

Effects of Ionic Strength on Thiocyanate Complexation Equilibrium

Introduction

Equilibrium concentrations for reactions can be measured spectroscopically when the products and reactants have different absorption peaks in their visible spectrum. By measuring the concentrations of the products and of the reactants spectroscopically (using the Beer-Lambert relationship), the equilibrium constant, K , can be easily calculated. For ideal reactive mixtures, the relationship between the equilibrium constant and the standard Gibbs energy of the reaction (ΔG_r°) is straightforward to determine:

$$\Delta G_r^\circ = -RT \ln K \quad (1).$$

where T is the temperature at which the equilibrium occurs and R is the ideal gas law constant. For reactions involving electrolyte solutions, however, equilibrium concentrations must be considered to be affected by the presence of the average electric field in the solution. Many biological solubilities, such as those of proteins, are enhanced by dissolving the solute into a solution that already contains a certain ionic strength, a phenomenon known as *salting in*. This is because the true equilibrium constant is the ratio of *activities* of the reactants and products, not the apparent concentrations. In such a case, the *thermodynamic equilibrium constant*, K_a , is different from the *apparent equilibrium constant*, K , which is determined spectroscopically:

$$K_a = K_\gamma K_c \quad (2).$$

K_a should therefore be independent of ionic strength, but K_c will vary based on the ionic strength. In Eq. 2, K_γ represents the ratio of the activity coefficients, γ , for the compounds involved in the equilibrium. In this laboratory, the apparent equilibrium constant for the complexation of thiocyanate ion (SCN^-) with iron will be measured. Upon complexation, the solution will take a tangerine orange color due to the formation of $\text{Fe}(\text{SCN})^{2+}$ in solution:



The color can be monitored. Because of the unique circumstances of this type of reaction (binary reaction, single product), the apparent equilibrium constant can be calculated based on only a single concentration at equilibrium. This works because the initial concentrations of Fe^{3+} and SCN^- (C_F and C_S , respectively) are known. Since the reaction is only a complexation, all iron in the solution is either in the reactants or in the products, and the same can be said for all thiocyanate. Thus,

$$\begin{aligned} C_S &= [\text{SCN}^-] + [\text{FeSCN}^{2+}] \\ C_F &= [\text{Fe}^{3+}] + [\text{FeSCN}^{2+}] \end{aligned} \quad (4).$$

The concentration of product can be calculated based on the absorbance, A , measured at a particular wavelength with the Spectronic-20 spectrophotometer. Appendix 1 shows that these three values can be related in a relatively simple formula for the determination of K_c :

$$\frac{C_F C_S}{A} = \frac{1}{ab} \left(\frac{1}{K_c} + C_F + C_S \right) \quad (5),$$

where A represents the measured absorbance corresponding to the iron thiocyanate complex. To determine the thermodynamic equilibrium constant, K_a , the activities of each compound must be calculated. Because all reaction components are electrolytes, activities are dominated by the ionic strength of the solution, I :

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (6).$$

For solutions with $I < 0.1$ M, Debye-Hückel Theory can be used to arrive at values for γ , which can be used to determine K_γ , according to

$$K_\gamma = \frac{\gamma_{\text{Fe}(\text{SCN})^{2+}}}{\gamma_{\text{SCN}^-} \gamma_{\text{Fe}^{3+}}} \quad (7).$$

In this case, however, the ionic strength is too high for the Debye-Hückel theory to be operational. Instead, we will need to use the Davies equation to determine each ionic activity coefficient:

$$\log \gamma = -0.509 z^2 \left[\frac{\left(\frac{I}{m^\circ} \right)^{1/2}}{1 + \left(\frac{I}{m^\circ} \right)^{1/2}} - 0.30 \left(\frac{I}{m^\circ} \right) \right] \quad (8).$$

where m° is the standard concentration of 1 M, and z is the charge of the ion being considered.

Experimental Procedures

Several solutions have been prepared for you in advance. You might notice that the iron nitrate solution has a faint orange color, but should not significantly alter the results. Several different initial concentrations of the iron nitrate solution will be measured, but by successively adding 1-mL aliquots to the same solution of potassium thiocyanate. Follow the procedures carefully to ensure that you will be able to properly carry out the calculations later.

Because equilibrium constant is temperature-dependent, you will need to provide a constant-temperature bath in which your reaction vessel will sit. Use a 1000-mL beaker with a magnetic stir-bar to ensure even temperature. A thermometer should be placed in the water near (but not touching) the edge of the beaker. You will add warm water or small portions of ice to maintain a constant temperature of 25°C.

In a 100-mL volumetric flask, pipette 1 mL of 0.02-M KSCN solution, then 25 mL of 2.0 M HNO₃. Dilute this mixture to the mark with deionized water, mix well, and pour the contents into a 250-mL Erlenmeyer flask for easy use during the experiments. Fill the spectrometer cuvette with a few mL of the KSCN/HNO₃ solution. This will serve as your blank – measure its absorption spectrum. You should be able to set it as a reference so that it will be automatically subtracted from the spectra of the samples. Remove the cuvette, return its contents to the 250-mL flask (do not dispose), and clean and dry the cuvette.

For each data point, you will measure the absorbance of your solutions. Begin by adding 1 mL of the 0.1-M Fe(NO₃)₃ (dissolved in 0.5-M HNO₃ solution to prevent iron hydrolysis) solution to the beaker of thiocyanate solution. Mix well with a glass stirring rod, and allow five minutes for thermal equilibration, then transfer a sample into the spectrophotometer cuvette. Measure a spectrum of the solution, then set the wavelength of the spectrophotometer to monitor absorbance at the peak of that absorption. **Do not dispose of your sample until you have measured your last concentration.** Instead, pour the contents of the cuvette back into the flask from which it came. Then, add your next 1-mL aliquot of Fe(NO₃)₃ solution, equilibrate, measure its absorbance at the same wavelength, and return the sample to the beaker after measurement. Continue this process until you have added a total of 10 mL of Fe³⁺ solution to the KSCN solution. Dispose of all used solutions as directed by the laboratory assistant.

Data Analysis and Lab Reports

The calculations for this lab are somewhat involved. A spreadsheet is definitely recommended. It will likely work well to do your work up independently of your lab mates to compare your results afterwards. This will allow you to check for typographical errors.

Calculations: For each addition of Fe(NO₃)₃, you will need to create a spreadsheet that lists the absorbance (A), initial concentration of iron (C_F), and initial concentration of thiocyanate (C_S). From this, you can determine the apparent equilibrium constant, K_c , using a graphical technique. Based on Eq. 5, the value of K_c can be determined by plotting $(C_F C_S / A)$ vs. $(C_F + C_S)$. This should produce a set of data with a straight line, which can be fit with a linear regression to determine the slope (m) and intercept (b) of the line. Based on Eq. 5, it can be shown that

$$K_c = \frac{m}{b} \quad (9).$$

Although you do not know the value of the molar absorptivity for FeSCN^{2+} , you can now use the value of K_c to calculate the concentration of the complex at equilibrium for each of your solutions. We show in Appendix 2 that this can be done without need of molar absorptivity, resulting in Eq. A8. You should briefly summarize this derivation in your theory section as well.

To determine the value of K_a , the thermodynamic equilibrium constant, you will need to use Eq. 2, demanding that you must first calculate the ionic activity coefficients (γ) for each compound so that you can calculate K_γ using Eq. 7. To do this, you will first need to separately calculate the ionic strength of each solution by accounting for all of the ions in the solution (don't forget about H^+ and NO_3^- from the acid as well as the dissolved K^+ and NO_3^- in the solution!). Then, you can use the Davies equation (Eq. 8) to determine the value of γ for each compound in the solution. Armed with K_γ , you should plot the thermodynamic equilibrium constant as a function of ionic strength. So... Here's what is needed for your short report:

1. A well-labeled, easy to follow Excel spreadsheet must be uploaded as your calculations, but as separate document.
2. Write a short (1-2 page) report that describes and shows two plots. The first should be your plot used to determine K_c . The second should be K_a as a function of I , which will give a sense of the range of values. These are not perfectly constant, but your values should be within a range that is about 5% of the mean value. Your report should do the following:
 - a. Compare your thermodynamic equilibrium constant to one determined based on tabulated thermodynamic data for this reaction. The values for $\Delta_f G^\circ$ for the relevant compounds are given in the table below. Now, compare your values for K_a and K_c to the value you calculate based on Gibbs energy for the reaction. Which is closer? Explain why in one to two sentences.

Ion	$\Delta_f G^\circ$ (kJ/mol)
Fe^{3+}	-4.7
SCN^-	+92.7
$[\text{Fe}(\text{SCN})]^{2+}$	+71.1

- b. Try predicting K_a at effectively zero ionic strength based on your plot of K_a as a function of I by extrapolating your data points back to $I = 0$. Does this agree better with the literature results? Discuss that result in one to two sentences.

References:

1. Chang, R. *Physical Chemistry for the Biosciences*; University Science Books: Sausalito, CA, 2005; pp. 243-254.
2. Cobb, C. L., and Love, G. A. "A Physical Chemistry Equilibrium Lab Incorporating Ionic Strength Effects," *J. Chem. Educ.* **75**(1), 90-02 (1998).

Appendix 1. Derivation of Eq. 5.

We know that equilibrium constant is defined as a ratio of concentrations of products over reactants:

$$K = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]} \quad (A1).$$

However, we seek a way to measure the concentrations of the iron thiocyanate complex without needing to perform a Beer-Lambert calibration (plotting concentration vs. absorbance). Even so, we know that the absorbance, A , is given by the Beer-Lambert relation, so that

$$A = \epsilon b [FeSCN^{2+}] \quad (A2),$$

where ϵ is the molar absorptivity of the absorbing species (the iron thiocyanate complex), and b is the cell pathlength. Using this and Eq. 4 from the introduction, we can express K_c as

$$K = \frac{\frac{A}{\epsilon b}}{\left[C_F - \left(\frac{A}{\epsilon b} \right) \right] \left[C_S - \left(\frac{A}{\epsilon b} \right) \right]} \quad (A3).$$

Now, we are left with only one variable ($A/\epsilon b$) to solve for, since C_F and C_S are known for each experimental trial. We can rearrange algebraically (you should prove this to yourself) to put the equation into a form that can use the quadratic formula:

$$\left(\frac{A}{\epsilon b} \right)^2 - \left(C_F + C_S + \frac{1}{K_c} \right) \left(\frac{A}{\epsilon b} \right) + C_F C_S \quad (A4).$$

This can now be solved to show that

$$\left(\frac{A}{\epsilon b} \right) = \frac{C_F C_S}{C_F + C_S + \left(\frac{1}{K_c} \right)} + \frac{(C_F C_S)^2}{\left[C_F + C_S + \left(\frac{1}{K_c} \right) \right]^3} \quad (A5).$$

Since the initial concentrations are quite small and $K_c < 1$, the second term is negligible compared to the first, and can be dropped, and the result rearranged to arrive at Eq. 5 from the introduction.

Appendix 2. Determination of $[FeSCN^{2+}]$.

We can rearrange Eq. A2 to solve for the value of ϵb :

$$\epsilon b = \frac{A}{[FeSCN^{2+}]} \quad (A6).$$

Inserting this into Eq. 5 from the introduction, we arrive at an expression with A in the denominator of all terms, which, when cancelled, leaves

$$C_F C_S = [FeSCN^{2+}] \left(\frac{1}{K_c} + C_F + C_S \right) \quad (A7).$$

Solving Eq. A7 for the concentration of the complex gives us an expression in three known quantities (K_c , C_F , and C_S):

$$[FeSCN^{2+}] = \frac{C_F C_S}{\left(\frac{1}{K_c} + C_F + C_S \right)} = \frac{K_c C_F C_S}{1 + K_c (C_F + C_S)} \quad (A8).$$