UV-Vis Absorption Experiment 5: Beer-Lambert Law and the Temperature Dependence of the Crystal Violet-Sodium Hydroxide Reaction

Overview

In Part A of this experiment, the absorption behaviour of crystal violet (CV) in aqueous solution will be investigated. Standard samples containing different concentrations of CV in deionised water will be prepared and UV-Vis absorption spectra recorded for each. A Beer-Lambert plot will be constructed in order to determine the molar extinction coefficient for CV in aqueous solution.

In Part B, the kinetics of the reaction between CV and NaOH as a function of temperature will be investigated using UV-Vis spectroscopy. CV absorbs strongly in aqueous solution but the product formed upon reaction with NaOH is colourless. Consequently, the rate constant for the reaction at different temperatures will be derived from absorbance measurements as a function of time.

Finally, you will establish whether the CV/NaOH reaction follows an Arrhenius type dependence and derive the activation energy for the process.

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Introduction

Ultraviolet-Visible (UV-Vis) spectroscopy[1] is concerned with measurement of the interaction of outer shell electrons with electromagnetic radiation[1] in the range 190 nm to 700 nm. Electrons of organic compounds with a high degree of conjugation[1] or aromaticity[1], transition metal ions and charge transfer complexes are active in this part of the spectral region[1]. Compounds with the ability to interact with or *absorb* UV-Vis radiation are given the general name *chromophores*. UV-Vis spectroscopy has many uses across science such as in, identification and quantification of aromatic species in an unknown sample through analysis of pharmaceutical substances and in biology, in investigation of proteins. This experiment is concerned with chemistry and kinetics and demonstrates how the progress of a chemical reaction and its thermal dependence can be monitored through use of UV-Vis spectroscopy. UV-Vis spectroscopy involves measurement of the fraction of incident electromagnetic radiation that is either absorbed or transmitted by a sample. The measurement can be performed at a single wavelength or across a broad range of wavelengths when a spectrum[1] is produced.

UV- Vis spectroscopy

The basis of UV-Vis spectroscopy is shown in Figure 1:

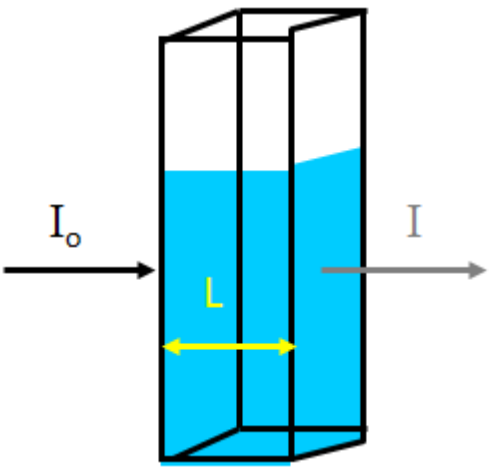

Figure 1 Basis of a UV-Vis measurement

This process can be described by The Beer-Lambert Law[1] which relates the incident light intensity (I_o) at the front of a cell of length, L, (in centimetres) of a single absorbing species of concentration, c, to that which is transmitted by the sample [i.e., the intensity of light (I) which emerges from the cell]. ε is known as the molar extinction coefficient and is a measure of the probability of absorption of a photon[1] of light by a compound. The Beer-Lambert law is expressed formally in equation 1:

$$\log_{10}(I_o/I) = -\log_{10}(\%T/100\%) = \varepsilon c L = A \qquad \text{Equation 1}$$

The ratio I/Io is known as the transmittance of the sample and is usually expressed as a percentage (%T). This is one method of describing the absorption of light by the chromophore. Clearly, from consideration of equation 1, the transmittance falls exponentially with concentration (as shown in Figure 2)

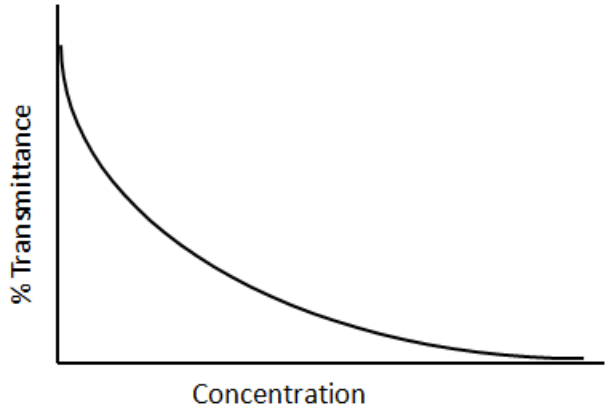

Figure 2 % Transmittance as a function of concentration

An alternative means of expressing the light absorbed by the sample is through the absorbance[1], A. Absorbance is related to the transmittance and percentage transmittance (% T) by equation 1. Since A is also directly proportional to concentration, from equation 1, it is more convenient for *quantitative* analysis, to work in terms of A rather than transmittance, see Figure 3:

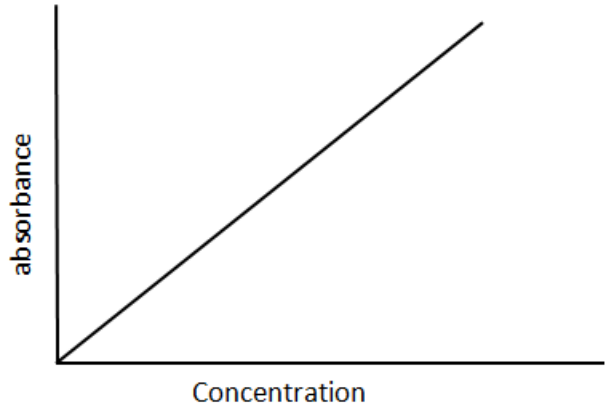

Figure 3 Beer-Lambert plot: absorbance vs concentration

Figure 3 is known as a Beer-Lambert plot[1] and ε can be derived from the slope of the straight line. Once ε is known for a compound, it is possible to estimate the concentration of a sample[1] by measuring A spectrophotometrically.

Kinetics of the Reaction between Crystal Violet and Sodium Hydroxide

Crystal Violet, CV, (see scheme 1 for the structure) is an intensely coloured triarylmethane dye due to extensive conjugation[1] present in the molecule. (Conjugation is a system of alternating single and

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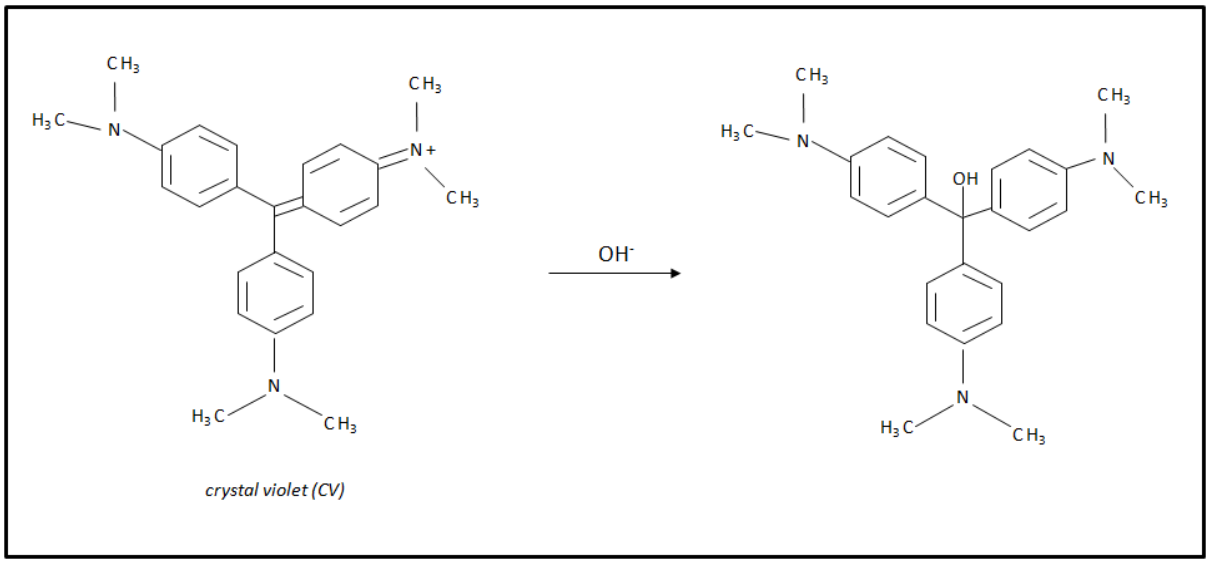
double bonds which extends over all three benzene rings and the central carbon atom in CV). It follows that the colourless product obtained on reaction with NaOH (see scheme 1) is due to a loss of conjugation: the three benzene rings are no longer in conjugation with one another. Consequently, the absorbance of a reaction mixture containing CV and NaOH will be proportional to the



Scheme 1 Reaction of crystal violet and the hydroxide ion

concentration of unreacted dye still present in solution. The reaction of CV and NaOH can therefore be monitored and the kinetics studied by measuring the absorbance of the mixture as a function of time. Since the CV/NaOH reaction follows first order kinetics[2] under the conditions adopted in this experiment then

$$ln\ [CV]_t = ln\ [CV]_o - k_R t \qquad \text{Equation 2}$$

where $[CV]_o$ is the initial concentration of CV, $[CV]_t$ is the concentration at some time, t, and k_R is the rate constant[2] for the reaction.

A plot of, ln [CV] vs time will be linear and k_R can be derived from the slope of the plot.

By using the Beer-Lambert law[1], if ε for CV is known, the concentration of CV can subsequently be derived as a function of time and k_R determined.

The rate of many chemical reactions and certain physical processes increase exponentially with temperature and can be described by the Arrhenius equation[2]

$$k_R = A\ exp^{-Ea/RT} \qquad \text{Equation 3}$$

where k_R is the rate constant[2], E_a, the activation energy for the process[2], R the gas constant and T the absolute temperature in degrees kelvin. A is known as the pre-exponential factor[2] (or frequency factor) and is a measure of the frequency of collisions between reactant molecules while E_a

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represents the minimum energy required for the reaction to proceed. Equation 3 shows that the rate constant (and therefore reaction rate) of many chemical reactions/physical processes increase exponentially with temperature.

Taking the natural logarithm of Equation 3 allows an alternative means of representing the Arrhenius equation

$$ln\, k_R = ln\, A - \frac{Ea}{RT} \qquad \text{Equation 4}$$

The linear form of the expression (Equation 4) allows E_a to be determined since a plot of ln k_R *vs* 1/T in degrees kelvin should be linear with the slope = -Ea / R

Aims

This experiment is divided into two parts: In Part A, you will study the absorption behaviour of CV in aqueous solution. You will prepare a series of samples containing different concentrations of CV in deionised water and then record UV-Vis absorption spectra for each. You will subsequently construct a Beer-Lambert plot and determine the molar extinction coefficient, ε, for CV in aqueous solution.

In Part B, you will investigate the temperature dependence of the reaction between CV and NaOH using UV-Vis spectroscopy. The reaction will follow first order kinetics under the conditions adopted in this experiment. You will derive the rate constant k_R at several different temperatures and determine whether the reaction shows Arrhenius behaviour.

Experimental Procedure

PART A: Absorption Behaviour of Crystal Violet

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References

1. Sim Pack 4: Download Notes on “UV-Vis Spectroscopy & the Beer-Lambert Law”, Copyright 2020, sim4t.com.

2. Sim Pack 3: Download Notes on “Rate of Reaction and Arrhenius Behaviour”, Copyright 2020, sim4t.com.

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