Equilibrium Dependence of Iron (III) Thiocyanate Complexation

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For the complexation reaction,

the apparent equilibrium constant Kc can be calculated using the initial concentrations of iron (III) CF and thiocyanate CS through the following linear relationship

for molar absorptivity ε, cuvette length b and absorbance A. Although, the ε and b variables disappear by taking the slope/y-intercept ratio of a plot of CFCS/A vs. CF+CS giving only Kc.

**Figure 1:** Plot for the calculation of Kc.

For our data,

Alternatively, the thermodynamic equilibrium constant Ka, can be calculated using standard Gibbs energy of reaction ΔGr, and temperature T from standard formation values.

We can compare our apparent equilibrium constant to the literature by the relationship to the thermodynamic equilibrium constant by . Kγ is calculated via the Davies equation. For each addition of iron (III), the ionic strength of solution changes. We find that Kγ 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 Kγ.

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

This value is closer to the literature calculated Ka than Kc due to the salting in effect. When Kγ is calculated for hypothetical much higher concentrations, the Kγ 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 Kγ=2.469, therefore

This result is even closer to the expected Ka than before.