X-ray Diffraction Study of the Coordination of Fe(III) in a Highly Hydrolyzed Solution of Iron(III) Chloride

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A highly hydrolyzed solution of iron(III) chloride is investigated by X-ray diffraction. The occurrence of six O atoms in the first coordination shell of iron(III) is demonstrated. The structural similarity of hydrolyzed solutions of Fe(III) chloride and nitrate is pointed out.

Introduction

The hydrolysis of iron(III) has been largely investigated because of the intrinsic interest and the technological importance of this subject, and detailed results have been reported in some reviews [1, 2].

One of the less clear points in this matter is the relationship between the hydrolysis products and the solid phases obtained from iron(III) solutions. It has been observed [1] that, in some conditions, the addition of a base to Fe(III) solutions gives rise to rapid formation of precipitates while, in different situations, hydrolysis phenomena result in the growth of polymers from which solid phases are produced very slowly. According to Spiro et al. [3], "precipitation occurs most readily via low molecular weight species and thus polymerization and precipitation are competing processes". The hypothesis has been advanced [3] that structural differences between polymers and precipitates are responsible for this competition effect; as a consequence structural information on the polymeric species is badly needed.

Further interest for these problems comes from the observation that some Fe(III) hydrolyzed products are analogs of natural compounds of biological importance, like the ferritin, so that they have been used as model compounds in investigations on these natural substances. To date, however, only two studies [4, 5] have been performed by X-ray diffraction on solutions containing polymeric species obtained from alkalized iron(III) nitrate solutions. These studies agree as far as the kind of short and medium range order is concerned (that is the succession of peaks appearing in the radial distribution function calculated from experimental data). But a different coordination is assigned to the iron(III) atom. In fact, Brady et al. [4] suggest a fourfold oxygen coordination with tetrahedral arrangement, while Magini [5] proposes a sixfold oxygen coordination, presumably with octahedral geometry. This contrast is singular, as connecting either tetrahedra or octahedra in order to build the polymeric units cannot lead to the same spectrum of medium range distances. In this connection, however, it can be observed that, in a recent EXAFS investigation on the structure of iron-containing polymers, Heald et al. [6] showed that the polymer investigated by Brady et al. was composed of two different fractions; while one form may be described in terms of octahedrally coordinated Fe(III), in the second one the iron(III) atoms are tetrahedrally coordinated. This observation may partly explain the discrepancy between the results of Brady et al. and the estimates of Magini.

Obviously the knowledge of the true Fe(III) coordination in the hydrolysis products is the first step towards the resolution of the structural problem. Therefore, as a first contribution to a better understanding of the structure of Fe(III) polymeric species, an investigation was started on a highly hydrolyzed solution obtained from $FeCl_3$. Aims of this study were: a) to ascertain the immediate environment of Fe(III) atom, b) to check the possible effect on polymerization of changing the anion.

Experimental and Data Treatment

Following the procedure of Magini [5], the sample was prepared from a solution of $FeCl_3 \cdot 6\,H_2O$ by extracting HCl with an organic solution of a primary amine. The composition of the sample was $Fe^{3+} : Cl^- : H_2O = 1 : 0.8 : 28.5$, the concentration of Fe(III) being $2\ mol \cdot l^{-1}$.

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The present results cannot be compared with a previous study of Brady et al. [7] on the structure of polymeric ferric chloride in aqueous solutions, as in that case polymerization was carried out by adding HCl to $FeCl_3$ neutral solutions, thus increasing the ratio Cl atoms/Fe(III) atoms.

The X-ray apparatus has been described elsewhere [8, 9]. As the solution is in a non-equilibrium state, in the choice of experimental conditions a compromise was looked for between the need of good statistics in the collected counts and reasonable experience times. Thus 100.000 counts per point were recorded between the scattering angles $2\vartheta = 3^\circ$ and 122°, which protracted the data collection for a week. During this time subsequent checks at prefixed angles allowed to verify that initial and final counting rates did not differ by more than 2%, that is only a bit more than the usual statistical accuracy. This confirms that Fe(III) hydrolyzed solutions change very slowly.

The measured diffraction intensities were worked out following a standard treatment [8–10] which includes background subtraction, correction for absorption, polarization and incoherent radiation and evaluation of the absolute intensities $I_{\mathrm{e.u.}}$. A fourth differencies smoothing procedure was cautiously applied in order to get rid of the strongest irregularities without modifying the experimental data beyond the statistical uncertainty.

The structure function was then constructed according to:

$$i(s) = \left(I_{\mathrm{e.u.}} - \sum_{i=1}^{m} x_i f_i^2\right) \Big/ \left(\sum_{i=1}^{m} x_i f_i\right)^2, \qquad (1)$$

where f_i are the scattering factors, x_i the stoichiometric coefficients in a structural unit containing m kinds of atoms, s is the usual scattering variable $= 4\pi \sin\vartheta/\lambda$, λ being the wavelength of the radiation employed (Mo Kα). The values of the f_i used were those proposed by Hajdu [11] for the water molecule and those by Cromer and Mann [12] for the other species. A correction for residual systematic errors in the structure function was also applied [8, 9].

The radial distribution function, $D(r)$, was obtained from $i(s)$ by Fourier Transformation according to:

$$\frac{D(r)}{r} - 4\pi r \varrho_0 = Q(r) = 2/\pi \int_{s_{\min}}^{s_{\max}} s\, i(s) \sin rs\, \mathrm{d}s, \qquad (2)$$

where r is the interatomic distance, $s_{\min}$ and $s_{\max}$ are the lower and the upper limits of the experimental data, and ϱ_0 is the bulk density of stoichiometric units. Because of the bad quality of the high angle data, the $s_{\max}$ value used was 14.4 Å^{-1}.

Results and Discussion

The structure function and the corresponding radial distribution function (in the differential form $Q(r)$) are given in Figs. 1 and 2, respectively. The structure function exhibits general features very different from the usual diffraction spectra from

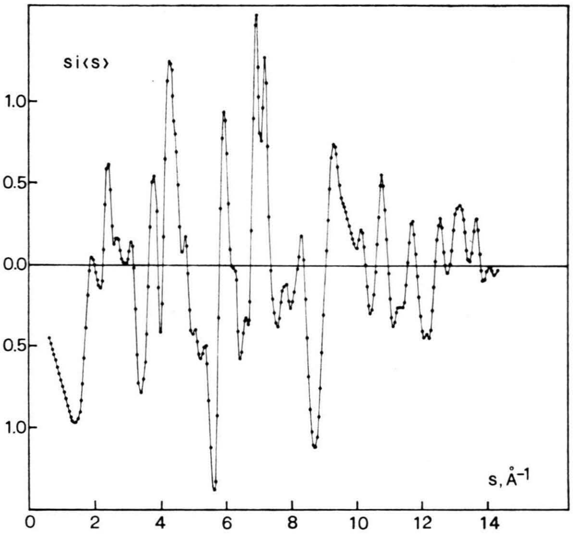

Fig. 1. Experimental structure function (a continuous line has been drawn through experimental points for clarity).

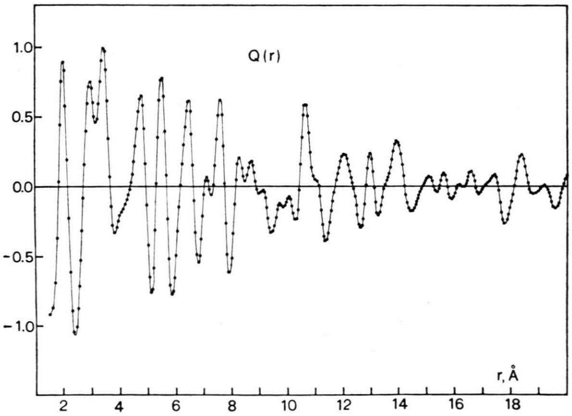

Fig. 2. Experimental radial distribution function in the differential form (a continuous line has been drawn through experimental points for clarity).

liquids. The number of peaks, their sharpness and the irregular distribution of their heights suggest much more remarkable and complex order phenomena than the ones usually observed in electrolyte solutions. This suggests that the hydrolytic polymerization has caused the formation of high molecular weight species (as expected) and, above all, that the connection of the monomeric units takes place in a regular way.

The radial distribution function confirms this supposition. In fact, peaks up to about 20 Å are observable, that cannot be confused with periodic spurious ripples and that, therefore, indicate meaningful positional correlation. As discussed in the following, it is impossible to ascribe these peaks to specific pair interactions, with the exception of the first peak. This peak, in fact, is centered at 2.00 Å; this is the value ascribed to the Fe(III)-O pair in aqueous solutions in a great number of investigations [5, 13 – 15]. Moreover, the peak is symmetric and well-resolved, thus giving a first indication that the immediate environment of Fe(III) atoms is formed essentially by oxygen atoms. The good resolution of the peak at 2.00 Å made possible its quantitative analysis. In fact, back-transforming the peak, a "filtered" structure function $s\,i(s)_f$ was obtained and analyzed by using the Debye formula modified, as usually done in constructing synthetic structure functions for liquids, solutions and amorphous substances [8 – 10]. A least squares refinement, based on the hypothesis that this partial structure function comes out from Fe(III)-O interactions alone, yielded a very good agreement between "experimental" and synthetic $s\,i(s)_f$'s, as observed in Figure 3. The final values of the parameters used were: Fe(III)-O distance, $r_{\text{Fe-O}} = (2.019 \pm 0.002)$ Å; root mean square deviation of the Fe(III)-O distance, $\sigma_{\text{Fe-O}} = (0.151 \pm 0.003)$ Å; coordination number of Fe(III) atom, $N_{\text{Fe-O}} = 5.9 \pm 0.1$.

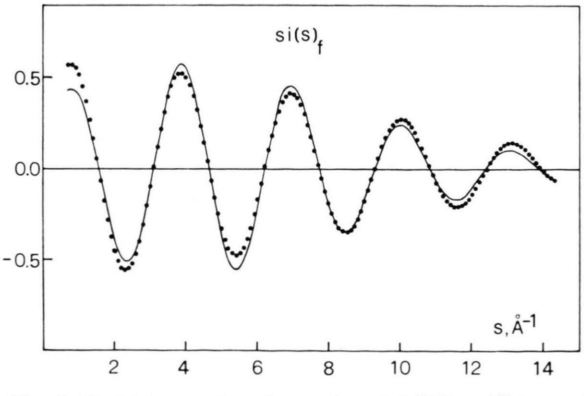

Fig. 3. Model (———) and experimental "filtered" (· · · · ·) partial structure functions for Fe(III)-O pair.

The coordination number (practically equal to six) and the Fe(III)-O distance (coinciding with the Fe(III)-O distances usually quoted in neutral-acid solutions) clearly point out that the arrangement of oxygen atoms in the first coordination shell of the Fe(III) atom should not be very different from the octahedral one found in $Fe(H_2O)_6^{3+}$. The value of the root mean squares deviation $\sigma_{\text{Fe-O}}$ is about twice the one reported for the Fe(III)-O pair in neutral-acid solutions; this could mean a distortion of the octahedral geometry that is not unexpected.

The occurrence of only O atoms in the first coordination shell of the iron(III) is an important (not completely expected) result. In fact, in the initial $FeCl_3$ solutions, the iron(III) atom is engaged in complexes containing a variable number of Fe-Cl contacts [16, 17]. Clearly, during extraction and polymerization processes, Cl^- ions are displaced from the first coordination sphere of Fe^{3+} ions. This hypothesis is supported by the succession of the peaks beyond the first one being identical to that reported by Magini [5] and by Brady et al. [4] in solutions of the polymers obtained from $Fe(NO_3)_3$ samples. In fact, peaks at 2.90 Å, 3.40 Å, 4.75 Å, 5.45 Å and 6.25 Å are present in the $Q(r)$ of Fig. 2, in very good agreement with the results reported in the above mentioned papers. Thus, it can be stated that the short and medium-range order in hydrolyzed solutions of Fe(III) chloride and nitrate is very similar, the influence of the residual anion being very week. Since in the mentioned papers information on the "order range" is missing, it is not possible to verify if the degree of hydrolysis and the polymer size are remarkably dependent on the anion present, as reported by Spiro et al. [3]. Furthermore, nothing can be said about the influence of chloride ions on the morphology of polymer particles that was evidenced in a study of Dousma et al. [18].

As regards the coordination number of Fe(III), the present result is in agreement with the proposal of Magini [5], while it is at variance with Brady et al.'s [4] evaluation.

A clear answer has been given to the questions raised in the Introduction. One may ask, at this point, if further information can be drawn from a deeper analysis of the sequence of the peaks above described. In the present state of the possibilities of the X-ray diffraction technique, this would be a mere exercise. In fact, on the one hand, a univocal assignment of the peaks is impossible (for example, Fe-Fe distances can fall either at 2.90 Å if regular FeO_6 octahedra are linked through an edge or at 3.40 Å if Fe-O-Fe bridges are bent with angles of about 125 degrees); on the other hand, a useful model should include interatomic distances up to 20 Å, this being the observed order range. As a consequence, lacking structural data from different techniques, a quantitative analysis more complete than that performed seems nowadays quite impossible.

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