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Influence of 5-Sulphosalicylic Acid on Redox Reaction between Fe(III) and Sn(II)

by V. Pautienienė, G. Rozovskis[*] and A. Survila

Institute of Chemistry, A. Goštauto 9, Vilnius LT–2600, Lithuania
E-mail: redox@ktl.mii.lt

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Kinetics of Fe(III) reduction with Sn(II) in 0.5–2 M H_2SO_4 solutions involving sulphosalicylic acid (H_3Ssal) has been studied. H_3Ssal acts not only as an indicator for spectrophotometric determination of Fe(III) but also takes part in the redox reaction as an accelerator. The data are described by the kinetic equation obtained for the rate-determining step of $FeSsal + Sn^{2+} \rightarrow Fe^{2+} + Sn^{3+} + Ssal^{3-}$ with rate constant $k_2 \approx 1.4 \cdot 10^{-4}$ $M^{-1}\,s^{-1}$ at 60°C. Effect of fluoride consists in the decrease of FeSsal concentration, due to the formation of extra Fe(III)–fluoride complexes, resulting in the decrease of the reaction rate.

Key words: iron(III), sulphosalicylic acid complexes, tin(II), redox kinetics

The investigation of redox reaction between Fe(III) and Sn(II) goes back to 19th century [1]. To explain its mechanism on the basis of the kinetic data, the existence of radical Sn(III) and its participation in this reaction was postulated for the first time in [2]. An accelerating effect of Cl^-, Br^- and I^- ions was found to be peculiar for this process [3,4]. It was also found that the reaction product, Fe(II), reduces the rate of the reaction in chloride-containing media [1]. Due to these peculiarities, this reaction was included in the textbook [5] as a classical example. As it is often the case, this fact implied a loss of interest in this system.

The following reaction scheme was proposed by Benson [5] to explain the revealed phenomena:

$$Fe^{3+} + SnCl_3^- \rightleftarrows Fe^{2+} + SnCl_3; \qquad Fe^{3+} + SnCl_3 \rightleftarrows Fe^{2+} + SnCl_3^+$$

Whereas the influence of I^- and Br^- could be interpreted by alternate oxidation and reduction of the catalysts ($I^- \rightleftarrows I_2$ and $Br^- \rightleftarrows Br_2$), an accelerating effect of Cl^- ions was explained in different ways, *e.g.* it was associated in [3] with participation of different chloride complexes of Fe(III) and Sn(II) in the reaction. Among the papers published later, only [4] is worthy to mention in the kinetic aspect. According to [4], the accelerating action of Cl^- ions is associated with the following reaction:

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[*] Author for correspondence.

$$\mathrm{FeCl}_m^{(3-m)} + \mathrm{SnCl}_n^{(2-n)} \rightleftarrows [\mathrm{FeSnCl}_{m+n}^{(5-m-n)}] \rightleftarrows [\text{an active complex}] \rightleftarrows \text{products}$$

The intermediate $\mathrm{FeSnCl}_{m+n}^{(5-m-n)}$ was supposed to be a charge transfer complex, but the structure of the next active complex was not identified in [4]. Similar complexes, in which SnCl_3^- acts as a ligand, are also known for Pd(II) [6] or Pt(IV) [7].

The mentioned above "classical" papers deal mainly with chloride-containing solutions, in which the reaction order according to Cl^- formally may be higher than three. The subject of the present paper is the investigation of redox reaction between Fe(III) and Sn(II) in solutions containing H_2SO_4 and sulphosalicylic acid. Since the latter compound involves 3 mobile protons, it will be symbolized as H_3Ssal. The Ssal^{3-} species are able to form complexes with Fe(III) [8], which are intensively coloured. This makes it possible to study kinetics of Fe(III) reduction by spectrophotometry. Similar reaction involving the Fe(III) sulphosalicylic complex was already described, when developing a kinetic method for determining of Re(VII) [9].

Preliminary experiments have shown that the reduction of Fe(III) by Sn(II) proceeds extremely slowly in concentrated (0.5–2 M) H_2SO_4 solutions. However, the addition of sulphosalicylic acid results in a distinct acceleration of this process. The change in kinetic regularities, as compared with those reported for chloride-containing solutions, has also been observed. Thus, H_3Ssal seems to act not only as indicator for Fe(III), but also to take part in the redox reaction. Its mechanism is worthy of a detailed consideration.

EXPERIMENTAL

The solutions were prepared by successive mixing of solutions containing H_3Ssal, $SnSO_4$, $NH_4Fe(SO_4)_2$ or only H_2SO_4. The basic molar concentrations in the solution obtained were 0.08, 0.37, 0.05 and 1.0 M, respectively, for the above components. The concentration of one of them was changed, whereas concentrations of the others were kept constant. Constant ionic strength was maintained by adding Na_2SO_4. Na_2CO_3 was used to change the acidity of the solution without changing $[\mathrm{SO}_4^{2-}]$. Taking into account the experimental results published earlier (see introduction), some experiments were carried out with solutions involving NaF, NaCl and $(NH_4)_2Fe(SO_4)_2$. The total concentration of Fe(III) in the initial solution was determined mercurymetrically [10], and that of Sn(II) was controlled iodometrically [10].

Absorbance of the solutions was measured by a photoelectric colorimeter KFK–2 (Russia) at wavelength $\lambda = 540$ nm and cell thickness $l = 0.1$ cm. The reference cell was filled with a solution similar to the working one but not containing Fe(III). To avoid the formation of colloids, each experiment was performed with a freshly prepared reference solution. Kinetic experiments were carried out at 60 ± 1°C. A series of solution samples was taken at different times and their absorbance was measured after abrupt cooling to room temperature, thus reaching a negligible reaction rate.

To relate the absorbance to the concentration of the certain complex of Fe(III), the absorption spectra were recorded using spectrophotometer KFK-3 (Russia) with $l = 0.1$ cm. An example of data obtained is given in Fig. 1. Absorption plots pass a maximum (A_{max}) at $\lambda = 510$ nm. When increasing the ligand concentration, a constant value of A_{max} is attained and no shift of λ_{max} is observed (Fig. 1). The results obtained are indicative of formation of a single Fe(III) complex. Though the amount of active ligand (Ssal^{3-}) is very low in highly acid media, the monoligand FeSsal complex is formed due to the large affinity of Fe^{3+} for Ssal^{3-}. This conclusion was confirmed by simulations (see below), which also showed that the system under investigation should be treated as ligand-deficient one.

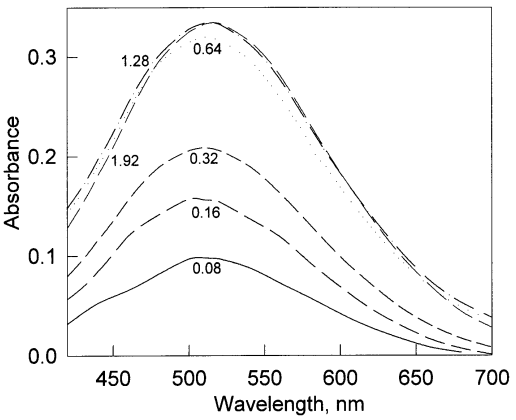

Figure 1. Absorption spectra recorded at 20°C for solutions containing 0.012 M Fe(III) and 1.0 M H_2SO_4. Total molar concentrations of sulphosalicylic acid are indicated on the curves.

The molar absorbtivity $\varepsilon = A_{max}/[\mathrm{FeSsal}]\cdot l = 269\ \mathrm{M^{-1}\cdot cm^{-1}}$ was calculated from the data in Fig. 1. Then the [FeSsal] = A/(εl) was calculated for each experiment and was expressed as a molar fraction of $[\mathrm{FeSsal}]/[\mathrm{Fe(III)}]_T$, where $[\mathrm{Fe(III)}]_T = [\mathrm{FeSsal}] + [\mathrm{Fe^{3+}}]$.

Since only the amount of FeSsal was available directly from absorption measurements, equilibrium concentrations of other species were obtained by simulation. Well-known equations (see, *e.g.* [11]) accounting for the material balance in the system were used. They relate the total concentrations of initial components ($[\mathrm{Fe(III)}]_T$, $[\mathrm{H_3Ssal}]_T$, $[\mathrm{H_2SO_4}]_T$, *etc.*) with equilibrium concentrations of species formed. Besides, they involve equilibrium characteristics of the system, which may be expressed in terms of cumulative stability constants of complexes and protonated species of ligand (β and β^H respectively). According to [8], β values depend, to some extent, on the ionic strength of solutions and on the nature of the supporting electrolyte.

We failed to find the data concerning sulphate media in the references. Therefore, the stability constant for FeSsal (β_1) was corrected on the basis of experimental data obtained (see below). Since the experiments were carried out with ligand-deficient solutions, the formation of such possible species as $\mathrm{Fe(Ssal)_2^{3-}}$ or $\mathrm{Fe(Ssal)_3^{6-}}$ was omitted from our consideration. The first step of dissociation of H_2SO_4 was assumed to proceed completely.

Equilibria, which were taken into account, are listed in Table 1. Their constants were selected from [8] for ionic strength close to that of the solutions. Data for 60°C were obtained using enthalpies (ΔH) or interpolating β dependencies on temperature given in [8]. For lack of literature data, no corrections have been made for ΔH dependence on temperature.

Table 1 Selected equilibrium characteristics of the solutions under investigation from [8].

Equilibrium	Type of the constant stability	Logarithm of constant	
		25°C	60°C
$H^+ + Ssal^{3-} \rightleftarrows HSsal^{2-}$	β_1^H	11.5	10.9
$2H^+ + Ssal^{3-} \rightleftarrows H_2Ssal^-$	β_2^H	13.9	~13.3
$H^+ + H_2Ssal^{2-} \rightleftarrows H_3Ssal$	K^H		1.52 (80°C)
$Fe^{3+} + Ssal^{3-} \rightleftarrows FeSsal$	β_1	14.4	14.2
$H^+ + F^- \rightleftarrows HF$	$\beta_1^{'H}$	3.2	3.4
$2H^+ + F^- \rightleftarrows H_2F^+$	$\beta_2^{'H}$	3.8	4.4
$Fe^{3+} + F^- \rightleftarrows FeF^{2+}$	$\beta_1^{'}$	5.2	5.4
$Fe^{3+} + 2F^- \rightleftarrows FeF_2^+$	$\beta_2^{'}$	9.2	9.5
$Fe^{3+} + 3F^- \rightleftarrows FeF_3$	$\beta_3^{'}$	11.9	12.4
$H^+ + SO_4^{2-} \rightleftarrows HSO_4^-$	K	1.9	2.5

RESULTS AND DISCUSSION

The conclusion that absorbance of the solutions depends on the concentration of FeSsal requires an additional support. In this connection, we carried out series of experiments varying the concentration of a single component. When increasing the total concentration of Fe(III), both the content of Fe^{3+} and that of FeSsal increase as well. This circumstance does make it possible to solve uniquely the above problem. Data given in Fig. 2 are more valuable. Increase of the acidity of the solutions diminishes the complexation degree. Increase in the ligand concentration leads to the opposite effect: the fraction of FeSsal increases, whereas the concentration of aqua-ions of Fe^{3+} decreases. It follows from the experimental regularities that the changes in absorbance should be ascribed to the variations of FeSsal concentration. This conclusion is supported quantitatively (Fig. 2) and makes it possible to improve the β values for sulphate media. Values of $\log \beta_1 = 14.45 \pm 0.05$ at 20°C and $\log \beta_1 = 14.0 \pm 0.1$ obtained in the present investigation at 60°C are close to those given in Table 1.

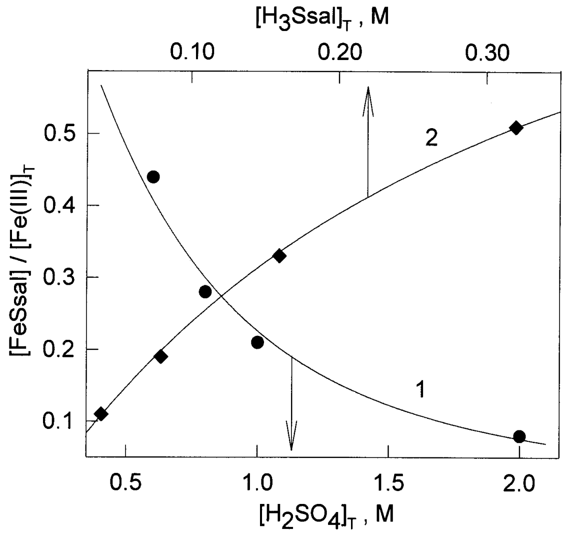

Figure 2. Effect of total concentration of H_2SO_4 (curve 1) and H_3Ssal (curve 2) on the molar fraction of FeSsal complex at 20°C. Experimental (symbols) and simulated (full lines) data are compared. The best fit is obtained at $\log\beta_1 = 14.54$ (curve 1) and 14.46 (curve 2). Initial composition of the solutions (M): Fe(III) – 0.05, H_3Ssal – 0.08 (curve 1), H_2SO_4 – 1.0 (curve 2).

It is worthy to note that the degree of complexation of Fe(III) increases with temperature, though both β_1 and β_1^H decrease. Two competitive processes cause this effect: decrease in the stability of the complex and increase in the amount of the active form of ligand. The latter effect was found to be predominating.

The influence of separate components on the rate of the redox process may be characterized as follows. While increasing total concentrations of Fe(III), Sn(II) or H_3Ssal, the rate increases as well. Respective experimental data are shown in Figs. 3 and 4.

The order in respect to Sn(II) is equal to about 1 at low concentrations, but tends to zero at higher [Sn^{2+}] (Fig. 3). All the kinetic measurements described below were performed at such Sn(II) concentration when the order of the reaction in Sn was equal to *ca* zero.

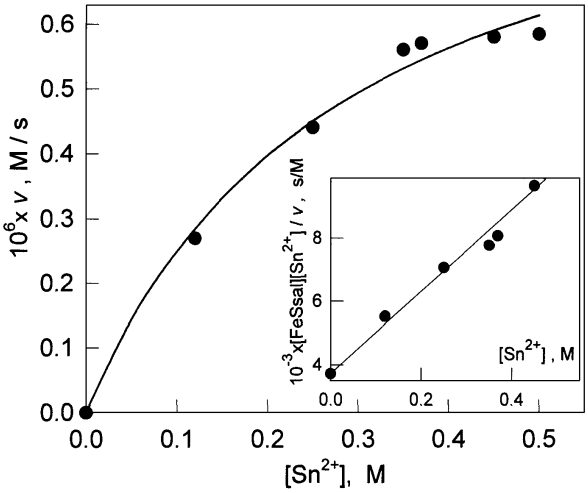

Figure 3. Dependence of Fe(III) reduction rate on concentration of Sn(II) at $Fe(III)_T$ – 0.05 M, H_3Ssal – 0.08 M, H_2SO_4 – 1.0 M, t = 60°C. Simulated data obtained with [FeSsal] = 0.012 M, k_2 = $1.4 \cdot 10^{-4}$ M^{-1} s^{-1}, $k_{-1} = 3.8 \cdot 10^{-5}$ s^{-1} (full line) are compared with experimental results (symbols). Plot linearized according to Eqn. (7) is given in the inset.

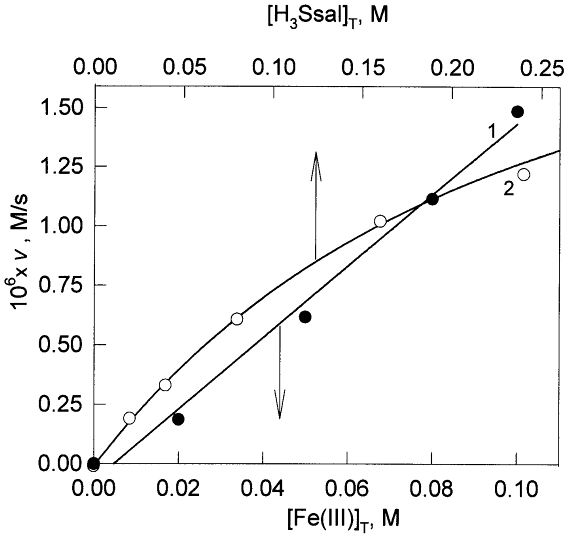

Figure 4. Dependence of Fe(III) reduction rate on the total concentration of Fe(III) (1) and [H_3Ssal] (2) at 60°C. Initial concentrations of other components (M): Sn(II) – 0.37, H_2SO_4 – 1.0. The experimental data for H_3Ssal (symbols) are compared with the results of simulation (full line) obtained with $k_2 = 1.4 \cdot 10^{-4}$ M^{-1} s^{-1} and $k_{-1} = 3.8 \cdot 10^{-5}$ s^{-1}.

The rate (*v*) varies approximately linearly with $[Fe(III)]_T$ and $[Fe^{3+}]$ (Fig. 4, curve 1). Formally, this indicates the first order in respect to Fe(III) and FeSsal concentrations. The addition of Fe(II) (up to 0.05 M) was found to have a negligible effect on the reaction rate.

Similar to the data given by curve 1 in Fig. 4 but weak effect is seen for $[H_3Ssal]_T$ (Fig. 4, curve 2). Finally, according to the data obtained (not shown), the rate varies approximately linearly with $[H_2SO_4]_T^{-1.42}$. In fact the reaction rate depends only on $[H^+]$ and does not depend on SO_4^{2-} ion concentration. For example, the reaction rate is the same in both 0.5 M H_2SO_4+0.5 M Na_2SO_4 and 0.5 M H_2SO_4 solutions. Two latter effects give ground to conclude that FeSsal is the species which takes part in the rate-determining step. Then, the following scheme based on the experimental results may be proposed.

$$H_3Ssal \overset{1/\beta^H}{\rightleftarrows} HSsal^{2-} + 2H^+ \tag{1}$$

where $\beta^H = K^H\beta_2^H/\beta_1^H$ (see Table 1),

$$Fe^{3+} + HSsal^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} FeSsal + H^+ \tag{2}$$

$$FeSsal + Sn^{2+} \xrightarrow{k_2} Fe^{2+} + Sn^{3+} + Ssal^{3-} \quad \text{(the rate-determining step)} \tag{3}$$

Next step, involving interaction between FeSsal and Sn^{3+} radical, is very rapid and it increases twice the reaction rate ($2k_2$). The kinetic equation for the steps (2) and (3) may be obtained using the method of stationary concentration which yields:

$$\nu = \frac{2k_1k_2[Fe^{3+}][HSsal^{2-}][Sn^{2+}]}{k_{-1}[H^+] + k_2[Sn^{2+}]} \tag{4}$$

Assuming that the process (2) proceeds under equilibrium conditions, it is possible to write that $k_1[Fe^{3+}][HSsal^{2-}] = k_{-1}[FeSsal][H^+]$. Then

$$\nu = \frac{2[FeSsal][Sn^{2+}]}{k_2^{-1} + k_{-1}^{-1}[Sn^{2+}][H^+]^{-1}} \tag{5}$$

At sufficiently low concentrations of Sn^{2+}, the second term in the denominator may be omitted. Then (5) shows the first order in Sn(II). On the contrary, the condition that $k_2^{-1} << k_{-1}^{-1}[Sn^{2+}][H^+]^{-1}$, which is valid at high $[Sn(II)]_T$, leads to the order of the reaction equal to zero. Experimental data (Fig. 3) are in agreement with the given theoretical predictions. Finally, (5) may be linearized to

$$[\mathrm{FeSsal}][\mathrm{Sn}^{2+}]/v = 0.5(k_2^{-1} + k_{-1}^{-1}[\mathrm{Sn}^{2+}][\mathrm{H}^+]^{-1}) \quad (6)$$

This modification is useful for analysis of experimental data. An example of linearized plot is shown in the inset of Fig. 3. Values of $k_{-1} = 3.8 \cdot 10^{-5}$ s^{-1} and $k_2 = 1.4 \cdot 10^{-4}$ M^{-1}s^{-1} obtained from the slope and intercept of approximating line, respectively, were used to calculate v–[Sn^{2+}] dependence according to (5). Experimental and simulated data coincide quite well (Fig. 3).

To reveal the effect of solution acidity, (4) may be modified inserting the expression for [HSsal^{2-}] obtained from stability constant, β^H, which characterizes the process described by (1). This procedure yields the relationship

$$\nu = \frac{2k_1 k_2 [Fe^{3+}][H_3Ssal][Sn^{2+}]}{\beta^H (k_{-1}[H^+] + k_2[Sn^{2+}])[H^+]^2} \quad (7)$$

At $k_2[\mathrm{Sn}^{2+}] \gg k_{-1}[\mathrm{H}^+]$, the reaction rate is in inverse proportion to $[\mathrm{H}^+]^2$. Strictly speaking, the term of [H$^+$] cannot be replaced by total concentration of H_2SO_4, because deprotonization $H_3Ssal \rightleftarrows H_2Ssal^- + H^+$ increases with the decrease of H_2SO_4 concentration. Therefore, the experimental value of the reaction order in $[H_2SO_4]_T$ is somewhat different (see above).

We have also investigated the influence of F$^-$ ions, which are capable to form complexes with Fe(III) (see Table 1). An addition of NaF up to 0.2 M decreases the absorbance of the basic solution and, consequently, the content of FeSsal. Such an effect is supported quantitatively (Fig. 5, curve 1). Mostly the inhibiting effect of fluo-

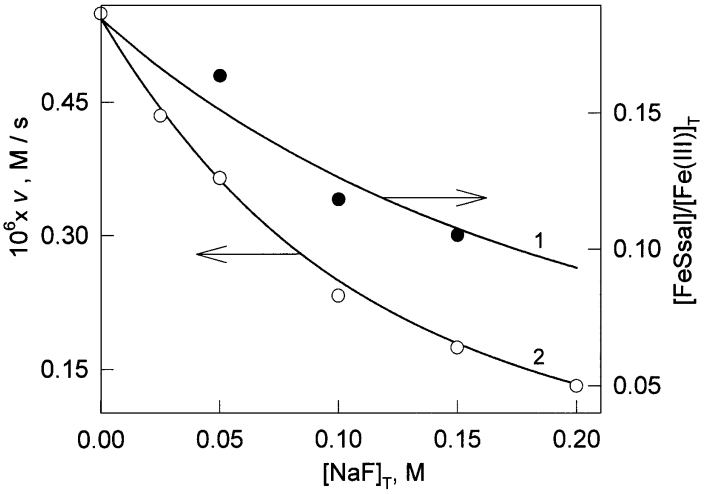

Figure 5. Influence of NaF on the molar fraction of FeSsal in the basic solution at 20°C (1). Comparison of experimental (symbols) and simulated (full line) data. The best fit is obtained at $\log\beta_1 = 14.42$. Effect of fluoride on Fe(III) reduction rate at 60°C (2). Experimental data (symbols) are compared with results of simulation (full line) with the same parameters as those in Fig. 3. Initial composition of the solutions (M): Fe(III)$_T$ – 0.05, H_3Ssal – 0.08, Sn(II) – 0.37, H_2SO_4 – 1.0.

ride is evident from the data in Fig. 5, curve 2 and seems to manifest itself through the changes in the concentration of FeSsal. The analysis of kinetic constants and calculated values of [FeSsal] results in satisfactory correlation between experimental and simulated data (Fig. 5). The action of chloride ions is different. According to the results obtained, an addition of 0.05–0.2 M NaCl results in significant acceleration of the redox process in the system studied. The change in its mechanism might be responsible for such behaviour, as it has been mentioned in the introduction.

The results of the present paper show that the FeSsal complex is the kinetically active oxidant, which determines the rate of the redox process between Fe(III) and Sn(II).

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