19. Practice: Kinetic study of iron(III) – thiocyanate reaction by stopped flow method

19.1 Introduction

Chemical reaction were classified into two main groups according to their rates. The first group involved the reactions the rate of which can be determined and the second those the rate of which (due to being extremely low or fast) cannot. Rapid reaction are the ones that proceed completely within one second. The co-called stopped flow method gives a way to measure such fast reactions. The stopped-flow spectrophotometer contains a special mixing chamber in which the mixing time is very short – in the range of 3 ms, typical for enzymatic reactions.

In the practice you will study the following reaction:

$Fe^{3+} + SCN^{-} = FeSCN^{2+}$

In aqueous solution, Fe^{3+} does not exist because of deprotonation of the aquacomplex. Likewise, $FeOH^{2+}$ will denote the deprotonated form. The iron(III) ion forms an intense reddish brown colored complex with a maximal coordination number of six. In sufficiently dilute solutions, and at high Fe(III) excesses, practically only the first coordination step takes place within fractions of seconds. The formed complexes have intense light absorption near 460 nm. The progression of the reaction can be monitored by the absorbance change. Due to the ease of the reaction mechanism and the reproducibility of the reaction it is used for the calibration of stopped-flow photometers.

19.2 Literature background

In aqueous solutions containing iron(III) and SCN^{-} ions, the following equilibrium complexation reactions take place (the equilibrium constants are denoted as K, while the standard concentration values of 1 mol/dm^3 as $c^{\ominus}$):

$$Fe^{3+} + SCN^{-} \underset{k/K_1}{\overset{k}{\rightleftharpoons}} FeSCN^{2+} \qquad K_1 = \frac{[FeSCN^{2+}]\cdot c^{\ominus}}{[Fe^{3+}]\cdot[SCN^{-}]} = 146$$

$$FeSCN^{2+} + SCN^{-} \rightleftharpoons Fe(SCN)_2^{+} \qquad K_2 = \frac{[Fe(SCN)_2^{-}]\cdot c^{\ominus}}{[FeSCN^{2+}]\cdot[SCN^{-}]} = 15,5$$

$$Fe(SCN)_{i-1}^{(4-i)+} + SCN^{-} \rightleftharpoons Fe(SCN)_i^{(3-i)+} \qquad K_i = \frac{[Fe(SCN)_i^{(3-i)+}]\cdot c^{\ominus}}{[Fe(SCN)_{i-1}^{(4-i)+}]\cdot[SCN^{-}]},$$

where i can vary between 3 and 6. Because K_1 is larger than any other equilibrium constants, practically the only species formed is the mono-thiocyanate if iron(III) ions are in a great excess compared to thiocyanate ions. In this case, only the first equilibrium should be taken into account. If the pH of the solution is greater than 1-1.5, the iron(III) aquacomplex deprotonates

significantly and may also form oligonuclear complexes. These processes cannot be described with the above equations, and the consideration of the following processes are also necessary:

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad K_H = \frac{[FeOH^{2+}]\cdot[H^+]}{[Fe^{3+}]\cdot c^{\ominus}} = 2,05\times10^{-3}$$

$$2\,FeOH^{2+} \rightleftharpoons Fe_2(OH)_2^{4+} \qquad K_D = \frac{[Fe_2(OH)_2^{4+}]\cdot c^{\ominus}}{[FeOH^{2+}]^2} = 390$$

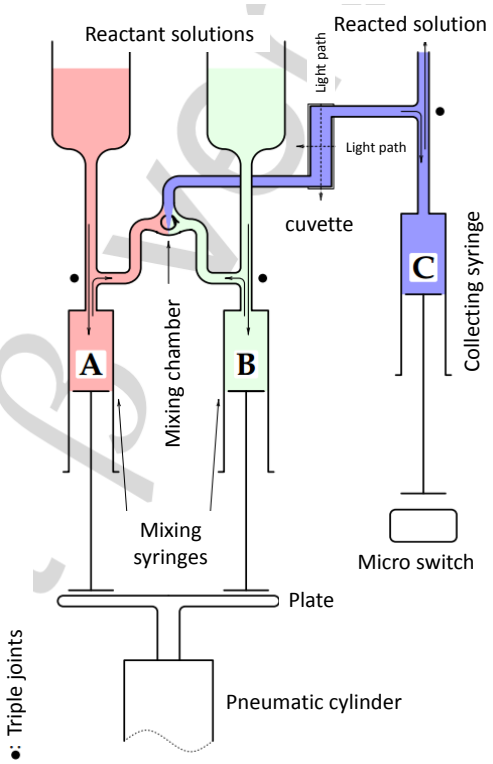
The following rate equation has been found for the reaction:

$$\frac{d\,[FeSCN^{2+}]}{dt} = k_1\cdot[Fe^{3+}]\cdot[SCN^-] + \frac{k_2\cdot[Fe^{3+}]\cdot[SCN^-]}{[H^+]} - \frac{k_1}{K_1/c^{\ominus}}\cdot[FeSCN^{2+}] - \frac{k_2\cdot[FeSCN^{2+}]}{K_1/c^{\ominus}\cdot[H^+]}$$

and the simple correlation between the formal second order rate constant and k_1 is the pH-independent and k_2 is the second order rate constant that is proportional to the hydroxide ion concentration (inversely proportional to the hydroxonium ion concentration):

$$k = k_1 + \frac{k_2}{[H^+]}$$

19.3 The stopped flow technique



Only a few companies produce commercially available stopped-flow devices. These are usually single beam photometers in which the absorbances of the samples are compared to a previously measured absorbance of a reference sample. The monochromatic light is obtained by an optical grating and is transferred via an optical glass cable into the thermostated reactor (mixture chamber) made of quartz. Two pneumatic syringes (A and B) are used to load the reagents into the mixture chamber as shown by the scheme of the instrument. The mixing chamber is connected to a cell and another (C) syringe. If a solution is injected from (A) and (B) through the cell, then the new solution pushes the previous portion forward until the syringe (C) reaches a micro switch, which stops the flow and initiates the recording of the absorbance-time curve. During the injection of the solutions into the mixture chamber, the solution is first "cut" into distinct (several microliters or lower) volumes that are injected in an alternating manner from syringes (A) and (B). In the next stage, these tiny liquid elements are completely homogenized because the turbulent flow and the diffusion equalizes their concentration difference.

TASKS for WEEK1

1) Prepare a solution series according to the following instructions and table below.

Sorszám	1	2	3	4	5	6	7	8	9	10	11	12	13
Sorozatjel	a	a	a	a	b	b	b	b	c	c	c	c	a, b, c
$[Fe^{3+}]_0$	f1	f2	f4	f5	f3	f3	f3	f3	f3	f3	f3	f3	f3
$[SCN^-]_0$	s3	s3	s3	s3	s1	s2	s4	s5	s3	s3	s3	s3	s3
$[H^+]_0$	h3	h3	h3	h3	h3	h3	h3	h3	h1	h2	h4	h5	h3

You have 26 volumetric flasks of 50 mL volume. You have to prepare two 13-membered series of solutions.

The first series contains the iron salt, the acid and the background salt.

The second series contains the thiocyanate salt and the background salt.

A) The iron salt will be $Fe(NO_3)_3$. The Fe^{3+} concentration (f1-f5) needs to be varied between 0.02 and 0.002M so that it changes uniformly within this range.

B) The thiocyanate salt will be NaSCN or KSCN. Its concentration (s1-s5) needs to be varied between 0.002 and 0.0002M so that it changes uniformly within this range.

C) The added acid will be nitric acid. The hydroxonium ion concentration must range between 0.8 and 0.02M but the range may change according to the instructor.

D) The ionic strength also affects the rate of the reaction so it must be kept constant with an inert, well soluble salt. The ionic strength will be set by $NaNO_3$ to a value between 0.6-1 M.

It is worth preparing a table with the necessary concentrations and ionic strengths and volumes of stock solutions. NOTE the following:

- the iron(III) stock solution must contain the acid at least in a 0.005M concentration in order to avoid hydrolysis and precipitation. If this step is forgotten, the iron(III) ions (originally in the form of aquacomplexes) will deprotonate and oligonuclear iron species will form, that will not undergo the same complex formation reaction with the thiocyanate ions.

- the concentrations in the real reaction system (in the mixture chamber) may be different than those in the solution series because two liquid aliquots are mixed.

- Analytical balance must be used for weigh-in. Ferric nitrate is hygroscopic and the exact concentration must be determined by complexometric titration. The measurement plan should be shown to the instructor before the experiments.

2) Complexometric determination of iron(III) concentration

Direct titration can be used for determining the Fe(III) concentration by using EDTA ligand that forms very stable chelate complex with 1:1 stoichiometry at pH of ca. 2-3 (acidic conditions are used to avoid hydrolysis and precipitation. Tiron or sulfo-salycilic acid can be

used for the indication of the equivalence point: the iron(III) ions form violet complexes with sulfo-salycilic acid and blue complex with tiron. In both cases, the initially colored complex solutions of iron(III) ions must be titrated until they are fully decoloured. Decoloration occurs because the indicator-Fe(III) complex undergoes ligand exchange because the added EDTA molecules have higher affinity to coordinate to the metal ion and during titration they replace the indicator ligands from their complexes.

If needed, we check the pH of the solution by HCl or NaOH solution (pH checked by indicator paper) and upon addition of 3 droplets of indicator solution, the solutions are warmed up to 40-50 ^{o}C and they are titrated with EDTA solution from the burette until the colour change occurs.

TASKS for WEEK2 AND EVALUATION

1) Prepare the solutions containing the reactants and additives (salt and acid for the iron(III) ions and salt for the thiocyanate ions) from the stock solutions.

2) Perform the kinetic measurements according the description of the instrument.

3) Evaluate the obtained experimental curves by the software using nonlinear curve fitting. The main result is the formal second order rate constant (with the respective errors), which must be noted in the report and used for the calculation of the k1 and k2 rate constants, which will be obtained from plotting the k as a function of the inverse of the hydroxonium ion concentration.

4) Tabulate the result as the following: initial Iron(III) concentration, initial thiocyanate concentration, initial hydroxonium ion concentration, ionic strength, and the k values.

Short test questions (some may not be explicitly found in the description – then consult textbooks or undisputed Wikipedia content)

WEEK 1

1) What kind of complex formation processes can occur in the highly acidic solutions containing iron(III) and thiocyanate ions?

2) What kind of condition must be fulfilled to ensure that only complexes of a 1:1 composition are formed?

3) Write down the studied reaction and specify the color of the formed species!

4) How does the rate constant of the studied reaction change with the hydroxonium ion concentration?

5) Shortly describe the stopped-flow technique!

6) Why do you need to add a small (0.005 M) acid when you prepare the stock solution of the iron(III) salt?

WEEK 2

1) How would you determine the iron(III) content of a solution by complexometry?

2) Note the essence of the stopped flow method in several sentences!

3) Draw a schematic picture of the stopped-flow instrument!

4) What is the correlation between the apparent rate constant and the pH?

5) Calculate the weight of $Fe(NO3)_3$ *9 H_2O needed to prepare 250,0 mL of 0.04 M Fe(III) stock solution! $A_r(Fe) = 55.85$, $A_r(O) = 16.00$, $A_r(N) = 14.01$, $A_r(H) = 1.01$

INSTRUMENTAL OPERATIONS FOR STOPPED FLOW SPECTROPHOTOMETER

1) Turn on the mains switch at the rear side of the grey box, down to the bottom.

2) Turn on the visible lamp on the front panel of the grey box.

3) The PC must be booted under the DOS operation system choosing the "Command prompt only" and then the "for….for RKBIN mainly" menu points.

4) load the measurement and evaluation software with the command "rk", and omit the choice of the printer by "Esc"

Settings after the preparation of solutions

1) The mechanic unit is first flushed with distilled water. For that, the triple-way switch is set to "FLUSH". In this setting, the injected solutions flow directly to the waste beaker without pushing the third syringe.

2) Screw the two, black dual-way switches at the front of the instrument to the "FILL" setting. Fill the two plastic syringes at the top of the instrument with water. Note that they must always contain liquids (water or the reactant solutions) to avoid bubble formation in the system.

3) Draw liquid into the mixing syringes made of glass by dragging downwards the metal pistons simultaneously, holding them together by the movable black plate. Beware that the liquid level should not fall below the part of the plastic syringe where it narrows near its bottom. After the glass syringes were filled, the dual-way black switches are switched to "DRIVE" and the content of the glass syringes are flushed to the waste beaker. This operation is repeated multiple times with several milliliters of water.

If the liquid levels in the plastic syringes are not the same, the pistons must be moved individually making sure that the other container is not changing position.

4) We need to set the baseline and the dark current in the software, for this go to "Acquire Menu/Live Mode". Then increase the voltage of the photoelectron multiplier by "Voltage adjust" button until the absorbance displayed on the screen (AU) reaches zero. Next, the dark current shutter at the rear side of the instrument is pushed to cut the beam path and press twice the "-" button on the keyboard. Then remove the shutter and retune the zero baseline and press twice "+" button.

5) Quitting "Live mode" by ESC, we need to set a directory name in the "Storage menu", where we store the data. ("Change directory"). We also set the first six characters of the measurement files ("Change Series Name") "For all buffers".

6) Note that the measurement data are saved to "buffers". Their numbers are noted in the screen and changes automatically. Always note down for yourself which buffer refers to which solution pair so that you can withdraw the correct data during evaluation.

Measurements

1 Fill the plastic syringes with the reactant solutions. Add 3-4 mL to each after you are sure that they contain water only at the very bottom part and the liquid meniscus in located where the syringe is narrowed. In this way, one can avoid the dilution of the solutions.

2 Flush the cell with several portions of solutions (three-way switch is at “FLUSH”). Then the syringes are completely filled again, the liquid content (if there is any) of the collecting syringe is emptied into the waste beaker (the three-way switch is at “WASTE”). Both switches are then put to “DRIVE”.

3 In the software, go to “Live mode”. Press the space on the keyboard, and by gentle but fast push-up, the solutions are “shot” together, and the third syringe reaches a button due to which the flow stops and starts recording the absorption. The software then quickly plots the measured voltage-time curve.

4 After measurement, we set the three-way switch to “WASTE”, empty the collecting syringe and then we turn it back to “DRIVE”. Then the measurement should be repeated several (4-5) times. Later on we will evaluate these repeated experiments and average the fitted rate constants.

5 Repeat the measurements with the other solution pairs!

Turning the instrument off

1) First we flush the plastic syringes with water and flush also the whole mechanic unit by water. Leave ca. 3-3 mL water in each plastic syringe.

2 Screw down the voltage button on the grey box to zero, turn of the visible lamp and turn of the mains switch at the rear panel.

Evaluation of rate constants

1) Return to main menu by ESC

2) Getting to “Analysis Menu/Fit Menu” the kinetic curves can be fitted and the rate constants are obtained. Only the kinetic data that are displayed can be evaluated. To load another curve, go to “Display menu/Select buffer”.

3) In the “Fit menu” and then “Equation menu”, choose the proper curve shape (here: “1 exp +off”, that is, an exponential curve with a possible baseline.

4) Then mark the first and the last measurement point that will be taken into account for the curve fitting by “End Cursor” and “Start cursor”. “Run fit” then performs the fitting procedure and plots the results. These, especially the rate contant, should be noted.

5) PC is turned off manually after quitting the software.