RSC | Advancing the Chemical Sciences

Reckitt Benckiser

Distribution of 2-hydroxybenzoic acid between water and an organic solvent

Student worksheet

Health and safety note

Wear eye protection and ensure no naked flames. 10% v/v ethyl ethanoate in hexane is highly flammable and harmful.

Principle

Solubility and ionisation of 2-hydroxybenzoic acid

2-hydroxybenzoic acid (figure 1) is the main metabolite of aspirin. It forms when aspirin hydrolyses. It is only slightly soluble in water (2 g dm^{-3} at 20 °C), but it dissolves in alkaline solutions forming the 2-hydroxybenzoate ion,

$$\mathrm{HOC_6H_4COOH + OH^- \rightarrow HOC_6H_4COO^- + H_2O}$$

The solubility of sodium 2-hydroxybenzoate at 20 °C is 660 g dm^{-3}.

2-hydroxybenzoic acid is a weak acid. The carboxylic acid group ionises and exists in aqueous solution in dynamic equilibrium with the 2-hydroxybenzoate ion:

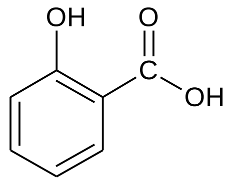

Figure 1 2-hydroxybenzoic acid.

$$\mathrm{HOC_6H_4COOH \leftrightarrow HOC_6H_4COO^- + H^+}$$

$$\text{Acidity constant, } K_\mathrm{a} = \frac{[\mathrm{H^+}][\mathrm{HOC_6H_4COO^-}]}{[\mathrm{HOC_6H_4COOH}]} = 1.07\ \times 10^{-3}\mathrm{mol\ dm^{-3}}$$

$$\mathrm{p}K_\mathrm{a} = -\log_{10} K_\mathrm{a} = 2.97$$

The solubility of 2-hydroxybenzoic acid depends on pH. Increasing pH moves the position of equilibrium to the right (formation of the 2-hydroxybenzoate ion), increasing solubility.

Partition coefficient and distribution coefficient

The distribution of 2-hydroxybenzoic acid between water (aq) and an organic solvent (org) is given by its distribution coefficient, *D*:

$$D = \frac{[\mathrm{HOC_6H_4COOH(org)}]}{[\mathrm{HOC_6H_4COOH(org)}][\mathrm{HOC_6H_4COO^-(aq)}]}$$

The distribution constant is pH dependent.

The partition coefficient, *P*, of 2-hydroxybenzoic acid is a measure of the distribution that would happen if it did not ionise.

$$P = \frac{[\mathrm{HOC_6H_4COOH_{(org)}}]}{[\mathrm{HOC_6H_4COOH_{(aq)}}]}$$

For solutes that do not ionise, partition coefficients can be determined by direct measurement. However, if the solute does ionise, measurements of *D* at different pHs may be made to calculate *P* (figure 2).

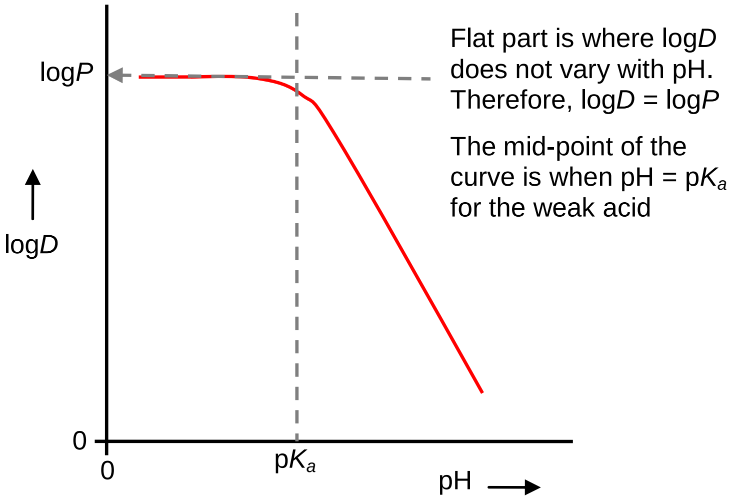

Figure 2 Graph of log*D* against pH for a weak acid.

Equipment and materials

Distribution

- Organic solvent (10% v/v ethyl ethanoate in hexane) – Highly flammable, Harmful
- Range of buffer solutions, each containing 0.2 g dm^{-3} 2-hydroxybenzoic acid

  pH's of buffer solutions: 1.0, 1.6, 2.3, 2.8, 3.2, 4.0, 4.5, 5.1
- Boiling tube with stopper x 8
- 5 cm^3 measuring cylinder x 2

Colorimetric analysis

- Colorimeter and suitable filter (green/yellow)
- 2 cm^3 pipette
- 5 cm^3 measuring cylinder x 2
- 10 cm^3 measuring cylinder
- 0.025 mol dm^{-3} iron(III) nitrate solution

Method

Carry out the following procedure for each of the buffer solutions 0.2 g dm^{-3} 2-hydroxybenzoic acid. You may need to work in a small group, sharing the work.

1. Pipette 2.0 cm^3 of the buffered 2-hydroxybenzoic acid solution into a test tube. Add 8.0 cm^3 of 0.025 mol dm^{-3} iron(III) nitrate solution. Allow the colour to form, and measure the absorbance (A_1).
2. Use a measuring cylinder to put 5.0 cm^3 of 0.2 g dm^{-3} 2-hydroxybenzoic acid solution into a boiling tube. Using another measuring cylinder, add 5 cm^3 of ethyl ethanoate/hexane solvent. Stopper and shake the test tube for 5 minutes to complete the extraction. Allow the two phases to settle.
3. Pipette 2.0 cm^3 of the aqueous phase (the lower layer) into a test tube and add 8.0 cm^3 of 0.025 mol dm^{-3} iron(III) nitrate solution. Allow the colour to form and measure the absorbance (A_2).

4. Record the measurements of A_1 and A_2 in a table similar to this:

pH	A_1	A_2	D =($A_1 - A_2$)/A_2	log$D$
1.0				
1.6				
2.3				
2.8				
3.2				
4.0				
4.5				
5.1				

Processing data

In the samples taken, absorbance of the coloured solutions is directly proportional to concentration (in other words, they obey the beer-Lambert law).

- A_1 is proportional to the concentration of 2-hydroxybenzoic acid in the buffer solution before extraction.
- A_2 is proportional to the concentration of 2-hydroxybenzoic acid in the buffer solution after extraction.
- ($A_1 - A_2$) is proportional to the concentration of 2-hydroxybenzoic acid in the organic layer after extraction.

$$D = \frac{(\mathrm{A}_1 - \mathrm{A}_2)}{\mathrm{A}_2}$$

1. Use this equation to calcuate D at each of the pH values. Write the values into the table.
2. Calculate log$D$ for 2-hydroxybenzoic acid in each buffer solution.
3. Plot a graph of log$D$ against pH (figure 2).
4. From the graph, estimate log$P$ and pK_a.