and one would expect dioxane to be a poor solvating solvent. These observations indicate the importance of both solvent donor strength and solvating ability in accounting for anion displacement.

In conclusion, it must be emphasized that solvent interactions make significant contributions to the measured enthalpy values of adduct formation. Specific interactions between the solvent and a reacting species significantly change the observed equilibrium constant and enthalpy; even contributions from nonspecific solvation have pronounced effects. Therefore, great care must be taken before comparing enthalpies measured in different solvents. The interpretation of changes in the equilibrium constant with changes in solvent appears formidable at present. Although the equilibrium constant appears to increase, as expected in a more polar solvent, little else can be said about the changes in the equilibrium constant in different solvents. Until a better understanding of all the factors affecting the equilibrium constant is reached, it is hazardous to interpret small differences between equilibrium constants measured in various solvents.

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The Hydrolytic Polymerization of Iron(III)

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Abstract: Hydrolysis of ferric nitrate with bicarbonate leads to solutions which contain a discrete high polymeric component. This component has been isolated by gel filtration and characterized. The weight-average molecular weight of the polymer, as determined with the analytical ultracentrifuge, is 1.4×10^5. Its empirical composition corresponds to $Fe(OH)_x(NO_3)_{3-x}$, where x lies between 2.3 and 2.5. Polymer size and composition are nearly independent of the degree of hydrolysis of the ferric nitrate solutions between 1.0 and 2.0 base equiv/mole of Fe. Formation of the polymer is rapid, while dissociation is very slow. Although ferric hydroxide precipitates from partially hydrolyzed ferric nitrate solutions within a few days, solutions of the isolated polymer remain clear indefinitely. Electron microscopy reveals that the polymer particles are isolated spheres, most of which are close to 70 A in diameter.

The hydrolysis of ferric ion, a problem of very long standing in solution chemistry, has been considerably clarified in recent years. On the basis of a careful potentiometric study, Hedström[2a] proposed that the initial product of hydrolysis in perchlorate solution is primarily a dimer, $Fe_2(OH)_2^{4+}$. This result was corroborated by Mulay and Selwood[2b] who established that the dimer is essentially diamagnetic, indicating strong electronic interaction between the ferric ions. Although considerable quantities of base (bicarbonate) can be added to ferric perchlorate before a lasting precipitate is produced, Hedström found that solutions containing more than about 0.5 equiv of base per mole of iron gave drifting potentials, and he attributed the drift to incipient precipitation of ferric hydroxide. Feitknecht and Michaelis[3] observed in fact that all iron(III) solutions to which base has been added, even those studied by Hedström, are unstable with respect to eventual precipitation of various forms of ferric hydroxides. This two-phase system reaches an apparent equilibrium after 200 hr as indicated by Biedermann and Schindler,[4] who obtained a reproducible solubility product constant for ferric hydroxide from hydrolyzed ferric perchlorate solutions.

It is evident, therefore, that the hydrolytic polymerization of ferric ion, which begins with the formation of $Fe_2(OH)_2^{4+}$, continues, with time, to the precipitation of ferric hydroxide. There remain the questions of mechanism of polymerization and chemical composition of the intermediates.

Diffusion measurements with partially hydrolyzed solutions of iron salts led Jander and Winkel[5] to suggest that polynuclear iron–hydroxy complexes were present. These complexes were thought to contain from 1 to 50 metal atoms. More generally, however, it is felt that these intensely colored solutions contain colloidal ferric hydroxide of indeterminant composition.

We wish to present evidence that the hydrolysis of ferric nitrate can lead to formation of a high molecular weight polymer of composition $[Fe(OH)_x(NO_3)_{3-x}]_n$ where x lies between 2.3 and 2.5 and n is of the order of 900. This polymer has been isolated and characterized.

Experiments and Results

The Preparation of Hydrolyzed Iron Solutions. Most solutions were prepared by dissolving a weighed amount of reagent ferric nitrate (Mallinckrodt) in a small volume of distilled water and adding the requisite

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[1] (a) Princeton University; (b) Research Career Development Awardee, U. S. Public Health Service.

[2] (a) B. O. A. Hedström, *Arkiv Kemi*, **6**, 1 (1953); (b) L. N. Mulay and P. W. Selwood, *J. Am. Chem. Soc.*, **76**, 6207 (1954).

[3] W. Feitknecht and W. Michaelis, *Helv. Chim. Acta*, **45**, 213 (1962).

[4] G. Biedermann and P. Schindler, *Acta Chem. Scand.*, **11**, 731 (1957).

[5] G. Jander and A. Winkel, *Z. Anorg. Allgem. Chem.*, **193**, 1 (1930).

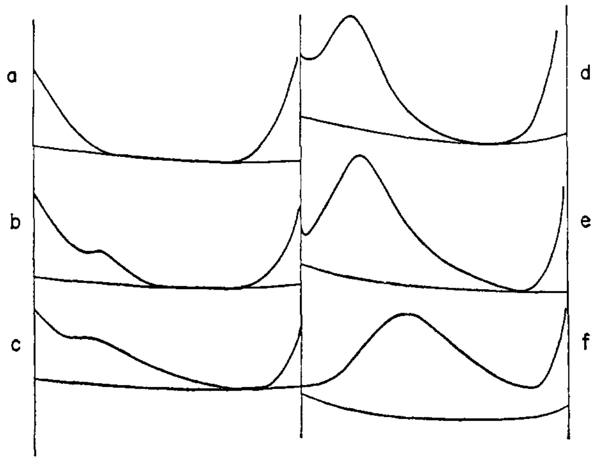

Figure 1. Schlieren patterns after 16-min ultracentrifugation at 56,100 rpm of 0.3 *M* ferric nitrate solutions containing (a) 0.5, (b 0.75, (c) 1.0, (d) 1.5, (e) 2.0, and (f) 2.5 base equiv/mole of iron.

weight of reagent potassium bicarbonate (Baker and Adamson). To remove all dissolved CO_2 formed in the reaction, nitrogen was bubbled briefly through the solution which was then diluted to the required volume. The final solutions were in most cases 0.3 *M* in iron, a concentration found to give good schlieren patterns in the ultracentirfuge. Bicarbonate was used as base to prevent local high concentrations of hydroxide and the irreversible formation of a precipitate which results when strong base is added directly to iron solutions. With the addition of up to 2.5 equiv of bicarbonate per mole of iron, clear reddish brown solutions were obtained; the color intensity increased with the degree of hydrolysis. These solutions contained no visible precipitate for at least 2 days. Addition of more than 2.5 equiv of base produced an immediate thick brown precipitate.

For exploratory investigation of the effect of other anions, 0.3 *M* iron solutions with 2 equiv of base per mole of iron were also prepared from ferric chloride (Mallinckrodt) or ferric perchlorate (G. F. Smith). The latter reagent initially contained an excess of perchloric acid and therefore an excess of sodium perchlorate on hydrolysis, for which the base used in this case was sodium bicarbonate to avoid precipitation of $KClO_4$. It should be noted that in all solutions the concentration of inert salt is proportional to the number of base equivalents added per mole of iron. The total anion concentration is independent of the degree of hydrolysis. Potassium nitrate is a particularly good supporting electrolyte for ultracentrifuge studies since potassium and nitrate ions have very similar sedimentation coefficients.[6]

Analytical Ultracentrifuge Studies. Centrifugations were carried out using a Spinco Model E analytical ultracentrifuge equipped with an AN-D rotor and schlieren optics. A Wratten No. 49 red filter was placed over the mercury lamp source, and Kodak F-103 red-sensitive photographic plates were used. Sedimentation velocity experiments were performed at a velocity of 56,100 rpm. For this purpose, a double-sector epon cell was used, one sector containing 0.45 ml of the iron solution under study, the other sector filled with 0.45 ml of a solution containing the same concentration of potassium nitrate (or other salt as appropriate) as was present in the iron solution. All solutions were centrifuged within an hour of their preparation to avoid aging effects as noted below.

Table I. Ultracentrifuge Data of Hydrolyzed Ferric Nitrate Solutions

Equiv of base/mole of Fe	Sedimentation coeff, S	Fraction of Fe as polymer	pH
1.00	7.1	0.23	1.85
1.50	6.1	0.37	1.90
2.00	7.1	0.52	2.00
2.50	12.8	0.66	2.24

Typical schlieren patterns for hydrolyzed 0.3 *M* ferric nitrate solutions obtained after 16 min of sedimentation are shown in Figure 1. It is evident that a polymeric fraction, polydisperse, but nevertheless reasonably discrete, is present in all solutions containing more than 0.5 equiv of base per mole of iron. The amount of polymer increases with increasing degree of hydrolysis. It is of great interest that the modal sedimentation coefficient of the polymeric fraction, as determined by classical techniques, is practically the same, 7 ± 1 S (Svedbergs), for solutions containing 1, 1.5, and 2 equiv of base per mole of iron. The reproducibility of the sedimentation coefficients for separately prepared solutions is of the order of 1 S. The sedimentation coefficient for the solution containing 2.5 equiv of base per mole of iron, on the other hand, is 13 S. For each of the schlieren patterns, the area under the peak, after a small correction for radical dilution, is proportional to the concentration of the polymer fraction in the particular solution. The fraction of iron present as polymer was determined for each solution by calibrating the total iron concentration in terms of refractive index units using the peak area generated in a synthetic boundary run of a solution containing 2 equiv of base per mole of iron. Table I lists the sedimentation coefficients and fractional amounts of polymeric iron for various extents of hydrolysis. Also given are the pH values of these solutions as measured with a Beckman Zeromatic pH meter. While it is clear from these results that a hydrolytic polymer of iron does form in proportion to the degree of hydrolysis, its composition is not immediately apparent.

Since these solutions are all unstable with respect to eventual precipitation of ferric hydroxide, it was of interest to determine the effect of aging on sedimentation behavior of the polymeric fraction. The sedimentation coefficient for a solution containing 2 equiv of base per mole of iron was determined repeatedly over several days. The gradual increase of the sedimentation coefficient during this time is shown in Figure 2. After 3 days, a Tyndall effect was also observed. From this point on, an aliquot of the original solution was centrifuged for 10 min at 12,000*g* in order to remove the precipitate prior to analytical ultracentrifugation. The fraction of iron precipitated, calculated from the dry weight of the precipitate, assuming it to be FeOOH, is also shown in Figure 2. The shapes of the two curves suggest that polymer growth and precipitation are not parallel processes.

On the second day of the aging study, the concentration dependence of the sedimentation coefficient was also determined. The 0.3 *M* iron solution was diluted to 0.15 and 0.075 *M* with 0.6 *M* potassium nitrate

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(6) K. O. Pedersen, *J. Phys. Chem.*, **62**, 1282 (1958).

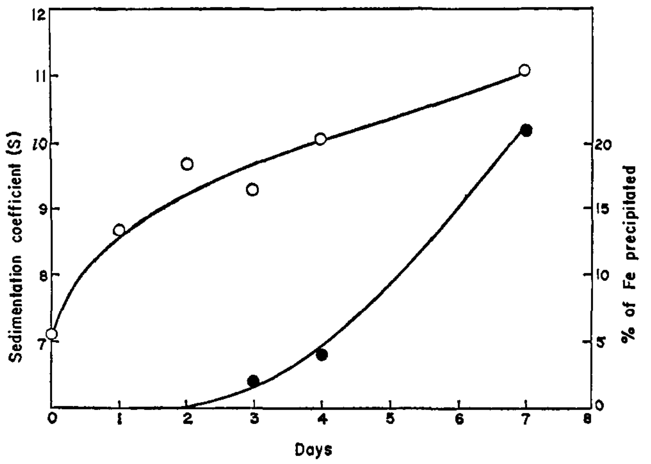

Figure 2. The effect of aging on sedimentation coefficients (○) and per cent of iron precipitated (●) in 0.3 *M* ferric nitrate containing 2 base equiv/mole of iron.

adjusted to pH 2.0 with nitric acid. As is shown in Figure 3, the sedimentation coefficient increased slightly with increasing dilution, and there was negligible dissociation of the polymer into lower molecular weight species over this concentration range. Evidence is presented below that dissociation of the polymer is a very slow reaction.

The effect of two other anions was investigated using the chloride and perchlorate solutions as described above. Similar schlieren patterns were observed for these solutions as for the nitrate solutions, but the sedimentation coefficients turned out to be unexpectedly much higher for both of these anions: 23 S for the perchlorate and 25 S for the chloride. The pH values of these solutions were also much lower than those of the nitrate solutions: 1.10 for the perchlorate and 1.38 for the chloride.

Dialysis Experiments. In order to investigate further the polymeric behavior of hydrolyzed iron solutions, we have employed the membrane dialysis technique of Lindskog and Malmström.[7] The solutions were prepared with ^{59}Fe as tracer in the manner described above. The apparatus consists of two identical chambers separated by a cellulose acetate dialysis membrane (Visking Corp). Activity was determined in a scintillation well counter peaked at the 1.1 Mev γ emission of ^{59}Fe. At various time intervals, aliquots of solutions were calibrated using solutions of $^{22}NaCl$ which reached equal concentrations on both sides of the membrane within 5 hr. The fraction of iron undialyzed at various times is plotted in Figure 4. The hydrolyzed solutions contain a low molecular weight fraction of iron which moves rapidly across the dialysis membrane. There is also a high molecular weight fraction that does not move across. The differences in iron concentration on either side of the membrane are in agreement with the fraction of polymer formed as determined by the ultracentrifuge. It is evident that the polymer dissociates very slowly indeed.

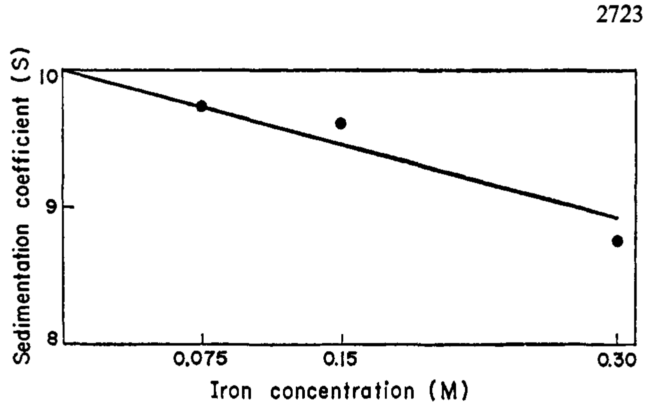

Figure 3. Effect of iron concentration on sedimentation coefficient of 24-hr-old ferric nitrate solutions containing 2.0 equiv of base/mole of iron.

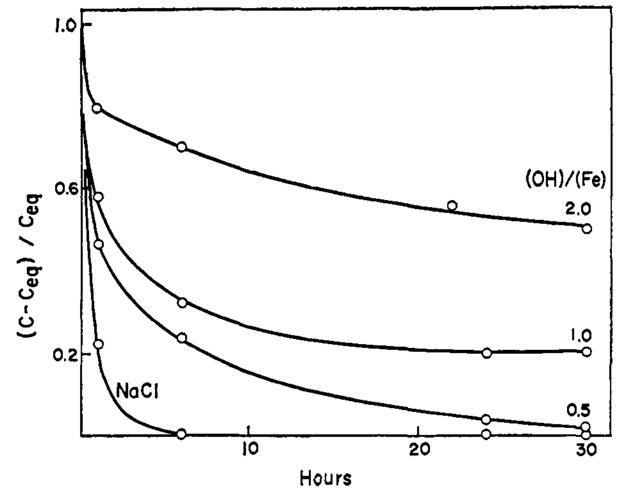

Figure 4. Fraction of iron undialyzed as a function of time for solutions containing different base equiv/mole of iron, (OH)/(Fe). The fraction is given as $(C - C_{eq})/C_{eq}$, where C is the concentration of iron in the initial compartment at any time, and C_{eq} is the equilibrium concentration, *i.e.*, half of the initial concentration. The sodium chloride curve indicates the dialysis kinetics of a low molecular weight material.

An indication of the rate of polymer dissociation was obtained in another experiment. A solution was prepared to contain 2 equiv of base per mole of iron and allowed to stand for 1 hr, and then enough nitric acid was added to bring the net proton deficiency back to zero. Although ferric nitrate itself moves rapidly across the dialysis membrane, the freshly acidified solution took approximately 20 hr to achieve equilibrium. Dissociation of the polymer is a slow reaction even with acid present. A sedimentation velocity experiment in the ultracentrifuge was performed on the same freshly acidified solution. A peak was observed which failed to clear the meniscus throughout the run, and therefore corresponds to a polymer of much lower molecular weight than that observed in the hydrolyzed solutions. The schlieren pattern for this solution after 16 min is compared with that of ferric nitrate in Figure 5.

Potentiometry. Glass electrode and Fe(III)/Fe(II) oxidation-reduction potentials were determined for perchlorate solutions containing ferric and ferrous iron, as a function of added base, following the titration technique of Hedström.[2a] As in his study, the ionic medium was 3 *M* $NaClO_4$, the base added was sodium bicarbonate, and the temperature was kept at 25.0°.

The early part of the titration gave data which are in excellent agreement with those of Hedström.[2a] At higher degrees of hydrolysis, we also observed large potential drifts. The titration was continued, but on a strict time sequence, in which base additions were spaced 10 min apart and the potentials followed. At 2.0 equiv per mole of iron(III), base addition was stopped and the solution was back-titrated with per-

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(7) S. Lindskog and B. G. Malmström, *J. Biol. Chem.*, 237, 1129 (1962).

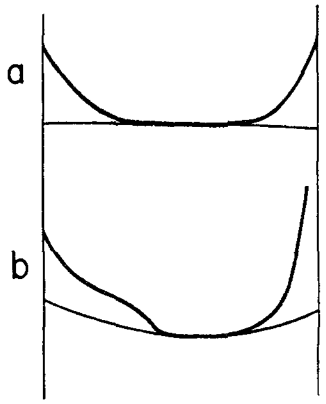

Figure 5. Schlieren patterns of (a) 0.3 M ferric nitrate and (b) a similar solution which had been hydrolyzed and acidified (see text).

chloric acid (the iron and perchlorate concentrations being kept the same) using the same time sequence. The course of the titration is illustrated in Figure 6.

Drifting potentials occur in the same region of hydrolysis where polymer formation is observed in the ultracentrifuge. The platinum electrode drifts to higher potentials, the direction expected if addition of base produces a local excess of polymer which dissociates slowly. The drift to lower pH of the glass electrode is difficult to understand, since the same mechanism should produce the opposite effect. Perhaps spurious potentials arise from surface effects on the glass electrode in the polymerizing solutions. During the back-titration, the drifts of both electrodes are in the anticipated direction for continuing slow dissociation of the polymer. The most noticeable feature, however, is the large hysteresis effect. The platinum potentials are lower (less free iron), and the glass potentials are higher (more free hydrogen ion) than at the corresponding points in the forward titration. Evidently a sizeable fraction of the iron remains polymerized throughout the back titration. For example, at 20.2 mM acid excess, the fraction of free iron is over 95% in the forward titration, but only about 60% in the back-titration. Even at 194 mM acid excess, the final point in the back-titration, the platinum potential was considerably lower than at the start of the titration, and the solution was light brown. Allowed to stand overnight, the solution turned colorless and the platinum potential increased to within 1.5 mv of the starting potential.

At no time in the titration up to 2.0 equiv of base per mole of iron(III) was a precipitate observed. In a separate experiment, it was found that extension of the titration to 2.5 base equiv did lead to clouding of the solution. On subsequent back-titration, the precipitate remained undissolved until after addition of a large excess of acid. Because equilibrium is never attained beyond the first portion of the titration, it is not feasible to extract quantitative information from the potentiometric data. The kinetic behavior of the potentials is consistent with a rapid formation and slow dissociation of the polymer.

Isolation of the Polymer. Attempts were made to obtain the polymeric fraction free from low molecular weight components and from the supporting electrolyte by dialysis. The length of time required for this separation method, however, led to formation of colloidal ferric hydroxide. We found that the technique of gel filtration admirably suited our purpose. A column of Sephadex G-25, 3 × 30 cm, was washed several times and allowed to equilibrate with 0.01 M nitric acid; 20 ml of 0.3 M ferric nitrate with 2 equiv of base per mole of iron (pH 2.0) was placed on the column and eluted with the dilute nitric acid.

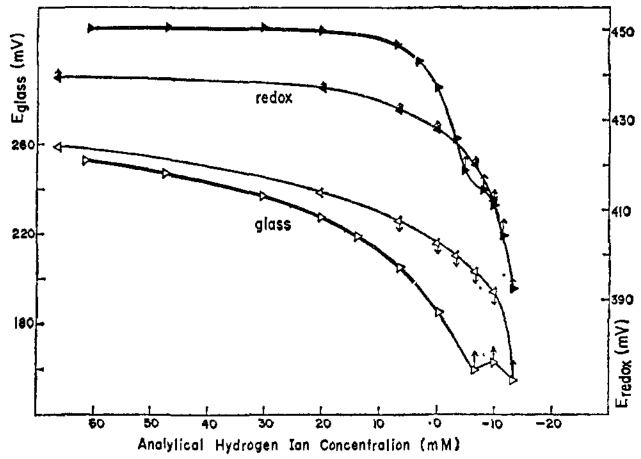

Figure 6. Glass electrode and Fe(III)/Fe(II) potentials in the bicarbonate titration of Fe(III) in 3.0 M sodium perchlorate. The concentrations of Fe(III) and Fe(II) are held constant throughout the titration at 6.6 and 3.0 mM, respectively. The glass electrode potentials in the forward titration are represented as ▷, and in the back-titration by ◁. The oxidation-reduction potentials are represented in the forward titration as (▶) and the back titration as (◀). The arrows represent the magnitude and direction of the potential drifts in the 10-min periods following addition of titrant. Initial portions of curves (heavy lines) are fitted using Hedström's equilibrium constants.

A distinct dark band emerged from the column at the void volume, 110 ml, indicating that it contained a high molecular weight form of iron which was excluded by the gel. Approximately 35 ml of this intensely colored solution was collected and taken to dryness immediately by lyophilization; 250 mg of a reddish brown solid was obtained, which corresponds to a yield of about 30% of the iron placed on the column. Much of the remaining iron was rather firmly bound to the Sephadex and could not be eluted with dilute nitric acid. It was found, however, that the iron could be removed by washing the Sephadex with phosphate solution which had been adjusted to a pH of 2.0.

Properties of the Polymer. The lyophilized material dissolves readily in water or salt solutions. A polymer solution 0.1 M in iron, 0.6 M in potassium nitrate, and 0.01 M in nitric acid shows no Tyndall effect and does not form a precipitate on standing for at least 3 months. A sedimentation velocity determination was made on this solution. The resulting schlieren pattern resembled that observed for the ferric nitrate solution containing 2 equiv of base per mole of iron (Figure 1e). The modal sedimentation coefficient was 7.1 S. The solution of isolated polymer was also used for a determination of the weight-average molecular weight, M_w, of the macromolecule with the Archibald method, as outlined by Schachman.[8] Polymer solution, 0.15 ml, was placed over 0.2 ml of dense silicone oil in a Spinco ultracentrifuge cell. The approach-to-equilibrium experiment was conducted at 3617 rpm, 22.4°, for 99 min, and four schlieren patterns were analyzed at

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[8] H. K. Schachman in "Methods in Enzymology," Vol. 4, S. P. Colowick and N. O. Kaplan, Ed., Academic Press Inc., New York, N. Y., 1957, p 32.

different times within this period. Although the buoyant molecular weight values $M(1 - v\rho)$ at the two menisci diverged from one another with increasing time, extrapolation to zero time gave the same result at each meniscus. The specific volume, v, of the polymer was determined by weighing samples of polymer solution and polymer-free solvent in a 10-ml pycnometer. At 20–23°, for solutions 0.1 *M* in iron, $v = 0.40$. There was some evidence that v decreases with increasing polymer concentration over the range 0–20 g/l., and a more detailed investigation of this effect is underway. A weight-average molecular weight of 1.4×10^5 can be assigned to the iron polymer in the solution analyzed.

Polymer Composition. The polymeric fraction was isolated from ferric nitrate solutions containing 1.0, 1.5, and 2.0 equiv of base per mole of iron in the manner described above. The polymeric solids, which were kept in a vacuum desiccator over P_2O_5, were analyzed for their iron, hydroxyl, and nitrate content. Iron was determined by reduction to iron(II) with stannous chloride (after acidification) and titration with permanganate. Nitrate was determined by titration of acid eluted from a cation-exchange resin (Dowex 50) in the acid form after equilibration with an aliquot of polymer solution. Equilibration of the polymer with the cation exchanger is slow, and it was found necessary to stir the solution with a portion of the resin for 15 min at an elevated temperature before pouring it onto the cation-exchange column. If this was not done, variable amounts of the iron were eluted out of the column with the acid.

The hydroxyl ion content was determined by digesting the polymer with excess standard acid and back-titrating with base. In order to suppress interference from ferric ion, an excess of potassium oxalate was added, following the suggestions of Blaedel and Panos,[9] and the titration was followed potentiometrically, using the linear extrapolation method of Gran.[10]

The compositions obtained for these preparations are given in Table II. The polymer composition is almost independent of the degree of hydrolysis, although there is a small increase in hydroxyl/iron ratios with increasing degree of hydrolysis. The fact that the weight of polymer per mole of iron is slightly lower than the calculated formula weight implies some condensation of hydroxyl groups with accompanying loss of water.

Table II. Chemical Composition of Isolated Polymers

Base equiv/mole of Fe	Mole ratio OH/Fe	Mole ratio NO_3/Fe	Wt of polymer/mole of Fe	Formula wt[a]
1.0	2.27	0.72	138.4	139.1
1.5	2.44	0.56	127.8	132.0
2.0	2.52	0.51	123.2	130.3

[a] The formula weight is calculated on the basis of $Fe(OH)_x(NO_3)_y$, where *x* and *y* are given in columns 2 and 3.

Electron Microscopy of Isolated Polymer. A dilute solution of the solid material was prepared for electron microscopy as follows. Isolated polymer from a solution containing 2 equiv of base per mole of iron was dissolved in 0.03 *M* nitric acid, 0.25 mg of polymer/ml. It was further diluted with an equal volume of solution containing polystyrene spheres, diameter 880 A, for calibration purposes. This mixture was sprayed onto freshly cleaved mica with a high-velocity glass spray gun. The particles were then shadowed at an angle of 1:10 with platinum, and a thin carbon layer was added normal to the surface. The preparation was scored, floated off, and picked up on a fine-mesh, uncoated copper grid. The micrographs were obtained using an RCA EMU-3F electron microscope. A representative area is shown in Figure 7.

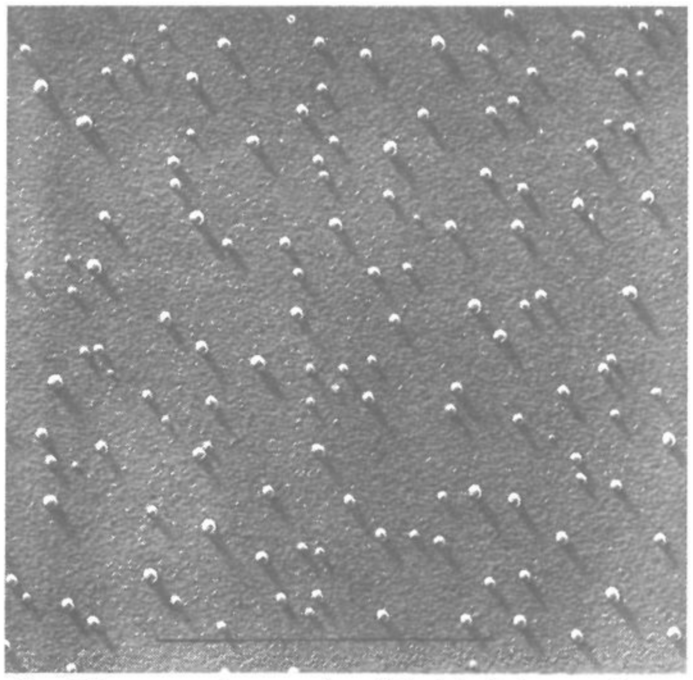

Figure 7. Electron micrograph of isolated iron polymer. The calibration mark represents 1 μ.

The polymer appears as discrete spheres with diameters distributed as shown in Figure 8. Most spheres have diameters of about 70 A. These spheres are well separated, not clumped together as would be expected of ordinary ferric hydroxide colloid. Their appearance is reminiscent of proteins and other biopolymers. Calculations of the expected molecular weights of the 70-A spheres based on a density of 2.5 for ferric polymer (see above) give a value of 2.4×10^5, in reasonable agreement with sedimentation measurements.

Discussion

Colloidal ferric hydroxide has been studied for many decades. There are several procedures for the preparation of ferric hydroxide sols, one of which involved hydrolyzing ferric salts with carbonate and dialyzing the resultant dark solutions against water.[11] Therefore it might have been expected that the polymeric fraction we observed was, in fact, colloidal ferric hydroxide. However, the analytical results on the isolated polymer fraction make it clear that we are dealing with polycations, $[Fe(OH)_x{}^{(3-x)+}]_n$, where values for *x* lie between 2.3 and 2.5, or, more generally, $[FeO_{x/2}(H_2O)_z{}^{(3-x)+}]_n$. Presumably the polycations are hydrated and extensively bound to the nitrate counterions which neutralize their high charge density.

These polycations are probably chains of ferric ions held together by double hydroxyl bridges. An extended linear configuration appears unlikely in view of the electron microscope pictures showing isolated spherical particles. Preliminary viscosity measurements (to be published) also point to a spherical conformation for

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(9) W. J. Blaedel and J. J. Panos, *Anal. Chem.*, **22**, 910 (1950).

(10) G. Gran, *Analyst*, **77**, 661 (1952).

(11) F. E. Bartell, "Laboratory Manual of Colloid and Surface Chemistry," Edwards Brothers, 1936, p 34.

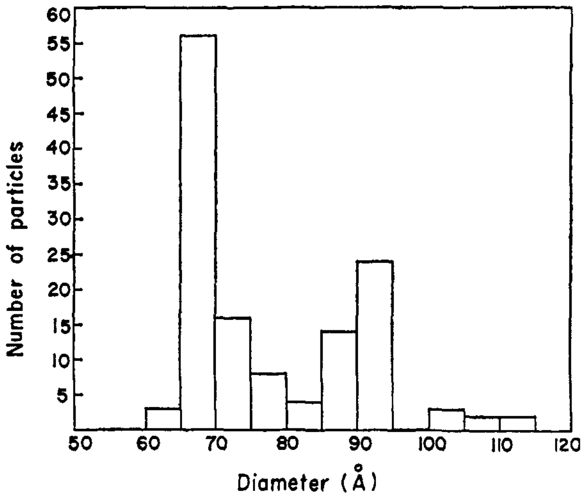

Figure 8. Size distribution of isolated polymer particles as measured on electron micrographs.

the polymer. On the other hand, there is no requirement that double hydroxyl bridges be colinear. If iron retains its normal octahedral coordination, the angle between successive double hydroxyl bridges could be either 180 or 120°. The 120° configuration would result in tightly coiled chains. These would not be readily uncoiled, because of the rigidity of the two-point hydroxyl bridging. Similarly there is no *a priori* reason for assuming colinearity of any oxo bridges which might be present. The hydroxyl groups in excess of those required for double-bridge formation could themselves participate in interior intrachain bridging. The resulting cross-linked coil would not be essentially different from a variety of three-dimensional networks which could also be postulated.

The ultracentrifuge measurements show that the polycations are very large, comprised of about 900 iron atoms. The average size is independent of the degree of hydrolysis, up to 2 base equiv per mole of iron. The exact distribution of molecular sizes remains to be determined, but there is no evidence for an extended series of polymers, of the type proposed by Jander.[5] The onset of polymerization evidently leads to a rapid buildup to a limiting size and chemical composition. It is not clear what factors limit polymer growth. The depletion of available iron cannot play a significant role since all hydrolyzed solutions show appreciable concentration of low molecular weight components. The polymer does continue to grow, as shown by the gradual increase of its sedimentation coefficient with age, but at a rate much slower than that of the initial formation reaction.

Perhaps the most remarkable property of the isolated polymer is that solutions of it form no precipitate for an indefinite period, despite the instability of hydrolyzed iron solutions. This behavior implies a high activation energy for the conversion of the polymer to insoluble ferric hydroxide. It appears that a structural change is involved. It may be significant in this regard that we observed no correlation between the time required for a precipitate to appear and the degree of hydrolysis of our ferric nitrate solutions, and also that polymer aging and precipitation are apparently not parallel processes (Figure 2). It may well be that precipitation proceeds not from the polymer, but from low molecular weight components of the hydrolyzed solutions. The slowness of polymer dissociation may account for the metastability of the isolated polymer solutions. We have noted, in fact, that these solutions will turn cloudy after about a week if made moderately acid (0.1 M HNO_3). Polymer dissociation is enhanced, but the concentration of acid is not sufficiently high to prevent precipitation.

It is evident that the polymer formation described in this work fits into the "irreversible" category of hydrolytic processes discussed by Kraus in his review of heavy metal hydrolysis.[12] His description of plutonium(IV) hydrolysis contains some striking parallels to the observations reported here. There may well be other systems with similar characteristics. Large polyanions occur in silicate and aluminate systems. To the best of our knowledge, this is the first report of the isolation of a discrete high polymer obtained by hydrolysis of a metal ion.

These iron polymers are of interest not only with respect to inorganic solution chemistry, but also are relevant to certain problems in biochemistry. In connection with work on the metabolism of iron, Saltman[13] has presented evidence that sugar complexes with iron exist in a polymeric form. The high molecular weight may be a consequence of iron hydrolysis; chelation by sugar serves to maintain the polymer in soluble form even at higher pH. Further work on polymeric chelates of iron is in progress. It is also of interest to point out that the size and shape of the inorganic iron polymer observed in these experiments are similar to the iron hydroxide units found within the molecule of ferritin.[14] Another intriguing biological phenomenon which may be related to the polymeric properties of iron is the morphological structure of the ferric hydroxide stalks elaborated by the iron bacterium *Gallionella ferriginea.*[15] These stalks are about 100 A in diameter and have a bead-like or segmented appearance.

The application of physical and chemical techniques so often employed in biochemical experiments has been most fruitful in the present study of iron polymerization. Attractive possibilities for further investigation of polymeric inorganic systems are apparent. The characterization of the iron polymer system is far from completed by this study. It would be highly desirable to define precisely the structure of the macromolecule and to elucidate the mechanism of hydrolytic polymerization. Such information should permit a clearer understanding of the chemical and biological behavior or iron and other polyvalent metal ions.

Acknowledgments. This work was supported by the John A. Hartford Foundation, Inc. We wish to thank Sue Ricket, Leslie Olsen, and Clyde Stitt for their valuable technical assistance in many phases of the research. Dr. Jerome Vinograd was most helpful with suggestions and encouragement.

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(12) K. A. Kraus, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, **7**, 245, (1956).

(13) P. Saltman, *J. Chem. Educ.*, **42**, 682 (1965).

(14) P. M. Harrison, *J. Mol. Biol.*, **6**, 404 (1963).

(15) A. E. Vatter and R. S. Wolfe, *J. Bacteriol.*, **72**, 250 (1956).