

DETERMINATION OF STABILITY CONSTANTS AND OPTIMAL SYNTHESIS CONDITIONS FOR THIOCYANATE COMPLEX OF FE (III)

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Abstract:

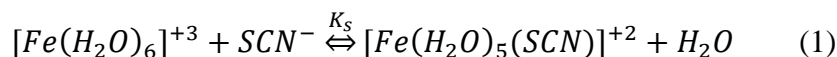
In this paper the formation of thiocyanate complex of Fe(III) was studied. We proposed to determine the optimal formation condition into a synthesis from FeCl₃ and KSCN mixture. Achieving of thiocyanate complex was favored by room temperature, pH 2 and a reaction time by minimum 50 minutes. It was recommended using of HCl for acidulation of reaction medium and it was indicated to avoid sulfuric acid and acetate acid. Stability constant recorded the highest value to pH 2 and decreasing at pH growth. The study was accomplished in 1-4 pH range.

Key words: thiocyanate, iron, stability constant, spectrophotometry

INTRODUCTION

Substitution reaction (1) between iron (III) aquacomplex and thiocyanate took place just to an equilibrium

point, defined by a stability constant, noted in equation (2) [1-5]. Equilibrium concentrations of both iron and thiocyanate were characterized by equations (3) and (4):



$$K_s = \frac{[Fe(H_2O)_5(SCN)]^{+2}]_{eq}}{[Fe^{+3}]_{eq} \cdot [SCN^-]_{eq}} \quad (2)$$

$$[Fe^{+3}]_{eq} = [Fe^{+3}]_{initial} - [Fe(H_2O)_5(SCN)]^{+2}]_{eq} \quad (3)$$

$$[SCN^-]_{eq} = [SCN^-]_{initial} - [Fe(H_2O)_5(SCN)]^{+2}]_{eq} \quad (4)$$

External factors like pH, temperature, reaction time, reaction medium (counterions, solvent) may involve in the reaction evolution. Such as we proposed to determine the optimal synthesis conditions of complex [Fe(H₂O)₅(SCN)]²⁺ from FeCl₃ and KSCN: pH, type of acid from reaction medium, reaction time and work

temperature. More we calculated the stability constant for this reaction conditions [6,7].

Materials and methods

All substances used in our experiments were analytical purity and the solutions were prepared with distilled water. All determinations

were effectuated with a spectrophotometer T60.

pH influence in $[Fe(H_2O)_5(SCN)]^{2+}$ synthesis

The study was realised for pH values from 1 to 4. In four tubes 0.25 mL 0.02 M $FeCl_3$ and 0.25 mL 0.02 M KSCN were added. The pH control from 1 to 4 was realized with HCl solution by different concentration and distilled water just a final volume by 5 mL in all four samples prepared. Absorbances of solutions were measured with spectrophotometer at 470 nm, after 30 minutes reaction at room temperature beside a blank (0.25 mL 0.02 M $FeCl_3$ solution raised with distilled water to 5 mL). Results were recorded in Fig. 1. The higher absorbance was determined for reaction mixture prepared to pH 2. More, in range pH 1-4, the absorbance values of $[Fe(H_2O)_5(SCN)]^{2+}$ decreased from pH 2 to pH 4 [8].

In this experiment, we prepared four samples mixture reaction like in previous study at pH 2, with the difference that the acid added was not the same in all sample tubes (Table 1).

Absorbances were measured after 30 minutes reaction at room temperature at 470 nm using the blank solution from Table 1.

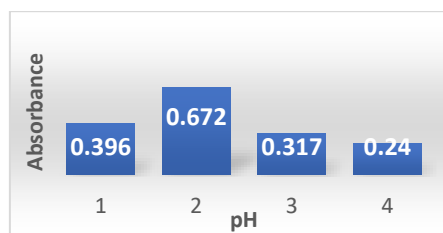


Fig. 1. pH influence in $[Fe(H_2O)_5(SCN)]^{2+}$ synthesis

The influence of the acid nature in $Fe(H_2O)_5(SCN)]^{2+}$ synthesis

At pH=2, the highest value of absorbance was recorded for reaction mixture prepared in acetic acid solution, but in this case the increasing of absorbance may be due to suppose of absorbance value of red solution from very stable complex $[Fe_3(\mu_3-O)(OAc)_6(H_2O)_3]^+$. In these conditions, the synthesis of $[Fe(H_2O)_5(SCN)]^{2+}$ was favored by HCl presence and was the worst in H_2SO_4 .

Table 1. The reaction mixtures prepared in different acid medium at pH 2 for $[Fe(H_2O)_5(SCN)]^{2+}$ synthesis

Reaction medium	0.02 M $FeCl_3$ (mL)	0.02 M KSCN (mL)	Vacid/Vwater (mL)	Absorbance
HCl	0.25	0.25	4.5	0.405
H_2SO_4	0.25	0.25	4.5	0.05
HNO_3	0.25	0.25	4.5	0.286
$H_3C-COOH$	0.25	0.25	4.5	0.415
Distilled water	0.25	0	4.75	0

Influence of temperature in $[Fe(H_2O)_5(SCN)]^{2+}$ synthesis

In five samples tube were added reaction mixtures between 0.02 M $FeCl_3$ and 0.02 M KSCN prepared like in Table 1 in HCl solution to pH 2. Each samples was put to react for 30 minute at 20 °C, 40 °C, 60 °C, 80 °C and 100°C. After reaction time, samples were could and the absorbance were determined at 470 nm related to the same blank. The highest values of absorbance were recorded at 20-40 °C and the absorbance decrease to increasing of temperature, so it was seen in Fig. 2 [9].

Influence of the reaction time in $[Fe(H_2O)_5(SCN)]^{2+}$ synthesis

A reaction mixture was prepared exactly in previous experiment and was stated measured the absorbance values at 470 nm between 5-120 minutes, every five minutes. The absorbance started to be constant

from 50 minutes by reaction and kept unmodified after 24 hours (Fig. 3) [10].

Determination of the stability constant for $[Fe(H_2O)_5(SCN)]^{2+}$ at different pH

Values of absorbance for different complex concentrations resulted from reaction mixtures between 0.002 M KSCN and 0.2 M $FeCl_3$ were recorded in Table 2. Measurements of absorbances were effectuated after 30 minutes at room temperature at 470 nm to blank [11-13].

In Fig. 4, the equation from the linear variation of absorbance with complex concentration was determined and was used for calculated of $[Fe(H_2O)_5(SCN)]^{2+}$ concentration to equilibrium for reaction mixtures mentioned before in Table 3.

In Table 4, the values of stability constant (K_s) for each reaction mixture studied were determined with the help of equation (1), (2) and (3). For the median value of constant stability was calculated $\log K_s$.

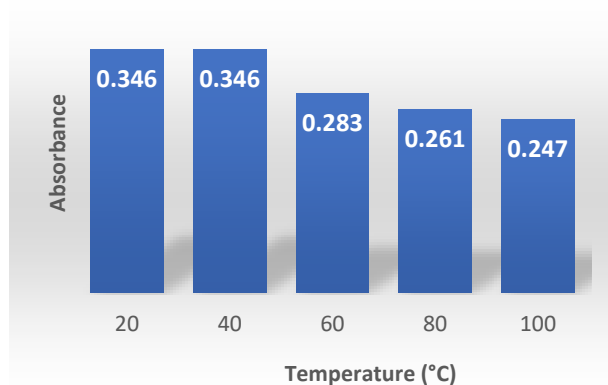


Fig. 2 Influence of the temperature in $[Fe(H_2O)_5(SCN)]^{2+}$ synthesis

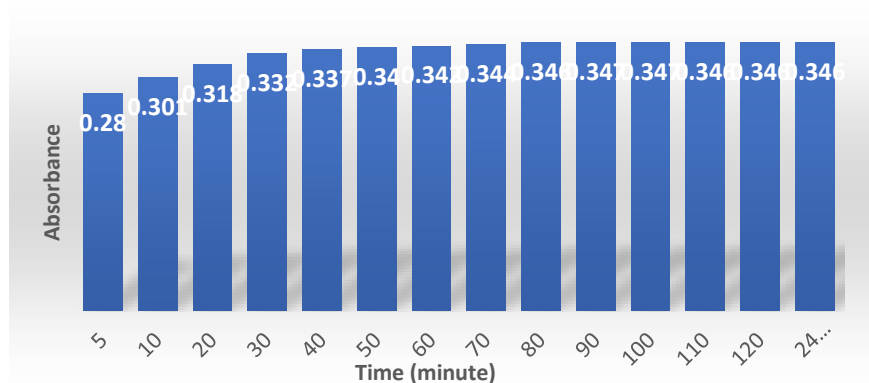


Fig. 3. Variation in time of $[Fe(H_2O)_5(SCN)]^{2+}$ absorbance

Table 2. Determination of absorbance for different $[Fe(H_2O)_5(SCN)]^{2+}$ concentrations to pH 1

0.002M KSCN (mL)	0.2M FeCl ₃ (mL)	HCl (mL)	$[Fe(H_2O)_5(SCN)]^{2+}$ (mmol/L)	Absorbance
0	1,25	3,75	0	0
0,05	1,25	3,7	0,02	0,078
0,1	1,25	3,65	0,04	0,146
0,2	1,25	3,55	0,08	0,296
0,3	1,25	3,45	0,12	0,432
0,4	1,25	3,35	0,16	0,574
0,5	1,25	3,25	0,2	0,735

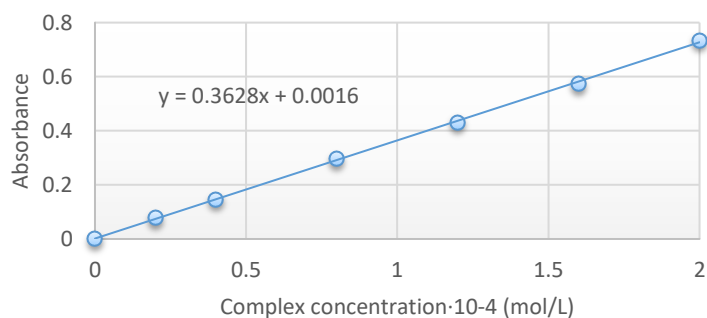


Fig. 4. Determination of equation from linear variation of absorbance with $[Fe(H_2O)_5(SCN)]^{2+}$ concentration to equilibrium at $pH=1$

Table 3. Determination of $[Fe(H_2O)_5(SCN)]^{2+}$ concentration at equilibrium to pH 1

KSCN 0,02M (mL)	FeCl ₃ 0,02M (mL)	HCl (mL)	Absorbance	$[Fe(H_2O)_5(SCN)]^{2+} \cdot 10^{-4}$ (mol/L)
0,05	0,25	4,7	0,195	0,537
0,1	0,25	4,65	0,387	1,177
0,15	0,25	4,6	0,598	1,648
0,2	0,25	4,55	0,815	2,246
0,25	0,25	4,5	1,027	2,831
0,5	0	4,5	0,05	

Table 4. Determination of stability constant of $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$ to pH 1

Initial		Equilibrium			
$[\text{SCN}^-]$ (mmol/L)	$[\text{Fe}^{3+}]$ (mmol/L)	$[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$ (mmol/L)	$[\text{SCN}^-]$ (mmol/L)	$[\text{Fe}^{3+}]$ (mmol/L)	K_s
0.2	1.0	0.0537	0.1435	0.9435	396.63
0.4	1.0	0.1177	0.2795	0.8795	478.8
0.6	1.0	0.1648	0.4214	0.8214	486.5
0.8	1.0	0.2246	0.5616	0.7616	525.12
1.0	1.0	0.2831	0.7169	0.7169	547.33
					486.876
					$\log K_s = 2.687$

Stability constants were calculated for similar reaction mixtures in HCl solution prepared at room temperature but at different pH values. Absorbance of all these solutions were found at 470 nm after 30 minutes.

The values of stability constants and $\log K_s$ from these conditions were noted in Table 5. The highest stability constant was recorded at pH 2, in concordance with data resulted from influence pH study.

Table 5. The values of stability constant of $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$ at different pH

pH	K_s	$\log K_s$
1	486.876	2.687
2	917.52	2.963
3	403.183	2.606
4	202.66	2.307

CONCLUSION

The synthesis of $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$ from a mixture between FeCl_3 and KSCN took place better in HCl solution, to pH 2, at room temperature after 50 minutes of reaction.

Following the variation of $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$ stability in time indicated touching of the equilibrium after 50 minutes and preservation of this for 24 hours surely.

The synthesis of $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$ from FeCl_3 and KSCN is recommended to be effectuated in HCl solution and avoided using of sulfuric acid or acetate acid.

Determination of stability constant to different pH values indicated a highest value at pH 2 and a decreasing at pH growing.

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