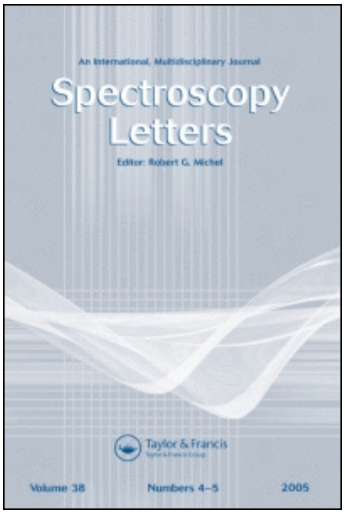

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A SPECTROSCOPIC STUDY OF POLYNUCLEAR COMPLEX OF IRON(III) WITH INULINE OLIGOMERS

Key words: inuline, iron(III) complex, IR spectra, ESR spectra

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ABSTRACT

The infrared spectra of the hydrates of inuline oligomers and the complex of iron(III) with inuline oligomers and their partial deuterated analogs were studied. From the appearance and frequencies of the bands in the range of OH and OD vibrations it was concluded that these crystalohydrates have one type of H_2O molecule, and relatively weak hydrogen bond (estimated

O_w...O distances are 280 and 283 pm for inuline and its complex, respectively). From the FTIR spectra of the complex the β_2-form for iron(III) oxihydroxide (FeOOH) was determined. On the basis of the electron spin resonance spectra it was concluded that Fe^{+3} ions of octahedral configuration (g-value 2.03 ± 0.01) were present in the complex. From the measured ESR linewidth (ΔH = 100 ± 5 mT) the approximate Fe interatomic distance of 0.21 nm was calculated, indicating a dense packing of Fe atoms in the cluster.

INTRODUCTION

For the prevention and treatment of iron deficiency different types of iron(III) hydroxide carbohydrate complex are used.[1,2] The structure of these complex systems has not been explained in details yet, despite a number of studies.

Electron spin resonance (ESR) spectra of the iron metal complexes of different carbohydrates, such as polyisomaltose, polymaltose and hydrogenated low molecular dextrane, are reported.[2,3] The interest of the investigators has mainly been centered on type of interactions between iron clusters and the ligand species,[2] or iron configurations.[3]

The infrared (IR) studies have been focused mainly on the ν(OH) and δ(OH) vibrations of the iron(III) hydroxide and their modifications.[2,4] The hydrogen bonds in the structure of hydrogenated low molecular dextrane and their complex with iron(III), conformation of glucopyranoze unit in their compounds were studied.[3]

Continuing our study on the complexes of iron(III) with oligosaccharides,[5-8] the present work deals with the polynuclear complex of iron(III) with inuline oligomers.

Inuline is a suitable ligand for complexing with iron(III) hydroxide because of its physicochemical characteristics (relative small molecular weigth, unreducing polysaccharid). Literature data on this complex is very rare. Only Müller[2] reported that this complex, with the content of iron of 39.7% w/w, was synthesized. The structure of this compound has not been studied in detail, but it is expected that it will be similar to the complexes of iron(III) hydroxide with other polysaccharides.

The IR spectra of inuline hydrates, the complex of inuline with iron(III) hydroxide and their partially deuterated analogs were studied in the present work. The main goals were to establish the types of H_2O molecules, to estimate the strength of hydrogen bond (between H_2O molecules, inuline and the complex) and to determine the form of FeOOH in the complexes. With the aid of ESR measurements an attempt to propose the type of coordination around the iron ions was also made.

EXPERIMENTAL

All compounds were prepared by the published methods.[6] The partial deuterated analogs were prepared from the hydrates of analogs. Deuteration was accomplished by suspending a sample in liquid deuterium oxide (5 D_2O : 1 sample by gross weight). The mixture was

kept in the special fused test tubes in vacuum, at room temperature for 48 h and then was dried in vacuum at room temperature.

The IR spectra were recorded at room temperature, on a Perkin-Elmer 1600 FTIR spectrophotometer, using KBr techniques.

The ESR spectra were recorded on a Bruker 200D ESR spectrometer, employing 100 KHz modulation and a nominal frequency of 9.5 GHz.

RESULTS AND DISCUSSION

Iron(III) hydroxide appears in several modifications described as α-, β_1-, β_2-, γ- and δ-FeOOH. For the synthesis of the pharmacologically important complexes only the β_2-form is used. The presence of β_2-FeOOH in the complexes can not be verified certainly by the method of IR spectroscopy because the bands of δ(OH) and ν(OH) vibrations are covered by the bands of ligands.[2] However, in the IR spectrum of the complex of FeOOH with hydrogenated low molecular dextrane (HDD),[3] which is refined by preparative column gel chromatography on Sephadex, presence of the β_2-form is verified by the band at about 690 cm^{-1}. In our case, the band of the δ(OH) vibration from β_2-FeOOH appears at about 687 cm^{-1}. The IR spectrum of FeOOH used in the present synthesis is identical to the spectrum for β_2-FeOOH found in the literature[2,4] (Fig. 1a).

The weak band at about 693 cm^{-1} appears in the spectrum of the complex of iron(III) with inuline oligomers (Fig. 1b) but not in the

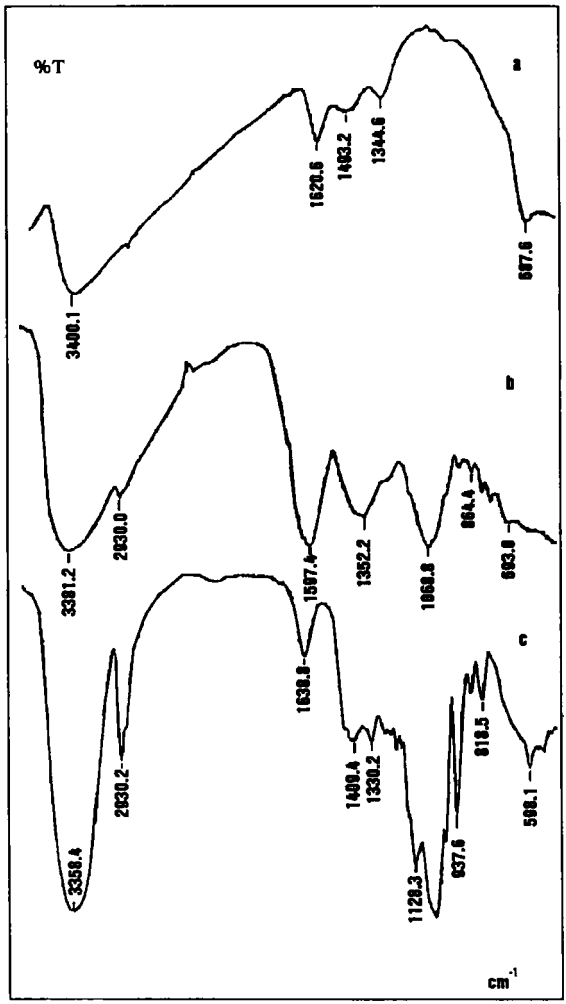

Fig. 1. Infrared spectra of samples: a) β_2-FeOOH; b) inuline-iron(III) complex; c) inuline

spectrum of inuline oligomers (Fig. 1c). Thus, it can be concluded that β_2-FeOOH is present in the complex of iron(III) with inuline oligomers.

By the isotopic excange method, both inuline and its complex are shown to be crystallohydrates. Namely, in the spectrum of inuline with a low content of deuterium (Fig. 2) in the range of ν(OD) vibrations from HDO molecules one band appears at about 2495 cm^{-1}, and for the complex there are a band with the center at 2510 cm^{-1} and the low-frequency side inflexion (Fig 3). The number of bands and the frequencies can not be changed by an increase in the isotopic excange degree, i.e. by an increase in the content of deuterium.

The corresponding partners of these vibrations in the ν(OH) region, which are expected at about 3400 cm^{-1}, are difficult to find. Namely, in both compounds a wide intensive band appears in this region with the centre at about 3358 cm^{-1} and 3381 cm^{-1} in the spectra of inuline and the complex, respectively. As well known,[9] in this region the bands of ν(OH) vibrations of saccharides are expected and thus, the band at 3380 cm^{-1} should be assignated as the ν(OH) vibration of inuline. However, the reduction in the intensity of this band by deuteration shows that it is also due to the ν(OH) vibration of H_2O molecules, but its frequency can not be determined precisely because of the covering effect.

On the basis of the spectrum in the valent OD region of HDO molecules, it can be concluded, using criterion of Falk et al.[10], that both inuline and its complex with iron(III) have one crystallographic type of H_2O molecule. Water protons take part in the formation of

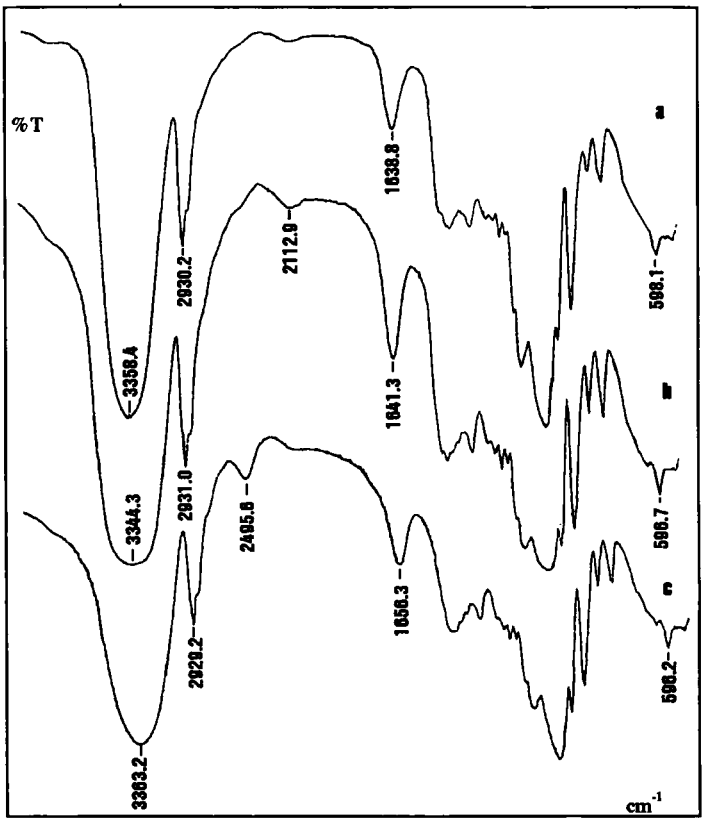

Fig. 2. Infrared spectra of samples: a) inuline; b,c) partially deuterated inuline

relatively weak hydrogen bonds. On the basis of corelation Berglund,[11] the estimated O_w...O distances are 280 and 283 pm, for inuline and their complex, respectively. These resultes are very similar to those obtained by studying HDD and its complex with FeOOH.[7]

The ESR spectrum of the complex of iron(III) with oligomers of inuline in the solid state, recorded at room temerature is presented

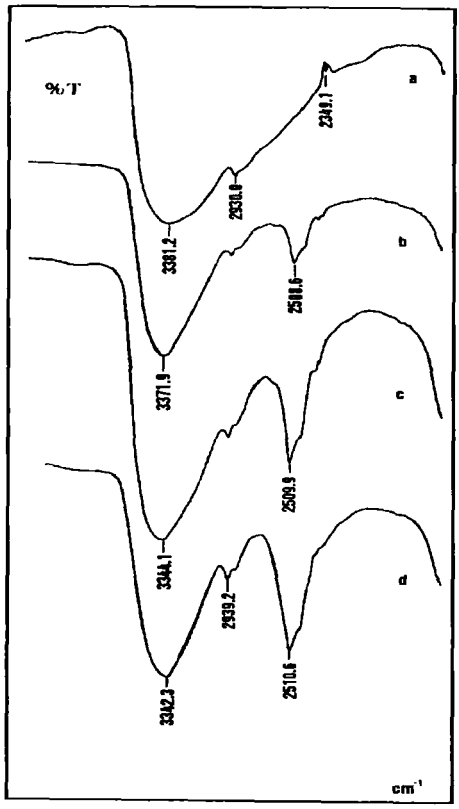

Fig. 3. Infrared spectra of samples: a) inuline-iron(III) complex; b,c,d) partially deuterated inuline-iron(III) complex

in Fig. 4. The most probable source of the intense resonance that is characteristic of the inulin-iron system is Fe^{+3}. An effective g-value of 2.03 ± 0.01 and a linewidth $\Delta H_{p\text{-}p}$ of 100 ± 5 mT are evidence that these parameters are determined by the strong magnetic interaction between the paramagnetic ions.[2,12,13] For the complex of HDD with

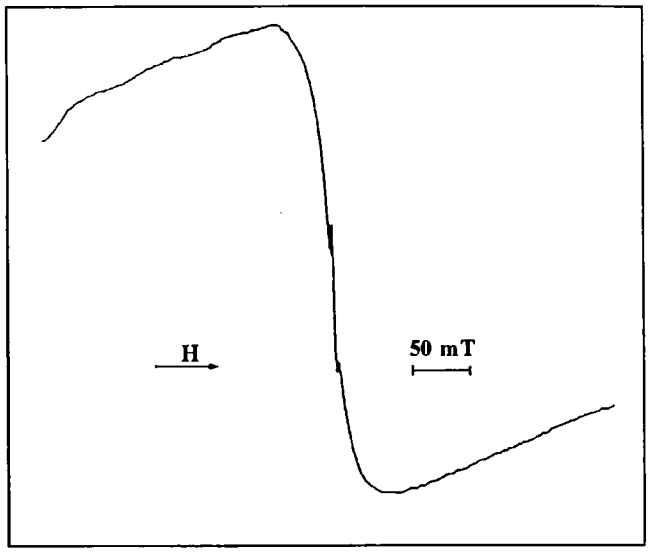

Fig. 4. ESR spectrum of inuline-iron(III) complex

FeOOH the effective g-value of 2.02 ± 0.01 and a linewidth $\Delta H_{p\text{-}p}$ of 90 ± 5mT are determined.[3]

The interatomic distance between Fe atoms in a molecule of the complex can be calculated by using the literature data,[14] from the experimental g-value and the ESR linewidth. The linewidth depends on the magnetic dipole-dipole alternating effect between Fe atoms. This effect increases by decreasing the interatomic distance.

An approximate distance between Fe atoms of 0.21 nm is determined from the measured ESR linewidth of 100 ± 5 mT. A somewhat smaller value of Fe interatomic distance (0.15 nm) was

published earlier.[2] The values of which was explained by a dense packing of Fe atoms in cluster.

In addition, the *g*-value for the complex of iron with inuline oligomers is in the range commonly found for the octahedraly bound iron ions in compounds with hydrogenated dextrane, polyisomaltose, polymaltose and similar carbohydrates, which indicates the similar interaction between iron ions and ligands in these compounds.[2]

In spite of the difficulties concerning the determination of the band of FeOOH vibrations on the basis of the available evidences from the ESR spectra and the literature data, we suggest that the most probable coordination around iron ions is octahedral.

CONCLUSION

From the IR spectral data it is concluded that β_2-FeOOH is probably present in the complex of iron(III) with inuline oligomers. The inuline and its complex with iron(III) have one crystallographic type of water molecule. Water protons take part in the formation of relatively weak hydrogen bonds.

The ESR spectra indicate that the coordination around the iron ion in the complex is probably octahedral.

The structure of the complex iron(III) with inuline oligomers is probably similar to the structure of the complexes of iron(III) hydroxide with other oligo- and polysaccharides.

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