Dissociation equilibrium constant determination by spectrophotometric method

Background: P.W. Atkins & J. de Paula: *Physical Chemistry* (10th ed.), Chapters 5F (activity of ions), 6 (chemical equilibrium), and 12A (Beer–Lambert law).
Type of practice: Individual.
Aim of practice: Illustrate how to determine the dissociation equilibrium constant of bromocresol green (tetrabromo-m-cresolsulfonphthalein) or other similar acid – base indicator.

1 Introduction

Acid – base indicators act as weak acids (or bases) in aqueous solutions, thus their deprotonation (or protonation in case of bases) is an equilibrium process. For example, in the case of weak acid we can write

$$\mathrm{HB_{aq}} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{B^-}, \tag{1}$$

where HB and $\mathrm{B^-}$ denote the protonated (not dissociated) and deprotonated (dissociated) forms, respectively. The equilibrium is characterized by the acid dissociation constant defined by ion activities

$$K_a = \frac{a_{\mathrm{H_3O^+}}\, a_{\mathrm{B^-}}}{a_{\mathrm{HB}}} = \frac{c_{\mathrm{H_3O^+}}\, c_{\mathrm{B^-}}}{c_{\mathrm{HB}}\, c^0}\, \frac{\gamma_{\mathrm{H_3O^+}}\, \gamma_{\mathrm{B^-}}}{\gamma_{\mathrm{HB}}} = K_c\, \Gamma, \tag{2}$$

where K_c is the equilibrium constant defined by molar concentrations and the activity coefficients are merged into Γ. Therefore,

$$pK_c = pK_a \; + \; \lg \Gamma. \tag{3}$$

In the case of small ionic strength, the activity coefficient of uncharged particles is unity according to the Debye – Hückel theory, thus eq. (3) can be written as

$$pK_c = pK_a \; + \; \lg \left(\gamma_{\mathrm{B^-}}\, \gamma_{\mathrm{H_3O^+}}\right). \tag{4}$$

In solution, the mean ion activity coefficient for electrolytes dissociating into monovalent ions can be expressed by the ion activity coefficients of the separate ions as $\gamma_\pm = \sqrt{\gamma_+\, \gamma_-}$, thus applying that for eq. (4) we obtain

$$pK_c = pK_a \; + \; 2 \lg \gamma_\pm. \tag{5}$$

According to the extended Debye – Hückel theory, the mean ion activity coefficient is defined as

$$\lg \gamma_\pm = -\frac{\mathcal{A}\sqrt{I}}{1 + D\sqrt{I}} = -\mathcal{A} \cdot I', \qquad \text{where} \qquad I' = \frac{\sqrt{I}}{1 + D\sqrt{I}}, \tag{6}$$

where $\mathcal{A}$ and D are constants ($D = 2.3\,\mathrm{M}^{-1/2}$ at 25 °C) and I denotes the ionic strength of the solution. The ionic strength is defined as $I = \frac{1}{2}\sum c_i \cdot z_i^2$, where z_i is the charge of ion i and c_i is its molar concentration. Finally, substituting eq. (6) into eq. (5) leads to

$$pK_c = pK_a - 2\, \mathcal{A}\, I'. \tag{7}$$

Therefore, K_c must be known for solutions of various ionic strength in order to determine K_a. First, the concentration of hydroxonium ions ($c_{\mathrm{H_3O^+}}$) must be obtained at each ionic strengths, then the calculations require the ratio of the concentrations of dissociated and not dissociated forms ($c_{\mathrm{B^-}}/c_{\mathrm{HB}}$) as well. We obtain pK_a from the intercept of the linear fitted to the $pK_c - I'$ function.

Applying acid – base indicators, the color of the protonated and deprotonated forms significantly differs (e.g., see bromocresol green in Figure 1) thus their concentration ratio can be measured spectrophotometrically. The method requires the existence of a wavelength at which there is a remarkable absorbance difference

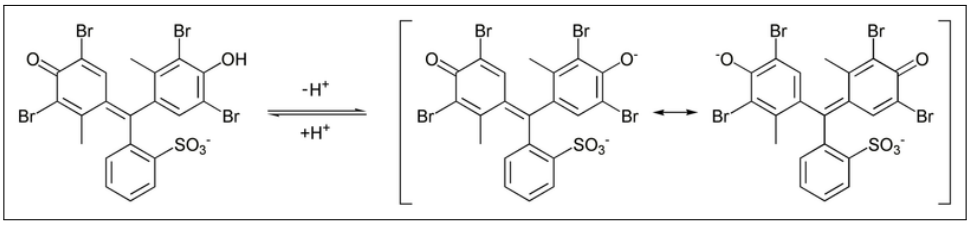

Figure 1: The structure of bromocresol green: left – HB form (yellow in water), right – B^- form (blue in water).

between the two forms of the chemical compound in the solution of given *p*H. If the solution of the chemical system is colorful, the measurement can be performed in the visible range, whereas a transparent system might be investigated in the UV region. If both forms are present in the same solution, the absorbance is calculated as

$$A = A_{\mathrm{HB}} + A_{\mathrm{B^-}} = \varepsilon_{HB}\,\ell\,c_{HB} + \varepsilon_{B^-}\,\ell c_{B^-}\,, \tag{8}$$

and for the analytical concentration of the chemical compound (c) we can write $c = c_{\mathrm{HB}} + c_{\mathrm{B^-}}$. The molar absorption coefficients of the two forms are obtained from the absorbance of the solution containing only one of them with concentration c, i.e., from the absorbance of the fully deprotonated form ($A_{\mathrm{B^-}}$) and from that of the fully protonated form (A_{HB}):

$$\varepsilon_{\mathrm{HB}}\,\ell = \frac{A_{\mathrm{HB}}}{c} \quad \text{and} \quad \varepsilon_{\mathrm{B^-}}\,\ell = \frac{\mathrm{A_{B^-}}}{\mathrm{c}}\,. \tag{9}$$

Upon substituting eqs. (9) into eq. (8) we obtain $A = A_{\mathrm{B^-}}\dfrac{c_{\mathrm{B^-}}}{c} + A_{\mathrm{HB}}\dfrac{c_{\mathrm{HB}}}{c}$ expression, from which – after rearrangement – the concentration ratio of the two limiting cases can be calculated as

$$\frac{c_{\mathrm{B^-}}}{c_{\mathrm{HB}}} = \frac{A - A_{\mathrm{HB}}}{A_{\mathrm{B^-}} - A}\,. \tag{10}$$

Therefore, preforming the measurements in cuvettes with identical optical path (or in the very same cuvette) eliminates the need of knowing the molar absorption coefficients or that of optical path.

Consequently, three type of solutions are required for the spectrophotometric measurements. The hydrogen ion concentration must be set by buffers in a way that one solution contains the dissociated form only, an other one purely contains the not dissociated form, whereas dissociation takes place to some extent in the third type of solution. The analytical concentration of the investigated chemical compound must be the same in each solution. pK_a of the compound can be determined by applying eq. (7) if a series of the third type solution is prepared where the ionic strength changes from one solution to the other one while other experimental parameters are kept constant.

2 Experimental

2.1 Preparations

If not ready yet, prepare the following stock solutions:

500 $\mathrm{cm^3}$	10^{-4}	mol $\mathrm{dm^{-3}}$	bromocresol green
500 $\mathrm{cm^3}$	0.25	mol $\mathrm{dm^{-3}}$	acetic acid
500 $\mathrm{cm^3}$	3	mol $\mathrm{dm^{-3}}$	HCl
500 $\mathrm{cm^3}$	10^{-2}	mol $\mathrm{dm^{-3}}$	HCl
1000 $\mathrm{cm^3}$	0.2	mol $\mathrm{dm^{-3}}$	sodium acetate
500 $\mathrm{cm^3}$	1	mol $\mathrm{dm^{-3}}$	KCl

Prepare the solutions below by dilution from the stock solutions:

1. Measure 5 cm^3 indicator and 2.5 cm^3 sodium acetate stock solutions into 50 cm^3 volumetric flasks. According to the Instructor's request, add the following volumes (in cm^3) of KCl stock solution to prepare a solution series with varying ionic strength.

aa:	0,0	0,5	1,0	2,0	4,0	8,0	16,0	32,0
ab:	0,0	0,5	1,0	1,5	3,0	7,0	15,0	30,0
ac:	0,0	0,5	1,2	2,5	5,0	9,0	20,0	40,0
ad:	0,0	0,3	0,7	1,0	2,0	5,0	10,0	22,0

   Add 2 – 2 cm^3 0.25 mol dm^{-3} acetic acid stock solution to each solutions. Fill up the volumetric flasks with ion exchanged water. These solution are referred to as **A** in the following. (If no sufficient amount of volumetric flask is provided in order to store the solutions in them, prepare each solution in the same volumetric flask then pour the solutions into dry beakers.)

2. At a selected ionic strength, prepare the solution containing only the deprotonated form of the indicator (referred to as **B**) as follows: Measure 5 cm^3 indicator and 2.5 cm^3 sodium acetate stock solutions into a 50 cm^3 volumetric flask. Do not forget to add the volume of KCl solution belonging to the selected ionic strength (i.e., the solution is prepared in a similar way than the previous ones, only the acetic acid is not added).

3. At the same ionic strength, prepare the solution containing only the protonated form of the indicator (referred to as **C**) as follows: Prepare the solution on the same way as described in the first point but also add 0.4 cm^3 3 mol dm^{-3} HCl stock solution before filling up the volumetric flask.

4. The *p*H-meter must be calibrated at each ionic strength in order determine the hydrogen ion concentration in the different solutions. Therefore, prepare 50 – 50 cm^3 calibration standards for each ionic strength maintained in the **A** solution series. Each calibration standard must contain 10^{-3} mol dm^{-3} HCl; use the HCl stock solution with exact concentration for dilutions. When setting the ionic strength of the calibration standards, consider all compounds of **A** solutions which contribute to the ionic strength. Do not forget to take HCl into account as well.

   Summarize the calculation details in the table below:

   $[HCl]_{stock}$= M, $V_{solution}$= cm^3

V_{HCl} / cm^3	V_{KCl} / cm^3	I / M

2.2 Measurements

1. As a first step, determine the wavelength of the measurements, i.e., the wavelength where the difference of absorbance between the two solutions containing either the protonated or the deprotonated forms only is the most significant. Record the spectra of the two limiting cases (**B** and **C** solutions) between 400 and 700 nm with at least 10 nm resolution. (If no automatic spectrum recording is available, measure the absorbance at the selected wavelengths and then make a plot of the measured data.) If several regions are adequate for the measurements, then select the wavelength where the absorbance difference is high and the maximum absorbance does not exceed 1.2.

2. Measure the absorbance of solutions at the selected wavelength. Be aware that ∼35 cm^3 solution is required for *p*H measurements.

3. For the solutions remained after absorbance measurements, determine the hydrogen ion concentrations with the aid of calibration standard as follows:

   (a) Calibrate the *p*H-meter before each measurement by applying the calibration standard having the appropriate ionic strength, i.e., set *p*H = 3.00 for the selected 10^{-3} mol dm^{-3} HCl solution. By

definition, the instrument displays the negative logarithm (base ten) of hydroxonium ion activity. With this calibration performed on solutions of identical ionic strength, however, the displayed value is a good approximation of the negative logarithm (base ten) of hydroxonium ion concentration (the *p*H scale is simply shifted by lg γ).

(b) Thoroughly rinse the electrode with ion exchanged water, then use a paper towel to gently dry its surface. Measure the „*p*H" of each element of solution series **A**.

(c) Thoroughly rinse the electrode with ion exchanged water, then use a paper towel to gently dry its surface.

2.3 Evaluation

1. Plot the absorbance spectra corresponding to the two limiting case (i.e., either deprotonated or protonated compound only).
2. Calculate the ionic strength, its square root, and I' (see eq. (6)) for each measurement.
3. Calculate the concentration ratio of the deprotonated and protonated forms applying the absorbance data (c_{B^-}/c_{HB}, see eq. (10)).
4. Calculate the hydrogen ion concentration of the solutions applying the measured *p*H. Calculate K_c and pK_c as well.
5. Summarize your results in the following table:

$\lambda =$ nm, $A_{B^-} =$ $A_{HB} =$

Solution composition	A	I / M	$\sqrt{I/\mathrm{M}}$	$I'/\mathrm{M}^{1/2}$	*p*H	$[H^+]$ / M	$\frac{c_{B^-}}{c_{HB}}$	K_c	pK_c

6. Make a $pK_c - I'$ plot. Fit a linear through the data applying the least square method. From the fitted parameters, determine pK_a and $\mathcal{A}$ together with their standard deviation.
7. Compare the results to literature data and discuss the findings.

Note: This laboratory practice is experimentally demanding. Thus, the measurements can only be finished successfully within the allotted time, if the calculations necessary for solution preparation (especially that of the ionic strength) are done routinely. If the student is aware of her/his calculation difficulties, strongly advised to practice in advance.

Questions

1. Define the Beer – Lambert law and the notations in it.
2. What are the limitations of applying a spectrophotometric method for the determination of an equilibrium constant?
3. What is the relationship between the dissociation constants defined with either activities or molar concentrations? What is pK_a and pK_c?
4. Derive the equation used for the experimental determination of pK_a.
5. Given a chemical substance, what kind of wavelength should be used for the absorbance measurements and how do you determine its exact value?
6. Define ionic strength. Why is this quantity useful in physical chemistry?
7. Calculate the ionic strength of the solutions for the following cases:

- $2.0\,cm^3$ 0.25 M acetic acid, $2.5\,cm^3$ 0.2 M sodium acetate and $5.0\,cm^3$ 1.0 M KCl solutions mixed and diluted by ion exchanged water up to $50\,cm^3$ total volume.
- The solution contains the following compounds: 10^{-4} M indicator (HB), 0.025 M sodium acetate and 0.01 M KCl.
- $5\,cm^3$ 10^{-4} M indicator (HB), $2.5\,cm^3$ 0.2 M sodium acetate, $2.0\,cm^3$ 0.25 M acetic acid and $5.0\,cm^3$ 1.0 M KCl solutions mixed and diluted by ion exchanged water up to $50\,cm^3$ total volume.

8. Calculate the volume (in cm^3) of 1.0 M KCl solution which has to be added to $10\,cm^3$ 0.1 M HCl solution in order to maintain 0.4 M ionic strength upon diluting the mixture up to $50{,}0\,cm^3$ total volume.
9. Derive the equation which describes the ratio of the concentrations of dissociated and not dissociated forms.
10. In a few sentence, elaborate on how could you set up similar measurement protocols to determine pK_a of different indicators. Keep your statements generally valid.
11. What kind of experimental data will be obtained during the measurements and how will you determine K_a on their basis?
12. Given a solution which only contains either the dissociated or the not dissociated form of an indicator. Why is the absorbance of this solution independent of ionic strength?