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Interaction Mode Between Poly(acrylic acid) and Fe^{3+} Ions. Gelation Mechanism of the System

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The successful preparation of homogeneous gels from aqueous poly(acrylic acid) and Fe^{3+} systems is described first. It has been revealed by optical absorption, ESR, and magnetic susceptibility measurements that Fe^{3+} ions in the gels exist as clusters analogous to polynuclear basic iron(III) carboxylates.

It is well-known that many polysaccharides, especially acidic ones, gel on addition of metal ions such as Ca^{2+} and Mg^{2+}, together with the fact that most of them in nature really exist in such gel forms.[1) Poly(acrylic acid) (PAA) also gels easily on addition of Ca^{2+}, Fe^{3+}, and analogous metal ions as gelling agents, although the gels thus prepared are usually inhomogeneous. In general, the polymer gelation results from the formation of three dimensional network of polymer chains crosslinked tightly to each other. In the above PAA gels, it is believed that each of the metal ions interacts with two carboxyl groups of adjacent polymer chains to form a crosslink. However, it is doubtful whether the crosslink thus formed is tight enough for gelation or not, because all the stability constants of metal monocarboxylates are very samll.2) The purpose of this paper is to obtain fundamental information on the interaction mode between PAA and Fe^{3+} ions in aqueous solutions and in their gels by optical absorption, ESR, and magnetic susceptibility techniques. Furthermore, the method for preparing these gels of a homogeneous type will also be reported here.

Three PAAs with the average molecular weights of 5000, 17000, and 90000 were purchased from the Aldrich Chemical Co. $Fe(NO_3)_3{\cdot}9H_2O$ and the other reagents were of reagent grade or higher and were used without further purification. In this work, the concentration of PAA is expressed as [PAA polymer residue] in terms of monomeric residues, and R is defined as [PAA polymer residue]/[Fe^{3+}].

The preparative procedure for homogeneous PAA-Fe^{3+} gels is as follows: 4 ml of a 0.10, 0.20, or 0.30 M $Fe(NO_3)_3$ aqueous solution is added dropwise to 10 g of 20 wt% PAA solution with vigorous stirring (1 M = 1 mol dm^{-3}). At this stage, inhomogeneous gelation takes place in most cases. Furthermore, 4 ml of a NaOH (1.0 or 2.0 M) or NaCl(2.0 M) solution or distilled water is added similarly to this inhomogeneous gel in order to change pH or ionic strength in the gel. An homogeneous gel is finally obtained by heating this inhomogeneous gel at 90°C for an hour or by allowing it to stand for at least a month in a sealed state at room temperature. However, gelation did not take place in all the cases of the PAA of the average molecular weight of 5000 and in the high pH cases of that of 17000.

Figure 1 shows typical absorption spectra of both PAA-Fe^{3+} gel and solution. Both spectra are almost identical, demonstrating that the gel is completely homogeneous and transparent as well as the solution. However, these spectra were quite different from those for Fe^{3+} ions in a solution at pH 1.5 and in an acetate buffer solution at pH 5. Figure 2 shows the ESR spectra observed for the same samples as in Fig.1. Both ESR spectra are essentially the same, and look a very broad absorption, which is apparently indistinguishable from a large undulation of the base-line. These observations indicate that the interaction mode between PAA and Fe^{3+} ions in the gels is essentially the same as in more dilute aqueous solutions. Figure 3 shows a plot of μ_{eff} against pH for the aqueous solutions, where μ_{eff} expresses the effective magnetic moment (in units of B.M.) determined by the usual Gouy method. The result of Fig. 3 is understandable on the basis of the facts that the spin-only μ_{eff} value for Fe^{3+} ions is 5.9 B.M. and that the μ_{eff} value becomes smaller, when two or more Fe^{3+} ions are brought close enough to each other for antiferromagnetic interaction between them. In the pH range of 1.5 to 5.5, the μ_{eff} value is almost constant and at its minimum of about 3.2 B.M. This pH range is considered as most suitable for the formation of stable gels, since the pH of the mixture of aqueous PAA and ferric salt solutions, which is immediately followed by gelation, is around 1.5. The fact that Fe^{3+} ions in the gels have a subnormal μ_{eff} value indicates that these Fe^{3+} ions exist in a form of cluster with antiferromagnetic

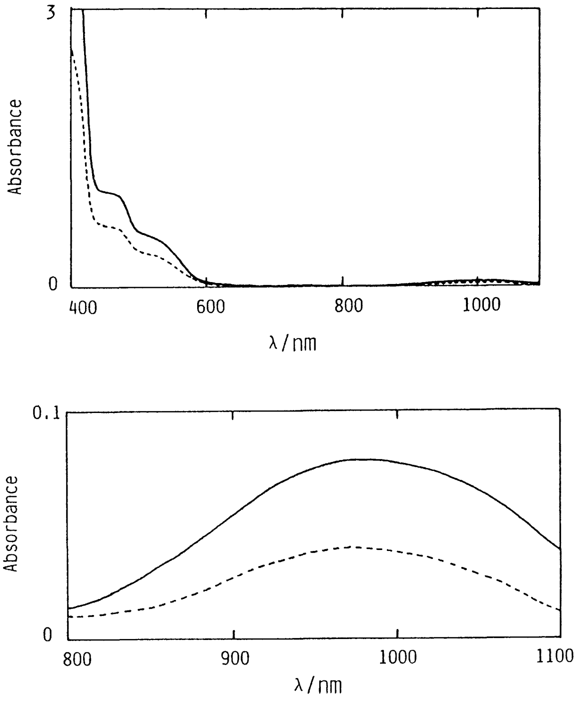

Fig. 1. Absorption spectra of the PAA-Fe^{3+} gel and solution systems at room temperature (PAA, av. MW = 90000; 10 mm quartz cell): (————) and (------), gel and solution with $[Fe^{3+}]$ = 0.022 and 0.010 M respectively (R = 10; pH 1.5).

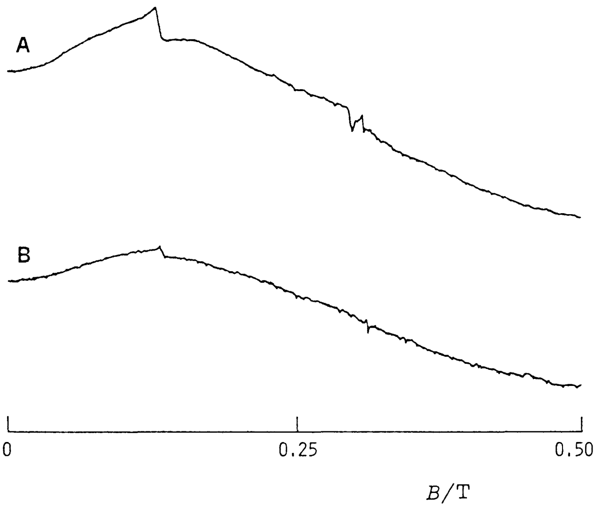

Fig. 2. X-Band ESR spectra of the PAA-Fe^{3+} gel and solution systems at 77K: A and B, the same samples as those for solid and dotted lines in Fig. 1 respectively.

interaction. This fact seems to be consistent with the ESR result mentioned above.

At this stage of discussion, recent studies on polynuclear basic iron(III) carboxylate complexes by Lippard et al. are very suggestive in a structural consideration of the above cluster.[3,4] One of these interesting complexes is a novel hexairon(III) complex derived from a trinuclear basic iron(III) benzoate whose structure is schematically shown in Fig. 4.[3)] Its μ_{eff} value of 2.94 B.M. is very close to the one described above for Fe^{3+} ions in the gelation systems, suggesting that the iron(III) cluster in the system may be analogous in structure to the one shown in Fig. 4, apart from the cluster size. However, it seems probable that the present iron(III) cluster is about 20 Å in diameter or less, since the present gel and solution systems are not turbid and, therefore, do not contain any colloidal particles, judging from such transparent absorption spectra as exemplified in Fig. 1; the situation was the same as for the systems of poly(vinyl alcohol) and Cu^{2+} or Fe^{3+} ions.[5)] This is also supported by the fact that a slight but significant raise of the base-line of absorption spectra is really observed for the colloidal dispersion with Fe_3O_4 particles of 40 – 100 Å in diameter.[6)]

It has been reported that a sort of hydrophobicity is necessary for the formation of such complexes as shown in Fig. 4.[3,4)] However, the condition of hydrophobicity may also be satisfied in aqueous PAA-Fe^{3+} systems, because there is a related fact that hydrophobic domains including binuclear metal centers are formed in aqueous PAA-Cu^{2+} systems.[7)]

The iron(III) cluster of Fig. 4 contains 10 carboxylate groups each of which acts as a bridging ligand between two Fe^{3+} ions, while many carboxylate groups of PAA must likewise be incorporated in the iron(III) cluster formed in the gels. It is reasonably considered that a

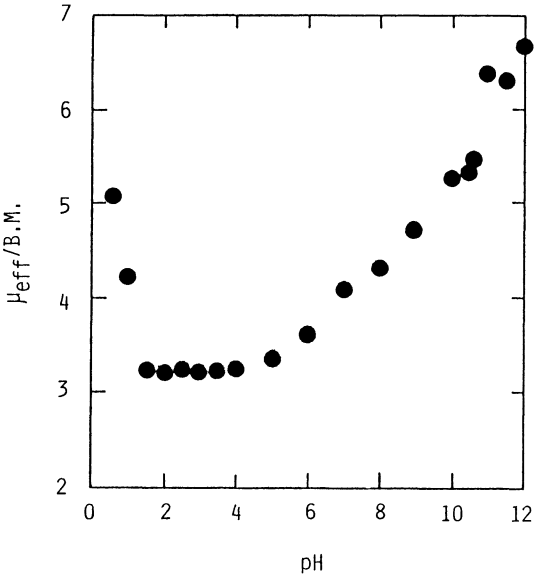

Fig. 3. A plot of μ_{eff} against pH for the PAA-Fe^{3+} solutions with $[Fe^{3+}]$ = 0.010 M and R = 1 (PAA, av. MW = 17000; measured at room temperature).

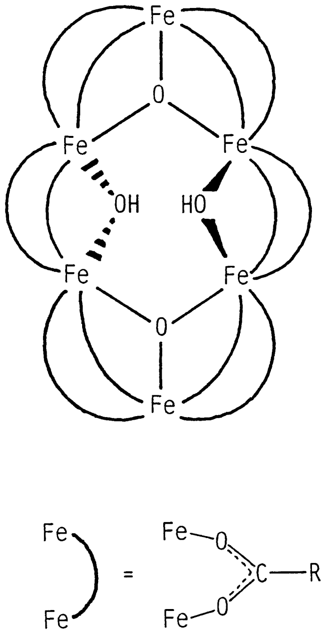

Fig. 4. Structural illustration for a novel hexairon(III) cluster prepared from a basic iron(III) benzoate.[3)]

tight crosslinking in the gels is made by many cooperative bonds between Fe^{3+} ions and PAA carboxylate groups in each cluster, even if each bond is weak. In conclusion, the formation of a large number of such tight crosslinks in the whole PAA-Fe^{3+} solution is responsible for the gelation. This conclusion also suggests that a similar mechanism may be applicable to the aqueous PAA-Ca^{2+} gel system, which is much more familiar in nature.

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