

Revisiting the Substitution Kinetics for the Formation of Iron (III) Thiocyanate $[Fe(SCN)]^{2+}$ Complex^{1,2} Using Applied PhotoPhysics Stopped-flow Spectrometer

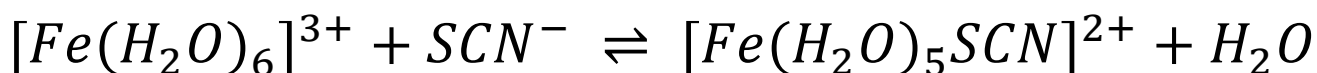
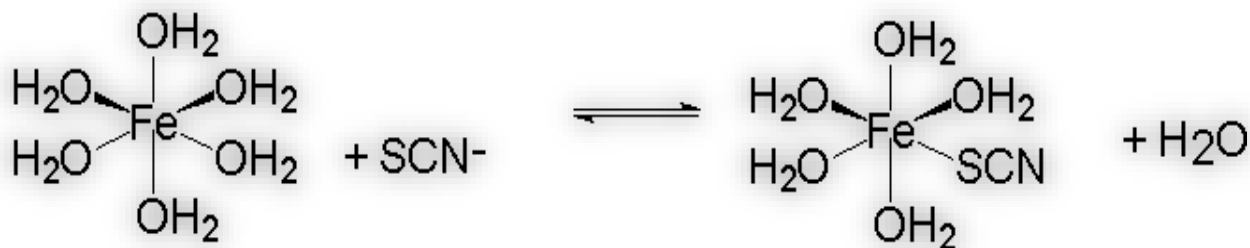
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ABSTRACT

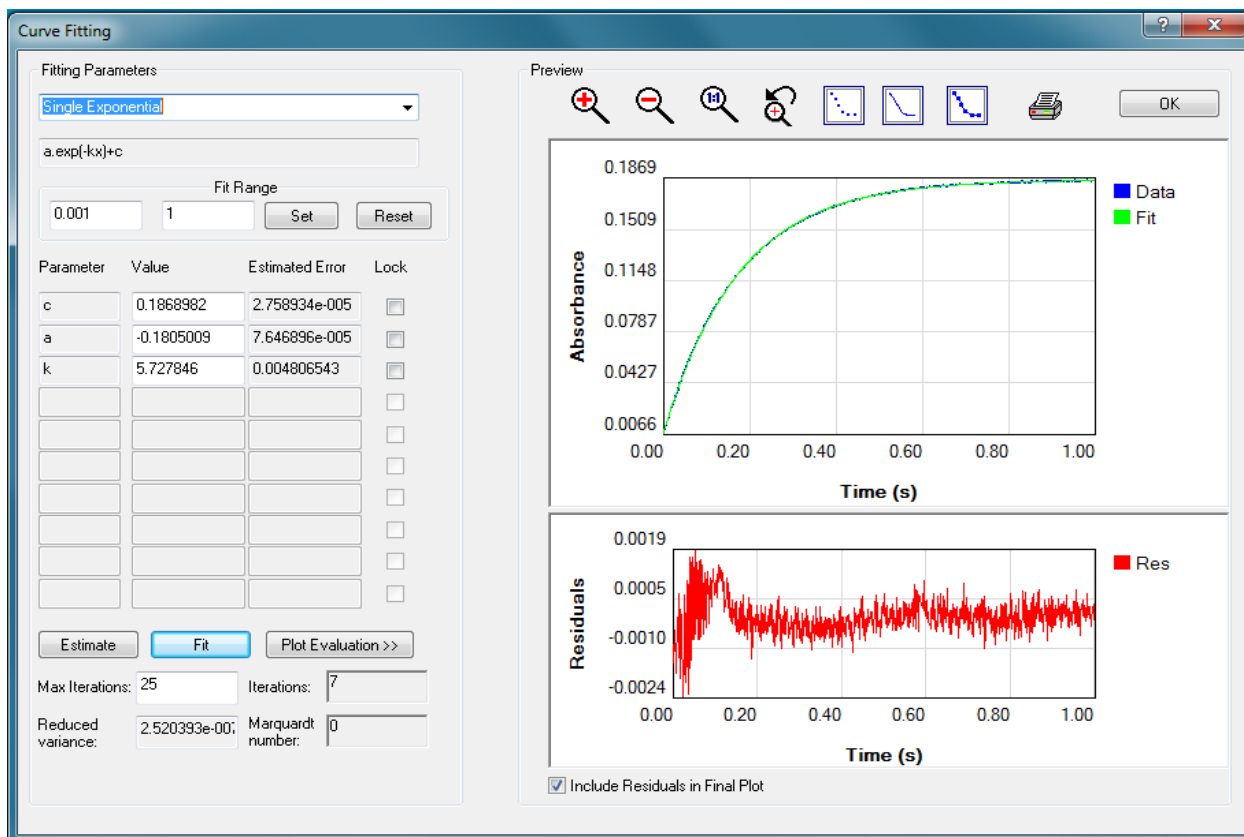
A Stopped-flow Spectrometer serves as a source for monitoring reactions that occur in timeframes as fast as milliseconds. The instrument mixes the reactants and examines the reaction's kinetics using a suitable spectroscopic probe. The experiment explores the Stopped-flow kinetics of the formation of Iron (III) Thiocyanate Complex – a four-step reversible system, governed by various rate and acid dissociation constants¹. The experiment was performed under Pseudo-first order conditions and the rate constants for the overall reaction, as collected by the spectrometer at 440 nm, 450 nm, and 460 nm for different Fe^{3+} and H^+ concentrations, were used to ultimately find the rate constants derived in the integrated rate law equation. The results were then compared with the reported values.



INTRODUCTION

The metal ion substitution kinetics for the formation of M (III) complexes has been studied mainly due to the very fast reaction rate, the high coordination number for metal (III) ion, and the complexity of the reaction scheme¹. One such example is the kinetics for the formation of Iron (III) thiocyanate complex in acidic conditions, observed in this experiment. The spectral and thermodynamic properties of the complex are well-known. However, discrepancies among kinetic rate constants as described in the proposed scheme² led us to revisit the kinetics using modern Stopped-flow Spectrometer acquired from Applied PhotoPhysics Inc.

The spectrometer offers Photodiode Array (PDA), Monochromator, and Fluorescence and is capable of taking 100 points in 0.1 seconds. It uses a suitable spectroscopic probe to monitor the reaction while the reagents are being mixed and passed through the optical observation cell. The Pro-Data SX Program records the change in spectroscopic signal as a function of time and Curve Fitting, using the correct Fitting Parameter, allows the determination of the overall rate constant (k_{observed})³. The instrument also offers a mathematical program named Pro-KIV. Single Exponential Curve Fitting ($y=a^{-kx}+c$) was used to find rate constants at 440 nm, 450 nm, and 460 nm, which were then compared with the reported ones^{1,2}.

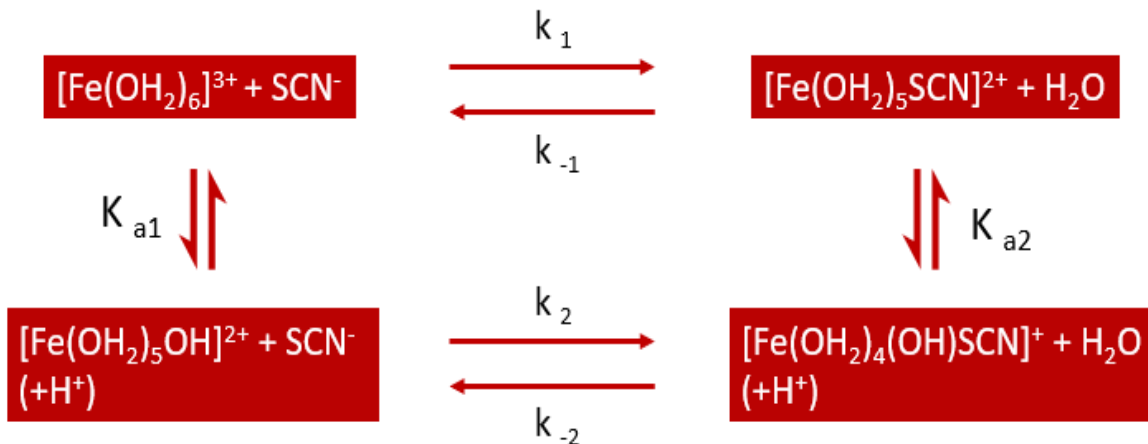


OBJECTIVE

The experiment was directed to look at the effects of varying Fe^{3+} and H^+ concentrations on the rate constants for the formation of Iron (III) thiocyanate complex, to gain hands-on experience with the SX20 Stopped-flow Spectrometer, and to explore the discrepancies in rate constants that have been reported for the system.

REACTION SCHEME

The formation of Iron (III) thiocyanate complex is a four-step reversible loop system, involving rate (k_1, k_2, k_{-1}, k_{-2}) and acid dissociation (K_{a1} and K_{a2}) constants. It follows second order kinetics but can be conditioned to pseudo-first order kinetics; the concentration of the ferric ions was in excess over the concentration of the thiocyanate ions. The reactants are essentially colorless, while the main product, $[\text{Fe}(\text{OH}_2)_5\text{SCN}]^{2+}$, is dark red and absorbs readily at 450 nm. The detail scheme is given below:



The Reversible Formation of Iron (III) Thiocyanate Complex

THE RATE LAW

$$\frac{-d[\text{SCN}]}{dt} = k_1[\text{Fe}][\text{SCN}] + k_2[\text{FeOH}][\text{SCN}] - k_{-1}[\text{FeSCN}] - k_{-2}[\text{Fe}(\text{OH})\text{SCN}]$$

$$\frac{-d[\text{SCN}]}{dt} = \left(k_1 + \frac{k_2 K_{a1}}{[\text{H}^+]}\right) [\text{Fe}][\text{SCN}] - \left(k_{-1} + \frac{k_{-2} K_{a2}}{[\text{H}^+]}\right) [\text{FeSCN}]$$

$$k_{\text{forward}} = k_1 + \frac{k_2 K_{a1}}{[\text{H}^+]}$$

$$k_{\text{reverse}} = k_{-1} + \frac{k_{-2} K_{a2}}{[\text{H}^+]}$$

$$\frac{-d[\text{SCN}]}{dt} = k_f[\text{Fe}]_T[\text{SCN}] - k_r[\text{FeSCN}]$$

$$[\text{SCN}] = [\text{SCN}]_{\text{eq}} + x$$

$$[\text{FeSCN}] = [\text{FeSCN}]_{\text{eq}} - x$$

$$\frac{-dx}{dt} = (k_f[\text{Fe}]_T + k_r)x$$

$$\text{At equilibrium, } \frac{-d[\text{SCN}]}{dt} = 0$$

$$k_f[\text{Fe}]_T[\text{SCN}]_{\text{eq}} = k_r[\text{FeSCN}]_{\text{eq}}$$

x represents the displacement from equilibrium concentration, $[\text{SCN}]_{\text{eq}}$

$$\frac{-d[\text{FeSCN}]}{dt} = (k_f[\text{Fe}]_T + k_r)([\text{FeSCN}]_{\text{eq}} - [\text{FeSCN}]) \implies \ln\left(\frac{[\text{FeSCN}]_{\text{eq}}}{[\text{FeSCN}]_{\text{eq}} - [\text{FeSCN}]}\right) = (k_f[\text{Fe}]_T + k_r)t$$

$$A = \epsilon_{\text{FeSCN}}[\text{FeSCN}]l$$

$$\ln\left(\frac{A_{\text{eq}}}{A_{\text{eq}} - A}\right) = (k_f[\text{Fe}]_T + k_r)t$$

$$k_{\text{obs}} = \left(k_1 + \frac{k_2 K_{a1}}{[\text{H}^+]}\right) [\text{Fe}]_T + k_{-1} + \frac{k_{-2} K_{a2}}{[\text{H}^+]}$$

EXPERIMENT

1. The following reagents were made using DI water as solvent:

- For vials (Syringe 1): 2.0 M KNO_3 , 1.0 M HNO_3 , 0.10 M KSCN , 3.0×10^{-4} M KSCN , 0.40 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.80 M HNO_3 , 0.20 M

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ & 0.40 M HNO_3 (0.40 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.80 M HNO_3 mixed in 1:1 volumetric ratio)

- For Syringe 2: 1.0 M KNO_3 & $1.5 \cdot 10^{-4}$ M KSCN (2.0 M KNO_3 & $3.0 \cdot 10^{-4}$ M KSCN mixed in 1:1 volumetric ratio:



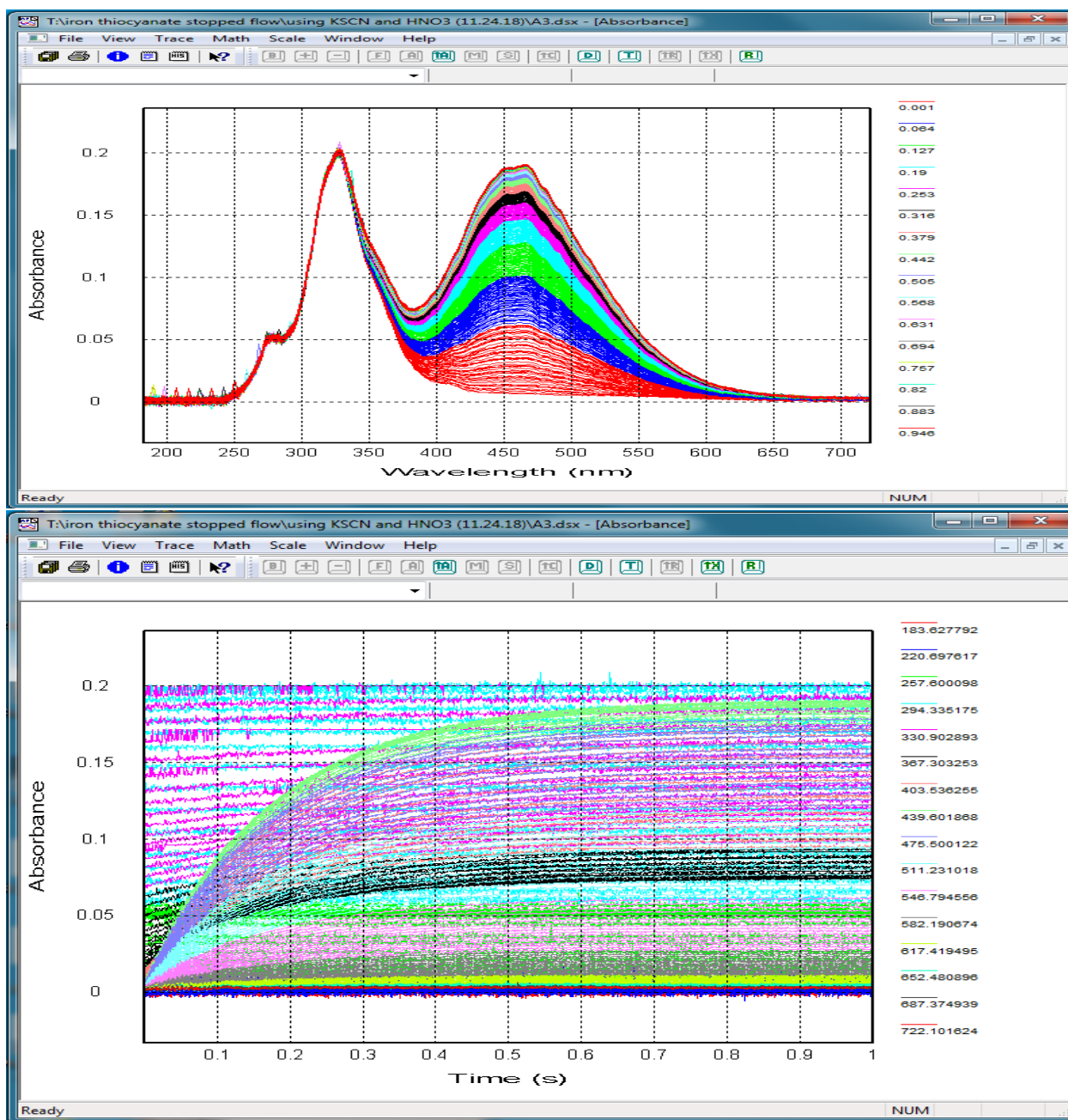
- 1. Three sets of vials were prepared as shown in the table (under ‘results’)¹.
 2. Photodiode Array, with 10 mm path length and 1.0 seconds timescale was used.
 3. Deionized water (DI) was used to record the baseline.
 4. One syringe had Fe^{3+} reagent (vial) while the other had SCN^- reagent. The syringes’ contents were mixed in 1:1 ratio by the Stopped-flow. Kinetic runs were performed for each vial and SCN^- reagent solution and the k values at 440 nm, 450 nm, and 460 nm were used in graphs and calculations.
 - ❖ For every run, a different syringe was used to avoid contamination and the system was flushed with DI water sufficiently between each run.

RESULTS AND DISCUSSIONS

The following table shows the contents of each Vial and the overall rate

Vials (Syringe 1)	0.2M Fe(NO ₃) ₃ x 9H ₂ O & 0.4M HNO ₃	1.0M HNO ₃	2.0M KNO ₃	[Fe ³⁺] in vials	[Fe ³⁺] in Stopped- flow after 1:1 mixing	[H ⁺] in vials	[H ⁺] in Stopped- flow after 1:1 mixing	k _{observed} at 450 nm (abbrev. k _{obs})
A1	250	1900	3850	0.005	0.0025	0.2	0.1	2.145583
A2	1000	1600	3400	0.02	0.01	0.2	0.1	3.620988
A3	2000	1200	2800	0.04	0.02	0.2	0.1	5.727846
B1	250	3900	2850	0.005	0.0025	0.4	0.2	1.792967
B2	1000	3600	2400	0.02	0.01	0.4	0.2	2.922793
B3	2000	3200	1800	0.04	0.02	0.4	0.2	4.444477
C1	250	5900	1850	0.005	0.0025	0.6	0.3	1.626882
C2	1000	5600	1400	0.02	0.01	0.6	0.3	2.735441
C3	2000	5200	800	0.04	0.02	0.6	0.3	4.053198

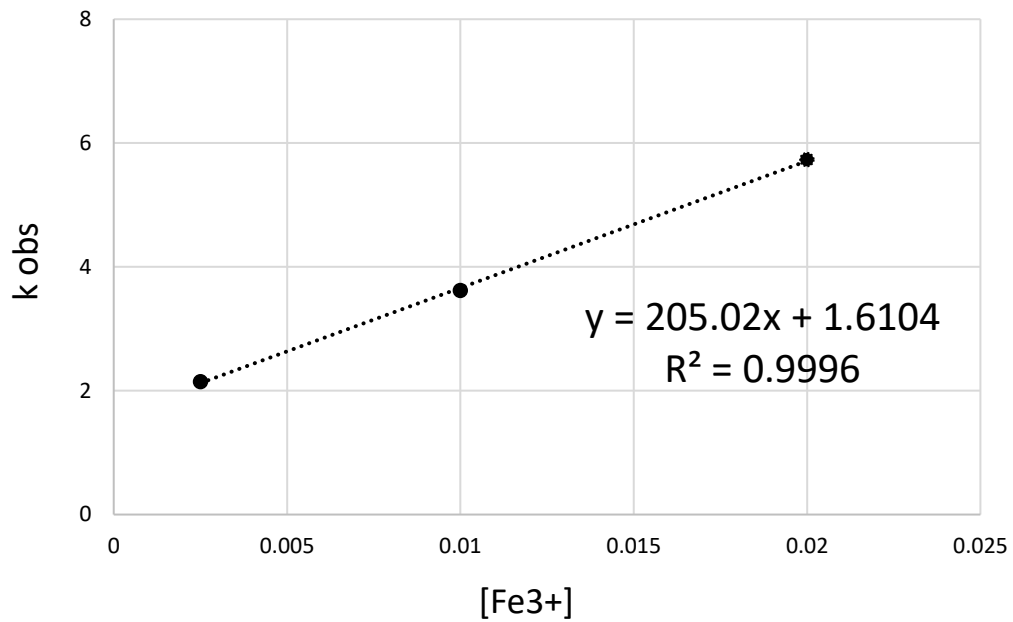
constants (k_{observed}) for the formation of Iron (III) thiocyanate complex for different Fe³⁺ and H⁺ concentrations. For simplicity, only the rate constants determined at 450 nm are stated in the table below. Comparable data was also obtained at 440 & 460 nm.



The two images show the display on the Pro-Data SX Program for Vial A3. The instrument took **1000 points in 1.0 second** over a range of wavelengths using Photodiode Array.

The k_{observed} values (y-axis) were plotted against the corresponding $[\text{Fe}^{3+}]$ (x-axis) to yield k_f and k_r for all three sets of vials. It should be noted that the Fe^{3+} and H^+ concentrations were halved after mixing in stopped-flow.

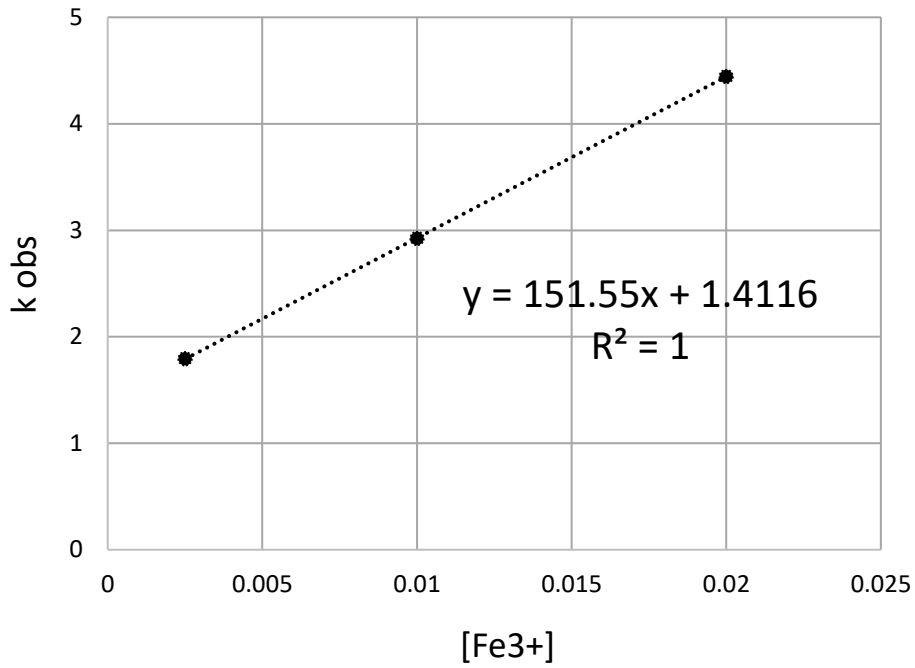
k obs vs. $[\text{Fe}^{3+}]_{\text{stopped-flow}}$
A1-A3



$m = k_f = 205.02$

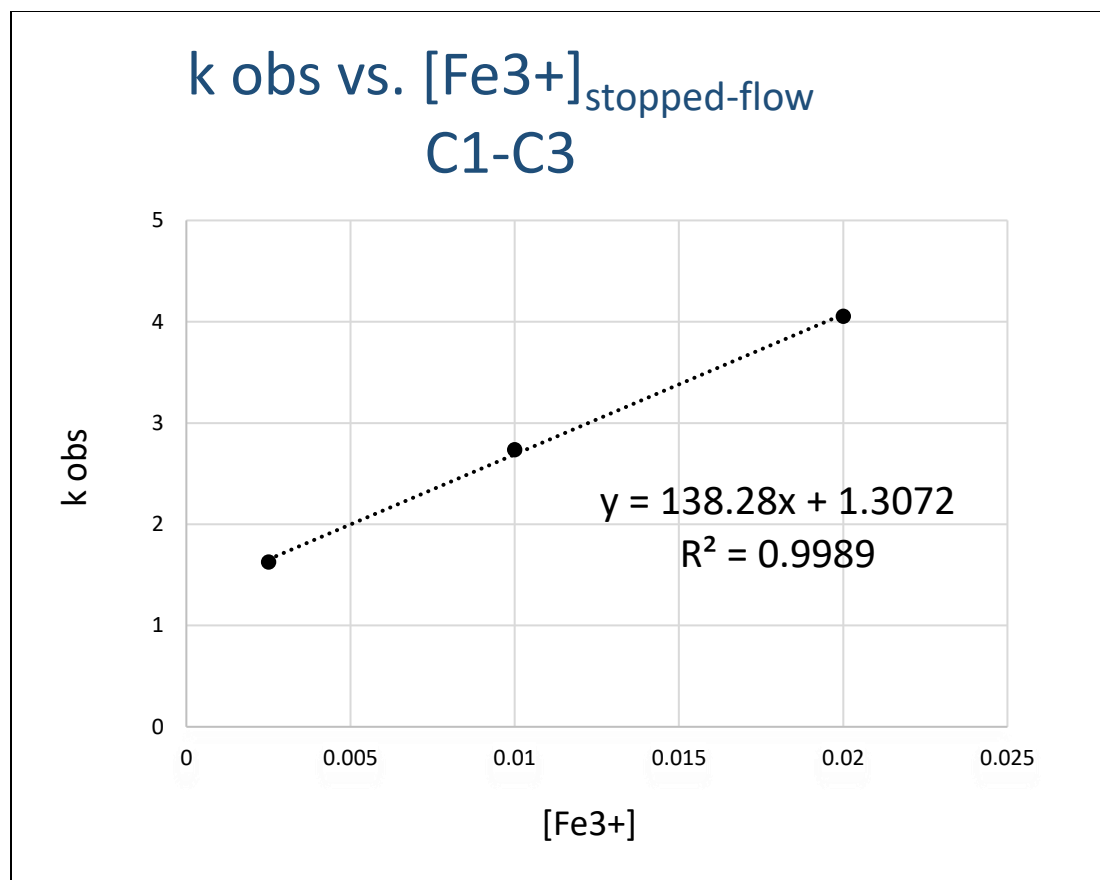
$\text{int} = k_r = 1.6104$

**k obs vs. $[\text{Fe}^{3+}]_{\text{stopped-flow}}$
B1-B3**



$m = k_f = 151.55$

$\text{int} = k_r = 1.4116$

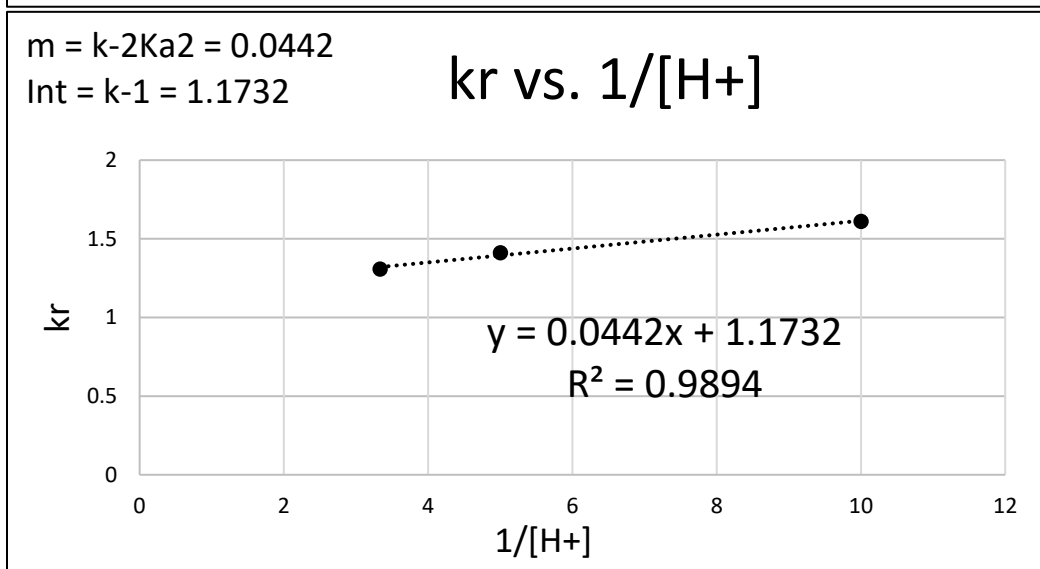
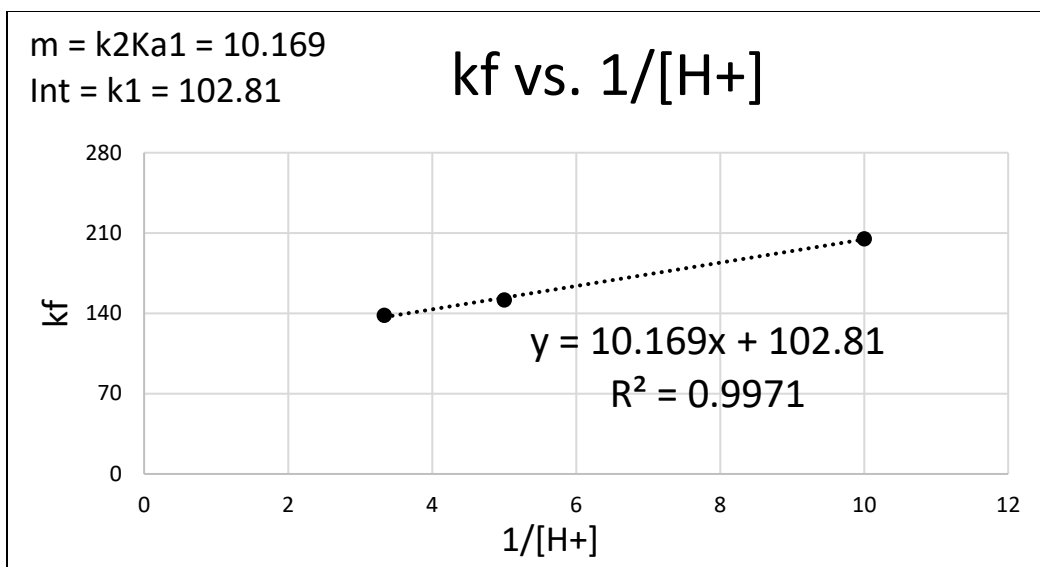


$$m = k_f = 138.28$$

$$\text{int} = k_r = 1.3072$$

The k_f and the k_r values for the 3 sets were plotted against the reciprocal of H^+

Set	$[\text{H}^+]_{\text{stopped-flow}}$ (M)	$1/[\text{H}^+]$ (M^{-1})	k_f	k_r
A	0.1	10	205.02	1.6104
B	0.2	5	151.55	1.4116
C	0.3	3.33333	138.28	1.3072



The slopes and intercepts from the graphs and the literature values of K_{a1} and K_{a2} (as reported in the research papers used for reference^{1,2}) were used to calculate k_1 , k_{-1} , k_2 , and k_{-2} values for the formation of Iron (III) Thiocyanate Complex. In the table below, all the calculated rate constants for 440 nm, 450 nm, and 460 nm are reported for this experiment, along with the reported ones from the two research papers^{1,2}.

	440 nm	450 nm	460 nm	Experiment by Mieling and Pardue (Anal. Chem. 1978) at 450 nm	Experiment by Clark (J. Chem. Educ 1997) at 450 nm
k ₁ [M ⁻¹ s ⁻¹]	103.73	102.81	103.49	97	109
k ₂ [M ⁻¹ s ⁻¹]	6018.48485	6163.030303	6068.48485	9600	8020
k ₋₁ [s ⁻¹]	1.1678	1.1732	1.1667	0.75	0.79
k ₋₂ [s ⁻¹]	703.076923	680	703.076923	2200	2630
Ka ₁ (literature)				0.00165 M	0.00204 M
Ka ₂ (literature)				0.000065 M	0.000065 M

CONCLUSION

The calculated rate constants (k₁, k₋₁, k₂, and k₋₂) were compared to the reported values. The slight discrepancies were noticed due to the complexity of the formation of the Iron (III) Thiocyanate complex in the presence of Nitrate-nitric acid (NO₃⁻/H⁺) combination instead of Perchlorate-perchloric acid (ClO₄⁻/H⁺) combination⁴; the apparent discrepancies could be attributed to the different strength of ion-pairing effects of perchlorate ion and nitrate ion. Further studies are needed to quantitatively assess the correlation between ion-pair effects and the rate constants (k₁,k₂,k₋₁,k₋₂) for such Fe(III)-SCN system. We also detected that an increase in [Fe³⁺] led to an increase in k_{obs}, while an increase in [H⁺] that led to a decrease in k_{obs}. These observations align with the reported results.

Nevertheless, as a sophomore student at MCC, I was thrilled to learn this sophisticated stopped-flow technique, observe the trend of a pseudo-first order kinetic reaction, and deal with the math of complex kinetics.

REFERENCES

1. Clark, C. R. (1997). A Stopped-Flow Kinetics Experiment for Advanced Undergraduate Laboratories: Formation of Iron (III) Thiocyanate. *Journal of Chemical Education*, 74(10), 1214. doi:10.1021/ed074p1214
2. Mieling, G. E., & Pardue, H. L. (1978). Evaluation of a computer-controlled stopped-flow system for fundamental kinetic studies. *Analytical Chemistry*, 50(9), 1333-1337. doi:10.1021/ac50031a036
3. Applied Photophysics Ltd. User Manual SX20 Stopped Flow Spectrometer. Online version: http://www.biophysics.bioc.cam.ac.uk/wp-content/uploads/2011/02/SX20-User-Manual_1.00.pdf
4. Both the experiments described in the research papers used Perchlorate salts and Perchloric Acid. However, due to safety regulations, we were unable to use them.

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