Mononuclear, oligonuclear and polynuclear iron(III) complexes with polyalcohols formed in alkaline aqueous media

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Abstract

Low molecular weight complexes of Fe(III) with selected diols, glycerol and sorbitol and their hydrolysis products in alkaline aqueous media have been prepared and characterized. The three types of ligands interfered distinctly different with hydrolysis. According to solubility measurements of Fe in the presence of the two monomethylethers of glycerol, deprotonated 1,2-diolato entities are bound to Fe(III) in strongly alkaline aqueous solutions. The magnetic susceptibility measurements and Vis spectra indicate the formation of a mononuclear glycerol complex at high base and ligand concentration ($\geqslant$1M). At pH 12–13, the growth of polynuclear complexes was investigated by laser light scattering and by kinetic measurements of the rate of degradation in 2 M HCl. A monotonic increase of the hydrodynamic radius (11–40 Å) and half life (0.5–10 s) over a period of four weeks was observed. Polynuclear Fe(III)–sorbitol complexes have a pH-dependent molecular weight, hydrodynamic radius and half life of degradation, with a small low molecular weight complex (pH$\geqslant$10.5) and a gel (pH$\geqslant$7) as the extremes of the series. The polymerization of these Fe(III)–sorbitol complexes is completely reversible.

Introduction

It has been known for more than 150 years that polyhydroxy compounds in aqueous alkaline solutions enhance the solubility of metal oxides or hydroxides such as FeOOH, $Cu(OH)_2$ and $Pb(OH)_2$ [1–3]. This effect has been explained either by the formation of soluble complexes [4, 5] or by the stabilization of colloidal solutions [3, 6]. Due to the low solubility of FeOOH in water on the one hand and the importance of iron in biological systems on the other hand, the sequestering ability of sugars [7–11], sugar-alcohols [10–13] and sugar-acids [10, 11, 14–16] has been extensively investigated. Already Goldschmidt *et al.* [2] found that in alkaline solutions of glycerol, mannitol or glucose, both forms, i.e. low molecular complexes and colloids, can appear depending on the concentrations of iron, base and ligand. Moreover, they postulated that "all conceivable intermediates of these two forms can be found in these solutions". Since that time, a variety of investigations, based on the analysis of precipitated solids [6, 7, 9, 10, 13], pH or redox titrations [7, 12, 14], EXAFS studies [11], Mössbauer [10, 13, 15], ESR [10], IR [10, 13] and UV–Vis spectroscopy [7, 14] has been performed. To solutions containing polynuclear species, electrophoresis [1], dialysis [3], ultrafiltration [2] and gel filtration [13] have also been applied. However, there still remain open questions about the structure and reactivity of these complexes.

In a previous investigation in our laboratory, a variety of methods was used to identify a set of well defined ferric complexes of sorbitol [17]. In the present contribution the different chelating ability of a series of polyols is discussed and it will be demonstrated that laser light scattering combined with stopped-flow kinetic measurements of acid degradation in 2 M HCl is a suitable method of getting additional information about the growth and structure of the species formed in solution.

Experimental

Ligands

Glycerol-1-methylether was prepared following the procedure given in ref. 18. Colourless liquid, b.p. 117 °C (22 Torr), n_D(25 °C) 1.4425. ^{1}H NMR ($CDCl_3$, δ (ppm) versus TMS) 4.16 (1 H), 3.94 (1 H), 3.77 (1 H) 3.3–3.6 (4 H), 3.29 (3 H). ^{13}C NMR ($CDCl_3$, δ (ppm) versus TMS) 74.1, 70.8, 63.8, 59.2. *Anal.* Calc. for $C_4H_{10}O_3$: C, 45.27; H, 9.50. Found: C, 45.11; H, 9.66%.

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Glycerol-2-methylether [19] was prepared by methylation of 3,5-dioxacyclohexanol (NaH, CH_3I, dioxane, yield 85%) followed by methanolysis of the obtained 1-methoxy-3,5-dioxacyclohexane (CH_3OH, H_2SO_4, yield 82%): Colourless liquid, b.p. 117 °C (13 Torr), n_D(25 °C) 1.4473. ^1H NMR ($CDCl_3$, ppm) 3.7 (4 H), 3.6 (2 H), 3.4 (3 H). 3.3 (1 H). ^{13}C NMR ($CDCl_3$, ppm) 81.5, 61.3, 57.5 *Anal.* Calc. for $C_4H_{10}O_3$: C, 45.27; H, 9.50. Found: C, 44.94; H, 9.74%.

All other ligands used were commercially available chemicals of analytical reagent grade.

Preparation of complex solutions

Aqueous solutions with a diol as ligand. An acidic solution of $FeCl_3$, containing an appropriate amount of the diol (0.1–1M) was added (0.5 ml/min) to an alkaline solution containing the same amount of ligand as the acidic $FeCl_3$ solution and an appropriate amount of NaOH to achieve the final desired pH. After addition, the suspension was allowed to stay in the dark until the precipitation of a brown solid was completed (1–3 days). The supernatant was then decanted from the solid, centrifuged for 2 h (12 000 rpm) and filtered. Fe was determined spectrophotometrically as the tris-phenanthroline complex of Fe(II) [20]. The content of base was checked by titration of a sample with 0.1 M HCl.

Aqueous solutions with glycerol as ligand. Four stock solutions were prepared:

(a) Fe = 0.1 M, glycerol = 1 M, HCl = 0.05 M;
(b) KOH = 0.5 M, glycerol = 1 M;
(c) glycerol = 1 M;
(d) KOH = 3 M, glycerol = 1 M.

The solutions (b) and (d) were kept under N_2; solutions (b), (c) and (d) were freshly prepared prior to use. During the preparation of the test solutions, the mixture was stirred vigorously and kept under N_2. A pale yellow solution of the mononuclear complex was prepared by the addition (0.5 ml/min) of equal volumes of (a) to (d). Dark brown solutions containing polynuclear species were either prepared by 1:10 dilution of the yellow solution with (c) or by the addition (1 ml/min) of equal amounts of (a) to (b). The pH of the polynuclear solutions was lowered by further dilution with (c) and adjusted to the range of 12.9 to 12.2.

Aqueous solutions with sorbitol (H_2sor) as ligand. A green solution containing the dinuclear $[Fe_2(OH)_2(sor)_4]^{4-}$ [17] was prepared by adding (1 ml/min) a solution of 1 M $FeCl_3$, 1 M H_2sor, 0.1 M HCl to a vigorously stirred 5 M NaOH, 1 M H_2sor solution in a 1:1 ratio. The solution of the oligonuclear Fe(III)–sor complex was prepared by lowering the pH to about 10.5 with imidazole buffer (7.5 M imidazole, 6.8 M HCl, pH = 6, rate of addition = 1 ml/min). For further experiments this solution was diluted with water to give a total iron concentration of 0.15 M. The same imidazole buffer as mentioned above was used to lower the pH to 7. NaOH solutions were used to increase the pH. Solid samples were prepared by precipitation with ethanol. The yellowish brown solid was washed with ethanol and dried *in vacuo*. *Anal.* Calc. for $Na_n[Fe_nO_{2n}H_{2n}(sor)_n]$: C, 24.60; H, 4.82; Cl, 0; Fe, 19.06; Na, 7.85. Found: C, 24.90; H, 4.90; Cl, 0.7; Fe, 18.3; Na, 5.88%.

Dry methanolic solutions with diols or glycerol as ligand and tetramethylammoniummethoxide as base were prepared as previously described [21]. However, with the ligands used in this investigation, no precipitation of solid phases was observed during the entire preparation procedure. The molar ratio of Fe:ligand:base was 1:6:10 with a total iron concentration of 0.05–0.1 M. The hydrolysis of these solutions was achieved by the addition of a solution of H_2O (10 M) in methanol.

Polynuclears in acidic aqueous chloride media were prepared by slow addition (0.4 ml/min) of 35.24 ml Na_2CO_3 solution (4.26 M) to 100 ml of an acidic $FeCl_3$ solution ($FeCl_3$ = 1 M, HCl = 1 M) with a Mettler DV 11 burette. During the addition of base, the mixture was kept under N_2. One day after preparation, 10 ml of this solution were diluted by addition of 138.3 ml of a $NaClO_4$ solution (0.92 M).

Kinetic measurements of acid decomposition

A Durrum-Gibson stopped flow spectrophotometer was used to follow the decomposition of ferric polyol complexes in solution. Equal volumes of 4 M hydrochloric acid and the complex solution ($7 \leqslant pH \leqslant 13$) were mixed (25 °C) and the absorbance was monitored at 450, 500 and 560 nm. The large excess of hydrochloric acid compared to the base in the complex solution provided a constant activity of H^+ and Cl^-. However, the kinetics of degradation of the polynuclears could not be expressed by the simple rate law discussed elsewhere [22]. Some 5–20% increase of the subsequent half lives was observed during the course of reaction. In this investigation, the first half life is used to characterize the reactivity of the polynuclears with regard to acid attack. It was not possible to investigate the polynuclears formed in acidic solutions under the conditions described above, due to precipitation of solid phases after the mixing of the polynuclear solution with 4 M HCl. The corresponding half life was derived from an experiment with lower HCl concentration (pH = 1, $[Cl]_t = 0.2$ M, $[ClO_4]_t = 0.85$ M) using the well established rate-law $1-(p_w(t)/p_w(0))^{1/3}=kt$ [23], were p_w is the number of Fe atoms per polynuclear and $k=(k_1+k_3K^s_{Cl}[Cl^-])[H^+][Cl^-]/(1+K^s_{Cl}[Cl^-])$ with $k_1=0.32$ h^{-1} M^{-2}, $k_3=0.23$ h^{-1} M^{-1} and $K^s_{Cl}=5$ M^{-1}. pH 1 was maintained with a Mettler DK 11 pH-stat. The total amount of Fe in polynuclear species was determined after removing the low molecular weight complexes by chromatography on an acidic ion exchange resin [24].

Physical measurements

For NMR measurements, a WM-250 spectrometer (Bruker) was used. Vis spectra were recorded with an Uvikon 820 spectrophotometer. pH was measured with a Philips (0-14) glass electrode combined with an ORION pH-meter.

Magnetic measurements

0.9–1 g of the alkaline solution, containing a Fe(III)–polyol complex, was sealed in a polypropylene tube and cooled immediately to 77 K with liquid nitrogen. The magnetic susceptibility of the frozen samples was measured by the Gouy method with a Varian V 4005 electromagnet operating at 6 kG and a Mettler ME 21 microbalance. Temperature control was achieved by a stream of N_2 in an evacuated variable temperature cryostate (Oxford Instruments). The sequence $T_1,T_1',p,g_1,g_2,g_3,T_2,T_2'$ was applied for 500–600 datapoints in the range of 77–300 K where T and T' denote the measurement of the temperature with two different thermocouples, p the measurement of the pressure, g_1 and g_3 the measurement of the weight in the presence and g_2 in the absence of the magnetic field. The magnetic susceptibility was then evaluated from $g_2(g_1+g_3)/2$ after correction for diamagnetism using Pascal constants. $\mu_{eff}=2.84(\chi T)^{1/2}$ was calculated according to the Curie law. An acidic aqueous solution of $FeCl_3$ was used for calibration.

Laser light scattering

The commercially available low angle laser light scattering photometer KM-6 from Chromatix was used for static and dynamic measurements. Irradiance of scattered and incident light was recorded on a strip chart recorder. The autocorrelation function of the scattered light intensity was calculated by a 64 channel Langley Ford digital correlator and subsequently evaluated on a Hewlett Packard 1000 computer.

Determination of the refractive index n of sample solutions and the refractive index increment dn/dc of the colloids were made with a refractometer type Atago 1T and a differential refractometer KMX-16 from Chromatix, respectively. Solvent viscosities were measured with a KPG Ubbelohde viscosimeter no. 0. Prior to the light scattering measurements, the solutions were filtered through a 0.2 μ Fluoropore filter from Millipore.

Static scattering (intensity measurements). The size of the iron colloids described in this work was much smaller than the wavelength of the laser light ($\lambda=632.8$ nm). Therefore, the theory of Rayleigh–Debye scattering may be applied to these systems [25] and the relations

$$Kc/R_\theta=1/M_wP+2A_2c/P+\ldots \tag{1}$$

$$K=(1+\cos^2\theta)(\mathrm{d}n/\mathrm{d}c)^2 2\pi^2 \mathrm{n}^2/\lambda^4 N_A) \tag{2}$$

are valid for dilute polymer solutions [26], where c is the polymer concentration (g/ml), R_θ denotes the Rayleigh ratio and M_w is the weighted average molecular weight. The form factor P is a function of the scattering angle θ and reaches unity for small values of θ as used in this investigation (2°–7°). The second virial coefficient A_2 represents the interaction between the polynuclears. Measurements at different colloid concentrations showed a linear correlation between R_θ and c which leads to $A_2=0$. Considering the relations $c=M_{Fe}c_{pn}/1000$ and $M_w=p_wM_{Fe}$ (M_{Fe} = formula mass of the iron hydroxide in g/mol) the nuclearity p_w can be calculated from eqn. (1) by $p_w=R_\theta/K'c_{pn}$, where c_{pn} is the concentration of Fe(III) bound in polynuclears and $K'=K\times 1000\,(\mathrm{d}c/\mathrm{d}c_{pn})^2$. In this investigation, the concentration of mononuclear Fe is negligible and c_{pn} is therefore equal to the total concentration of Fe in the solution. The Rayleigh ratio R_θ was calculated from the measured photomultiplier signals of incident (I_0) and scattered (I_s) light: $R_\theta=I_s/I_0S$. S is a constant determined by the optical geometry of the light scattering photometer.

Dynamic scattering (photon correlation spectroscopy). The translational diffusion coefficient D of the iron polynuclears was determined by analysis of the autocorrelation function $G(t)$ of the photocurrent $i(t)$ detected by the photomultiplier: $G(t)=\langle i(0)i(t)\rangle=\langle i^2\rangle(1+g_1^2(t))$. For monodisperse systems, $g_1(t)$ can be expressed as $g_1(t)=\exp(-Dq^2t)$ [27], where q denotes the scattering vector. For polydisperse systems, the autocorrelation function $G(t)$ was analyzed with the method of cumulants and nonlinear cumulants [28]. Both methods gave very similar results. Hydrodynamic radii r were calculated according to the Stokes–Einstein equation $r=kT/6\pi\eta D$.

Results and discussion

Fe(III) and diols

The chelating ability of a variety of diols in alkaline aqueous solution has been tested by the addition of an acidic solution of $FeCl_3$ and the diol to a solution containing the diol and a sufficient excess of base. A suspension, consisting of an almost colourless supernatant and a brown solid was always obtained. The chelating ability of the diol was determined by measuring the concentration of Fe remaining in solution. The results, together with the corresponding values for glycerol, are summarized in Table 1. It is obvious that the chelating ability of ligands with only two OH groups is inferior compared to glycerol. 1,3-Propanediol showed no interaction with Fe(III) as demonstrated by the same low Fe concentration regardless of the amount of ligand added. The observed value corresponds to the expected equilibrium concentration of $Fe(OH)_4^-$ [29]. The most striking result is the difference between the two methylethers of glycerol. Glycerol-2-methylether resembled 1,3-propanediol and caused almost no increase in dissolved Fe, whereas glycerol-1-methylether enhanced the solubility of Fe(III) dramatically.

A more comprehensive understanding of the nature of ferric diol complexes could be obtained by stepwise hydrolysis of the complexes in an alkaline methanolic medium. Hydrolysis was achieved by the subsequent addition of distinct amounts of water to rigorously dried complex solutions. Some spectroscopic and magnetic properties of partially hydrolyzed solutions are summarized in Table 2. The observed depression of the magnetic moment is an unambiguous indication for the formation of polynuclear complexes and can be used as a tool for structural assignments [30, 31]. A representative dataset from the literature is given in Table 3. According to the results presented in Table 2, the depression of the magnetic moment as observed in the polynuclear complexes is strictly correlated with an increase of a characteristic shoulder at 470 nm. Thus the lack of absorbance above 420 nm (Fig. 1) observed for complexes in aqueous media indicates that virtually no oxo, hydroxo or alkoxo bridged polynuclears were formed [33]. The present data suggests therefore the requirement of a 1,2-dihydroxy structure in the ligand for the formation of stable, mononuclear ferric complexes in strongly alkaline aqueous solution.

Fe(III) and glycerol

Under strongly alkaline aqueous conditions ($[OH^-] \geq 1$ M) and with a large excess of glycerol, pale yellow solutions were obtained upon addition of Fe(III). Both, magnetic measurements and the UV–Vis spectrum indicate the formation of a mononuclear complex. A temperature independent μ_{eff} of 5.7 μ_B was observed over the range 78–298 K and no absorption was detected above 420 nm. At lower pH ($0.01 \leq [OH^-] \leq 0.1$ M) the solutions were still clear, but the colour changed to a deep reddish brown (Fig. 1(e)). The growth of the polynuclears formed was examined by dynamic laser light scattering. Over a period of several weeks, a monotonic increase of the average hydrodynamic radius of polynuclears could be detected (Fig. 2). This result is in agreement with the observed rate of decomposition of the polynuclears in 2 M hydrochloric acid where they decay to $FeCl_4^-$ (Fig. 2). A linear interrelation between the half life of decay and the hydrodynamic radii of the polynuclears was found (Fig. 3).

Fe(III) and sorbitol

It has already been reported that in strongly alkaline solutions, Fe(III) forms mononuclear and dinuclear complexes in the presence of sorbitol [17, 38]. By careful and slow addition of a weak acid to an alkaline solution of the dinuclear $[Fe_2(OH)_2(C_6H_{12}O_6)_4]^{4-}$, the colour of the solution changes from green to brown at pH $\leq$ 10.5. According to static and dynamic laser light scattering, a uniform low-molecular-weight polynuclear of 5–8 Fe(III) atoms and a hydrodynamic radius of 8–11 Å was formed. The half life of degradation in 2 M hydrochloric acid is 0.1 s, i.e. four times lower than for the smallest polynuclears formed in alkaline solutions containing glycerol as sequestering agent. The magnetic moment μ_{eff} was found to be 4.4 μ_B (298 K).

The further decrease of pH by slow addition of a weak acid causes an increase of the average number

TABLE 1. Concentration of Fe(III) (mM) in alkaline aqueous solution in the presence of different polyhydroxy compounds

	Total Fe: 10 mM NaOH: 1.3 M Ligand: 1.0 M	Total Fe: 10 mM NaOH: 1.0 M Ligand: 1.0 M	Total Fe: 1 mM NaOH: 1.0 M Ligand: 0.1 M
Glycerol	10	10	0.9
Glycerol-1-methylether	9	8	0.13
Glycerol-2-methylether	0.03	0.02	0.009
1,2-Ethanediol	2	1	0.05
1,2-Propanediol	3	2	
1,3-Propanediol	0.01	0.008	0.009

TABLE 2. Magnetic and spectroscopic properties of partially hydrolyzed Fe(III)–1,2-ethanediol and Fe(III)–glycerol complexes in alkaline methanolic media

Ligand	$[H_2O]$ (M)	$[Fe]_t$ (M)	μ_{eff} (295 K) (BM)	ϵ (470 nm)
1,2-Ethanediol	0	0.059	4.4	15
	0.03	0.059	4.2	54
	0.12	0.059	3.9	96
	0.57	0.057	3.5	138
Glycerol	0	0.11	4.9	27
	0.038	0.076	5.0	42
	0.16	0.08	5.0	42
	0.74	0.074	4.9	51
	9.4	0.094	4.6	74

TABLE 3. Magnetic moment per ferric ion of selected polynuclear complexes

Structure type	μ_{eff} (298 K)	Reference
$[Fe(OH)_2Fe]^{4+}$	4.9–5.2	30, 31
$[Fe(OR)_2Fe]^{4+}$	4.9–5.2	32
$[FeOFe]^{4+}$	1.7–1.9	33
$[Fe_3O]^{7+}$	3.2–3.5	34, 35
$[Fe_3(OR)_9]$	4.4–4.5	36
α-FeOOH	2.7	37

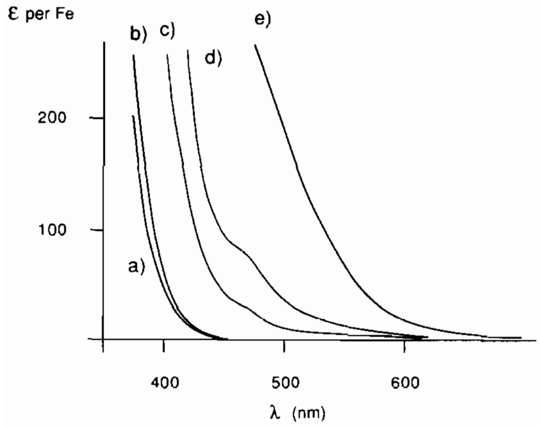

Fig. 1. Vis spectra of polyol Fe(III) complexes in alkaline media: (a) aqueous solution, Fe 0.008 M, OH^- 1.0 M, glycerol-1-methylether 1.0 M; (b) aqueous solution, Fe 0.05 M, OH^- 1.3 M, glycerol 1.0 M; (c) methanolic solution, Fe 0.1 M, glycerol 0.6 M, base 1 M; (d) methanolic solution, Fe 0.1 M, glycerol 0.6 M, base 1 M, H_2O 10 M; (e) aqueous solution, Fe = 0.05 M, OH^- = 0.08 M, glycerol = 1.0 M.

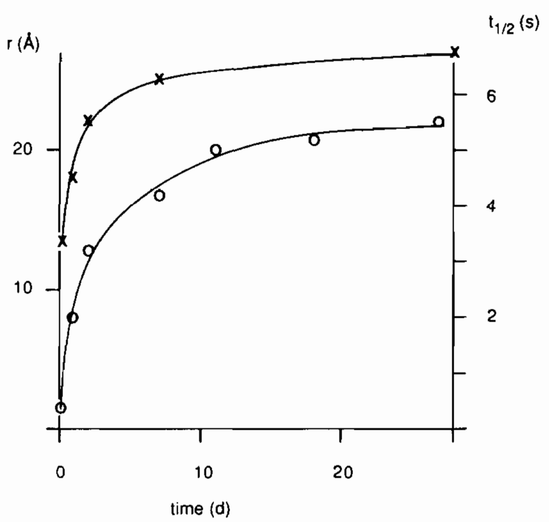

Fig. 2. Time course of the growth of polynuclear Fe(III) glycerol complexes in an alkaline aqueous solution (pH ≈ 13, 25 °C). ×, average hydrodynamic radius; ○, first half life for attack by 2 M HCl.

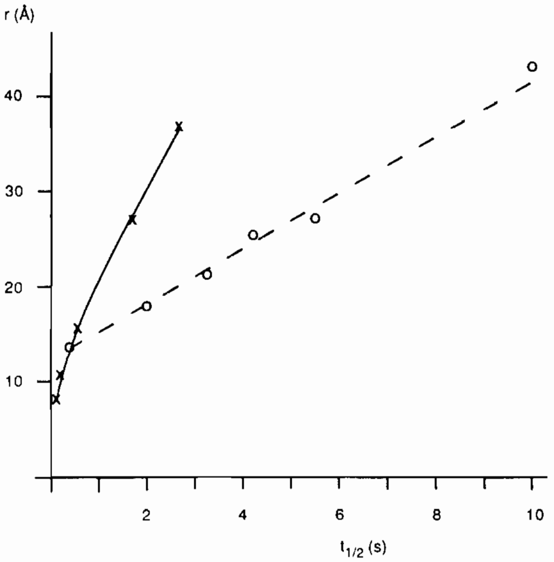

Fig. 3. Average hydrodynamic radius vs. first half life of decomposition in 2 M HCl for polynuclear Fe(III) complexes in alkaline aqueous solution (25 °C) in the presence of glycerol (– – –, ○) and sorbitol (——, ×).

of Fe(III) per particle, the average hydrodynamic radius and half life of acid decomposition (Fig. 4). This phenomenon obviously indicates the growth of these polynuclears as a function of pH which finally resulted in gelation at pH 6. It should be noted that both the growth of the polynuclears and the gelation are completely reversible. On raising the pH to 12.5, the initial polynuclears reformed. Moreover, after preparation, the polynuclear glycerol complexes continue their growth over a period of several weeks whereas the sorbitol complexes stop growing a few days after adjusting the system to a lower pH, to form uniform particles of a characteristic pH-dependent size (Fig. 4). Addition of ethanol to a solution

TABLE 4. Acid decomposition of polynuclear Fe(III) complexes

Compound	pH of formation	First half life (s)	Hydrodynamic radius (Å)
Glycerol complex	12.2–12.9	0.5–10	12–50
Sorbitol complex	10.5–7	0.1–3	8–44
Amorphous $Fe(OH)_3$	7–9	0.5–2	
Polynuclear FeOOH	2–3	200–300	60–80

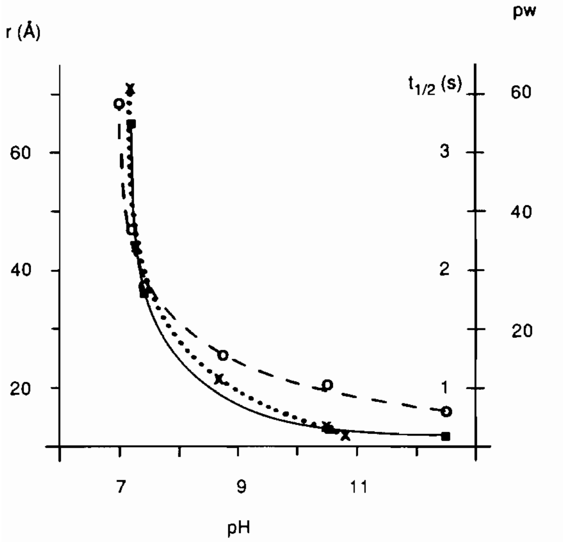

Fig. 4. Average hydrodynamic radius (– – –, O), average number of Fe(III) per particle (· · · · ·, ×), and first half life of decomposition in 2 M HCl (——, ■) for polynuclear Fe(III) sorbitol complexes in alkaline aqueous solution (25 °C) as a function of pH.

of the low-molecular-weight polynuclears (pH 10.5) resulted in the precipitation of a brown solid. The elemental analysis demonstrates clearly a molar ratio Fe:sorbitol of 1:1. The solid could be redissolved (pH 10.5), even after several months, forming unchanged polynuclears with respect to the methods used in this investigation.

Conclusions

Due to the rather low acidity of the polyols used in this investigation (ethanediol: p*K*= 15, glycerol: p*K*= 14.5, sorbitol p*K*= 13.6), mononuclear complexes are only observed at a very high pH ($OH^- > 0.1$ M). The results, obtained by blocking one of the OH groups in glycerol, indicate the coordination of a fully deprotonated 1,2-diolato entity to Fe(III). The different chelating ability of the ligands, as presented in Table 1, is well explained by the availability of the 1,2-diol structure and the acidity of the ligands. All these ferric complexes hydrolyze at a pH below 13. However, using glycerol or sorbitol as ligands, the formation of polynuclear complexes precedes the final precipitation of solid phases. Thus it seems that ligands, providing additional not coordinated hydroxyl groups, protect the polynuclear complexes from complete hydrolysis to solid products. Moreover, an increased number of such OH groups obviously enhances this protection. According to the magnetic moment of polynuclear sorbitol complexes, the polynuclears consist of an iron-oxide–hydroxide core, which is surrounded by a shell of polyols, coordinated on the surface of this core. The polynuclear solutions are generally supersaturated with respect to solid FeOOH [38]. However, the shell of coordinated polyols prevents the formation of the thermodynamically favoured solid, indicating severe kinetic constraints to the structural reorganization as required for the formation of crystalline phases.

The results obtained in this investigation seem to contradict an earlier report from Davis and Deller [8], where the 1,3-diol structure is claimed to be necessary for effective sequestering ability. However, the authors investigated complex formation at pH 8. Considering the hydrolysis of mononuclear polyol complexes below pH 13, it must be taken into account that the complexes investigated by Davis and Deller were of polymeric nature. Unfortunately, no data are given by the authors about the properties of the observed complexes.

It is well established that hydrolysis of Fe(III) in acidic media by continuous base addition occurs stepwise via Fe^{3+}, $FeOH^{2+}$, $Fe_2(OH)_2{}^{2+}$, large polynuclears and solid phases [29, 38]. Some of the polynuclears can be stabilized by surface complexation with suitable ligands like citrate [39, 40]. In alkaline solutions a related sequence can be observed following the addition of acid to solutions containing low molecular weight complexes with polyhydroxy-compounds. In both cases, polymerization results in the formation of solid phases around pH 7. It is remarkable that the acid decomposition of these polynuclears is faster than that of polynuclears of corresponding hydrodynamic radii obtained from acidic media (Table 4). Since the polynuclears from acidic solutions represent the structure type of crystalline FeOOH [41] it is obvious that the cores of the polynuclears from alkaline solution are much less compact and rather resemble freshly precipitated amorphous iron hydroxides.

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