5. Determination of the dissociation constant for a weak acid

Student Sheet

This practical uses some of the skills you acquired at AS level, as well as reinforcing your understanding of indicator theory and the strengths of weak acids.

Intended lesson outcomes

At the end of this exercise you will be able to:

- use a pipette and a burette to produce solutions of different concentration
- prepare a buffer solution
- use and understand indicator theory
- calculate dissociation constants

Background information

The pH of an aqueous solution of a weak acid gives some indication of the strength of an acid, but the pH varies with concentration. Dissociation constants, E_a values, give a much more accurate guide to the actual strength of an acid because their values are unaffected by changes in concentration.

A weak acid dissolved in water dissociates by reacting with the water as shown in the equation below.

$$HA(aq) \; + \; H_2O(l) \; \rightleftharpoons \; H_3O^+(aq) \; + \; A^-(aq)$$
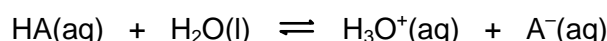
The K_c expression for this equilibrium process is:

$$K_c = \frac{\left[H^+(aq)\right]\left[A^-(aq)\right]}{[HA(aq)][H_2O]}$$

As the concentration of water, $[H_2O]$, is so large compared to the other concentrations, it may be regarded as being constant, and so this equilibrium equation is often simplified as below
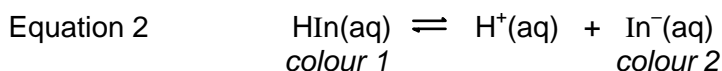
Equation 1 $\qquad HA(aq) \; \rightleftharpoons \; H^+(aq) \; + \; A^-(aq)$
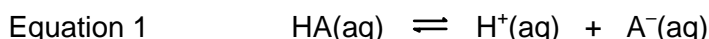
The dissociation constant for this reaction, K_a, is calculated using the expression shown below, where $K_a = K_c \times [H_2O]$.

$$K_a = \frac{\left[H^+(aq)\right]\left[A^-(aq)\right]}{[HA(aq)]}$$

Indicators

Indicators are also weak acids, or weak bases. The dissociation of a weak acid indicator, such as *bromocresol green*, is similar to that of any other weak acid but is usually represented as below. In this equation, the undissociated indicator is represented by HIn, while the dissociated anion is shown as In⁻.

Equation 2 $\qquad HIn(aq) \; \rightleftharpoons \; H^+(aq) \; + \; In^-(aq)$
$\qquad\qquad\qquad\qquad$ *colour 1* $\qquad\qquad\qquad$ *colour 2*

Excess acid drives the equilibrium to the left, while excess of alkali drives the equilibrium to the right. If a large excess of acid or alkali is added, *colour 1* or *colour 2* respectively is seen, otherwise an intermediate colour is seen. The colour observed will depend on the proportion of each the two colours present, i.e. the colour observed will depend on the [In⁻]/[HIn] ratio.

The experiment

In this experiment you will determine the dissociation constant of ethanoic acid in an ethanoic acid/sodium ethanoate buffer solution.

In the first step of this experiment you will dilute, to different extents, solutions containing bromocresol blue and either HCl or NaOH. These solutions will contain predominantly either HIn or In¯, the concentrations of which will depend on the degree of dilution used. By placing one test tube containing HIn in front of one containing In¯, and viewing through the two test tubes, a *combined* colour will be seen.

The combined colour observed will depend on the ratio of the concentrations of HIn and In¯ in the two test tubes. If this same colour is observed in a sample of the buffer, the [In¯]/[HIn] ratio in the buffer will be the same as the [In¯]/[HIn] ratio between the two separate test tubes. For example, if tubes 3 and 12 in the table below give a combined colour the same as that of the buffer, then the [In¯]/[HIn] ratio in the buffer is 7:3. Once the ratio of [In¯]/[HIn] in the buffer solution is known, the value of K_a for ethanoic acid can be calculated.

Note: You may be more familiar with bromocresol blue as a titration indicator. The endpoint of a titration is reached when the two forms of the indicator are present in equal concentrations. Therefore, with bromocresol blue, the endpoint colour would be the colour observed when tubes 5 and 14 in the table below are viewed together.

Safety

In step 1 of this exercise, concentrated solutions of hydrochloric acid and sodium hydroxide are used; both are hazardous. MSDS sheets should be consulted so that the correct action can be taken in event of a spillage and/or accident.

😎	**You must wear eye protection throughout this experiment**
🧪	Ethanoic acid (glacial acetic acid), sodium hydroxide and concentrated hydrochloric acid are **corrosive**
🔥	Ethanol is **Highly flammable**

Method

1. Make up solutions **A** and **B** as described below. It is crucial that the amounts used are accurately measured. Use the same pipette to measure the acid and alkali. You must wash the pipette with the acid or alkali prior to use.

    Solution A: Add one drop of concentrated HCl to 5 cm^3 of aqueous bromocresol green. In this form almost all the indicator is in the undissociated form, HIn. Mix the solution thoroughly.

    Solution B: Add one drop of 4M NaOH to 5 cm^3 of aqueous bromocresol green. In this the indicator will be mainly dissociated as In¯. Mix the solution thoroughly.

2. Arrange 18 test tubes in an array of two parallel rows of 9, so that it will be possible to look straight through each pair to see the combined colour of each pair.

Number the tubes and make up the following solutions using a burette to measure the water and the same pipette to add the correct number of drops of **A** or **B**. These drops must be the same size. Mix all the solutions thoroughly.

tube number	1	2	3	4	5	6	7	8	9
volume of water (cm^3)	10	10	10	10	10	10	10	10	10
drops of **A**	1	2	3	4	5	6	7	8	9

tube number	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
volume of water (cm^3)	10	10	10	10	10	10	10	10	10
drops of **B**	9	8	7	6	5	4	3	2	1

3. Mix together 5.00 cm^3 of aqueous ethanoic acid, of concentration 0.0200 mol dm^{-3}, and 5.00 cm^3 of aqueous sodium ethanoate, of concentration 0.0200 mol dm^{-3}. This gives a buffer solution of ethanoic acid and sodium ethanoate in which the [CH_3COOH] and [CH_3COONa] are equal. Such a solution is said to be *equimolar*. To this buffer:

- add 10 drops of the original aqueous bromocresol green; mix thoroughly, then

- compare the colour of this solution with that of the corresponding of pairs of test tubes in the array, then

- identify the pair of test tubes in the array whose combined colour most closely matches the colour of the buffer solution.

Calculation

Note: The ratio of [In^-]/[HIn] in the buffer solution $= \dfrac{\text{number of drops of } \textbf{B}}{\text{number of drops of } \textbf{A}}$

1 Write an expression, based on equation 2, for the K_{In} (i.e. the K_a) of the indicator.

2 Use your K_{In} expression, together with your ratio of drops, to calculate the [H^+] of the buffer solution.

(The K_a value for bromocresol green is 2.00 x 10^{-5} mol dm^{-3})

3 Write an equation for the dissociation of aqueous ethanoic acid.

4 Write a K_a expression, similar to the general one obtained from equation 1, for the dissociation of ethanoic acid.

Use this expression, together with your calculated value for the [H^+] of the buffer solution, to deduce the K_a value for ethanoic acid.

5 Compare your value with the data book value for the dissociation constant of ethanoic acid, which is 1.7×10^{-5} mol dm^{-3}.

5. Determination of the dissociation constant for a weak acid

Teachers' Notes

It is common to deduce the K_a value for a weak acid by using a pH meter, as shown in Experiment 6. The approach adopted in this exercise is somewhat novel and provides a 'low technology' route to determining this value.

A number of solution pairs are prepared in which the concentrations of the undissociated indicator, HIn, or the anion from the dissociation of the indicator, In^-, are known. When viewed together, the combined colour observed is the same as that which would be observed when the two species are present in the same $[In^-]/[HIn]$ ratio as the ratio between the two separate tubes. For example, if tubes 3 and 12 give a combined colour the same as that of the buffer, then the $[In^-]/[HIn]$ ratio in the buffer is 7:3.

The exercise requires considerable care and patience in making up the different solutions, together with a sound understanding of chemical equilibria, but proves popular with students.

Intended learning outcomes

These are detailed on the Student Sheet.

Technical information

Requirements per student/group

- one test tube labelled 'solution **A**'

- one test tube labelled 'solution **B**'

- one test tube labelled 'buffer solution'

- 18 test tubes

- labels for the 18 test tubes

- one burette, clamp and stand

- two teat pipettes with undamaged tips

- sufficient test tube racks to form an array 9 tubes wide and 2 tubes deep

- access to a burette filled with aqueous ethanoic acid, of concentration 0.0200 mol dm^{-3}

- access to a burette filled with aqueous sodium ethanoate, of concentration 0.0200 mol dm^{-3}

- access to a burette filled with aqueous bromocresol green, made by dissolving 0.1 g in 20 cm^3 of ethanol and making the solution up to 100 cm^3 with water

- access to a supply of aqueous sodium hydroxide of concentration 4.0 mol dm^{-3}, labelled with the appropriate hazard symbol

- access to a supply of concentrated hydrochloric acid (approx 8 mol dm^{-3}), labelled with the appropriate hazard symbol

Safety

The main points are included on the Student Sheet but it is the teacher's responsibility to ensure that a full risk assessment is carried out prior to the practical session.
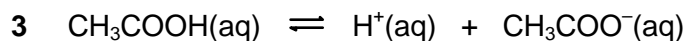
Answers to the questions on the Student Sheet

1 $K_a = \dfrac{[H^+(aq)][In^-(aq)]}{[HIn(aq)]}$

2   If the $[In^-]/[HIn]$ ratio in the buffer were 7:3

$$[H^+(aq)] = \frac{K_a \times [HIn(aq)]}{[In^-(aq)]} = \frac{2.00 \times 10^{-5} \times 3}{7}$$

$$= 8.57 \times 10^{-5} \text{ mol dm}^{-3}$$

3 $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

4 $K_a = \dfrac{[H^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$

As the salt and acid concentrations have been chosen to be equal (both diluted to 0.0100 mol dm^{-3} upon mixing) they cancel. So:
$K_a = [H^+(aq)] = 8.57 \times 10^{-5}$ mol dm^{-3}