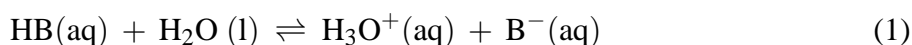


# Equilibrium constant determination of bromocresol green

**Goals:** To determine the acid dissociation constant ( $K_a$ ) for bromocresol green (BCG), an acid-base indicator.

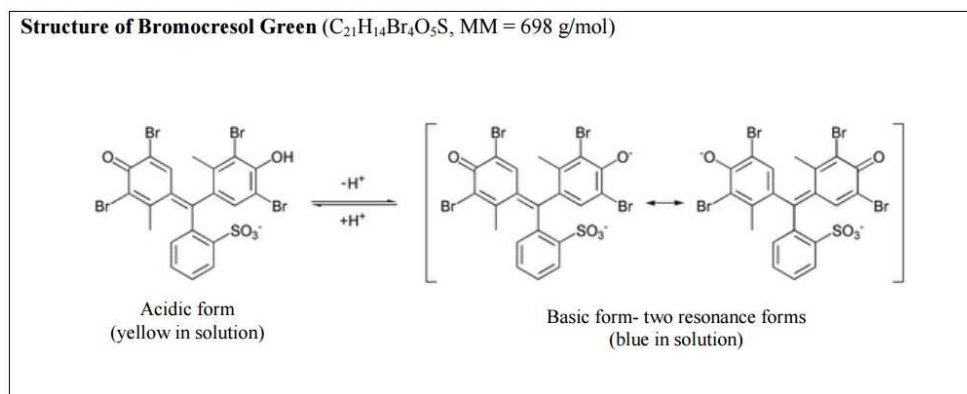
## 1. Introduction

Acid-base indicators, e.g. methyl red, phenolphthalein, are often used to indicate the end-point of an acid-base reaction. These indicators are weak acids (or bases) that dissociate into a hydronium ion ( $H_3O^+$ ) and a conjugate base anion ( $B^-$ ). This dissociation can be represented through the following equation and the corresponding equilibrium expression:



$$K_c = \frac{c_{H_3O^+} c_{B^-}}{c_{HB}} \quad (2)$$

In order for a compound to be a useful indicator, the acidic form (HB) and the basic form ( $B^-$ ) of the indicator should differ in color. Since equilibrium in acidic solution favors the formation of HB, this species is called the acidic form of the indicator. Likewise, the  $B^-$  form is called the basic form since it is favored in basic solutions. An equilibrium mixture of the indicator will be colored according to the relative concentration of each form of the indicator. The position of the equilibrium and, therefore, the relative concentration of the two forms of the indicator will depend on the  $H_3O^+$  concentration.



The relation between equilibrium constants can be expressed by including the activity coefficients as

$$K_a = \frac{a_{H_3O^+} a_{B^-}}{a_{HB}} = \frac{c_{H_3O^+} c_{B^-}}{c_{HB}} \cdot \frac{\gamma_{H_3O^+} \gamma_{B^-}}{\gamma_{HB}} = K_c \cdot \Gamma \quad (3)$$

For ionic species, the activity coefficient can be calculated from the Debye–Hückel limiting law at very low concentrations by introducing the mean activity coefficient as  $\gamma_{\pm} = \sqrt{\gamma_+ \gamma_-}$ . We

find that for the acid-base indicator  $\gamma_{\pm}^2 = \gamma_{\text{B}^-} \gamma_{\text{H}_3\text{O}^+}$  and that

$$\text{pK}_c = \text{pK}_a + \lg \Gamma = \text{pK}_a + \lg(\gamma_{\text{B}^-} \gamma_{\text{H}_3\text{O}^+}) = \text{pK}_a + 2\lg\gamma_{\pm} \quad (4)$$

The activity coefficients are modified based on the extended Debye–Hückel law as

$$\lg\gamma_{\pm} = -\frac{\mathcal{A}\sqrt{\mathbf{I}}}{1 + \mathbf{D}\sqrt{\mathbf{I}}} = -\mathcal{A} \cdot \mathbf{I}' \quad \text{with} \quad \mathbf{I}' = \frac{\sqrt{\mathbf{I}}}{1 + \mathbf{D}\sqrt{\mathbf{I}}} \quad (5)$$

where  $\mathcal{A}$ ,  $\mathbf{D}$  are constants ( $\mathbf{D} = 2.3 \text{ M}^{-1/2}$  at  $25^\circ\text{C}$ ) and  $\mathbf{I}$  is the ionic strength defined as  $\mathbf{I} = \frac{1}{2} \sum c_i \cdot z_i^2$  with  $z_i$  being the charge number of an ion  $i$  (positive for cations and negative for anions) and  $c_i$  its concentration. This yields

$$\text{pK}_c = \text{pK}_a - 2 \mathcal{A} \mathbf{I}' \quad (6)$$

The absorption curve of an indicator at different pH values can be studied to determine the equilibrium constant of the indicator. In this experiment, we will determine the equilibrium constant of bromocresol green (BCG) indicator that is yellow in acidic solutions and blue in basic solutions. When dissolved in water, the conjugate pair (acidic and basic forms) display different absorptions spectra since they have different colors.

## 1.1. Absorbance and spectrophotometry

Solutions that possess colors absorb visible light of specific wavelengths. Recall that a red solution appears red because it absorbs much of the blue–green part of the spectrum (complementary colors). Measurements of the amount of light absorbed by a substance plotted as a function of the appropriate wavelength is called an absorption spectrum. The shape of this curve depends almost entirely on the electronic structure of the substance and is almost unique for each substance.

At a given wavelength the amount of light absorbed by a solute is proportional to its molar concentration, thus providing a widely used method for concentration analysis. The Beer–Lambert law states that

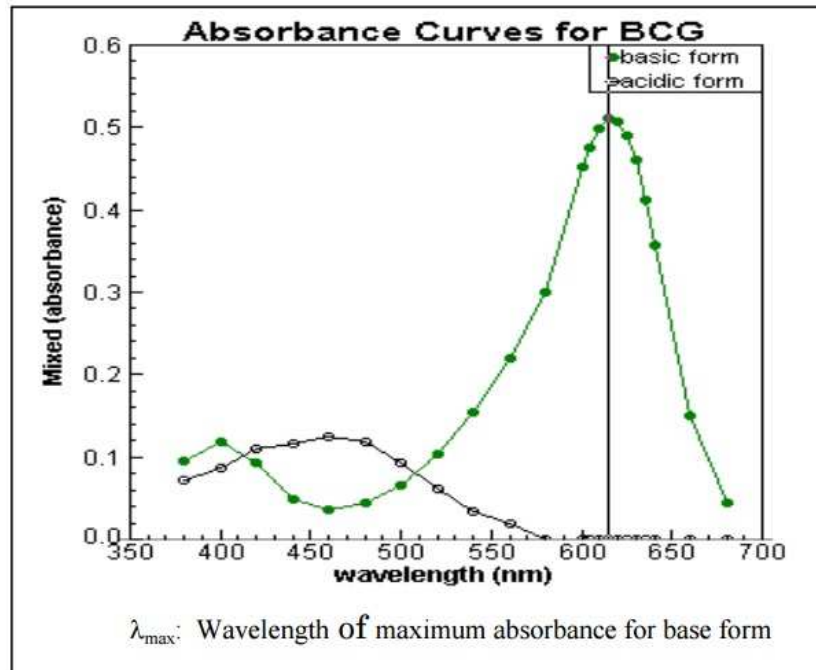
$$A = \varepsilon \cdot \ell \cdot c, \quad (7)$$

where  $A$  is the absorbance,  $\varepsilon$  is the molar absorption, a constant characteristic of the absorbing molecule,  $\ell$  is the path length, and  $c$  is the concentration.

## 1.2. Determining the equilibrium constant

If both the acidic form (HB) and the basic form ( $\text{B}^-$ ) of an indicator absorb light, the ratio  $\frac{c_{\text{B}^-}}{c_{\text{HB}}}$  can be determined by measuring light absorption at a wavelength where the difference in absorbance is the greatest between the two forms. The graph below shows that the basic form

has maximum absorption ( $A_{B^-}$ ) at  $\lambda_{max}$  while the absorbance of the acidic form ( $A_{HB}$ ) is small (almost zero).



When both forms are present, the measured absorbance is

$$A = \epsilon_{HB}lc_{HB} + \epsilon_{B^-}lc_{B^-} \quad (8)$$

and the overall concentration is

$$c = c_{HB} + c_{B^-} \quad (9)$$

The molar absorbance can be determined by measuring the absorbance of the pure basic ( $A_{B^-}$ ) and the pure acidic form ( $A_{HB}$ ) with concentration  $c$  from which

$$\epsilon_{HB}l = \frac{A_{HB}}{c} \quad \text{and} \quad \epsilon_{B^-}l = \frac{A_{B^-}}{c} \quad (10)$$

The substitution of them into Eq. 8 leads to the expression

$$A = A_{B^-} \frac{c_{B^-}}{c} + A_{HB} \frac{c_{HB}}{c} \quad (11)$$

from which the ratio of the two forms can be calculated as

$$\frac{c_{B^-}}{c_{HB}} = \frac{A - A_{HB}}{A_{B^-} - A} \quad (12)$$

Thus, besides having a solution containing both forms with overall concentration  $c$ , one has to prepare a solution containing the acidic form (HB) only and another one where only  $B^-$  is

present and their concentration is  $c$ . By measuring the  $\text{H}_3\text{O}^+$  concentration ( $c_{\text{H}^+}$ ) independently, we can calculate  $K_c$  from Eq. 2.

By preparing a series of solutions where the overall concentration,  $c$ , is constant, only the ionic strength is varied, one can determine  $K_a$  from Eq. 6. The task of the experiment is to find the equilibrium constant of bromocresol green and compare it with literature data.

## 2. Experimental

### 2.1. Chemicals

1000 cm <sup>3</sup>	0.2 mol/dm <sup>3</sup>	sodium acetate
500 cm <sup>3</sup>	1.0 mol/dm <sup>3</sup>	acetic acid
500 cm <sup>3</sup>	3.0 mol/dm <sup>3</sup>	hydrochloric acid
500 cm <sup>3</sup>	0.01 mol/dm <sup>3</sup>	hydrochloric acid
1000 cm <sup>3</sup>	0.01 mol/dm <sup>3</sup>	hydrochloric acid
500 cm <sup>3</sup>	1.0 mol/dm <sup>3</sup>	potassium chloride
500 cm <sup>3</sup>	2.0 mol/dm <sup>3</sup>	potassium chloride
500 cm <sup>3</sup>	10 <sup>-4</sup> mol/dm <sup>3</sup>	bromocresol green

### 2.2. Equipment

UV-vis spectrophotometer, glass pH electrode, three cuvettes, 1-cm<sup>3</sup> graduated pipette, two 2-cm<sup>3</sup>-graduated pipette, 5-cm<sup>3</sup> graduated pipette, 10-cm<sup>3</sup> graduated pipette, 25-cm<sup>3</sup> graduated pipette, 2-cm<sup>3</sup> bulb pipette, 250-cm<sup>3</sup> beakers, 11 50-cm<sup>3</sup> volumetric flask, 16 50-cm<sup>3</sup> beakers, distilled water bottle.

### 2.3. Solution preparation

**Solution A:** Dilute 12.5 cm<sup>3</sup> of 1.0 mol/dm<sup>3</sup> acetic acid solution in a 50 cm<sup>3</sup> volumetric flask with distilled water. The concentration of the acetic acid in this solution is 0.25 M.

**Solutions B:** Ask the instructor for the solution series to be prepared. For each solution pour 5.0 cm<sup>3</sup> of 10<sup>-4</sup> mol/dm<sup>3</sup> bromocresol green and 2.5 cm<sup>3</sup> of 0.2 mol/dm<sup>3</sup> sodium acetate to a 50 cm<sup>3</sup> volumetric flask. Then add the appropriate volume of the potassium chloride solution, with which you change the ionic strength in the solution. After that add 2 cm<sup>3</sup> of Solution A and dilute it to 50 cm<sup>3</sup> with distilled water.

	1 mol/dm <sup>3</sup> KCl (cm <sup>3</sup> )									2 mol/dm <sup>3</sup> (cm <sup>3</sup> )								
ba.	0.0	0.5	1.0	2.0	4.0	8.0	16.0	32.0	be.	0.0	0.5	1.0	2.0	4.0	8.0	16.0	32.0	
bb.	0.0	0.5	1.0	1.5	3.0	7.0	15.0	30.0	bf.	0.0	0.5	1.0	1.5	3.0	5.0	10.0	20.0	
bc.	0.0	0.5	1.2	2.5	5.0	9.0	20.0	40.0	bg.	0.0	0.3	0.5	1.0	2.0	5.0	15.0	35.0	
bd.	0.0	0.3	0.7	1.0	2.0	5.0	10.0	22.0	bh.	0.0	0.4	1.0	1.6	3.0	6.0	10.0	18.0	

**Solution C:** From the solution series, choose an ionic strength (i.e., a volume of KCl solution). Prepare that Solution **B** but without adding Solution **A**. This solution should be blue and will be the basic BCG solution.

**Solution D:** Prepare another Solution **B** with the same ionic strength as above and add  $0.4 \text{ cm}^3$  of  $3.0 \text{ mol/dm}^3$  hydrochloric acid solution to that. This solution should be yellow and will be the acidic BCG solution.

**Hydrochloric acid solutions for the pH-measurements:** Prepare a series of  $0.001 \text{ mol/dm}^3$  hydrochloric acid solutions from the  $0.01 \text{ mol/dm}^3$  HCl solution in a  $50 \text{ cm}^3$  volumetric flask. The ionic strength of each solution should be the same as of the appropriate Solutions **B**. Calculate the volume of the KCl solution necessary for each solutions. Write the calculated volume and the ionic strength in the table.

$[\text{HCl}]_{\text{stock solution}} = \quad \text{M}, \quad [\text{KCl}]_{\text{stock solution}} = \quad \text{M}, \quad V_{\text{solutions}} = \quad \text{cm}^3$

$V_{\text{HCl}}/\text{cm}^3$	$V_{\text{KCl}}/\text{cm}^3$	$I/(\text{mol/dm}^3)$

## 2.4. Experimental procedure

1. Measure the absorption spectra of the basic BCG solution (Solution **C**) and the acidic BCG solution (Solution **D**) starting from 400 nm up to 700 nm at 10 nm intervals. Record these measurements in your report.
2. From the absorbance data, determine the greatest change in the absorbance between the basic and acidic solutions. Note the wavelength this absorbance change corresponds to.
3. Measure the absorbance of the basic and the acidic BCG solutions at 2 nm intervals from 10 nm below to 10 nm above this wavelength.
4. Determine the greatest change in the absorbance between the basic and acidic solutions and find the corresponding wavelength ( $\lambda_{\text{max}}$ )
5. Measure the absorbance of solutions **B** at wavelength  $\lambda_{\text{max}}$ . Do not waste the solutions, you'll need  $\approx 30 \text{ ml}$  for pH measurements.
6. Determine the pH of the solutions
  - (a) Before each pH measurement, the pH-meter has to be calibrated with the equivalent  $0.001 \text{ mol/dm}^3$  hydrochloric acid solution and ionic strength. After reaching equilibrium, the pH should be set to 3.00.
  - (b) Rinse the electrode with distilled water and wipe carefully with tissue paper.
  - (c) Place the electrode into Solution **B**, read and record the pH from the pH-meter.

- (d) Rinse the electrode with distilled water and wipe carefully with tissue paper.
- (e) Repeat the previous 4 points for each solution.

### 3. Data evaluation

1. Prepare the absorbance–wavelength graph of bromocresol green in basic and acidic solutions.
2. Calculate the ionic strength of each solution **B**.
3. Calculate the  $\frac{c_{B^-}}{c_{HB}}$  ratio based on Eq. (12).
4. Calculate the hydrogen ion concentration and based on Eq. (2) determine  $K_c$ .
5. Summarize the measured and calculated data in the following table:

$\lambda_{max} =$	nm	$A_{B^-} =$			$A_{HB} =$					
Solution composition	A	I/M	$\sqrt{I/M}$	$I/M^{1/2}$	pH	$[H^+]/M$	$\frac{c_{B^-}}{c_{HB}}$	$K_c$	$pK_c$	

6. Plot  $pK_c - I$  graph, and fit linear regression. Estimate  $pK_a$  and  $\mathcal{A}$  from the parameters of the fitted line (with standard deviation). Draw the fitted line as well.
7. Try to find literature data of  $\mathcal{A}$ , discuss the results.

*Notes:* This experiment requires a lot of time. Think over the preparation of solutions, and practice the calculation of ionic strength in advance.

### 4. Possible test questions

1. Define the Beer–Lambert law. Define the symbols.
2. What circumstances allow the spectrophotometric determination of the dissociation constant?
3. What is the relationship between the dissociation constants, defined with activities and concentrations? Define  $pK_a$  and  $pK_c$ .
4. Deduce the formula which allows the determination of  $pK_a$ .
5. For a given compound, on which wavelength do you perform the absorbance measurements? How do you determine this wavelength?
6. Define ionic strength. Why was it introduced to physical chemistry?

7. Calculate the ionic strength of the following solutions:
  - a.  $2.0 \text{ cm}^3$   $0.1 \text{ M}$  HAc,  $2.5 \text{ cm}^3$   $0.2 \text{ M}$  NaAc and  $5.0 \text{ cm}^3$   $1.0 \text{ M}$  KCl, diluted to  $50 \text{ cm}^3$ .
  - b.  $10^{-4} \text{ M}$  indicator (HI),  $0.025 \text{ M}$  NaAc and  $0.01 \text{ M}$  KCl.
  - c.  $5.0 \text{ cm}^3$   $10^{-4} \text{ M}$  indicator,  $2.5 \text{ cm}^3$   $0.2 \text{ M}$  NaAc,  $2.0 \text{ cm}^3$   $0.1 \text{ M}$  HAc,  $5.0 \text{ cm}^3$   $1.0 \text{ M}$  KCl, diluted to  $50 \text{ cm}^3$ .
8. How large volume of  $1.0 \text{ M}$  KCl should be given to  $10 \text{ cm}^3$   $0.1 \text{ M}$  HCl, to achieve ionic strength of  $I = 0.4 \text{ M}$  after dilution to  $50 \text{ cm}^3$ ?
9. Deduce the formula, related to the concentration ratio of the protonated and deprotonated form of the indicator.
10. What considerations must be taken into account when planning the solutions, used for the determination of the  $\text{pK}_a$  value of an indicator?
11. What parameters are to be determined during the experiment? How is the value of  $\text{pK}_a$  determined from these?
12. Why is the absorbance of the fully protonated/deprotonated form of the indicator independent of the ionic strength?