Original Article

http://www.bpasjournals.com/chemistry

Bulletin of Pure and Applied Sciences.
Vol.39 C (Chemistry), No.1, 2020: P.14-20
Print version ISSN 0970 4620
Online version ISSN 2320 320X
DOI 10.5958/2320-320X.2020.00002.3

Spectrophotometric Determination of Equilibrium Constant

Abstract

The main purpose of the experiment is to obtain Keq's value of an unknown solution. It was obtained by means of a calibration graph by plotting the concentration of $FeSCN^{2+}$ ions vs. its absorbance. Formed the best fit line acted as the graph of calibration. The unknown solution's measured absorbance was then plugged into the y variable in the best fit line equation in order to get the concentration of $FeSCN^{2+}$ at equilibrium. The concentration of $FeSCN^{2+}$ at equilibrium was subtracted to the initial concentrations of Fe^{3+} and SCN^{-} for finding equilibrium in their respective concentrations. K_{eq} was calculated by the ratio of the product concentration and the reactant concentration of the reaction to their stoichiometric coefficients.

Keywords: Spectrophotometer, Equilibrium Constant, Calibration, Absorption, Standard Solutions.

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Received on 17.11.2019
Accepted on 21.03.2020

1. INTRODUCTION

A relation between the amount of light absorbed by a substance and its concentration is known as Spectrophotometry. In order to obtain the amount of a substance this method is employed.

The equilibrium constant, K, which is the "ratio" of the products to reactants, is a tool in the explanation of reactions at equilibrium. The extent to which reactants are converted to products is expressed by K. At equilibrium, if product is favoured, the value of large K is obtained whereas small value of K represents that reactant side is favoured. The values of K for reactions which is directly proportional to temperature are required for the optimization of the yield of chemical reactions (1).

The absorbance value of the penta aquathiocyanatoiron (III) ions is measured by means of a spectrophotometer, whereas the Beer-Lambert law is used for the direct absorption relationship (the ability of the material to absorb light) and analyte concentration (2). The law also shows that the length of the solution in which light passes or the path length b is proportional to the absorbance. Thus Beer-Lambert's law may be written in this way:

$$A = \in bC$$

Where $\in$ is the absorptivity coefficient in $M^{-1}Cm^{-1}$. A is absorbance, b the path length in Cm^{-1} and C denotes the concentration of the solution (in M).
Following reaction takes place:

$Fe^{3+} + 5H_2O(l) + SCN^-$ (aq)↔ $[Fe(H_2O)_5)SCN]^{2+}$ (1)
This equation may be simplified as given below:

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

Thus a coloured complex $FeSCN^{2+}$ is formed; the colour intensifies as soon as the concentration of the complex formed rises. The equilibrium constant for the reaction shown in Eq. [2] can be calculated by substituting values to the reaction's equilibrium constant expression shown as Eq. [3].

$$K_{eq} = \frac{[\mathrm{FeSCN}^{2+}]_{eq}}{[\mathrm{Fe}^{2+}]_{eq}[\mathrm{SCN}^{2+}]_{eq}} \quad (3)$$

The aim of this experiment is to relate the colour of the solution with the wavelength of the chromophore. This has been done with the help of spectrophotometry to obtain the concentration (equilibrium) of the chromophore, the part of molecule responsible for its colour which is absorbed.

In the present programme, The spectrophotometry calibration curve has been used to determine the molar absorption coefficient of $[\mathrm{FeSCN}]^{2+}$.

The resulting graph was then linked to Beer-Lambert's law (Eqn.2). The following relation has been observed:

$$y = mx + b$$

Where the slope m denotes for the molar absorptivity constant (ε), and y indicates the absorbance (A), x is the concentration (C) and Y-intercept given as b is the error, since absorbance and concentration should be directly related. The length of the solution for the experiment was 1 cm so it didn't affect the calculations as long as ε is in $M^{-1}Cm^{-1}$.

2. METHODOLOGY

For doing this experiment, a wavelength of 466 nanometers was used because the colour of $[FeSCN^{2+}]$was within the range of the yellow-orange color with maximum absorption wavelengths of 440-470 nanometers(3) It is necessary to use a concentrated and colored solution because in an incredibly dilute solution, it may be very difficult to see that it is coloured at all. The absorbance is going to be very low and changes in concentration would be difficult to notice.

Before calibration of UV-Vis spectrophotometer, solutions were prepared.

A. Solution Preparation

The main part of solution preparation is the requirement of adding HCl to $FeCl_3$.This is to provide excess Cl^- ions to favor the formation of the colorless diaquatetrachloroiron (III) ions in the solution, as given in Eq. [4]. This is preferred for spectrophotometric determination because Fe^{3+} is brown, while $FeCl_4(H_2O)_2$- is colourless.

$Fe^{3+} + 4Cl^- \leftrightarrow FeCl_4\,(H_2\,O)_2$ (4)

B. Stock Solutions

The following solutions were prepared: 1000 mL HCl(0.1M), 50 mL of KSCN(0.2M), 100mL of 0.002 M KSCN in 0.2 M HCl, 50 mL of 0.2 M $FeCl_3$ in 0.2 M HCl, and 100 mL 0.002 M $FeCl_3$ in 0.2 M HCl.

The calibration of UV-Vis spectrophotometer was done using six solutions of varying reactant concentrations, as listed in Table 1. The Blank was used to zero the spectrophotometer, so that only the absorbance of the pentaaquathiocyanatoiron (III) ions was displayed and recorded. The proportionality constant can be calculated using linear regression.

C. Determination of [FeSCN2+] of Unknown Solutions

Three different test tubes with varying initial concentrations of iron (III) ions and constant concentration of thiocyanate ions were subjected to the same UV-Vis spectrophotometer. The concentration of each reactant is listed in Table 2. Unlike in Calibration, the initial concentration of KSCN is relatively smaller, and that the test tubes can be set to equilibrate in time. Upon setting the zero for the spectrophotometer, every test tube absorbance was measured and noted. the absorbance of each test tube was measured and recorded. There is no need for corrected absorbance because the spectrophotometer was zeroed.

D. Preparation of the Unknown Solutions

Various quantities of 0.002 M FeCl3, 0.20 M KSCN, and 0.10 M HCl were prepared in 6-inch test tubes for preparation of unknown solutions. A blank solution was filled with 5.0 mL KSCN (0.002 M), and 5.0 mL of HCl (0.1 M). Unknown 1 was filled with 3.0 mL of $FeCl_3$ (0.002 M), 5.0 mL of 0.002 M KSCN, and 2.0 mL of HCl (0.1 M). Unknown 2 was filled with 4.0 mL of $FeCl_3$ (0.002 M), 5.0 mL of KSCN (0.002 M), and 1.0 mL of 0.1 M HCl. Unknown 3 was filled with 5.0 mL of $FeCl_3$ (0.002 M), and 5.0 mL of KSCN (0.002 M).

Calibration of the UV-Vis Spectrophotometer

Four times the cuvette was rinsed with distilled water and the blank solution was followed. The cuvette has been put inside the spectrophotometer in the sample holder. It's been achieved by Autozero. Standards 1 to 5 have been used to determine the maximum absorption wavelength. The wavelength was recorded. Removed the cuvette containing the blank solution and was rinsed three times with distilled water. Then rinsed the cuvette with Standard 1. The rinse was discarded and Standard 1 re-filled the cuvette. The cuvette was put inside the spectrophotometer in the sample holder and the absorption was recorded. Removed the cuvette and disposed of the solution in a waste bowl. Regarding Standards 2 to 5, the same absorbance monitoring system has been used.

Determination of Equilibrium Constant for the formation of $[FeSCN]^{2+}$

The same approach was used to position the cuvette with the solutions in the spectrophotometer. There was a different blank solution, but the same wavelength remained from the previous part.

For such a device, all measurements using the UV-Vis spectrophotometer are performed by setting the wavelength to a widely accepted analytical wavelength (which is 466 nm). This wavelength is similar to blue (4). Because the solutions are red-orange, it follows that they have to reflect light waves of the red-orange wavelength, which is about 570-650 nm, and they have to absorb those of other wavelengths, particularly their complement (5). Therefore, the absorbance in 466 nm must be greater than zero for this red-orange coloring system.

For analytical wavelength, absorbance measurements are performed to eliminate experimental errors. The graph maximum of wavelength versus absorbance illustrates this: a marginal deviation in wavelength when using the analytical wavelength will cause a relatively smaller deviation in absorbance compared to when using a wavelength in the graph's steeply sloping sides, where a slight deviation in testing can cause a larger deviation in the absorbance calculation (6).

3. RESULT AND DISCUSSION

The excess of KSCN during preparation of sample as given in Table 1, assures that the equilibrium in Eq. [2] shifts largely to the right, as suggested by Le Chatelier’s Principle. In other words, only the forward reaction takes place. This implies that all iron (III) ions are now converted to pentaaquathiocyanatoiron (III) ions, and that the initial concentration of iron (III) ions is the same as the equilibrium concentration of pentaaquathiocyanatoiron (III) ions. The Blank was used to zero the spectrophotometer, so that only the absorbance of the pentaaquathiocyanatoiron (III) ions was displayed and recorded.

A. Calibration

Figure 1 shows the calibration results. A linear fitting regression line is consistent with the Beer-Lambert Law on direct absorption proportionality to analyte concentration. The slope is the constant of proportionality related to the absorption of [$FeSCN^{2+}$]. The constant corresponding to the regression line's y-intercept is negligible.

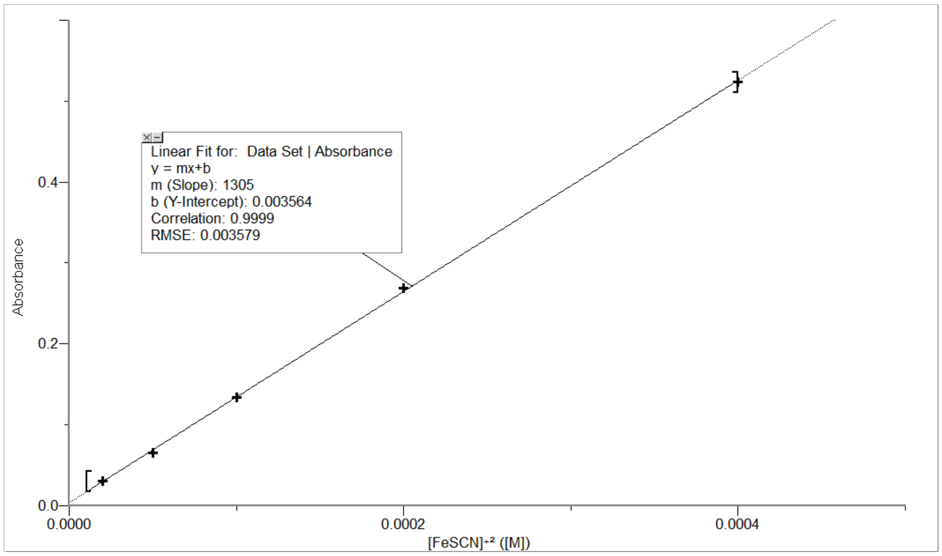

Figure 1: Linear relationship of [$FeSCN^{2+}$]$_{eq}$ and absorbance.

B. Determination of [$FeSCN^{2+}$] of Unknown Solutions

The fitting regression line of the plot of analyte concentration against absorbance allowed for the interpolation or extrapolation of data. That is, given the measured absorbance of the test tube whose reaction is at equilibrium, [FeSCN2+] at equilibrium can be calculated. Mathematically:

$$[FeSCN^{2+}]_{eq} = \frac{Absorbance}{proportionality\ constant}$$

$Proportionality\ Constant = \in b$

The slope in the regression line in Figure 1 and the value b = 1 cm, the experimental $\varepsilon = 1305\ M^{-1}\ cm^{-1}$.

In the determination of Keq, it was assumed that the reaction between$Fe^{3+}$and SCN^{-} was complete. Without this assumption,Beer-Lambert's law cannot be used. This is one of the limitations for this experiment. In addition, there were several sources of error. One is the presence of stray light. The spectrophotometer might not have been properly covered during the reading and stray light might have entered. Another source of error is the assumption that spectrometer only detects monochromatic light from the solution.

C. Errors

Probably the most important mistakes in the experiment are the preparation of the solution. Because the solutions used in the experiment were simply prepared using more concentrated stock solutions, random error could have occurred in this phase. The very high percentage of error (38%, see Table 5) value suggests that there may have been significant errors. Potential sources of error may include inadequate solution preparation, inappropriate spectrophotometer handling, and spectrophotometer systematic error. Prepared solutions may not have been properly measured, or may have been diluted by improper glassware washing._The cuvette may not have been sufficiently rinsed with the solution that could have caused the solution in the cuvette to dilute significantly.__Finally, the spectrophotometer may not have functioned properly as evidenced by the strange spike in the spectrophotometer graph when measuring the analytical wavelength. It is suggested that the reagents used be of high purity.

Calculations

1. Formula for calculating initial molarity of Ferric ion(Fe^{3+} or SCN^-) in the unknown and standard solutions:

$$\frac{Molarity\ of\ required\ solution\ X\ volume\ of\ required\ solution}{total\ volume\ of\ solution}$$

$$\frac{0.002\ M\ Fe^{3+}\ X\ 0.10\ mL\ FeCl_3}{10mL} = 2X\ 10^{-5}\ \ MFe^{3+}$$

2. Concentration determination of complex ($FeSCN^{2+}$) at equilibrium:

From the best fit line of figure 1,

(i) Unknown 1

$$\boldsymbol{Y = mx\ + b}$$

$$\boldsymbol{0.246 = 1350\ x\ + 0.0036}$$

$x = [\mathbf{FeSCN}]^{2+} = \frac{0.246-0.0036}{1305} = 0.000186$ M

(ii) Unknown II

$[\mathbf{FeSCN}]^{2+} = \frac{0.312-0.0036}{1305} = 0.00024$ M

(iii) Unknown III

$$[\mathbf{FeSCN}]^{2+} = \frac{0.387 - 0.0036}{1305} = 0.000294\ M$$

3. For calculating equilibrium concentration of Fe^{3+} or SCN^- :

$Initial\ concentration\ of\ \ Fe^{3+}\ or\ SCN^- - Equilibrium\ concentration\ obtained\ for$ $FeSCN^{2+}$

Also, through the stoichiometry of Eq. [2] and the ICE table method, the equilibrium concentrations of the reactants can be calculated.

Table 1: Initial concentration of reactants for spectrophotometric determination

Test Tube	$[\mathbf{Fe^{2+}}](\boldsymbol{initial})\boldsymbol{M}$	$[\mathbf{SCN^-}](\boldsymbol{initial})\boldsymbol{M}$
1	0.00002	0.09
2	0.00005	0.088
3	0.0001	0.084
4	0.0002	0.08
5	0.0004	0.07

Table 2.1: Sample ICE table for unknown 1 solution

Conc.	Fe^{3+}	SCN^-	$FeSCN^{2+}$
Initial Conc.	0.0006	0.001	0
Change in Conc.	-0.00018	-0.00018	0.00019
Equilibrium Conc.	0.00042	0.00082	0.00019

Table 2.2: ICE table for unknown 2 solutions

Conc.	**Fe^{3+}**	**SCN^-**	**$FeSCN^{2+}$**
Initial Conc.	$8X10^{-4}$	$1X10^{-3}$	0
Change in Conc.	-0.00022	-0.00022	0.00024
Equilibrium Conc.	0.00058	0.00078	0.00024

Table 2.3: Sample ICE table for unknown 3 solutions

Conc.	**Fe^{3+}**	**SCN^-**	**$FeSCN^{2+}$**
Initial Conc.	$1X10^{-3}$	$1X10^{-3}$	0
Change in Conc.	-0.000284	-0.000284	0.000294
Equilibrium Conc.	0.000716	0.000716	0.000294

Table 3: Initial concentration of reactants for spectrophotometric determination

Test Tube	$[\mathbf{Fe^{2+}}](\boldsymbol{initial})\boldsymbol{M}$	$[\mathbf{SCN^{-}}](\boldsymbol{initial})\boldsymbol{M}$
1	0.0006	0.001
2	0.0008	0.001
3	0.001	0.001

Table 4: Absorbance value of various standard solutions

Solution	**$[FeSCN^{2+}](M)$**	**Absorbance**
Blank	0	0
Standard1	$2X10^{-5}$	0.031
Standard2	$5X10^{-5}$	0.065
Standard3	$1X10^{-4}$	0.134
Standard4	$2X10^{-4}$	0.269
Standard5	$4X10^{-4}$	0.524

4. Calculation of the K_{eq} for the reaction:

$$K_{eq} = \frac{[\text{FeSCN}^{2+}]_{eq}}{[\text{Fe}^{2+}]_{eq}[\text{SCN}^{2+}]_{eq}}$$

Table 5: K_{eq} of unknown solution

Solution	**Equilibrium Constant, K_{eq}**
Unknown solution 1	552
Unknown solution 2	530
Unknown solution3	573
Mean	552

5. Calculation of the percent error of K_{eq}:

$$\text{Percent error} = \frac{average\ experimental\ value - Theoretical\ value}{Theoretical\ value} \text{ X } 100\%$$

$$\text{Percent error} = \frac{552-890}{890} \text{ X } 100\%$$

$$=38\%$$

Acknowledgment: Authors are extremely grateful to Principal, Dr. R.K. Dwivedi, and the Head, Dr. Varun Kumar Singh (Chemistry Department), Faculty of Engineering, Teerthanker Mahaveer University,Moradabad, for providing laboratory facilities during course of this investigation.

REFERENCES

1. Masterton, W.L.; Hurley, C.N. Chemistry: Principles and Reactions, 3rd ed.; Saunders College Publishing: Florida, 1997; pp 361-363.
2. The University of Adelaide, Australia: Department of Chemistry. Beer-Lambert Law. http://www.chemistry.adelaide.edu.au/ external/soc-rel/content/beerslaw.htm (accessed Jan 24, 2013).
3. Clark J. The Beer Lambert Law. Retrieved from http://www.chemguide.co.uk/analysis/uvvisible/beerlambert.html.
4. National Aeronautics and Space Administration (NASA). What Wavelength Goes With Color? http://scienceedu.larc.nasa.gov/EDDOCS/Wavelengths_for_C olors.html (accessed Jan 24, 2013)
5. Davidson College Chemistry Resources. Spectrophotometry. http://scienceedu .larc.nasa.gov/EDDOCS/Wavelengths_for_C olors.html (accessed Jan 24, 2013)
6. SimuLab Resources and Training Room. Study Notes: Analytical Wavelength. http://toolboxes.flexiblelearning.net.au/demosites/series5/ 508/laboratory/studynotes/snAnalyWavelength.htm (accessed Jan 25, 2013)