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SPECTROPHOTOMETRIC DETERMINATION OF THE EQUILIBRIUM CONSTANT OF A REACTION

ABSTRACT

The objective of the experiment was to determine the equilibrium constant of the reaction forming ferric thiocyanate through the use of Spectrophotometry. For the calibration, five standard solutions were prepared, then their respective absorbance values that were obtained through the use of the spectrophotometer, were plotted versus the concentration of the analyte so that a calibration curve would be obtained. The calibration curve was then used to determine the molar absorptivity coefficient. The unknown solutions were then tested, resulting in absorbance values. The molar absorptivity coefficient obtained in the calibration curve and the absorbance values were used to determine the equilibrium concentrations of all the species involved in the reaction. These concentrations were then used to calculate the equilibrium constant. An equilibrium constant of 549.0 was found. Compared to the literature value of 890 there was a 177.11% difference. Even if there was a high percent difference, this was enough to prove that spectrophotometry can be used to determine the equilibrium constant of a given reaction.

INTRODUCTION

In this experiment spectrophotometry was used which involves an instrument called a spectrophotometer. A spectrophotometer is a light measuring device that measures intensity as a function of the light source wavelength. The amount of light that had passed through the system is called the transmittance. The amount of light absorbed by the system is called the absorbance. However, the absorbance of $[Fe(SCN)]^{2+}$ is the one that the experiment is concerned with.

The concept of the Q, the reaction quotient is needed. There are infinitely many Q's for a given reaction. The reaction quotient at state where the rate of the forward reaction and the reverse reaction are equal is called the K_{eq}. The equal reaction rates means equal production of products and reactants which would result in constant ratio of products and reactants, thus there is only one K_{eq} for a given reaction.

In the first part of the experiment, calibration was performed. Calibration was done by testing five standard samples with known $[Fe(SCN)^{2+}]_{eq}$ with a spectrophotometer to get their absorbances. A calibration curve was then constructed. The calibration curve was obtained when the values of the equilibrium concentrations of $[Fe(SCN)]^{2+}$ and their respective absorbance values were plotted. After obtaining the calibration curve, linear regression was used to find the equation of the best fit line of the plot of the points. The εb is the slope m of the best fit line, absorbance is the y value, and the equilibrium concentration is the x value.

In the next part of the experiment, absorbance readings from five unknown solutions (with unknown $[Fe(SCN)^{2+}]_{eq}$'s) were taken. The $[Fe(SCN)^{2+}]_{eq}$ was obtained by substituting the absorbance to the equation of the best fit line. Then $[Fe(SCN)^{2+}]_{eq}$ was then subtracted from the initial concentrations of Fe^{3+} and SCN^- to get their respective equilibrium concentrations. The main objective of the experiment was to find the equilibrium constant of the reaction:

[1] $Fe^{3+} + SCN^- \leftrightarrow [Fe(SCN)]^{2+}$

Equation 1 produces a blood red complex. To determine this equilibrium constant, the following equation was used:

[2] $K_{eq} = [Fe(SCN)^{2+}]_{eq} / [Fe^{3+}]_{eq}[SCN^-]_{eq}$

RESULTS AND DISCUSSION

There are two existing light sources within a UV-VIS spectrophotometer, one for each (UV and visible light) spectrum. The usual light source used to generate visible light is the tungsten-halogen lamp emitting 200-340 nm wavelengths (Boyer, 1993). The UV source can be either a high-pressure hydrogen lamp or deuterium lamp. When measuring absorbance at the UV spectrum, the other lamp has to be turned off. The same goes when measuring visible light absorbance. This is to prevent interference of unnecessary

wavelengths in the incident light on the sample. Following the light source is a monochromator, the purpose of which is to filter light and select a specific wavelength by using either a prism or a diffraction grating. After the monochromator is a series of lenses, slits, mirrors, and filters that act as an optical system to concentrate, increase spectral purity of, and direct monochromatic light towards the sample chamber with cuvettes containing solutions to be tested. However, since the instrument has only a single beam, every time the wavelength has to be changed a blank reading must precede any sample reading. The light-sensitive detector follows the sample chamber and measures the intensity of light transmitted from the cuvette and passes the information to a meter that records and displays the value to the operator on an LCD screen. There are two general designs of spectrophotometers, single-beams and double-beams. When using any kind of spectrophotometer, one must perform auto-zero.

The absorbance measured from the spectrophotometer can be related to the concentration of the analyte by the Beer-Lambert's Law (Beer-Lambert-Bouguer's Law):

[3] $A = \varepsilon bC$,

Where:
A = measured absorbance
ε = wavelength – dependent molar absorptivity coefficient
b = path length (cm)
C = molar concentration

The linearity of the Beer-Lambert law's is limited by chemical and instrumental factors alike. Hence, there are deviations from the law on certain conditions, here are some:

- If the concentration of the analyte is too high, there can be deviations in absorptivity due to electrostatic interactions between molecules in close proximity. Also, there can be changes in the refraction index of the analyte due to its high concentration.
- The beam used was not monochromatic.
- The absorbing species was not distributed properly leading to a non-consistent absorptivity of the analyte.
- Scattering of light due to very small particles (contaminants) like dust.
- The place where the spectrophotometer was used. In some places, stray light can cause some abnormalities on the absorbance/transmittance readings

The wavelength was set to 447nm because this was the wavelength were the absorbing species will have the maximum absorbance. If the wavelength was set higher (lower frequency and lower frequency light can travel longer distances without being absorbed), the absorbance of the analyte would be lower and the calculated $[Fe(SCN)^{2+}]_{eq}$ would be smaller.

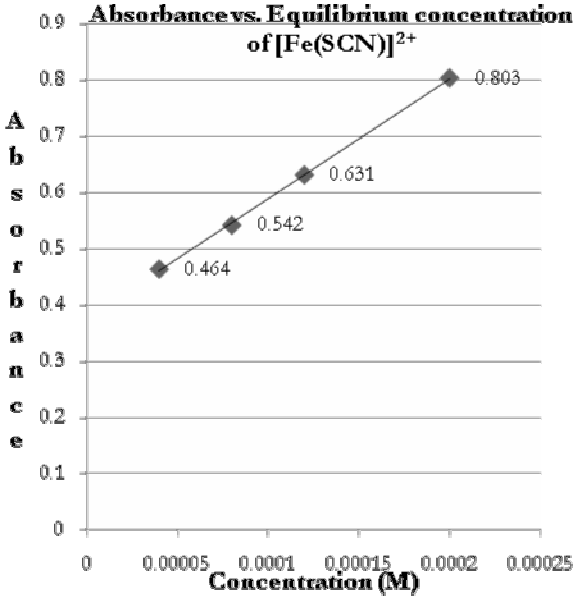
Table I. The Data of the Standard Solutions
Molar Concentration of KSCN: 2×10^{-3} M

Solution	Absorbance	$[SCN^-]$	$[Fe(SCN)^{2+}]$
Standard 1	0.464	4.00×10^{-5}	4.00×10^{-5}
Standard 2	0.542	8.00×10^{-5}	8.00×10^{-5}
Standard 3	0.631	1.20×10^{-4}	1.20×10^{-4}
Standard 5	0.803	2.00×10^{-4}	2.00×10^{-4}

The absorbance recorded from standard 4 was discarded because it clearly deviated from the other points when absorbance was plotted versus concentration of the analyte. This was done so that the best fit line is more accurate.

A spectrophotometer was used to obtain the absorbance of the standard solutions. A plot of the values of $[Fe(SCN)^{2+}]_{eq}$ versus Absorbance is shown below:

Figure I. The Graph of the Calibration Curve



Equation of the best fit line: $y = 2131.428571x + 0.375542857$

R^2 value: 0.999557262

The value of the R^2 obtained from the plot of the points is near to 1, which means that the plot of the points is near to a perfect line. The equation of the best fit line is important because it is related to the Beer-Lambert's Law. The slope, m, being εb (because b, the path length was kept at 1cm), the y being the absorbance and the x being the equilibrium concentration of $[Fe(SCN)]^{2+}$. However there is a non-zero y-intercept in the equation of the best fit line which suggested that the Beer-Lambert's law had some limitations.

From figure I, it was observed that as the equilibrium concentration of $[Fe(SCN)]^{2+}$ increased, the absorbance value also increased. The intensity of the color is related to the concentration of $[Fe(SCN)]^{2+}$. In the standard solutions, there was excess $[Fe^{3+}]_{initial}$ and limited $[SCN^-]_{initial}$. Therefore, by stoichiometric analysis, one can assume that the limiting reagent of the reaction was SCN^-, hence the product produced which was the absorbing species, $[Fe(SCN)]^{2+}$, was equal to the concentration of SCN^-.

The calibration curve was very essential because it related the absorbance of the analyte and concentration of $[Fe(SCN)]^{2+}$. The concentrations of $[Fe(SCN)]^{2+}$ in the unknown solutions were found using the graph and its equation. The next part of the experiment was the measurement of the absorbance of unknown solutions.

The absorbances of the unknown solutions are shown below:

Table II. Absorbance of Unknown Solutions

Initial molar Concentration of $Fe(NO_3)_3$: 2×10^{-3}
Initial molar Concentration of KSCN: 2×10^{-3}

Solution	Absorbance	$[Fe^{3+}]_{initial}$	$[SCN^-]_{initial}$
Unknown 1	0.110	1.00×10^{-3}	2.00×10^{-4}
Unknown 2	0.232	1.00×10^{-3}	4.00×10^{-4}
Unknown 3	0.389	9.09×10^{-4}	7.27×10^{-4}
Unknown 4	0.473	8.33×10^{-4}	1.00×10^{-3}
Unknown 5	0.528	7.69×10^{-4}	1.23×10^{-3}

Here, a different blank solution was used to re-zero the spectrophotometer before reading the absorbances of the unknown solutions because the molar concentration of Fe^{3+} in the unknown solutions is different from the standard solutions and according to Beer-Lambert's law the concentration of Fe^{3+}, an absorbing species is proportional to its absorbance leading to different values of absorbances. The spectrophotometer must subtract a different value from the absorbance of the whole solution to negate the absorbance of Fe^{3+} in the unknown solutions.

Table II shows that the absorbance increases as the concentration of SCN^- increases. The data from Unknowns 1 and 2 had been disregarded because from Beer-Lambert's law, one would get negative $[Fe(SCN)^{2+}]_{eq}$.

The $[Fe^{3+}]_{eq}$'s, $[SCN^-]_{eq}$'s, $[Fe(SCN)^{2+}]_{eq}$'s, and K_{eq}'s of Unknowns 3 to 5 are summarized in the table below:

Table III. Determination of the Equilibrium Constant, K_{eq}

Solution	$[Fe^{3+}]_{eq}$	$[SCN^-]_{eq}$	$[Fe(SCN)^{2+}]_{eq}$	K_{eq}
U 3	9.02×10^{-4}	7.18×10^{-4}	6.33×10^{-6}	9.77
U 4	7.87×10^{-4}	9.54×10^{-4}	4.57×10^{-5}	64.0
U 5	6.98×10^{-4}	1.16×10^{-3}	7.15×10^{-5}	88.3

Average Equilibrium Constant, K_{eq}: 54.0

The average equilibrium constant, 54.0, deviated greatly from the literature value 890 with a percent difference of 177.11%. One can say that the preparation of solutions was done correctly because the experimentally obtained K_{eq} values were close to each other (9.77 – 88.3) although they are very far from the literature value. This may be due to some other chemical reactions that compete with the production of $[Fe(SCN)]^{2+}$. For example the following reaction, $Fe^{3+} + 4Cl^- \leftrightarrow FeCl_4^-$, the reaction above occurs when there are excess Cl^- ions present, which is quite possible because both standard and unknown solutions were diluted with HCl. When the reaction took place, it will now hinder the production of $[Fe(SCN)]^{2+}$ also $FeCl_4^-$ does not contribute to the absorbance of the solution because it is colorless. The actual equilibrium concentration of $[Fe(SCN)]^{2+}$ was maybe smaller than the one calculated and that could cause the large difference from the literature value.

CONCLUSIONS AND RECOMMENDATIONS

There were many important observations made. First, the significance of the absorbing species, $[Fe(SCN)]^{2+}$ is discussed. The relationship suggested by the Beer-Lambert's law between the absorbance and the absorbing species was confirmed. The absorbance of $[Fe(SCN)]^{2+}$ made it possible for the absorbance to be obtained by using the spectrophotometer and for the equilibrium concentrations and constants of the unknown solutions to be calculated. Second, it was confirmed that spectrophotometry is an effective way of measuring absorbances due to the absorptivity of the analyte which was proved to be directly proportional to the concentration by the Beer-Lambert's law. Without the spectrophotometer, the solutions' absorbances

would not be measured hence there would be no proper way to obtain the equilibrium concentration of the analyte. And last, a calibration curve was obtained. It is useful in determining the equilibrium concentrations of the ions in the unknown solutions. With all of this, the calculation of the equilibrium constant was achieved.

The experiment yielded results that were consistent with what must be obtained although the percent error and the percent difference were high. The large discrepancies in the values of the experimental K_{eq} can be explained by the improper handling of the equipment and the place where the UV-Vis Spectrophotometer was used.

ANSWERS TO QUESTIONS

1. HCl is significant in the solution preparation because it helps to attain the desired concentration of the reactants by keeping the total volume of the solutions constant. Also the HCl used in the solution acidifies the solution. It minimizes the yellow – brown color of Fe^{3+} minimizing its absorbance and making $[Fe(SCN)]^{2+}$ the only absorbing species.

2. This is done to subtract the absorbance of Fe^{3+} to the absorbance of the whole solution so that the absorbance readings displayed are only due to $[Fe(SCN)]^{2+}$.

3. This may be due to some limitations of the Beer-Lambert's law leading to deviations in the calculated K_{eq}. Also there were measurement discrepancies and improper solution preparation. Measurements were made in graduated cylinders instead of a more accurate burette. Some apparatus were not completely dried and may have diluted the solutions. Also this maybe due to some other chemical reactions that compete with the production of $[Fe(SCN)]^{2+}$.

APPLICATIONS

Some applications of Spectrophotometry are:

- Analysis of some biochemicals in microbiology, also spectrophotometry is a way to determine the relative numbers of bacteria in a sample.
- Determination of the authenticity of some fruit juices, especially orange juice.
- Measurements of various properties of painted surfaces. Some properties of these surfaces include color, specular gloss, contrast gloss, bloom and sheen.
- Estimations of the cholesterol concentrations in blood plasma.
- Determination of the quality of honey based on its color.

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A. WORKING EQUATIONS

Beer-Lambert's Law:

$$A = \varepsilon bc,$$

Where:
A = measured absorbance
ε = wavelength – dependent molar absorptivity coefficient
b = path length (cm)
c = molar concentration

Equation of the Best Fit Line:

$$y = 2131.428571x + 0.375542857,$$

Where:
x = concentration
y = absorbance

Dilution Equation:
$M_1V_1 = M_2V_2$,
Where:
M_1 = concentration
M_2 = new concentration
V_1 = volume
V_2 = new volume

Equilibrium Expression:
$K_{eq} = [C]^c[D]^d / [A]^a[B]^b$
Where:
C, D = products
A, B = reactants
a, b, c, d = coefficients in the stoichiometric equation

Average Equilibrium Constant:
$K_{eq\ ave} = (K_{eq\ U3} + K_{eq\ U4} + K_{eq\ U5}) / 3$
Where:
$K_{eq\ U3} = K_{eq}$ obtained in Unknown 3
$K_{eq\ U4} = K_{eq}$ obtained in Unknown 4
$K_{eq\ U5} = K_{eq}$ obtained in Unknown 5

Percent Error:
|actual – theoretical / theoretical| X 100 = %
Where:
% = percent error

Percent Difference:
|actual – theoretical / ((actual + theoretical) / 2) | X 100 % = %
Where:
% = percent difference

B. SAMPLE CALCULATIONS

Equation of the Best Fit Line: y = 2131.428571x + 0.375542857

Equilibrium Concentration of $[Fe(SCN)^{2+}]$ in Unknown 3:

Given: y = 0.389

Find: x
[1] 0.389 = 2131.428571x + 0.375542857
0.389 - 0.375542857 = 2131.428571x
0.013457143 = 2131.428571x
$x = 6.33 \times 10^{-6}$

$x = 6.33 \times 10^{-6}$ M $[Fe(SCN)^{2+}]$

Dilution Equation of Standard 1:

Given: 0.20 ml of 0.002 M KSCN, 2.50 ml of 0.20 M $Fe(NO_3)_3$ and 7.30 ml of 0.1 M HCl

Find: M_2
M1 = 0.002 M KSCN
V1 = 0.20 ml KSCN
V2 = total volume = 0.20 + 2.50 + 7.30 ml = 10 ml
(0.002 M)(0.20 ml) = (M_2)(10 ml)
0.0004 moles = 10(M2)

$M_2 = 4.00 \times 10\text{-}5$ M $[SCN^-]$

Equilibrium Expression of Unknown 3:

Given:
$[Fe(SCN)^{2+}]_{eq} = 6.33 \times 10^{-6}$ M,
$[Fe^{3+}]_{init} = 9.09 \times 10^{-4}$ M
$[SCN^-]_{init} = 7.27 \times 10^{-4}$ M

Find: K_{eq}

An ICE table of Unknown 3

Net-ionic Equation:
$Fe^{3+} + SCN^- \leftrightarrow [Fe(SCN)^{2+}]$

	$[Fe^{3+}]$	$[SCN^-]$	$[Fe(SCN)^{2+}]$
I	8.33×10^{-4}	1.00×10^{-3}	0
C	-6.33×10^{-6}	-6.33×10^{-6}	$+6.33 \times 10^{-6}$
E	9.02×10^{-4}	7.18×10^{-4}	6.33×10^{-6}

$K_{eq} = [Fe(SCN)^{2+}]_{eq} / [Fe^{3+}]_{eq} \times [SCN^-]_{eq}$
$K_{eq} = 6.33 \times 10^{-6} / (9.02 \times 10^{-4}) * (7.18 \times 10^{-4})$

$K_{eq} = 9.77$

Average Equilibrium Constant:

$K_{eq\ ave} = (K_{eq\ U3} + K_{eq\ U4} + K_{eq\ U5}) / 3$
$= (9.77 + 88.3 + 64.0) / 3$

$K_{eq\ ave} = 54.0$

Percent Error:

Given:
Actual = 54.0
Theoretical = 890

% Error = (890 – 54.0) * 100 % / 890
% Error = 93.932 %

Percent Difference:

Given:
Actual = 54.0
Theoretical = 890

% Difference = (890 – 54.0) * 100 % / ((890 + 54.0) / 2)
% Difference = 177.11 %