Studies on the Complex Formation between Iron(III) or Copper(II) and Poly(vinyl alcohol) in Terms of Inclusion of the Metal Hydroxide-Like Clusters by the Polymer

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The complex formation between iron(III) or copper(II) and poly(vinyl alcohol) (PVA) in aqueous solution has been investigated in some detail by using many PVAs ranging in degree of polymerization (DP) from 33 to 500. The minimum concentration of PVA required to form soluble complexes has been found to be inversely proportional to its DP, as expressed by the constancy of (DP of PVA)×[PVA]; the constants were 13 and 15 M in 10 mM iron(III) and copper(II) solutions (1 M=1 mol dm^{-3}), respectively. It has been revealed that iron(III) and copper(II) ions in the complexes exist in the form of metal hydroxide-like clusters comprising, at most, 120 metal ions per PVA chain. Transmission electron micrographs for the cast films of an iron(III) complex solution have shown the cluster size to be about 30 Å. Poly(vinyl methyl ether), a methyl ether derivative of PVA, was similar to PVA in complex formation with iron(III) up to pH 5. This fact also supports the conclusion that the present PVA complexes are of an inclusion type due to a hydrophobic interaction.

The green complexes of copper(II) with poly(vinyl alcohol) (PVA) formed at pH>6 have already been reported to be of an inclusion type due to a hydrophobic interaction between copper(II) hydroxide-like clusters and PVA, contrary to the general belief.[1,2] This type of complexation seems to be quite general for the aqueous systems of heavy-metal ions and water-soluble polymers, such as polysaccharides.[2—4] Therefore, it must be found everywhere in nature. Ferritin, an iron-storage protein widely distributed among biological systems, is a similar type of complex.[5] In recent years, there have also appeared papers concerning water-soluble polymer complexes with metal-oxide particles, instead of metal hydroxide-like clusters.[6—9] From a structural point of view, all of these polymer complexes may be considered to be new kinds of materials. Much attention has recently been paid to the usefulness of these complexes as functional materials.[8—10] The purpose of this study was to investigate the fundamentals of the complex formation of iron(III) and copper(II) with PVA in detail by using many PVAs ranging in the degree of polymerization (DP) from 33 to 500, with special emphasis on the iron(III) complexes, rather than the copper(II) complexes. Recently, we carried out detailed structural studies of the same complexes by NMR techniques.[11]

Experimental

Materials and Preparation of Metal Complexes with PVA in Aqueous Solution. $Fe(ClO_4)_3\cdot 6H_2O$, $Cu(ClO_4)_2\cdot 6H_4O$, NaOH (Kanto Chemicals), and $HClO_4$ (Koso Chemicals, 60% in water) were all of the highest grade. Seven PVAs of different DP–DS values (33–95, 77–97, 130–98, 180–100, 250–98, 400–99, 500–100), prepared and purchased previously, were used here, where DP and DS refer to the degrees of polymerization and saponification, respectively.[11] Poly(vinyl methyl ether) (PVME) (Tokyo Kasei, 30% in water) was also used in order to make a comparison with PVA in the complex formation. D_2O (Matheson, 99.9% atom D) and NaOD (Aldrich, 99% atom D) were utilized for preparing NMR sample solutions. The pD was determined by adding the factor of 0.4 to a usual pH-meter reading.[11]

Aqueous solutions of iron(III) or copper(II) complexes with PVA were prepared by mixing aqueous solutions of the metal perchlorate and PVA at various molar ratios R (=[PVA monomeric residue]/[metal ion]), followed by adjusting the pH with NaOH or $HClO_4$ solutions without any buffer, and by a slight dilution in volumetric flasks to give a final metal-ion concentration of 10 mM. The thus-prepared solutions were transparent, if the concentration of PVA or PVME was sufficiently high for complex formation; if not so, precipitation or turbidity occurred in the solutions. Therefore, whether or not all of the metal ions in the solutions are incorporated in the complex formation can be judged with a certain degree of accuracy by visual inspections of the solutions.

Measurements. Magnetic-susceptibility measurements for aqueous solutions at room temperature were carried out by the Gouy method,[12] in order to obtain experimental plots of an effective magnetic moment (μ_{eff}/B.M.) against the pH.

^{1}H NMR spectra were recorded at 25±0.1°C with a JEOL EX-90 NMR spectrometer at 90 MHz. Longitudinal relaxation times (T_1) for ^{1}H NMR signals were determined by the inversion-recovery technique.[13] In this process, at least 8 repetition times were selected properly enough for the determination of every T_1 value. The relaxation time was reproducible to about ±2% upon repeated runs. The metal ions employed here are paramagnetic. The observed relaxation rate ($(1/T_1)_{\mathrm{obsd}}$) is

$$(1/T_1)_{\mathrm{obsd}} = (1/T_1)_{\mathrm{p}} + (1/T_1)_{\mathrm{o}}, \quad (1)$$

where the two terms on the right-hand side are the relaxation rate due directly to the paramagnetic ions and that in the absence of those ions, respectively. In aqueous solutions of iron(III), the number of water molecules coordinated directly to each iron(III) ion (n) was estimated using[14]

$$(1/T_1)_{\mathrm{obsd}} = (1/T_1)_{\mathrm{solv}} + (n[\mathrm{iron(III)}]/55.5)(1/T_1)_{\mathrm{M}}, \quad (2)$$

where $(1/T_1)_{\mathrm{solv}}$ and $(1/T_1)_{\mathrm{M}}$ are the relaxation rates of a pure-water solvent and coordinated water molecules, respectively. $(1/T_1)_{\mathrm{M}}$ was determined under the condition of n=6 at pH 1.0;[15] n was then estimated based on the assumption of $(1/T_1)_{\mathrm{M}}$ being the same at any other pH value.

Transmission electron micrographs for an iron(III) complex with PVA in aqueous solution were measured on both JEOL JEM-2000FX-II and JEM-2000EX electron microscopes. Samples for these measurements were prepared as follows: After a copper grid was coated with a thin collodion film, it was then coated with a thin amorphous carbon film by vacuum evaporation. Next, it was ion-irradiated in order for the surface to become hydrophilic. The thus-treated grid was soaked with a sample solution, and then placed on adsorbent paper in order to remove any excess solution. It was finally allowed to dry in the air at room temperature.

Results and Discussion

Characterization of Metal Ions in the Complexes. Figure 1 shows a plot of μ_{eff} against the pH for aqueous solutions of iron(III) and PVA, together with those of iron(III) alone and of iron(III) and PVME. An inspection of this figure indicates that PVA and PVME are almost indistinguishable up to pH 5, above which precipitation occurs in the latter solution. In the case of iron(III) alone, the plot up to the precipitating pH value of 3 was quite the same as in the others. Similar plots have also been reported for aqueous solutions of iron(III) and sugars or related polyols.[3]

The μ_{eff} value of hydrated iron(III) ions at pH 1 was close to 5.92 B.M., calculated from the so-called spin-only formula for high-spin iron(III). Upon a gradual increase in pH, the hydrolysis of hydrated ions begins, and leads to the formation of hydroxo- and oxo-polynuclear iron(III) complexes in which μ_{eff} becomes much smaller, due to an antiferromagnetic interaction among the iron(III) ions.[3] All of the iron(III) ions are finally deposited as a red-brown gelatinous iron(III) hydroxide-like precipitate at pH ca. 3.

On the other hand, in the presence of PVA and PVME, solutions remained transparent without any precipitation or turbidity, even at pH>3. Figure 1 shows that all plots of μ_{eff} against the pH were quite similar in an initial low-pH range, whether PVA and PVME are present or not, and that μ_{eff} is kept small and constant at pH>3. These facts suggest the possibility that the above-mentioned precipitate or related ones are solubilized by PVA and PVME, and, moreover, that this solubilization process just corresponds to the complex formation concerned in this work, as is the case with aqueous solutions of copper(II) and PVA at pH>6.[1] Aqueous solutions of iron(III) complexes with PVA and PVME around pH 4 were red brown and transparent, and almost identical in UV-visible spectra, although the spectra are omitted here for brevity. Furthermore, there was almost no difference between PVA and PVME regarding the pH dependence of frozen-solution ESR spectra at pH<5; an ESR spectrum characteristic of hydrated iron(III) ions at pH 1 decreased in intensity with increasing pH, and was finally changed at pH>3 into such an extremely broad ESR spectrum over the field range 0 to 0.5 T that there apparently appeared no ESR signals. Small μ_{eff} values ranging from 3 to 5 B.M. and extremely broad ESR spectra are closely correlated with each other, since both of them are generally characteristic of iron(III) hydroxide or related substances with a fairly strong antiferromagnetic interaction among high-spin iron(III) ions.[3] All of these facts indicate that iron(III) hydroxide-like clusters of the same form are included in both complexes with PVA and PVME. By the way, the reason why the iron(III) clusters in these polymer complexes are always called iron(III) hydroxide-like clusters in this work is that the clusters magnetically and spectroscopically resemble the iron(III) hydroxide precipitate or colloid, together with the fact that the precipitate is not always

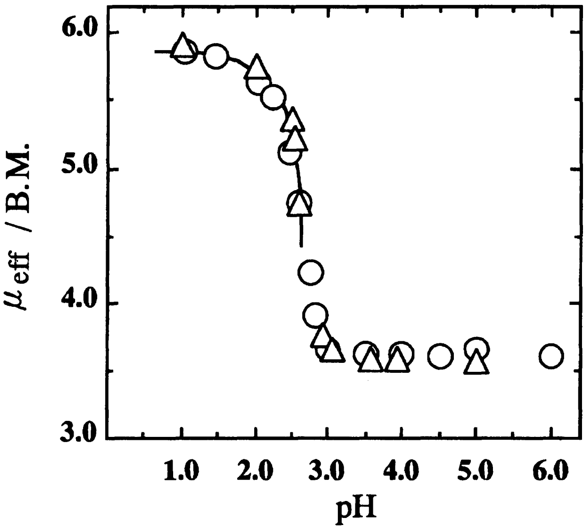

Fig. 1. Plots of μ_{eff} against pH for the aqueous solutions of PVA and iron(III) (○), PVME and iron(III) (△), and iron(III) alone (—) ([iron(III)]=10 mM; R=40; at room temperature).

constant in composition (described later).

Generally speaking, the iron(III) clusters, themselves, are hydrophobic-like particles, because they are nearly neutral in charge, and thus agglomerate and precipitate by themselves in water. The iron(III) hydroxide colloid is well known to be a typical hydrophobic type, as shown in any textbook on colloids.

The number of coordinated water molecules per iron(III) ion as a function of pD was determined by measuring the ^{1}H NMR relaxation rate of solvent water (Fig. 2). The hydrolysis of hydrated metal ions is regarded as being a reaction in which the number of coordinated water molecules is gradually reduced. In the absence of PVA, this number remarkably decreased with increasing pH in the pH range without precipitation, whereas, in the presence of PVA, the number similarly decreased at pH$<$3 and reached zero at pH 3, suggesting that there are no exchangeable water molecules in the iron(III) clusters of the complexes. This is additional evidence that this complex formation is accompanied by the hydrolysis of hydrated iron(III) ions, in conformity with a preliminary pH titration result.$^{2)}$ Interestingly, the number of coordinated water molecules in the presence of PVA at around pH 2.5 was somewhat smaller than that in its absence. This is probably because PVA molecules around the iron(III) clusters may have an inhibitory effect on the approach of bulk water molecules to the clusters.

Dependence of the DP of PVA and the Concentration of Metal Ions on the Complex Formation. It has been reported that the present complex formation is independent of the DP of PVA if DP$>$400.$^{16)}$ In this work, however, it has been found to be remarkably DP-dependent when DP$<$200, as described below. If PVA is insufficient to form complexes with a given amount of iron(III) in aqueous solution, precipitation or turbidity occurs upon the pH increasing above 3. This precipitation or turbidity is easily and sensitively detectable by a visual inspection of the solution. If is not the case for an initial period of several hours, all iron(III) ions were judged to form soluble complexes with PVA. Just for information, the complex formation was almost independent of the DS values ranging from 90 to 100. Figure 3 shows plots of the pH threshold of precipitation (pH$_{\text{ppt}}$) against the DP of PVA in aqueous solutions of 10 mM iron(III) or copper(II) and PVA at R=5. In the case of iron(III), precipitation did not occurred at any pH if DP$>$180, while it did occur at pH 3—3.5 if DP$<$130, as in the case without PVA. This fact indicates that the PVA of DP$<$130 has no ability to form iron(III) complexes, and, furthermore, that there is a large gap between the DPs of 130 and 180 in the complex formability of PVA. In the case of copper(II), the above-mentioned gap shifted to a little higher DP region between 180 and 250. The precipitation pH had a tendency to slightly increase with DP, even in the DP$<$180 range. On the other hand, a gummy precipitate was also produced at around pH 12, due to direct coordination of copper(II) to the OH groups of PVA accompanied by deprotonation in this pH range.$^{17)}$

Figures 4A and 4B show plots of the PVA-concentration threshold of precipitation ([PVA]$_{\text{ppt}}$) at pH 7.0 against the DP of PVA and their rearranged plots, respectively. These figures demonstrate that the minimum concentration of PVA required for complex formation is inversely proportional to the DP. The values of (DP of PVA)$\times$[PVA]$_{\text{ppt}}$ were 13 and 15 M for 10 mM iron(III) and copper(II) solutions respectively, indicating that iron(III) is more stable in the complex formation than copper(II), as has also been reported in

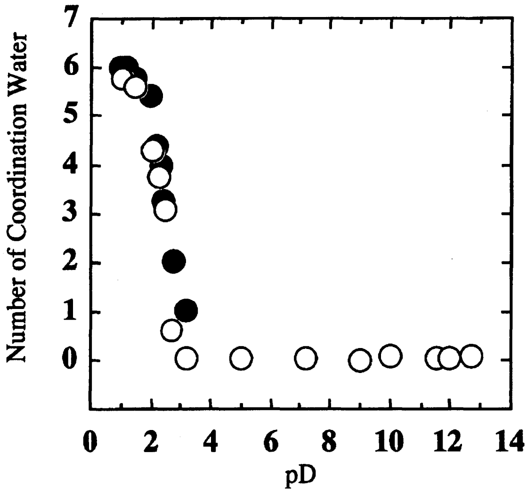

Fig. 2. pD dependence of the number of coordination water for iron(III) alone (●) and iron(III) complexes with PVA (○) ([iron(III)]=10 mM; R=40; 25±0.1 °C).

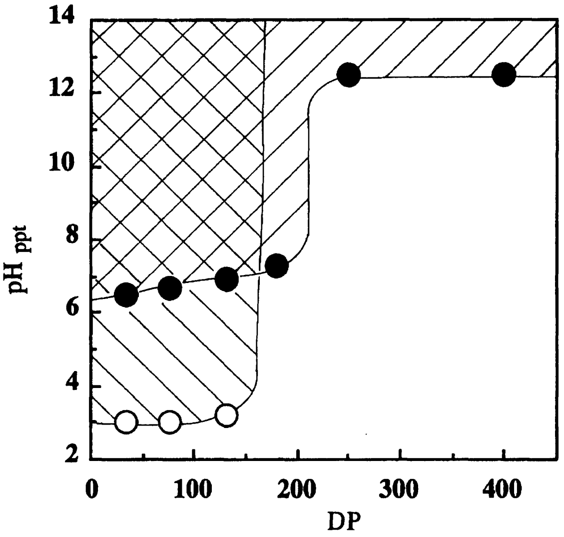

Fig. 3. Dependence of the DP of PVA on the lowest pH of precipitation (pH$_{\text{ppt}}$) in aqueous solutions of PVA and iron(III) (○) or copper(II) (●) ([iron(III)]=[copper(II)]=10 mM; R=5). Shaded areas in the figure indicate the precipitation regions.

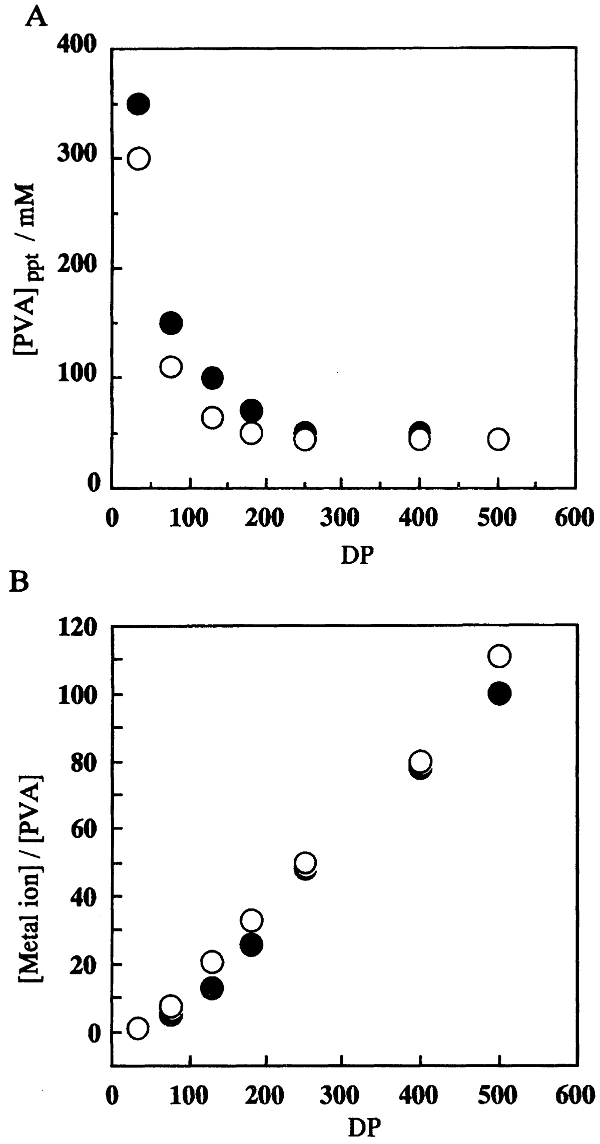

Fig. 4. Plots of the minimum PVA concentration of precipitation ($[PVA]_{ppt}$) against its DP (A) and plots of the values of [metal ion]/[PVA chain] against the DP (B) for aqueous solutions of PVA and iron(III) (○) or copper(II) (●) ([iron(III)] = [copper(II)] = 10 mM; pH 7.0); [PVA chain] = $[PVA]_{ppt}$/DP.

the literature.[18] Aqueous solutions of PVA and iron(III) or copper(II) decrease in viscosity upon the complex formation if DP < 500, as will soon be published elsewhere.[19] This viscosity decrease is interpreted as being due to a conformational contraction of individual PVA molecules upon complex formation in which they wrap coils around metal hydroxide-like cluster particles. Figure 4B clearly shows that a PVA molecule of DP 500 forms a complex including 100—110 metal atoms.

Transmission Electron Microscopic (TEM) Examination. The hydrolysis of iron(III) in aqueous solution produces a solid phase precipitate having a general formula of $FeO_{x/2}(OH)_{3-x}\cdot nH_2O$, where x and n are dependent upon the preparation condition.[15,20] The precipitate produced in a basic solution generally comprises amorphous $Fe(OH)_3$ with unknown hydroxide and oxide content and goethite (α-FeO(OH); *Pbnm*, $Z=4$; $a=464$; $b=998$; $c=303$ pm).[15] Lepidocrocite (γ-FeO(OH)) is also observed under a specific condition of the solution. Assuming that an α-FeO(OH) crystal is spherical in shape and contains 120 Fe atoms, its diameter is calculated to be about 20 Å. If amorphous $Fe(OH)_3$ is substituted for α-FeO(OH), the diameter must be somewhat larger.

In order to obtain reliable information concerning the particle size of iron(III) hydroxide-like clusters in the complexes, an attempt was made to take transmission electron micrographs for cast films of the present sample solutions. However, the question arose as to whether the particle images in the micrographs are clear or not, if we take into consideration that the images of crystalline magnetite particles of 40—100 Å in diameter in colloidal dispersions with PVA were not clear, probably due to the presence of PVA, which thickly coated the magnetite particles.[7] The resolution of the particle images in the micrographs might be anticipated to be lower for the present non-crystalline iron(III) hydroxide-like clusters than for the above-mentioned crystalline magnetite particles. Figure 5A shows one of the micrographs taken with a resolving power that was as high as possible.

The particle images in Fig. 5A are so low in resolution that they are almost indiscernible, as expected from above. However, a closer inspection of the fig-

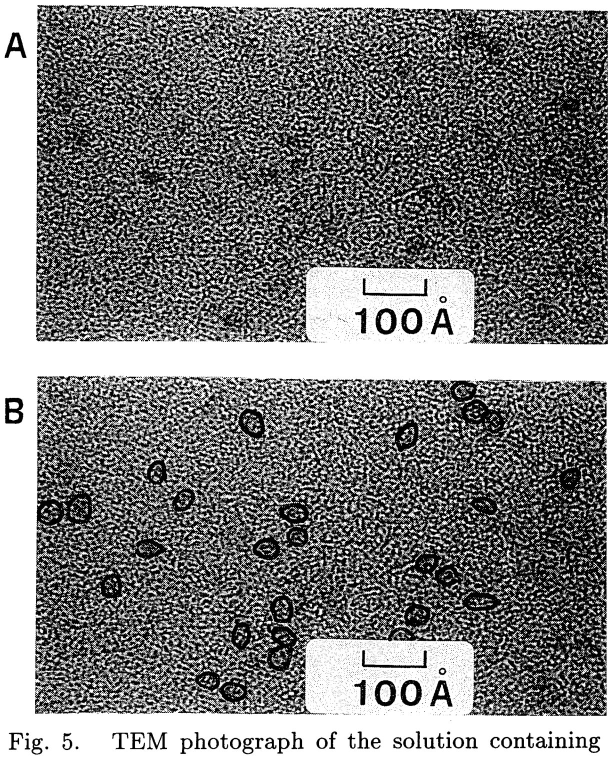

Fig. 5. TEM photograph of the solution containing iron(III) and the PVA of DP 500 and DS≈100 at $R=20$ ([iron(III)]=10 mM) at pH 7 (A) and the same one marked roughly with contour lines for particles (B).

ure indicates that there certainly appear vague image spaces of particles of about 30 Å in diameter. Figure 5B, which is marked roughly with contour lines for particles on Fig. 5A, is shown for convenience of a better understanding of the situation. The fact that there exist amorphous iron(III) hydroxide-like particles of about 30 Å in diameter in the iron(III) complexes with PVA under discussion is quite consistent with the above-mentioned estimate of each particle consisting of about 120 Fe atoms. In addition, this particle size seems to be reasonable in view of transparent solutions of the iron(III) complexes.[9)]

Concluding Remarks

Iron(III) and copper(II) complexes with PVA are of essentially the same kind, where metal hydroxide-like clusters are hydrophobically included by PVA. In this work, emphasis has been placed on studies concerning the complex formation of iron(III), rather than those of copper(II), according to the development of this series of work. It has been shown that iron(III) hydroxide-like clusters in the complexes have a considerably uniform size of about 30 Å and consist of about 120 Fe atoms. The fact that these complexes can be produced only by adding alkali to the solution of PVA and hydrated iron(III) suggests that the formation of those clusters may be induced by PVA, as well as by biopolymers in biomineralization.[21)]

The present metal complexes with PVA are very interesting and new kinds of materials comprising ultrafine particles of metal hydroxide-like clusters coated with PVA. It is noteworthy that polysaccharides, which have more complicated structures than PVA, also form similar complexes.[2,3)] Studies of PVA complexes are fundamentally important for a better understanding of polysaccharide complexes. Interestingly, PVA and polysaccharides can form complexes which include not only metal hydroxide-like clusters, but also metal oxides, themselves.[6—8)] All of these complexes are expected to be applicable as new materials in various fields in the future.

The structures of the present complexes with PVA remain uncertain regarding many points, even though detailed NMR studies on them have been carried out.[11)] X-ray crystal analysis is not applicable to them, because of a difficulty in obtaining crystals at present. Further detailed structures of them, along with their solution properties, are subject for a future study.

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