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The Hydrolysis of Ferric Complexes. Magnetic and Spectrophotometric Studies of Aqueous Solutions of Ferric Salts

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Ferric chloro, ferric aquo, and ferric sulfato complexes in acidic solutions have been hydrolyzed at temperatures below 70 °C to form polynuclear complexes of iron(III). Magnetic and spectrophotometric studies have then been carried out in order to clarify the nature of the polynuclear complexes. From these studies, their empirical formulas are presumed to be $Fe_2(OH)_2Cl_2O$, $Fe_2(OH)_3(NO_3)_3$, $Fe_2(OH)_3(SO_4)_{3/2}$, and $Fe_3(OH)_2(SO_4)_{7/2}$. The iron ions in these polynuclear complexes are in a high spin state, as are those in the ferric complexes, iron oxides, and oxyhydrates. It is proposed that, in all these polynuclear complexes except $Fe_3(OH)_2(SO_4)_{7/2}$, edge-shared octahedral dimer units are antiferromagnetically linked with one another by hydroxy or oxo bridging. When the hydrolysis temperature is raised, these polynuclear complexes are further hydrolyzed to form precipitates. The complexes of $Fe_2(OH)_2Cl_2O$, $Fe_2(OH)_3(SO_4)_{3/2}$, and $Fe_3(OH)_2(SO_4)_{7/2}$ give β-FeOOH, α-FeOOH, and $RFe_3(OH)_6(SO_4)_2$ (R=Na, K or NH_4) respectively, whereas the complex of $Fe_2(OH)_3(NO_3)_3$ gives α-FeOOH or α-Fe_2O_3, depending on the temperature.

When ferric salt solutions are heated or made alkaline, the ferric ions in them are hydrolyzed to form precipitates of various iron compounds. It is known that a ferric chloride solution gives β-FeOOH,[1-3] whereas a ferric nitrate solution gives α-FeOOH or α-Fe_2O_3, or a mixture of them, depending on the hydrolysis temperature.[4,5] Also, a ferric sulfate solution gives α-FeOOH or a basic sulfate, or a mixture of them, depending on the pH.[6] We consider that what kind of precipitate is formed by hydrolysis is closely connected with the nature of the ferric complexes present in the solutions just before the formation of precipitates.

The ferric complexes which are present as monomers in strongly acidic solutions of ferric salts have so far been studied by means of X-ray diffraction,[7,8] spectrophotometry,[9-13] magnetic measurement,[14-16] potentiometry,[17] *etc.* Among these methods the spectrophotometry in the region of electronic absorption has been used particularly for the study of Cl^-, SO_4^{2-}, and OH^- ligands. The electronic absorption curves of acidic solutions of ferric salts have been studied by many investigators. It has been clarified by these studies that such ferric complexes as chloro, sulfato, hydroxo, and aquo complexes are present in the strongly acidic solutions, depending on the kind and concentration of the anions in them. By decreasing the acidity of the solutions, polynuclear complexes of iron(III) are formed.

The polynuclear complexes formed in solutions of ferric perchlorate and ferric nitrate have also been studied by several investigators. From a potentiometric study, Hedstrom first proposed that the polynuclear complex formed by the hydrolysis of a diluted ferric perchlorate solution was a dimer.[17] The pH dependence of the magnetic susceptibilities and the optical absorption spectra of similar solutions was studied by Mulay and Selwood, who proposed that a diamagnetic dimer was formed by the hydrolysis of the same.[18] Also, Zvyagintsev and Loppato reported that a tetramer was formed by the hydrolysis of ferric nitrate.[19] The polynuclear complex in a ferric nitrate solution was studied in detail by Spiro *et al.* using various methods. Spiro *et al.* observed that the poly-

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nuclear complex consisted of a great number of iron ions.[20] Further, the structure of this complex was discussed by Schugar *et al.*, who pointed out that it was not a diamagnetic complex, but a paramagnetic one with a spin angular moment of $S=1$ per iron, and presumed that it was composed of many aquo dimers, $Fe=(OH)_2=Fe$.[21]

In order to discuss the mechanism of precipitation in solutions of different ferric salts, further investigations of the nature of complexes present in the solutions are needed. In this paper, the possible structure and the chemical composition of the polynuclear complexes will be discussed on the basis of the spectrophotometric and magnetic data.

Experimental

Sample Solution. Chemical reagents of an analytica grade were used in the present experiments. Desired quantities of ferric chloride, ferric nitrate, and ferric sulfate were dissolved in 1.00 N hydrochloric acid, nitric acid, and sulfuric acid solutions respectively. To each of these strongly acidic solutions of ferric salts, alkali solutions were added in various ratios below the chemical equivalent. By this addition, a precipitate was formed. However, it disappeared on agitation. The resultant acidic solutions were diluted with distilled water to desired concentrations of the ferric ion and stored in polyethylene bottles. The magnetic susceptibilities and the absorption spectra of these acidic solutions, which contained no visible precipitates, were then measured.

Apparatus. The measurements of the optical absorption spectra were carried out using a Shimadzu spectrometer, Model QR-50. The optical path in its sample container was selected from among 0.003, 0.010, and 1.0 cm by the use of quartz spacers of different sizes according to the concentration of the ferric ion and the frequency of the light. The absorbance value was obtained at intervals of 0.5 mμ. The extinction coefficient was calculated using Lambert-Beer's formula.

The magnetic susceptibilities of the solutions were measured as follows. A schematic illustration of the magnetic balance used is shown in Fig. 1. Each solution was introduced into a double cylindrical vessel (A) 2.5 cm in external diam., 1.8 cm in internal diam., and 40 cm in length, which was placed between the pole pieces of a magnet (B). A cylindrical quartz rod (C) with a cross-sectional area of 0.48 cm^2 and a length of 20 cm was hung in the vessel by means of a platinum wire from one arm of a chemical balance (D). The lower end of the rod was brought to the center between the pole pieces.

The repulsion force, F, of the lower end of the rod was measured by the chemical balance in the magnetic field range 0.2—13.5 kOe. The magnetic susceptibility, K, per unit of volume of the solution was calculated as follows:

$$2F/(H_A^2-H_B^2)A = K - K_0$$

where H_A is the strength of the magnetic field at the lower end of the rod; H_B, that at the upper end (negligibly small); K_0, the magnetic susceptibility per unit of volume of the rod, and A, the cross sectional area of the rod. The magnetic susceptibility of the rod was calibrated with a standard solution of $NiCl_2$ and was found to be

$$-0.395\times10^{-6}/\text{cm}^2(-0.878\times10^{-6}/\text{g}).$$

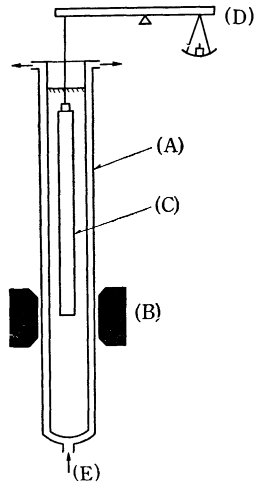

Fig. 1. Schematic illustration of vessel and magnetic balance used.
(A) Double cylindrical vessel, (B) Magnet, (C) Quartz rod, (D) Chemical balance, (E) Temperature-controlled water

The density of the solution was measured by using a density bottle, while the magnetic susceptibility per g-atom of the ferric ion in the solution was calculated making corrections for the diamagnetic elements in the solution. The magnetic moment, μ_{eff}, was calculated by the usual formula, $\mu_{\text{eff}}=2.84\sqrt{X_{\text{Fe}}\times T}$, where T is the absolute temperature. The pH was measured using a Horiba electrode pH meter.

Results

Spectrophotometric Data. Figures 2, 3, and 4 show the absorption curves of acidic solutions containing 0.3 N-ferric salt, 0.5 N-acid, and alkali in different concentrations from 0 to 0.7 N. There are absorption bands with peaks at 90 and 130×10^{13} Hz for the chloride, at 120×10^{13} Hz for the nitrate, and at 100 and 130×10^{13} Hz for the sulfate. When the acidity was decreased, the colors of these solutions (yellow for the chloride, light blue for the nitrate, and orange yellow for the sulfate) changed to reddish brown and these absorption bands broadened as may be seen in these figures. In order to find the relation between the frequencies of the peaks of absorption bands and the experimental conditions, optical measurements of acidic solutions with different concentrations of ferric salt, acid, and alkali were carried out in the frequency range from 70 to 140×10^{13} Hz at different temperatures. The results are given in Tables 1, 2, and 3.

Magnetic Data. Magnetic measurements of the same solutions were made in the range from 0.2 to 13.5 kOe at different temperatures. Their susceptibilities did not show any magnetic-field dependence at a given temperature. The magnetic moments, μ_{eff}, calculated from the magnetic data are given in the right-hand columns of Tables 1, 2, and 3.

In the above experiments, the pH values of the so-

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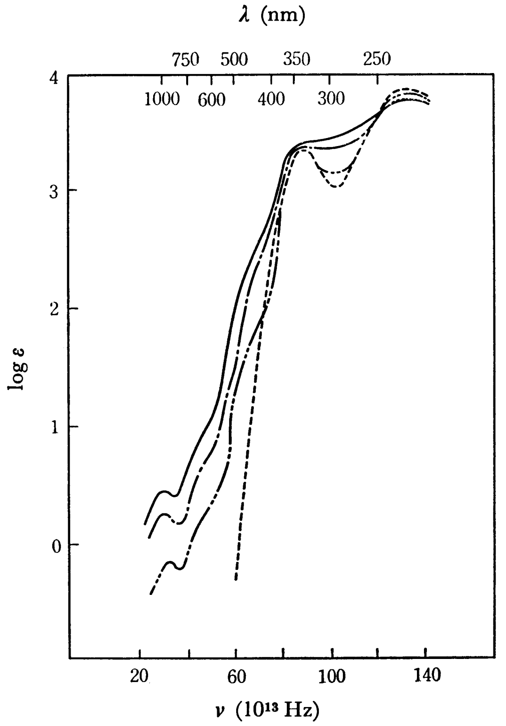

Fig. 2. Absorption curves of solutions containing 0.1 M-$FeCl_3$, 0.5 M HCl and *n*M NaOH at 25 °C: ---- $n=0$; ——— $n=0.5$; —·— $n=0.6$; —— $n=0.7$.

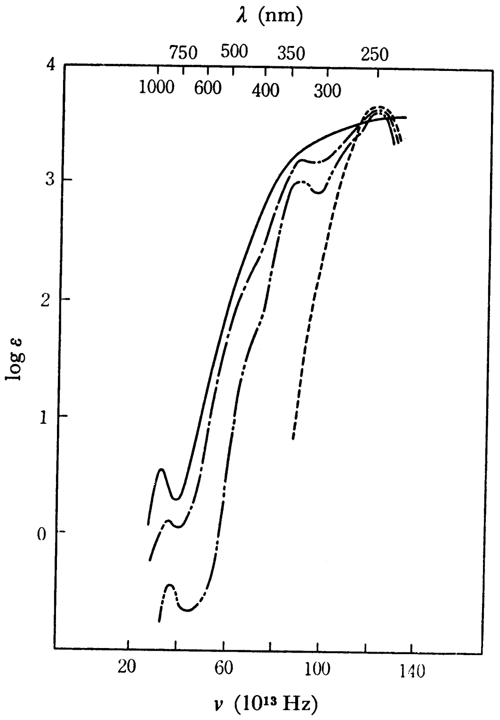

Fig. 3. Absorption curves of solutions containing 0.1 M $Fe(NO_3)_3$, 0.5 M HNO_3 and *n*M NaOH at 25 °C: ---- $n=0$; ——— $n=0.5$; —·— $n=0.6$; —— $n=0.7$.

lutions with no excess acid decreased with the time and the time dependence of the pH became smaller upon a decrease in the temperature. In order to obtain the susceptibility at different acidities, magnetic measurements of the solutions 0.1 g-iron atom/l at 17 °C were made at 13.5 kOe. The experimental results are summarized in Table 4.

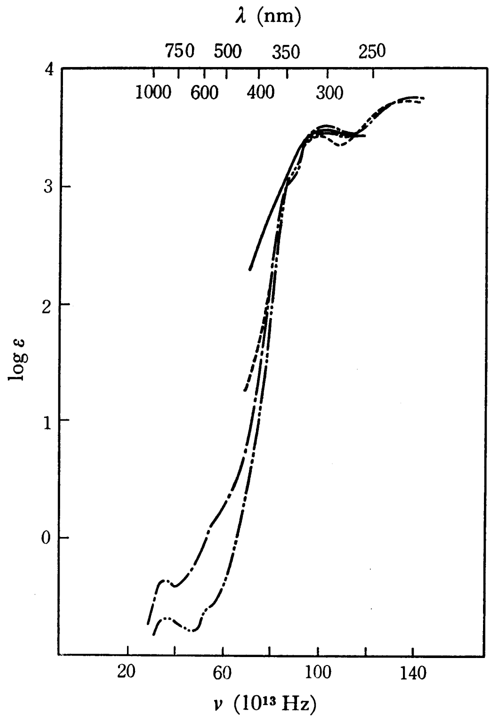

Fig. 4. Absorption curves of solutions containing 0.05 M $Fe_2(SO_4)_3$, 0.25 M H_2SO_4 and *n*M NaOH at 25 °C: ---- $n=0$; ——— $n=0.5$; —·— $n=0.6$; —— $n=0.7$.

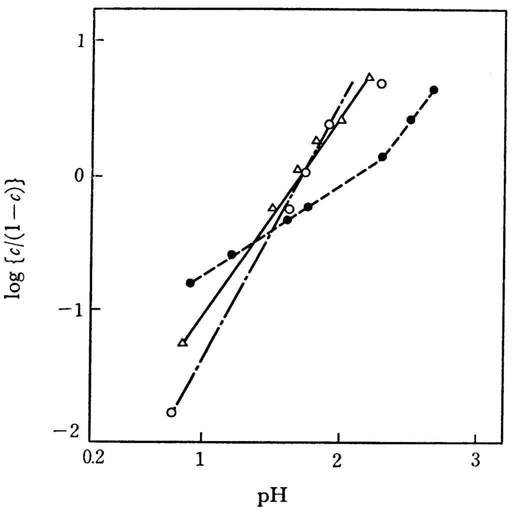

Fig. 5. Fraction of iron ions hydrolyzed in ferric salt solutions (0.1 g-iron atom/l) at various pH at 17 °C. The fraction is given by log $\{c/(1-c)\}$, where c is the concentration of iron ions present as polynuclear complexes: ○ = chloride, △ = nitrate, ● = sulfate.

Discussion

In strongly acidic solutions of ferric chloride, ferric sulfate, and ferric nitrate, ferric chloro, ferric sulfato, and ferric aquo complexes are formed respectively. These ferric complexes strongly absorb the light of frequencies in the ultraviolet region, the frequencies of the peaks of their absorption bands depending on the kind of ligands in them. Table 5 gives the frequencies and wavelengths of their peaks in the ultraviolet region.

Tables 1—3 indicate that the ferric complexes in

TABLE 1. SPECTROPHOTOMETRIC DATA AND MAGNETIC MOMENTS OF IRON IONS IN CHLORIDE SOLUTION (a=NH_4OH, b=NaOH used as alkali)

Composition (mol/l)			Temp. (°C)	ν (10^{13}/s)	log·ε	ν (10^{13}/s)	log ε	μ_{eff} (BM)
$FeCl_3$	HCl	Alkali						
0.01	0.5	0	30	90	3.0	132	3.7	5.8
0.01	0.5	0	50	90	3.1	134	3.7	5.8
0.01	0.5	0	70	90	3.2	134	3.7	5.8
0.01	0.5	0.45 a	30	90	3.0	136	3.7	5.8
0.01	0.5	0.45 a	60	90	3.2	136	3.7	5.8
0.01	0.5	0.51 a	30	92	3.3	136	3.7	4.4
0.01	0.5	0.52 a	30	105	3.4	136	3.7	
0.10	0.5	0	30	90	3.27	134	3.82	5.93
0.10	0.5	0	60	89	3.38			5.99
0.10	0.5	0.50 b	30	90	3.31	134	3.76	5.4
0.10	0.5	0.50 b	60	89	3.38			5.5
0.10	0.5	0.70 b	30	102	3.43	139	3.73	4.4

TABLE 2. SPECTROPHOTOMETRIC DATA AND MAGNETIC MOMENTS OF IRON IONS IN NITRATE SOLUTIONS (a=NH_4OH, b=NaOH used as alkali)

Composition (mol/l)			Temp. (°C)	ν (10^{13} Hz)	log ε	ν (10^{13} Hz)	log ε	μ_{eff} (BM)
$Fe(NO_3)_3$	HNO_3	Alkali						
0.004	0.022	0	35	120	3.46			5.8
0.004	0.022	0	70	102	3.10			5.8
0.004	0.022	0.008 a	35	103	3.16			
0.004	0.022	0.008 a	50	100	3.42			
0.004	0.022	0.008 a	70	100	3.42			
0.05	0.50	0	21	125	3.68			5.7
0.05	0.50	0	60	125	3.64			5.6
0.05	0.50	0.50 b	19	125	3.65	91	3.01	5.2
0.05	0.50	0.50 b	60	126	3.64	91	3.12	4.9
0.05	0.50	0.60 b	19	125	3.55	91	3.07	5.0
0.05	0.50	0.60 b	60	127	3.61			4.8
0.10	0.50	0.50 b	19	90	3.02			5.2
0.10	0.50	0.50 b	60	90	3.12			5.1
0.10	0.50	0.60 b	19	90	3.16			4.9

TABLE 3. SPECTROPHOTOMETRIC DATA AND MAGNETIC MOMENTS OF IRON IONS IN SULFATE SOLUTIONS (a=NH_4OH, b=$(NH_4)_2SO_4$, c=LiOH, d=CH_3COONa used as alkali or additive)

Composition (mol/l)			Temp. (°C)	ν (10^{13} Hz)	log ε	ν (10^{13} Hz)	log ε	μ_{eff} (BM)
$Fe_2(SO_4)_3$	H_2SO_4	Other						
0.005	0.025	0	27	135	3.5	98	3.2	5.8
0.005	0.025	0.05 a	27	137	3.5	101	3.3	5.0
0.005	0.025	0.06 a	27	138	3.8	104	3.5	4.5
0.025	0.25	0	20	135	3.73	100	3.42	5.6
0.025	0.25	0.5 b	20	137	3.73	101	3.52	5.6
0.025	0.25	1.0 b	20	101	3.55			5.6
0.025	0.25	2.0 b	20	101	3.60			5.5
0.025	0.25	0.5 c	20	137	3.78	100	3.51	5.4
0.025	0.25	0.6 c	20	139	3.77	101	3.51	5.1
0.025	0.25	0.5 d	20	100	3.49			5.2
0.025	0.25	0.5 d	60	99	3.09			5.0
0.025	0.25	1.0 d	20	89	3.19			3.1
0.025	0.25	1.0 d	60	89	3.1			3.4
0.025	0.25	2.0 d	20	89	3.24			3.1
0.025	0.25	2.0 d	60	89	3.3			3.5
0.050	0.25	0	30	137	3.72	100	3.47	5.7
0.050	0.25	0.5 c	30	138	3.74	101	3.47	5.4
0.050	0.25	0.6 c	30	139	3.75	103	3.50	5.1
0.050	0.25	0.7 c	30	109	3.50			4.1
0.050	0.25	0.5 d	20	97	3.45			5.2
0.050	0.25	2.0 d	20	89	3.2	121	3.3	3.1
0.050	0.25	2.0 d	60	89	3.3			3.6

Table 4. Magnetic data of solutions of ferric chloride, nitrate and sulfate at 17 °C

Composition (mol/l)			pH	Sp. gr.	$-F$ (mg)	$-K$ ($\times 10^6$)	X_{Fe} ($\times 10^2$)	μ_{eff}
Ferric salt	Acid	Alkali						
$FeCl_3$	HCl	NaOH						
0.10	0.50	0	0.5	1.021	66.5	0.731	1.41	5.96
		0.10	0.52	1.022	65.5	0.690	1.38	5.90
		0.20	0.57	1.026	65.5	0.690	1.38	5.90
		0·40	0.93	1.030	65.0	0.677	1.37	5.88
		0.50	1.64	1.032	54.0	0.414	1.11	5.30
		0.60	1.73	1.033	49.0	0.294	0.99	5.00
		0.70	1.90	1.035	42.7	0.144	0.84	4.62
		0.75	2.29	1.036	38.5	0.044	0.75	4.34
$Fe(NO_3)_3$	HNO_3	NaOH						
0.10	0.50	0	0.58	1.035	65.2	0.682	1.38	5.90
		0.10	0.63	1.038	66.0	0.702	1.39	5.91
		0.20	0.70	1.040	64.5	0.665	1.36	5.85
		0.40	0.86	1.043	63.0	0.630	1.33	5.78
		0.50	1.49	1.047	53.5	0.402	1.10	5.26
		0.60	1.69	1.048	48.5	0.282	0.98	4.98
		0.70	1.83	1.049	44.7	0.192	0.89	4.74
		0.75	2.00	1.050	42.3	0.134	0.83	4.58
		0.77	2.20	1.053	39.2	0.056	0.76	4.36
$Fe_2(SO)_4$	H_2SO_4	LiOH						
0.05	0.25	0	0.78	1.035	64.3	0.662	1.365	5.85
		0.10	0.80	1.039	63.2	0.634	1.28	5.69
		0.20	0.89	1.040	62.5	0.618	1.27	5.64
		0.40	1.18	1.047	61.0	0.582	1.22	5.53
		0.50	1.58	1.050	58.2	0.514	1.15	5.38
		0.55	1.73	1.050	56.5	0.453	1.10	5.24
		0.60	2.31	1.051	49.0	0.296	0.95	4.87
		0.65	2.42	1.051	43.5	0.163	0.83	4.56
		0.70	2.62	1.053	40.5	0.093	0.76	4.35

Table 5. Frequencies (ν in 10^{13} Hz) and wave lengths (λ in mμ) of absorption bands of various ferric complexes

Complex	ν	λ	ν	λ	ν	λ	Ref.
$[Fe(H_2O)_6]^{3+}$	111	270	125	240			10, 11, 18
$[FeOH]^{2+}$	125	240					18
$[Fe_2(OH)]_2^{4+}$	89	335					18
$[FeCl]^{2+}$	88	340	122	245			11
$[FeCl_2]^+$	88	340	122	245			11
$[FeCl_3]$	75	400	88	340	120	250	11
$[FeCl_4]^-$	83	360	96	310	120	250	11
$[FeSO_4]^+$	99	303					13
$[Fe(SO_4)_2]^-$	100	300					13

the strongly acidic solutions are paramagnetic in a high spin state, and that the frequencies of the peaks are determined by the kind and concentration of the anions in the solutions. Regardless of the concentration of ferric ions and the temperature,peaks appear at 89—90 × 10^{13} Hz, 120—125 × 10^{13} Hz, and 98—100 × 10^{13} Hz for strongly acidic solutions of ferric chloride, ferric nitrate, and ferric sulfate respectively. These peaks are due to ferric chloro, ferric aquo, and ferric sulfato complexes respectively. The strongly acidic solutions of ferric chloride and ferric sulfate show peaks (though not sharp) in the region of 132—137 × 10^{13} Hz, too. They are considered to be due to ferric chloro and ferric sulfato complexes respectively.

As the acidity of the strongly acidic solutions is decreased, the absorption bands become broad and obscure, as may be seen in Figs. 2, 3, and 4. This broadening may be due to the fact that a polynuclear complex containing a great number of ferric ions is formed in each solution and that its concentration increases with a decrease in the acidity, so that light in the ultraviolet region is strongly scattered. Also, the increase in the concentration of the polynuclear complex causes the magnetic susceptibility, X, of the ferric ions to decrease. The decrease in X may be due to the fact that the polynuclear complex contains antiferromagnetic couplings, though the ferric ions in the polynuclear complex as well as those in the strongly acidic solutions are in a high-spin state, as will be described later.

It is known that all the ferric ions present in crystals of α-FeOOH, β-FeOOH, and α-Fe_2O_3 are in a high spin state ($S=5/2$, five unpaired spins per iron) and are bound to O^{2-} and/or OH^- ions at angles of 90°

and either 120° or 180°.[22-25] When the bond angle between these ferric ions is between 120° and 180°, the spins can align themselves to each other by means of a superexchange interaction whose strength depends on the distance and angle between them. This bridging, called an antiferro magnetic coupling, causes the X value to decrease. Because both the iron ions in the ferric complexes and those in the final products of hydrolysis are in a high spin state, it is reasonable to consider that the iron ions in the polynuclear complexes, intermediates, are not in a low spin state, but in a high spin one, and that the polynuclear complexes must have antiferromagnetic couplings, causing the decrease in the X value.

It is known that upon a decrease in the acidity, the X decreases to a certain value. According to Mulay and Selwood's magnetic data, X of the ferric ions in a 0.04 M $Fe(ClO_4)_3$ solution at 16 °C decreased to 6.3 and 6.2×10^{-3} per g-iron atom when the pH was increased to 1.9 and 2.45 respectively.[18] Schuger et al. also reported that, in a 0.195 M $Fe(ClO_4)_3$ solution at 25 °C, X decreased to about 6.9×10^{-3} per g-iron atom.[21] It is supposed that when the solution reaches a state where a further decrease in its acidity causes hardly any decrease in X, most of the ferric complexes in it have been hydrolyzed to form a polynuclear complex.

The usual formula for the hydrolysis of the ferric ion is written as follows:

$$Fe^{3+} + nH_2O = Fe(OH)_n{}^{3-n} + nH^+$$

Let c represent the wt fraction of ferric ions as a polynuclear complex, $Fe(OH)_n{}^{3-n}$; X_{Fe}, the susceptibility/g-atom of the total ferric ions present at different acidities; X_T, that/g-atom of ferric ions present as a ferric complex, Fe^{3+}; and X_P, that/g atom of ferric ions present as the polynuclear complex. Assuming that $X_{Fe}=cX_P+(1-c)X_T$ and that X_P is independent of acidity, it is given as:

$$c = (X_T-X_{Fe})/(X_T-X_P)$$

In the present experiment, unfortunately, the X value independent of the acidity could not be obtained (the magnetic measurements were not made for the solutions with higher pH values than the values shown in Table 4, as the presence of a precipitate was observed). From the X_{Fe} values in Table 4, the c values at different acidities are calculated for the solutions at 17 °C using the $X_P=6.2\times10^{-3}$ obtained by Mulay and Selwood.[18] The c values thus obtained are plotted against the pH in Fig. 5. As may be seen in the figure, the points for the chloride and the nitrate are on straight lines, while those for the sulfate on a curved line. These lines have different slopes and intercepts. Since $\log K=\log(Fe(OH)_n{}^{3-n})\times(H^+)^n/(Fe^{3+})$ in the hydrolysis formula, the slope(n) and intercept ($\log K$) represent the OH^- (or $2O^{2-}$)/Fe^{3+} ratio in each polynuclear complex and its formation constant respectively. The n and $\log K$ values obtained are given in Table 6.

Table 6. Slopes (n) and intercepts ($\log K$) for each ferric salt solution in Fig. 5

Chloride		Nitrate		Sulfate			
n	$\log K$	n	$\log K$	n	$\log K$	n	$\log K$
2.2	−3.7	1.4	−2.5	0.7	−1.4	1.4	−3.0

It is supposed that the X_P value depends on the particle size and the structure of the polynuclear complex which are affected by the kind of ferric complex. Spiro *et al.* reported that the particle size of the polynuclear complex in the nitrate is nearly independent of the degree of hydrolysis of the aquo ferric complex.[20] The nature of the polynuclear complexes formed by the hydrolysis of the aquo ferric complex has been widely studied, but that of the polynuclear ones formed by the hydrolysis of other ferric complexes, such as the chloro ferric complexes, has not yet been sufficiently studied.

We believe that the X_P value of the polynuclear complex formed in the ferric chloride solution is not less than 3.4×10^{-3}, which is the room-temperature molar susceptibility of the final product, β-FeOOH, of the hydrolysis of the ferric chloro complexes. The c values for the chloride are also calculated using $X_P=3.4\times10^{-3}$. The n and pK values for the chloride obtained by the graphical method are 2 and 3.7 respectively.

These n values suggest that the polynuclear complex formed by the hydrolysis of the aquo ferric complex in the nitrate contains $[Fe_2(OH)_3]^{3+}$ cations. In the sulfate, a polynuclear complex containing $[Fe_2(OH)_3]^{3+}$ or one containing $[Fe_3(OH)_2]^{7+}$, or a mixture of them, is formed, depending on the pH. The polynuclear one formed in the chloride contains $[Fe(OH)_2]^+$ cations.

It is impossible to determine from the n values whether the ligand is OH^- or O^{2-}. Tables 2 and 3 show that when the acidity of ferric nitrate solutions is decreased, absorption peaks appear at 90—91 × 10^{13} Hz, and that when a ferric sulfate solution is added to excess sodium acetate, a peak appears at 89 × 10^{13} Hz. It was found by Schugar *et al.* that a dimeric complex, $[Fe(pic)_2OH]_2$(pic=picolinic radical), contains a dihydroxo-bridged structural unit, $Fe_2(OH)_2$.[26] Also, Anderegg pointed out that $[Fe(pic)_2OH]_2$ and polynuclear complexes formed by the hydrolysis of a ferric aquo complex must have a similar bridging structure, because they exhibit similar electronic spectral bands at 87.5 and 89 × 10^{13} Hz respectively.[27] It is evident that the dihydroxo-bridged structural units exist in the polynuclear complexes containing $Fe_2(OH)_3$ cations. Where edge-shared octahedral dimers, $[Fe_2(OH)_2(H_2O)_8]^{4+}$, are weakly bound by water molecules to form a polynuclear complex, the decrease in the X value may, however, be slight at room temperature, since magnetic superexchange

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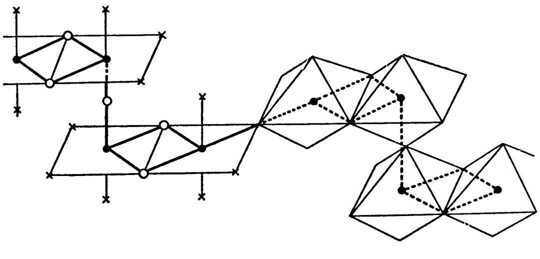
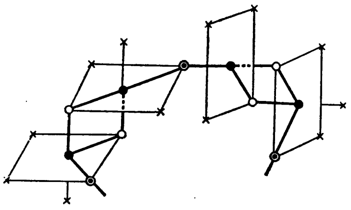
interaction is weak. We propose that the edge-shared octahedral dimers are antiferromagnetically bound together by monohydroxo-bridging to give a zigzag polynuclear cation of a structure such as is shown below:



where ●, O, and × are Fe^{3+}, OH^-, and H_2O respectively.

The ferric chloride solutions show absorption peaks at 90 × 10^{13} Hz regardless of the presence of polynuclear complexes. Therefore, it is impossible to determine from the spectroscopic data whether or not the polynuclear complex in the chloride contains the dimers. However, from the crystal structure and magnetic properties of the β-FeOOH formed by the hydrolysis of ferric chloride,[2,25] it can be presumed that the edge-shared octahedral dimers are antiferromagnetically bound together by oxo-bridging to give a ring-like polynuclear cation of a structure such as is shown below:



where ●, O, ⊙, and × are Fe^{3+}, OH^-, O^{2-}, and H_2O respectively.

The polynuclear complexes may be composed of the polynuclear cations and the acid ions, NO_3^-, $SO^2{}_4^-$, and Cl^-; they would thus be enabled to keep their electric neutrality. Among these anions, SO_4^{2-} and Cl^- are probably bound to the ferric ions as ligands in these complexes. The reactions by which the polynuclear complexes are formed may be roughly expressed by the following formulas, where the H_2O ligands are omitted:

$$2Fe(NO_3)_3 + 3H_2O = Fe_2(OH)_3(NO_3)_3 + 3HNO_3$$

$$Fe_2(SO_4)_3 + 3H_2O = Fe_2(OH)_3(SO_4)_{3/2} + (3/2)H_2SO_4$$

$$(3/2)Fe_2(SO_4)_3 + 2H_2O = Fe_3(OH)_2(SO_4)_{7/2} + H_2SO_4$$

$$2FeCl_3 + 4H_2O = Fe_2(OH)_2Cl_2O + 4HCl$$

On heating, these polynuclear complexes are further hydrolyzed. The $Fe_2(OH)_3(SO_4)_{3/2}$ and $Fe_2(OH)_3(NO_3)_3$ complexes form the precipitate of α-FeOOH, and the $Fe_2(OH)_2Cl_2O$ complex forms the precipitate of β-FeOOH. When Na^+, K^+, or NH_4^+ ion exists in the acidic solution of ferric sulfate, (Na, K or NH_4)-$Fe_3(OH)_6(SO_4)_2$ is formed as a crystalline precipitate of the basic sulfate.

When the temperature is raised, α-Fe_2O_3 is formed. Also, the formation temperature differs with the kind of polynuclear complex. For example, α-Fe_2O_3 began to be formed at about 60 °C in the ferric nitrate solution, and at about 90 °C in the sulfate and chloride solutions. Which is formed, α-Fe_2O_3 or FeOOH (α or β), may be determined by the change in the structures of the polynuclear complexes. It may also be supposed that the temperature at which the structural change begins is lower for the $Fe_2(OH)_3(NO_3)_3$ complex than for the others. The temperature dependence of the magnetic susceptibility of the ferric ions in acidic solutions of ferric nitrate, ferric chloride, and ferric sulfate was investigated by Bose at temperatures between room temperature and the boiling point.[15] His data suggest that the structure of the ferric ion in the nitrate solution varies with the temperature, since among these three kinds of ferric ions, the ferric ion in the nitrate solution has a magnetic transition point at about 343 K (70 °C) on the $1/X$ *vs.* temperature (K) curve.

Our proposal on the compositions and structures of the polynuclear complexes can well explain the experimental results obtained by many workers. It also gives a fundamental understanding of their nature. In order to clarify the mechanism of precipitation in ferric salt solutions, it will be necessary to determine precisely the compositions and structures of the polynuclear complexes present in them.

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