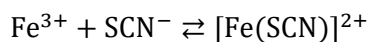


# Equilibrium Dependence of Iron (III) Thiocyanate Complexation

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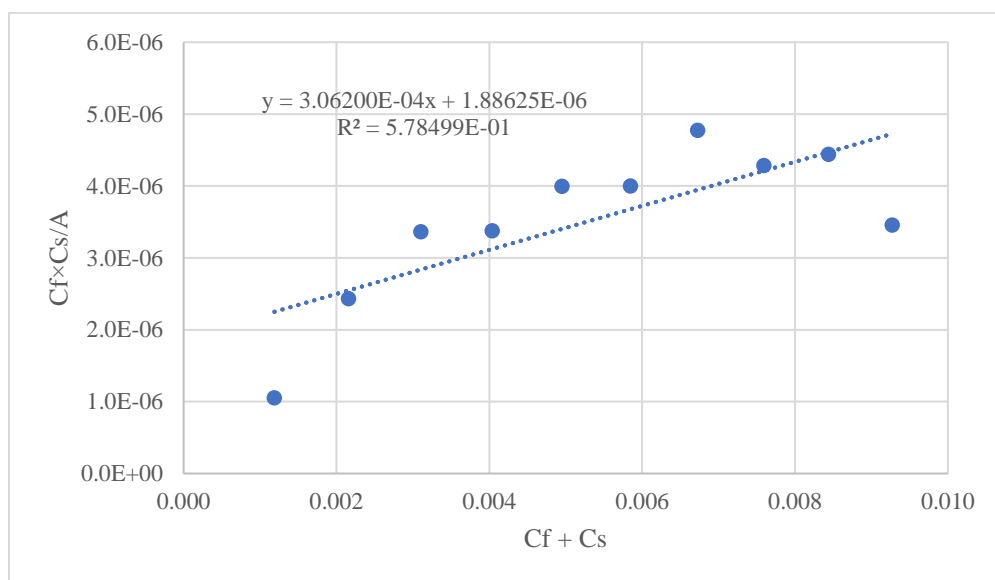
For the complexation reaction,



the apparent equilibrium constant  $K_c$  can be calculated using the initial concentrations of iron (III)  $C_F$  and thiocyanate  $C_S$  through the following linear relationship

$$\frac{C_F C_S}{A} = \frac{1}{\epsilon b K_c} + \frac{C_F + C_S}{\epsilon b}$$

for molar absorptivity  $\epsilon$ , cuvette length  $b$  and absorbance  $A$ . Although, the  $\epsilon$  and  $b$  variables disappear by taking the slope/y-intercept ratio of a plot of  $C_F C_S / A$  vs.  $C_F + C_S$  giving only  $K_c$ .



**Figure 1:** Plot for the calculation of  $K_c$ .

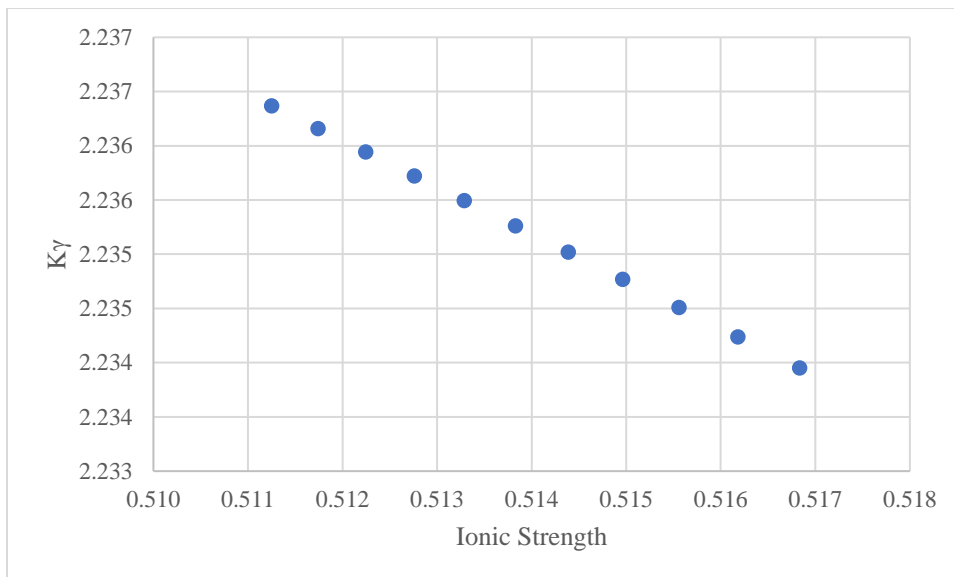
For our data,

$$K_c = \frac{0.0003062}{0.000001886} = 162$$

Alternatively, the thermodynamic equilibrium constant  $K_a$ , can be calculated using standard Gibbs energy of reaction  $\Delta G_r^\circ$ , and temperature  $T$  from standard formation values.

$$\Delta G_r^\circ = -RT \ln K \rightarrow K_a = \exp \frac{-16900 \frac{\text{J}}{\text{mol}}}{-8.314 \frac{\text{J}}{\text{K mol}} 298.15\text{K}} = 914$$

We can compare our apparent equilibrium constant to the literature by the relationship to the thermodynamic equilibrium constant by  $K_a = K_\gamma K_c$ .  $K_\gamma$  is calculated via the Davies equation. For each addition of iron (III), the ionic strength of solution changes. We find that  $K_\gamma$  does not deviate from the mean value of 2.235 by more than 0.06% for all ionic strengths in the reaction.



**Figure 2:** Demonstration of the stability of  $K_\gamma$ .

Because of this, we can find the calculated thermodynamic constant for our data.

$$K_a = K_\gamma K_c = 2.235 * 162 = 362$$

This value is closer to the literature calculated  $K_a$  than  $K_c$  due to the salting in effect. When  $K_\gamma$  is calculated for hypothetical much higher concentrations, the  $K_\gamma$  vs. ionic strength graph obeys an almost perfect exponential fit. Applying an exponential fit to the graph and extrapolating back to  $I=0$ , we find  $K_\gamma=2.469$ , therefore

$$K_a = K_\gamma K_c = 2.469 * 162 = 400.$$

This result is even closer to the expected  $K_a$  than before.