalch eqn:

$$pH = pK^{HAc} + log\frac{c^{NaAc}}{c^{HAc}} \tag{1.10.}$$

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. The detailed calculation of the ionic strength. **Common graph 1:** UV/VIS spectra for all sample solutions. **Next:** wavelength of absorption maxima of B^{2-} and HB^-, value *A₂* and *A₁* (**FIGURE 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 (1.9.)), $\log[(A_i - A_1)/(A_2 - A_i)]$, c^{NaAc} and c^{HAc} , *pH* value calculated using eqn (1.10.) and pK^{HAc} from literature. $pK_A^{'}$ (eqn (1.4.)), pK_A (eqn (1.8.)). **Next:** The mean value pK_A and its confidence interval according to the Student's t-distribution.