Calculating optical density of unknown substance

Aim: To prove Beer's Law and to determine the composition of an unknown dichromate/ permanganate mixture by determining its optical density.

Introduction:

Beer's Law is represented by the following equation: A = abc where " A" is the absorbance, " a" is the absorptivity of the sample, " b" is the path length of the quartz cuvette used (1cm) and " c" is the concentration of the sample. Beer's law states that when monochromatic light passes through a sample or absorption medium, the decrease in intensity rate is proportional to the light intensity, thus:

(Equation 1)

Ix = I0e-kx (Equation 2)

where " Ix" is the light intensity once the light passes through a path length of thickness " x" and I0 is the initial intensity of light.

Rearranging equation 2, the equation becomes:

= -kx (Equation 3) which becomes log10 = -Kx (Equation 4)

where K = k = 2. 3026.

Beer extended equation 4 and started to apply it to solutions of varying concentrations. Through his research he found out that:

log10 = ECx = D (Equation 5)

where " E" is known as the molar extinction coefficient, " C" is the molar concentration, " x" is the path length and " D" is the optical density.

In this experiment, the wavelength selected at which the optical density was read was determined by using a UV spectrophotometer on two samples, namely 0. 0005M potassium dichromate and 0. 0005M potassium permanganate. The wavelengths were chosen depending at which wavelength maximum absorption for 0. 0005M dichromate and 0. 0005M permanganate was observed. Optical density is a means by which one can prove Beer's Law for a particular sample. In this experiment, this was carried out by measuring the optical density of four solutions each of different concentrations of permanganate and dichromate respectively, namely, 0. 0001M – 0. 0004M.

Optical density, being an additive property can also be applied to two different samples instead of one and as a result, the optical density can further be used to determine the composition of an unknown dichromate/permanganate mixture by using the following simultaneous linear equations

D1 = ECr1CCr + EMn1CMn

D2 = ECr2CCr + EMn2CMn

Where 1 and 2 represent the two wavelengths selected respectively.

Method:

Chemicals used:

Potassium dichromate (GPR, BDH)

Potassium permanganate (GPR, BDH)

Apparatus:

UV spectrophotometer

Conical flasks

Cuvettes

Pipette

Procedure:

Spectra for 0. 0005M $KMnO_4$ solution and 0. 0005M $K_2Cr_2O_7$ solutions were recorded using a spectrophotometer. Attention was given to the 300-400nm and 500-600nm wavelength regions. The wavelengths where the absorptions of each solution were at a maximum were recorded.

From the spectra obtained, an appropriate wavelength for the permanganate and dichromate solutions was selected in order to test Beer's Law.

Four permanganate solutions and four dichromate solutions with concentrations between 0. 0005M and 0. 00005M were prepared. The optical density of each solution was measured using a non-recording spectrophotometer using the wavelengths selected in step 2.

Concentration against optical density for both wavelengths were plotted and using regression analysis it was made sure that for both permanganate and dichromate solutions, the expressions: D = EMnCMn and D= ECrCCr respectively hold.

Using the solutions prepared in step 3, four different mixtures of 0. 0005M permanganate and 0. 0005M dichromate were prepared and the absorbancies were measured at wavelengths selected in step 2.

The theoretical absorbance of the mixtures as the sum of the absorbancies obtained in step 3 was calculated. The measured absorbancies were plotted against the calculated absorbancies and using linear regression analysis it was made sure that the following expression: D = ECrCCr + EMnCMn holds at both wavelengths.

The composition of an unknown dichromate/permanganate mixture was determined by determining the optical density at the two wavelengths selected in step 2 using the following simultaneous linear equations: D1 = ECr1CCr + EMn1CMn and D2 = ECr2CCr + EMn2CMn.

Precautions:

It was made sure that prior to using the UV spectrophotometer, a standard was used to calibrate the instrument, namely a cuvette with distilled water.

It was made sure that all solutions prepared were homogenous.

Results and Calculations:

Results:

Absorbance for the unknown mixture at a wavelength of 525nm – 0. 699

Absorbance for the unknown mixture at a wavelength of 352nm – 0. 890

EMn525 = 1949dm2mol-1

Calculations:

Theoretical densities:

At 525nm using the equation D525 = ECr525CCr + EMn525CMn:

Mixture 1: -250(0. 0001) + 1949(0. 0004) = 0. 7546

Mixture 2: -250(0. 0002) + 1949(0. 0003) = 0. 5347

Mixture 3: -250(0. 0003) + 1949(0. 0002) = 0. 3148

Mixture 4: -250(0. 0004) + 1949(0. 0001) = 0. 0949

At 352nm using the equation D352 = ECr352CCr + EMn352CMn:

Mixture 1: 2908(0. 0001) + 1199(0. 0004) = 0. 7704

Mixture 2: 2908(0. 0002) + 1199(0. 0003) = 0. 9413

Mixture 3: 2908(0. 0003) + 1199(0. 0002) = 1. 1122

Mixture 4: 2908(0. 0004) + 1199(0. 0001) = 1. 2831

To determine what was the concentration of the unknown mixture of dichromate and permanganate using the following simultaneous linear equations;

D525 = ECr525CCr + EMn525CMn

D352 = ECr352CCr + EMn352CMn

From the data;

Absorbance for the unknown mixture at a wavelength of 525nm – 0. 699

Absorbance for the unknown mixture at a wavelength of 352nm – 0. 890

0. 699 = -250 CCr + 1949 CMn Equation A

0. 890 = 2908 CCr + 1199CMn Equation B

Using equation B, making CCr subject of the formula, CCr = (0. 890 – 1199CMn) / 2908 therefore, inserting this in equation A,

0. 699 = -250(0. 890 – 1199 CMn/2908) + 1949CMn

0. 699(2908) = -250(0. 890) + 250 (1199 CMn) +2908 (1949CMn)

2032. 692 = -222. 5 +299750 CMn + 5667692CMn

2255. 192 = 5967442 CMn

CMn = 0. 0003779M

Therefore using equation A and substituting CMn = 0. 0003779, CCr= 0. 000150M

Therefore, in the unknown mixture, concentration of permanganate was 0. 0003779M and concentration of dichromate was 0. 000150M.

Discussion:

Using linear regression on a plot of optical density against concentration of sample, one can confirm that that in both samples, Beer’s Law is obeyed. Therefore, in this experiment, it was made sure that the equations D = EMnCMn and D = ECrCCr hold. From the results obtained, it is clear that beer’s law holds since as the concentration of dichromate and permanganate decreased, the optical density decreased. An anomaly was however observed in the results obtained for dichromate at a wavelength of 525nm since as the concentration of dichromate decreased, the optical density increased. This anomaly could possibly be due to contamination of the samples.

As has been described previously, optical density is considered to be an additive property. As a result, if one considers a mixture of two species having overlapping absorption spectra, the absorbance measured for that mixture at a particular wavelength would correspond to the sum of the absorbancies of the individual species making up that mixture. Using the equation D = ECrCCr + EMnCMn, one can calculate the theoretical optical density of a mixture of two species. A graph of measured absorbancies against theoretical absorbancies can then be plotted and using linear regression analysis, it can be made sure that D = ECrCCr + EMnCMn holds. The graphs obtained should have had a gradient of one since the theoretical and measured optical densities should have matched. However, this was not the case since a gradient of 1. 102 and 1. 065 were obtained for the graphs at a wavelength of 525 and 352nm respectively. This might have been due to contamination in the samples prepared.

Two simultaneous linear equations were used in order to determine the concentrations of permanganate and dichromate in an unknown mixture and it was found out that the concentration of permanganate was 0. 0003779M where as the concentration of dichromate was 0. 000150M.

Conclusion:

This experiment has shown that Beer's law holds for the dichromate and permanganate mixtures prepared and that the optical density can be used to find the concentration of two species in an unknown mixture. In this case, in an unknown concentration of dichromate and permanganate mixture, the concentrations were 0. 0003779M and 0. 000150M for permanganate and dichromate respectively.

Bibliography:

Beer Lambert Law available at http://www. chemistry. adelaide. edu. au/external/soc-rel/content/beerslaw. htm (accessed on 3rd December 2010)

Optical density available at http://www. physicsclassroom. com/class/refrn/u14l1d. cfm (accessed on 3rd December 2010)

Christian G. D., (2004). Analytical Chemistry, 6th Ed., Wiley & Sons, USA pp. 1-800.

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Analytical 2B: Visible Region Spectrophotometry.

Aim: To determine the composition of the blue complex formed between salicylic acid and ferric ammonium sulfate using the optical density obtained for the solution.

Introduction:

The composition of a complex can be established using visible region spectrophotometry. If substances X and Y react together to form a complex with an empirical formula XmYn, the following equilibrium will be set up in a solution containing both substances:

K

mX + nY XmYn

where, K = [XmYn] / [X]m [Y]n.

The amount of complex that forms depends on the stoichiometric ratio m: n. The amount of complex formed will be less if either reactant X or Y is less than the stoichiometric ratio in order to maintain a constant rate constant (K). It is for this reason that the greatest concentration of complex will be formed when the reactants X and Y are of equal ratio as they are found within the complex.

Changes in optical density can be used in order to study reaction mixtures of equimolar solutions of X and Y due to the fact that optical density changes with complex formation. In this experiment, salicylic acid (acting as the ligand) and ferric ammonium sulfate (acting as the cation) form a blue complex upon reacting with one another. Eleven solutions of equimolar salicylic acid and ferric ammonium sulfate were prepared with each solution having a different ratio of reactants from the rest. Since both reactants are colorless when compared to the complex that forms, the optical density of the solution can be used as a measure of how much complex is present within the solutions since as the concentration of complex increases, the optical density increases, as expected according to Beer’s Law.

The maximum value for the optical density obtained from an absorbance against volume of one of the reactants will correspond to the solution where the volumes of reactants are in the same ratio as that in which they occur in the complex therefore, the composition of a complex can be determined.

Method:

Chemicals used:

- Salicylic acid (GPR, BDH)
- Hydrochloric acid (GPR, Sigma Aldrich)
- Ferric ammonium sulfate solution (GPR, BDH)

Apparatus:

- UV spectrophotometer
- Conical flasks
- Glass cell
- Burette
- Measuring cylinder
- Pipette

Procedure:

Two solutions, namely, 500mL 0. 001M salicylic acid (0. 069g) in 0. 002M HCl and 500mL 0. 001M ferric ammonium sulfate solution (0. 239g) in 0. 002M HCl were prepared.

Using two burettes, eleven mixtures of the two solutions, each of volume 10mL were prepared as follows:

The solutions were mixed at intervals of about two minutes and allowed to stand for five minutes. Their optical densities were determined in a 1cm glass cell against water as a blank at a wavelength of 520nm.

Optical density against composition of the solution was plotted and the composition of the blue complex that formed was determined.

Precautions:

It was made sure that both reactants were dissolved in 0. 002M hydrochloric acid in order to obtain an optimum pH of 2. 7 required for the complex to form.

The UV spectrophotometer was calibrated using a blank prior to any absorption measurements using distilled water.

It was made sure that solutions were mixed at intervals of about two minutes and allowed to stand for five minutes.

Results and Calculations:

Results:

Mass of ferric ammonium sulfate weighed – 0. 241g

Mass of Salicylic acid weighed – 0. 068g

Discussion:

The literature explains that phenolic compounds react with ferric ions to give a coloured complex. This is useful especially when one wants to determine the composition of a complex since individually; both ferric ions and phenolic compounds are colorless. The pH of complex formation is crucial and in this experiment it was made sure that the complex forms in a pH of around 2. 7. This was made sure by dissolving the salicylic acid and ferric ammonium sulfate in 500mL 0. 002M hydrochloric acid.

In this experiment, mixtures were prepared and they were made up of equimolar solutions of ferric ammonium sulfate and salicylic acid but in different ratios as has been outlined previously in the results section. The composition of the complex can be found from a graph of optical density against volume of a reactant and the composition must have the highest value for the optical density.

From the results obtained it was observed that mixture 7 had the highest value for the optical density therefore, mixture 7 consists of different volumes of equimolar solutions of the reactants and they are present in the same ratio as that in which they occur in the complex thus since 6mL salicylic acid: 4mL Ferric ammonium sulfate were used to prepare mixture 7, the ratio can be simplified to 3: 2. This was not as expected due to the fact that since equal molarity of reactants was used, it is expected that the composition of the complex is 1: 1 however, this was not the case

Conclusion:

This experiment has concluded that the unknown composition of a complex can be determined using visible region spectrophotometry at a wavelength of 520nm. It was determined that the complex was composed of 6mL salicylic acid: 4mL Ferric ammonium sulfate therefore 3: 2 ratio.