

An investigation of the Fe^{3+} -sulphonated pyrogallol system in aqueous solutions

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The electrochemical behaviour of the Fe^{3+} -sulphonated pyrogallol (SP) complex was investigated and its composition and stability constants were determined at pH 2.30. It was found by voltammetric and spectrophotometric measurements that Fe^{3+} and SP form a complex of the ML_2 type, which is relatively stable during the first 30 minutes. The optimal pH value for complex formation is between 2.30 and 2.80. The relative stability constants determined by voltammetric and spectrophotometric measurements are $\log \beta_2 = 5.08 \pm 0.26$ and $\log \beta_2 = 6.31 \pm 0.04$, respectively.

Keywords: cyclic voltammetry, spectrophotometry, Fe^{3+} ions, complex, sulphonated pyrogallol.

INTRODUCTION

The system metal–organic ligands in aqueous solution has been widely investigated, but very few data are related to the behaviour of Fe^{3+} ions with ligands of biologically active substance.^{1–5} Ferric ions form a complex $[\text{Fe}(\text{C}_6\text{H}_5\text{O})]^{2+}$ with monohydroxybenzen in aqueous solution⁴ in the pH range from 1.5 to 2.1. The stability constant of the complex for ionic strength $I = 0.3$ is $\log \beta = 9.78$. It is also well known that Fe^{3+} ions form a complex of type $[\text{Fe}(\text{O}_3\text{SC}_6\text{H}_3(\text{O})\text{COO})_3]^{6-}$ with sulphosalicylic acid in neutral and alkaline solution, with hydrolysis constant $\text{p}K_h = -42$.

Tiron (1,2-dihydroxybenzen-3,5-disulphonate) is a ligand which belongs to the group of sulphonated phenols and which forms complexes with Fe^{3+} ions: the ratio $\text{M:L}=1:1$ is found for $\text{pH} < 5.6$, $\text{M:L}=1:2$ for pH between 5.7 to 6.9 with a conditional stability constant $\log \beta_2 = 14.88$. At $\text{pH} > 7.0$ Fe^{3+} ions and tiron form a complex of the ML_3 type⁶ whose conditional stability constant is $\log \beta_3 = 19.14$.

Sulphonated phenol forms a complex of the $[\text{Fe}(\text{C}_6\text{H}_4\text{OHSO}_3)]^{2+}$ type⁷ with Fe^{3+} ion in pH range from 2.95 to 3.60 whose stability constant is $\log \beta = 3.95$.

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Sulphonated 1-naphthol forms the complex $[\text{Fe}(\text{C}_{10}\text{H}_6\text{OHSO}_3)_2]^+$ in the pH range from 1.87 to 3.53 with a stability constant⁷ $\log \beta = 7.78$. Sulphonated pyrogallol^{8,9} forms a complex with Fe^{3+} ions in 50 % ethanol with a ratio M:L=2:1. Data about the formation of complexes of Fe^{3+} ions with sulphonated pyrogallol in aqueous solutions have not been found in the literature. Other data of Fe^{3+} or Fe^{2+} complexes with simple sulphonated phenols have not been found in the literature.

EXPERIMENTAL

Apparatus

The following instruments were used:

- hardware and software for electrochemical investigations by the cyclic voltammetric method manufactured in the laboratories of the Faculty of Metallurgy and Technology and Faculty of Electric Engineering, Podgorica, "PKS system",
- UV-VIS spectrophotometer CARY 17D with 1 cm quartz cells,
- UV-VIS spectrophotometer JENWAY 6405,
- analytical balance METTLER H54AR,
- pH-meter PHM 64 Radiometer Copenhagen,
- universal thermostat type 10 MLW WHA 4 WEB Prüfgärete-Werk.

Reagents and solutions

All chemicals: $\text{Fe}_2(\text{SO}_4)_3$, H_2SO_4 , NaOH, pyrogallol, standard buffers pH 7.0 and pH 4.1 were of analytical grade purity, Merck. Distilled and double distilled water were used to prepare the solutions. The pH value was adjusted by the addition of either 0.1 mol dm^{-3} NaOH or 0.1 mol dm^{-3} H_2SO_4 . Standardization of the $\text{Fe}_2(\text{SO}_4)_3$ solution was performed by gravimetry and complexometry methods.^{8,9} The initial solution of sulphonated pyrogallol was prepared by dissolving the synthesized substance immediately prior to the experiment.

Synthesis of sulphonated pyrogallol¹⁰

Pyrogallol, 3.78 g, was dissolved in 100 cm^3 96 % H_2SO_4 at $298 \pm 0.1 \text{ K}$. The precipitate was separated after 48 h by filtration on a B-4 nutch and redissolved in water. A saturated solution of NaCl was added to the cooled solution. A precipitate of the Na-salt of sulphonated pyrogallol ($\text{C}_6\text{H}_2(\text{OH})_3\text{SO}_3\text{Na}$) formed after a certain time. After filtration on a B-3 nutch, repeated recrystallization was carried out from 96 % ethanol, followed by drying over P_2O_5 .

RESULTS AND DISCUSSION

A series of aqueous solutions with different ratios of the concentrations of metal ions and ligand, 1:0; 1:0.2; 1:0.5; 1:0.75; 1:1; 1:1.5; 1:3; 1:5; 1:5; 1:10 and 1:20, were prepared for the investigation of the Fe^{3+} – sulphonated pyrogallol (SP) system by cyclic voltammetry. The concentration of Fe^{3+} ions was always $5 \times 10^{-3} \text{ mol dm}^{-3}$ and the pH value was always 2.30. The voltammograms were recorded in the potential range from -0.30 V to 0.80 V vs. SCE at a potential sweep rate of 10 mV s^{-1} . Prior to the measurements, all the solutions were pretreated with argon. The results are shown in Fig. 1.

It can be seen that in the investigated potential range only the peak which corresponds to free Fe^{3+} ions reduction is found, while there is no reduction of the Fe^{3+} ions which belong to the complex. The values of the peak potentials and peak

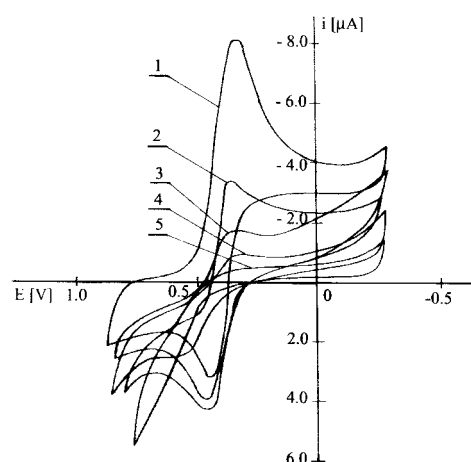


Fig. 1. Voltammograms of the Fe^{3+} - SP system; pH 2.30; $c_{\text{Fe}^{3+}} = 5 \times 10^{-3} \text{ mol dm}^{-3}$; 1) $c_{\text{SP}} = 0$, 2) $c_{\text{SP}} = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$, 3) $c_{\text{SP}} = 5 \times 10^{-3} \text{ mol dm}^{-3}$, 4) $c_{\text{SP}} = 5 \times 10^{-2} \text{ mol dm}^{-3}$ and 5) $c_{\text{Fe}^{3+}} = 0$, $c_{\text{SP}} = 5 \times 10^{-2} \text{ mol dm}^{-3}$, $v = 10 \text{ mV s}^{-1}$.

currents in the cathodic range as a function of mole ratio of ligand and metal are shown in Table I.

It can be seen that the peak of the voltammogram is shifted towards more positive potentials with decreasing concentration of Fe^{3+} ions, due to complex formation.

TABLE I. The value of the peak currents and peak potentials in cathodic range for different ratios of SP and Fe^{3+} and the values of the relative stability constants $\log \beta_2$ for the $\text{Fe}^{3+} : \text{SP} = 1.2$ complex; $c_{\text{Fe}^{3+}} = 5 \times 10^{-3} \text{ mol dm}^{-3}$; 298 0.1K

$c_{\text{SP}}/c_{\text{Fe}^{3+}}$	$i/\mu\text{A}$	E_k/V	$\log \beta_2$
0	7.9	0.335	$\log \beta_2 = 5.08 \pm 0.26$
0.2	5.3	0.345	
0.5	5.0	0.355	
0.75	4.6	0.360	
1.0	3.7	0.365	
1.5	3.4	0.365	
3.0	1.9	0.370	
5.0	1.5	0.375	
7.0	1.4	0.380	
10.0	1.4	0.385	
20.0	1.4	0.390	

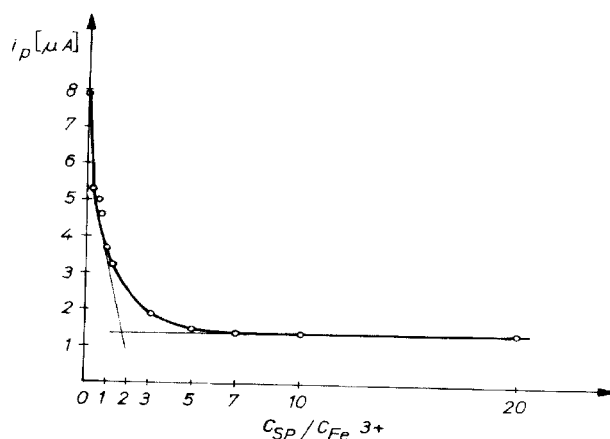


Fig.2. Dependence of the peak current in the cathodic range on mole ratio of ligand and metal $c_{SP}/c_{Fe^{3+}}$ ($c_{Fe^{3+}} = 5 \times 10^{-3} \text{ mol dm}^{-3}$; $c_{SP} = 1 \times 10^{-1} \text{ mol dm}^{-3}$); pH 2.30.

According to the obtained voltammograms, the dependence of the peak current on the mole ratio of SP and Fe^{3+} in the cathodic range is shown in Fig. 2.

The decrease of the peak current indicates complex formation between Fe^{3+} and SP (Fig. 1). The intersection point of the extrapolated linear part of the $i = f(c_{SP}/c_{Fe^{3+}})$ dependence indicates a chemical composition of the complex ML_2 (Fig. 2). The stability constant of this complex is given by the equation:

$$\beta_2 = [ML_2]/[M][L]^2 \quad (1)$$

Using the equilibrium values of the complex, as well as the ligand and metal ions concentrations obtained from the peak currents (Table I), Eq. (2) is obtained:

$$\beta_2 = (i_0 - i)/i[c_L - 2(i_0 - i)/k_M]^2 \quad (2)$$

This equation was obtained by taking: $c_M = i_0/k_M$, $[M] = i/k_M$, $[ML_2] = (i_0 - i)/k_M$, $[L] = c_L - 2(i_0 - i)/k_M$, where i_0 – the peak current in the absence of ligand, proportional to the total concentration of metal – c_M , i – the peak current in the presence of ligand, proportional to the equilibrium concentration of Fe^{3+} ions and c_L – the total concentration of SP.

The constant k_M was determined using the equation $i_0 = k_M c_M$. For $i_0 = 6.5 \mu A$ and $c_{Fe^{3+}} = 5 \times 10^{-3} \text{ mol dm}^{-3}$, k_M has the value 1300. At higher $c_{SP}/c_{Fe^{3+}}$ ratios, a straight horizontal line is obtained, since the peak currents are of the same value. The difference between the peak current i and the constant peak current is $6.5 \mu A$. Using this method, the stability constants for every concentration of ligand (Fig. 2), excluding three last points, were determined (Table I). The relative stability constant, calculated as the mean value of the obtained results and after application of Chauvenet's criterion¹⁴ has the value $\log \beta_2 = 5.08 \pm 0.26$.

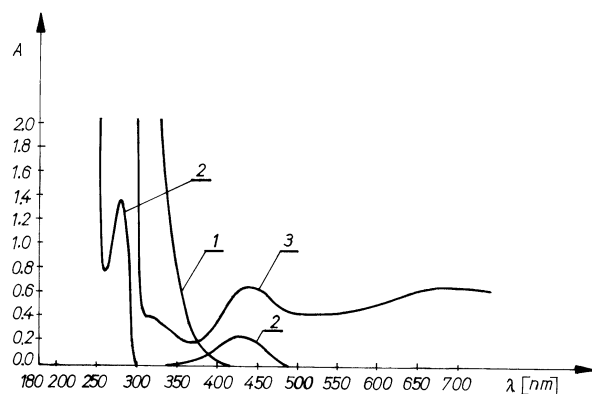


Fig. 3. Absorption spectra: 1. $\text{Fe}_2(\text{SO}_4)_3$, $c_{\text{Fe}^{3+}} = 1 \times 10^{-3} \text{ mol dm}^{-3}$; 2. SP, $c_{\text{SP}} = 1 \times 10^{-2} \text{ mol dm}^{-3}$; 3. Complex Fe^{3+} - SP, $c_{\text{Fe}^{3+}} = 1 \times 10^{-3} \text{ mol dm}^{-3}$; $c_{\text{SP}} = 1 \times 10^{-2} \text{ mol dm}^{-3}$. The reference solution was water and the pH was 2.30.

The investigation of the Fe^{3+} -SP system was also carried out using spectrophotometric measurements. Sulphonated pyrogallol and Fe^{3+} form a coloured complex in aqueous solutions. The absorption spectra of a $1 \times 10^{-3} \text{ mol dm}^{-3}$ Fe^{3+} ion solution, a $1 \times 10^{-2} \text{ mol dm}^{-3}$ SP solution and a mixture of Fe^{3+} and SP in water ($c_{\text{Fe}^{3+}} = 1 \times 10^{-3} \text{ mol dm}^{-3}$ and $c_{\text{SP}} = 1 \times 10^{-2} \text{ mol dm}^{-3}$) at pH 2.30 are shown in Fig. 3.

There is no characteristic maximum of Fe^{3+} and SP (curves 1 and 2, Fig. 3) in the wavelength range in which the Fe^{3+} -SP mixture absorbs. In the absorption spectrum of iron (curve 1, Fig. 3), one absorption maximum is observed in the range from 200 to 300 nm, while there are two absorption maxima, at 210 nm and 275 nm in the UV range, and one absorption maximum in the visible range at about 435 nm in the absorption spectrum of SP (curve 2, Fig. 3). The obtained results are in accordance with the literature data^{12,13} which point to Na-pyrogallol-5-sulphonate air oxidation, characterized by the formation of a coloured oxidation product with an absorption maximum at 436.8 nm. In case of the Fe^{3+} -SP mixture (curve 3, Fig. 3), two absorption maxima in the visible range, at 440 and 700 nm, are observed. The literature data^{12,13} suggest that iron catalyses the process of air oxidation of SP. Hence, the existence of the maximum at 440 nm in the spectrum of the Fe^{3+} -SP mixture can be ascribed to air oxidation of SP, while the maximum at 700 nm is due to complex formation.

The reaction of complex formation is faster than the reaction of SP air oxidation, which is confirmed by the change of absorbance with time in a solution with a ligand concentration of $5 \times 10^{-3} \text{ mol dm}^{-3}$ and a metal concentration of $1 \times 10^{-3} \text{ mol dm}^{-3}$ at pH 2.30. The intensity of the absorbance decreases slightly by about 2.3 % during 120 min in presence of excess ligand, which indicates that the complex is stable within 30 min.

The influence of the pH value on the formation of the Fe^{3+} -SP complex (Fig. 4) indicates its formation over the sulfo group. The initial increase in the absorbance of the complex with increasing pH is connected with the enhanced dissociation of the SP sulfo group. The highest values of absorbance were found in the pH range from 2.30 to 2.80, suggesting that this range should be optimal for investigating the complex. Further increase of the pH leads to a decrease in the absorbance,

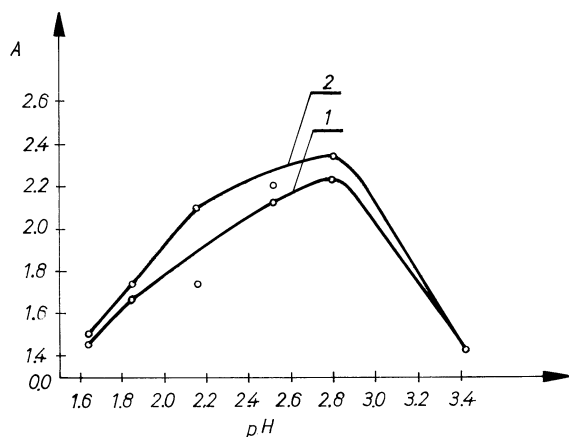


Fig. 4. Dependence of the absorbance of the Fe^{3+} - SP complex on the pH of the solution, $c_{\text{Fe}^{3+}} = 1 \times 10^{-3} \text{ mol dm}^{-3}$; $c_{\text{SP}} = 2 \times 10^{-2} \text{ mol dm}^{-3}$; $T = 298 \pm 0.1 \text{ K}$: 1. $\lambda = 670 \text{ nm}$ and 2. $\lambda = 690 \text{ nm}$.

due to the decomposition of the complex or the formation of a complex with a different ratio of metal and ligand.

The composition of the complex was determined by the mole ratio method.¹¹ At pH 2.30, the absorbances of a series of solutions with a constant iron concentration ($1 \times 10^{-3} \text{ mol dm}^{-3}$) and changing concentration of ligand ($2 \times 10^{-4} - 2 \times 10^{-3} \text{ mol dm}^{-3}$) were measured. Distilled water was used as the reference solution. The dependence of the absorbance at 700 nm on the concentration ratio of SP and Fe^{3+} is shown in Fig. 5.

The number of ligands in the complex was determined from the intersection point of the tangents of the initial and final part of the curve (Fig. 5) and was found to have a value of 2.

TABLE II. The values of the absorbances of solutions with different ratios of the concentration SP and Fe^{3+} and the relative stability constants $\log \beta_2$ for the $\text{Fe}^{3+} : \text{SP} = 1:2$ complex; $c_{\text{Fe}^{3+}} = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $298 \pm 0.1 \text{ K}$.

$c_{\text{SP}}/c_{\text{Fe}^{3+}}$	$A_{700 \text{ nm}}$	$\log \beta_2$
0	0.030	$\log \beta_2 = 6.31 \pm 0.04$
0.2	0.075	
0.5	0.270	
0.75	0.520	
1.0	0.780	
1.5	1.200	
3.0	1.660	
5.0	1.810	
7.0	1.910	
10.0	1.990	
20.0	1.990	

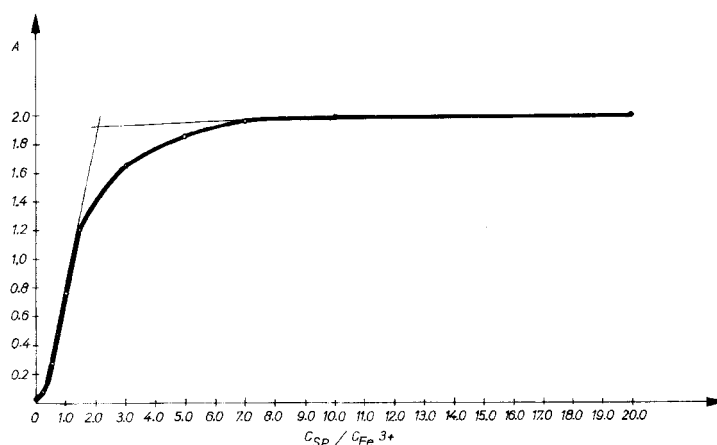


Fig. 5. Dependence of the absorbance of the Fe^{3+} - SP complex on the ratio of the concentrations of SP and Fe^{3+} ; $c_{\text{Fe}^{3+}} = 1 \times 10^{-3} \text{ mol dm}^{-3}$; $c_{\text{SP}} = 2 \times 10^{-4} - 2 \times 10^{-2} \text{ mol dm}^{-3}$; pH = 2.30, $T = 298 \pm 0.1 \text{ K}$; $\lambda = 700 \text{ nm}$.

The formation of the complex was confirmed by the Harvey-Manning method.¹¹ The absorption spectra were recorded for two series of solutions of Fe^{3+} - SP mixtures at pH 2.30. The concentration of ligand in the first series was constant at $c_{\text{SP}} = 2 \times 10^{-2} \text{ mol dm}^{-3}$ and the concentration of Fe^{3+} was varied between $c_{\text{Fe}^{3+}} = 1 \times 10^{-4} - 5 \times 10^{-4} \text{ mol dm}^{-3}$, while in the second series the concentration of Fe^{3+} was constant at $c_{\text{Fe}^{3+}} = 2 \times 10^{-2} \text{ mol dm}^{-3}$ and the concentration of ligand was varied between $c_{\text{SP}} = 1 \times 10^{-4} - 5 \times 10^{-4} \text{ mol dm}^{-3}$. The dependences of the absorbance of the complex at 700 nm on the concentration of metal and of SP are shown in Fig. 6.

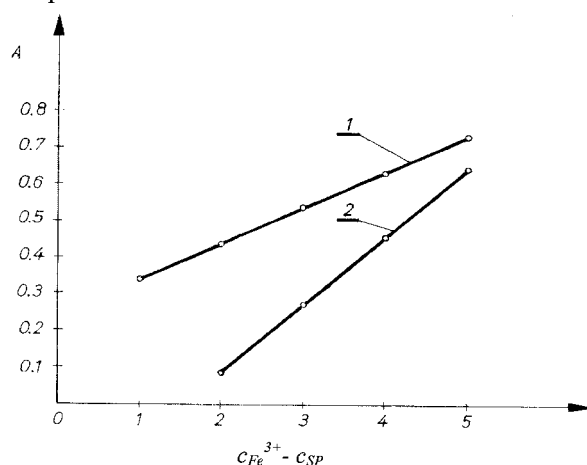


Fig. 6. Dependence of the absorbance of the Fe^{3+} -SP complex: 1) on the concentration of Fe^{3+} ($c_{\text{Fe}^{3+}} = 1 \times 10^{-4} - 5 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{SP}} = 2 \times 10^{-2} \text{ mol dm}^{-3}$); 2) on the concentration of SP ($c_{\text{SP}} = 1 \times 10^{-4} - 5 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{Fe}^{3+}} = 2 \times 10^{-2} \text{ mol dm}^{-3}$) at $\lambda = 700 \text{ nm}$; pH 2.30.

The ratio of the slopes of the straight lines from Fig. 6, $s_1 : s_2 = \tan \alpha : \tan \beta = 1.76$ represents the ratio of stoichiometric coefficients the ligand and metal in the complex, indicating that Fe^{3+} and SP form a complex with M:L = 1:2. The relative

stability constant of the Fe^{3+} -SP complex was calculated using the values of the absorbances obtained by the mole ratio method, Table II (Fig. 5).

The mean molar absorption coefficient was calculated using the equation:

$$a_k = A_0 / [\text{ML}_2] b \quad (3)$$

where $b = 1$ – the thickness of the absorption layer, A_0 – the absorbance corresponding to the horizontal part of the curve, $[\text{ML}_2] = c_M = 1 \times 10^{-3} \text{ mol dm}^{-3}$, because all the metal is included in the complex. The value of the mean molar absorption coefficient is 1.990. The values of the stability constant presented in Table II were obtained by calculating the equilibrium concentrations of the complex, the ligand and the metal in the part of curve which precedes the horizontal part and their subsequent substitution in Eq. (1). The relative stability constant has the value $\log \beta = 6.31 \pm 0.04$, obtained by discarding individual results using the Chauvenet criterion.¹⁴

The obtained results indicate that the complex $[\text{Fe}(\text{SP})_2]^+$ is significantly more stable than the complex $[\text{Fe}(\text{SP})]^{2+}$ whose presence could not be detected by the used methods. The obtained values of the stability constants which, although relative, because the dissociation constant of the sulpho group of SP is not known, are in accordance and prove the previous conclusion. The difference of mean $\log \beta_2$ values obtained using cyclovoltammetric and spectrophotometric measurements is partly the consequence of different ionic strength of investigated solutions, since it is five times higher in cyclovoltammetric than in spectrophotometric measurements. The composition of the investigated complex does not differ significantly from the composition of other complexes with similar ligands (sulphonated phenol ligands), mentioned in the introduction.

ИЗВОД

ИСПИТИВАЊЕ СИСТЕМА Fe^{3+} - СУЛФОНОВАНИ ПИРОГАЛОЛ У ВОДЕНИМ РАСТВОРИМА

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Испитивано је електрохемијско понашање и одређен је састав и константа стабилности Fe^{3+} -сулфопирогалола у киселој средини, рН 2,30. Утврђено је волтаметријским и спектрофотометријским мјерењима да Fe^{3+} и сулфопирогалол граде комплекс типа ML_2 и да је комплекс релативно стабилан током 30 минута. Оптимална рН вриједност за грађење комплекса је између 2,30 и 2,80. Одређене су релативне константе стабилности овог једињења ($\log \beta_2 = 5,08 \pm 0,26$ - волтаметријска мјерења и $\log \beta_2 = 6,31 \pm 0,04$ - спектрофотометријска мјерења).

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