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# Influence of sodium polyanethol sulphonate on the morphology of $\beta$ -FeOOH particles obtained from the hydrolysis of a $\text{FeCl}_3$ solution

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## Abstract

Influence of sodium polyanethol sulphonate on the hydrolysis of 0.1 M  $\text{FeCl}_3$  solution at 90°C has been investigated. In the absence of this polymer different shapes of submicron particles such as needles, X- and Y-shaped particles were obtained. The experimental conditions for the formation of spherical particles of micron dimensions, in the presence of sodium polyanethol sulphonate, were determined. At relatively high concentration of the polymer, large particles of irregular shape were dominant. FT-IR spectra (mid + far) of these particles showed the characteristic  $\beta$ -FeOOH phase and also indicated the incorporation of polyanethol sulphonate chains into the microstructure of the particles. The phenomenology of this process was discussed.

## 1. Introduction

Iron oxyhydroxide and oxide particles of submicron or micron dimensions have found applications in the production of pigments, catalysts, sensors, magnetic recording media, etc. In many cases, besides the required particle size, it is also important to control well the particle shape. The  $\text{Fe}^{3+}$  concentration, pH, temperature, as well as the presence of different inorganic ions, may affect the particle size, morphology and phase composition of the precipitates generated by the hydrolysis of iron (III) salts.

Akaganéite ( $\beta$ -FeOOH) is a typical product of slow hydrolysis of  $\text{FeCl}_3$  solution at room temperature [1–4]. After a certain period of hydrolysis of  $\text{FeCl}_3$  solutions, there is formation of  $\beta$ -FeOOH sediments which exhibit iridescent colors, the so-called Schiller layers [5]. The  $\beta$ -FeOOH particles were also obtained in the

early stage of the hydrolysis of 0.2 M  $\text{FeCl}_3$  solution at 120°C, which transformed to  $\alpha$ - $\text{Fe}_2\text{O}_3$  for longer autoclaving times [6]. In the mixed  $\text{Fe}(\text{NO}_3)_3 + \text{FeCl}_3$  solutions the phase composition of the hydrolytical products was determined by the concentration of the dominant Fe(III) salt. Structural investigations indicated that  $\beta$ -FeOOH particles possess hollandite-type crystal structure [7].

The present article describes the strong effect of sodium polyanethol sulphonate (SPAS) on the hydrolysis of  $\text{FeCl}_3$ , which was observed during our investigation of the colloidal properties of  $\beta$ -FeOOH particles. SPAS was originally developed as an anticoagulant for blood, and it also can stabilize biocolloids such as milk and gelatin [8].

## 2. Experimental

The  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$  salts of analytical purity and doubly distilled water were used. Sodium polyanethol sul-

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Table 1  
The chemical composition of the solutions and the conditions of FeCl<sub>3</sub> hydrolysis

Sample	FeCl <sub>3</sub> (mol dm <sup>-3</sup> )	SPAS <sup>a</sup> (wt %)	Time of heating at 90°C (h)	Starting pH	Final pH
S1	0.01		48	2.48	1.56
S2	0.02		120	1.65	0.70
S3	0.1		4	1.82	1.04
S4	0.1		8		1.00
S5	0.1		24		0.95
S6	0.1		48		0.93
S7	0.1		72		0.88
S8	0.1		120		0.81
S9	0.1		240		0.79
S10	0.1	0.1	4	1.70	1.31
S11	0.1	0.1	24		1.19
S12	0.1	0.1	72		
S13	0.1	0.1	120		1.15
S14	0.1	0.5	4		1.36
S15	0.1	0.5	8		1.08
S16	0.1	0.5	24		1.05
S17	0.1	0.5	72		0.90
S18	0.1	0.5	120		0.91
S19	0.1	0.5	240		0.96

<sup>a</sup> SPAS means sodium polyanethol sulphonate.

phonate (SPAS) was obtained from KOCH-LIGHT Ltd (anticoagulant,  $M_w = 10000$ ). The chemical composition of the solutions and the conditions for FeCl<sub>3</sub> hydrolysis are given in Table 1. The experiments were performed in glass autoclaves. The separation of solid hydrolytical products from the mother liquor was performed using an ultra-speed centrifuge (operational range up to 20000 rpm). The solid hydrolytical products were washed several times with doubly distilled water. pH measurements were performed using a PHM-26 pH meter and combined pH electrode, both produced by Radiometer.

Transmission electron microscopy (TEM) of all samples was performed with an electron microscope, EM 10, produced by Opton. Fourier transform infrared (FT-IR) spectra of all samples were recorded at room temperature with a Perkin-Elmer spectrometer (model 2000). The FT-IR spectrometer was coupled with a personal computer loaded with an IR Data Manager (IRDM) program. The samples were pressed into spectroscopically pure KBr or polyethylene to form discs.

### 3. Results and conclusions

In order to ascertain the effect of SPAS on the hydrolysis of FeCl<sub>3</sub>, it was first necessary to characterize the solid hydrolytical products in the absence of this polymer. Fig. 1 shows TEM micrographs of hydrolytical products obtained by hydrolysis of 0.01 M and 0.02 M FeCl<sub>3</sub> solutions. The FT-IR spectrum of the hydrolytical product (sample S1), formed in 0.01 M FeCl<sub>3</sub> solution at 90°C after 48 h, is shown in Fig. 2. This spectrum is characterized by a very strong band at 564 cm<sup>-1</sup>, strong bands at 480 and 352 cm<sup>-1</sup> and a weak band at 384 cm<sup>-1</sup>. These bands can be ascribed to α-Fe<sub>2</sub>O<sub>3</sub>. β-FeOOH colloids, as a hydrolytical product (sample S2), were obtained from 0.02 M FeCl<sub>3</sub> solution at 90°C after 120 h. Fig. 3 and Fig. 4 show TEM micrographs of the hydrolytical products formed by the hydrolysis of 0.1 M FeCl<sub>3</sub> solution at 90°C for different times. Fig. 3 shows different shapes of colloidal particles, such as needles, X- and Y-shaped particles, and the tendency to form a lateral arrangement of needle-shaped particles

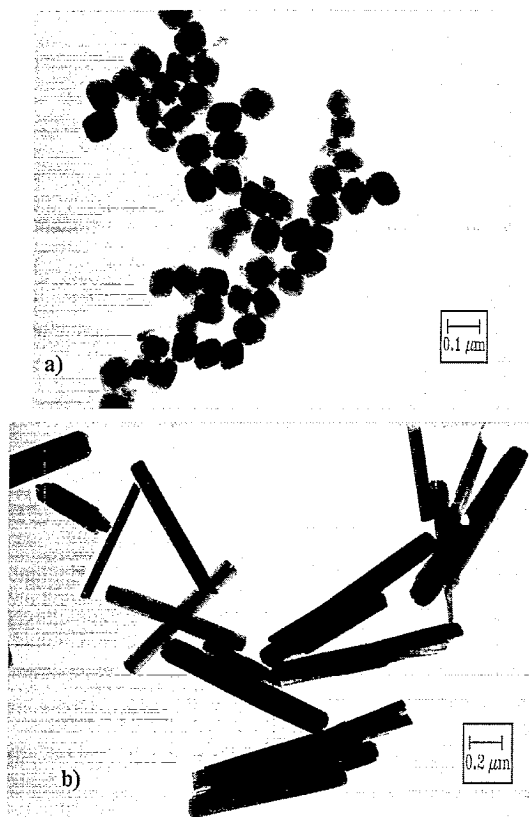


Fig. 1. TEM micrographs of (a) sample S1 and (b) sample S2. The particles of sample S1 correspond to  $\alpha$ - $\text{Fe}_2\text{O}_3$  and the particles of sample S2 correspond to  $\beta$ - $\text{FeOOH}$ .

is also visible. The size of the colloidal particles, generated during the hydrolysis of 0.1 M  $\text{FeCl}_3$  solution, increased with increasing hydrolysis time. FT-IR spectra (Fig. 5) of the hydrolytical products, formed by the hydrolysis of 0.1 M  $\text{FeCl}_3$  solution at 90°C for 4, 24 and 240 h, respectively, can be ascribed to the  $\beta$ - $\text{FeOOH}$  phase.

Fig. 6 shows a strong effect of SPAS (0.1 wt %) on the morphology of the hydrolytical product of the  $\text{FeCl}_3$  solution. In the presence of SPAS, spherical particles of micron dimensions were obtained, whereas only a small number of particles possessed no defined shape. FT-IR spectra of these samples also showed the spectral lines of SPAS, besides those typical of  $\beta$ - $\text{FeOOH}$ , as illustrated in Fig. 7. Since the solid hydrolytical products were well washed with doubly distilled water, it can be concluded that polymer chains are incorporated

in the microstructure of these particles. With an increase of the SPAS concentration (up to 0.5 wt %) more particles of irregular shape were observed in the corresponding TEM micrographs. FT-IR spectra of the hydrolytical products prepared in the presence of 0.5 wt % of SPAS also showed the main characteristics of the  $\beta$ - $\text{FeOOH}$  phase (Fig. 8). In these spectra the IR bands corresponding to  $\beta$ - $\text{FeOOH}$  interfere with the spectral lines of SPAS polymers at 631, 586 and 550  $\text{cm}^{-1}$ .

Influence of different ions on the precipitation of iron(III) oxyhydroxides and oxides was also investigated by other researchers. For example,  $\beta$ - $\text{FeOOH}$  particles were obtained by forced hydrolysis of 0.1 M  $\text{FeCl}_3$  solution at 100°C in the presence of citrate ions [9]. However, the crystallization of  $\beta$ - $\text{FeOOH}$  particles was inhibited by the presence of citrate ions, and the particles showed an amorphous structure for citrate concentrations > 5 mol %. Ishikawa et al. [10] monitored the hydrolysis of 0.1 M  $\text{FeCl}_3$  solution at 100°C for 5 h in the presence of various amines with different

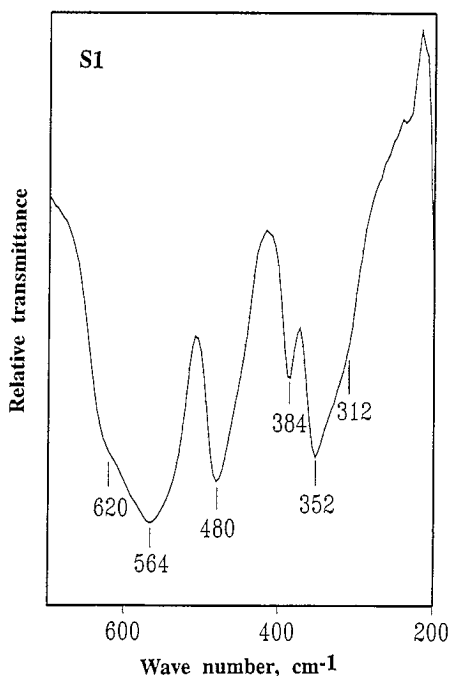


Fig. 2. FT-IR spectrum of sample S1, recorded in the KBr matrix.



Fig. 3. TEM micrographs of sample S3. Needles, X- and Y-shaped  $\beta$ -FeOOH particles are visible.

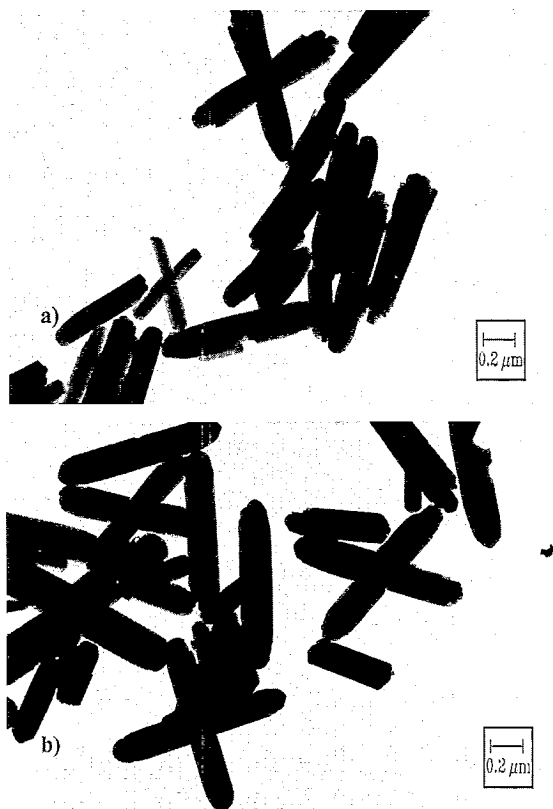


Fig. 4. TEM micrographs of (a) sample S6 and (b) sample S9.

numbers of nitrogen atoms. The particle and crystallite sizes of  $\beta$ -FeOOH decreased with increasing amine concentration; however, the particles produced did not contain amines. The morphology of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles, obtained by hydrolysis of 0.02 M FeCl<sub>3</sub> solution at 100°C, was affected by the addition of the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> anion [11]. Sugimoto et al. [12] prepared monodispersed peanut-type  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles by aging of condensed ferric hydroxide gel in the presence of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup> anions at 100°C for 8 days. The anisotropic growth of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles was explained by specific adsorption of these anions.

The mechanism of FeCl<sub>3</sub> hydrolysis in the presence of sodium polyanethol sulphonate is evidently more complex than the corresponding mechanisms of FeCl<sub>3</sub> hydrolysis in the presence of small inorganic or organic ions. The FeCl<sub>3</sub> hydrolysis in the presence of SPAS could be considered in several stages. In the first stage there is swelling and dissolution of SPAS. Uncoiled polyanethol sulphonate chains compete with OH<sup>-</sup> ions in the complexation of Fe<sup>3+</sup> ions. The iron(III) hydroxy polymers and the surface of  $\beta$ -FeOOH particles while forming are under strong attack of polyanethol sulphonate chains, and in the next stage the primary  $\beta$ -FeOOH particles are linked by uncoiled polymers into a rigid structure of spherical particles. It is

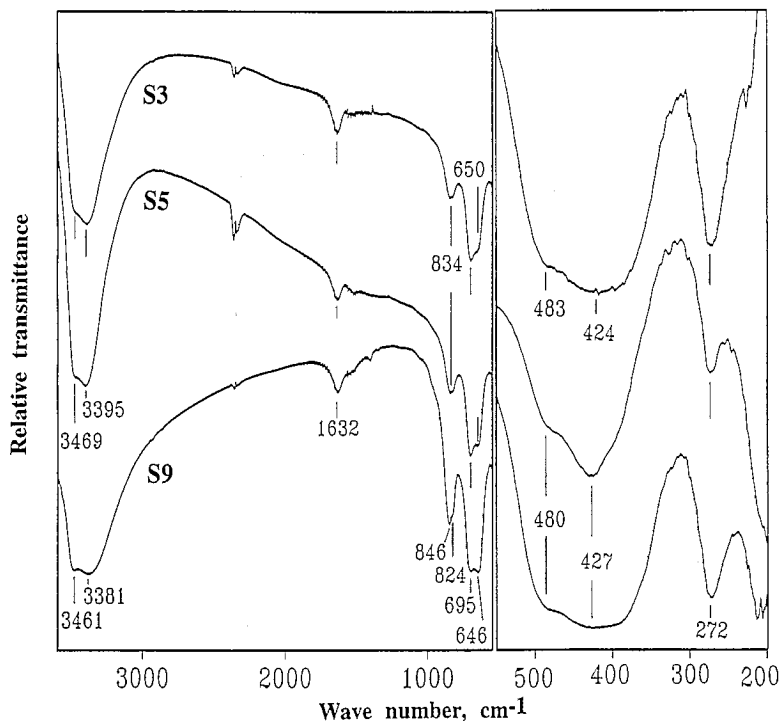


Fig. 5. FT-IR spectra of samples S3, S5 and S9, recorded in the KBr matrix. The samples were obtained by the hydrolysis of 0.1 M  $\text{FeCl}_3$  solution at  $90^\circ\text{C}$  for 4, 24 and 240 h, respectively.

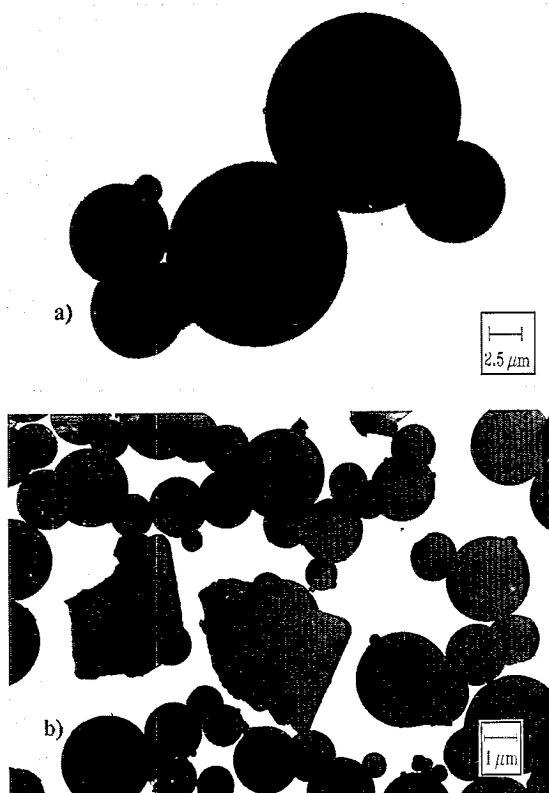


Fig. 6. TEM micrographs of the hydrolytical products of  $\text{FeCl}_3$  formed in the presence of 0.1 wt % of sodium polyanethol sulphonate: (a) after 24 h (sample S11); and (b) after 72 h (sample S12).

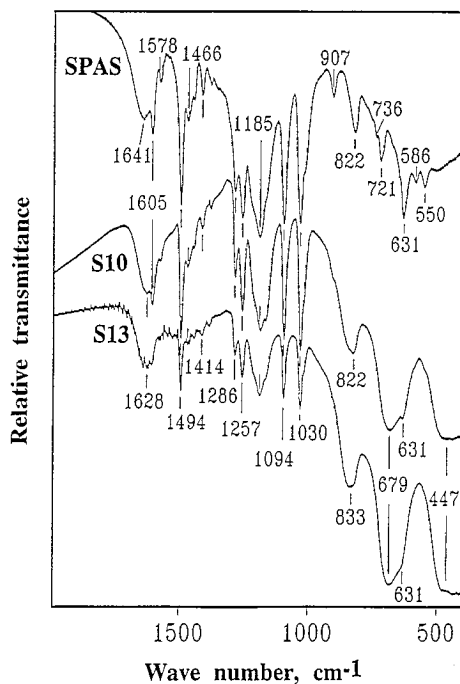


Fig. 7. FT-IR spectra of sodium polyanethol sulphonate (SPAS) and samples S10 and S13.

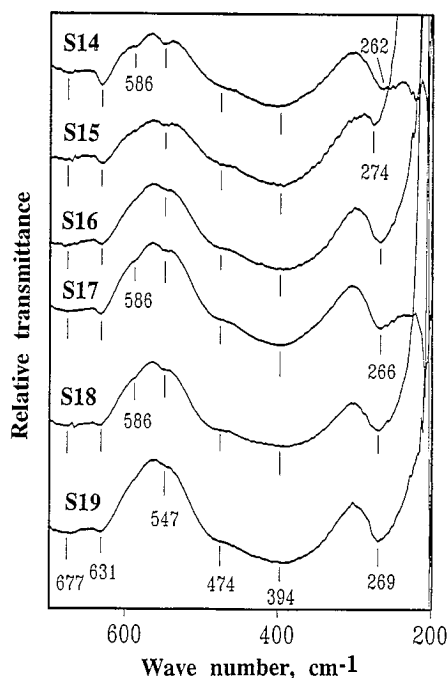


Fig. 8. FT-IR spectra of samples S14 to S19, recorded in the polyethylene matrix.

very probable that polyanethol sulphonate polymer at high concentrations inhibits the crystallization of  $\beta$ -FeOOH particles thus forming big particles of irregular shape. The specific influence of polymers on the other metal cations, which undergo hydrolysis easily, has also been investigated. For example, the precipitation of thorium(IV) hydroxide in the presence of gelatin has been discussed [13] with regard to three processes that occur with an increase in pH: (a) hydrolysis of  $\text{Th}^{4+}$  ions followed by formation of hydroxy complexes and colloidal thorium(IV) hydroxide, (b) dissociation of the functional groups of gelatin, and (c) interaction between the thorium(IV) hydroxide particles with gelatin. Reversible gel formation has been observed in the case of interaction of cupric ions with guar gum-graft-acrylamide [14]. It was concluded that acid groups, present in this polymer in small amounts, played an important role in the complexation and gel-

ling with cupric ions. We believe that the effect described in the present work, without regard to its origin, can be utilized in the production of micron size spherical and porous iron oxide particles after oxidizing the incorporated organic component at relatively low temperatures.

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