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Studies on the Formation of Magnetite Colloidal Dispersions in the Presence of Poly(vinyl alcohol)

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The formation of magnetite in aqueous solutions containing Fe^{3+} and Fe^{2+} ions in 2:1—1:2 ratio and poly(vinyl alcohol) at room temperature has been studied by magnetic susceptibility and optical absorption measurements. It has been found that the yield reaches a maximum after allowing the solutions at pH 10.5 to stand in a sealed state for 24 h. Transmission electron micrographs for their cast films have revealed that colloidal particles with diameters of 40—100 Å form either chain-like or cluster-like agglomerates. The particles have been identified as magnetite crystals by electron diffraction analysis and by direct observation of the crystal lattice structures.

Recently, much attention has been paid to biomagnetism, the main subject of which is the formation of fine magnetite particles in such biological systems as magnetotactic bacteria[1—3] and another organism.[4] Interestingly, the fine particles of magnetite in magnetotactic bacteria have found many biochemical and medical applications.[5] Furthermore, studies of immobilizing enzymes on synthetic magnetite particles have also been worthy of remark.[6] It is well-known that magnetite is easily synthesized as precipitates by adding a large quantity of 10% NaOH to an aqueous solution of Fe^{3+} and Fe^{2+} ions in 2:1 ratio and heating at 80 °C with stirring.[7] Magnetite colloidal dispersions have been prepared by boiling, sonicating, or shearing the mixtures of the above magnetite precipitates immersed in water and surfactants such as soap, dodecylamine, and sodium carboxymethylcellulose,[8] although these colloids are not always stable. Poly(vinyl alcohol) (PVA) also is a protective agent which can stabilize some inorganic colloids.[9,10] There have been brief reports on the preparation of magnetite colloidal dispersions in the presence of PVA and its modification.[11] The purpose of this paper is to investigate in detail the mode of formation of magnetite colloidal dispersions in the presence of PVA at room temperature and to examine the resulting colloidal dispersions by transmission electron microscopy.

Experimental

Materials. Hydrolyzed (100%) PVA with the average molecular weight of 14000 was purchased from the Aldrich Chemical Co. In this work, the concentration of PVA was expressed as [PVA polymer residue] in terms of monomeric residues. Iron(III) and iron(II) sulfates of guaranteed grade were used without further purification as sources of Fe^{3+} and Fe^{2+} ions respectively. The pH of the aqueous solutions was adjusted with NaOH without any buffer.

Measurements. Magnetic susceptibility measurements of colloidal dispersions were carried out at room temperature by the usual Gouy method for solutions.[12,13] The ultraviolet and visible absorption spectra of colloidal dispersions were recorded at room temperature with a Hitachi U-2000 spectrophotometer using 0.1 mm quartz cell. Transmission electron micrographs for the colloidal dispersions were measured on both JEOL JEM-2000FX-II and JEM-2000EX electron microscopes. The samples for these microscopes were prepared as follows: A copper grid was coated with a thin collodion film and then with a thin amorphous carbon film by vaccum evaporation. Next, it was ion-irradiated in order for the surface to become hydrophilic. The grid thus treated was soaked with a sample colloidal dispersion and then placed on absorbent paper to remove excess solution. It was finally allowed to dry in the air at room temperature.

Results and Discussion

Preparation of Magnetite Colloidal Dispersions. Figure 1 shows the change of effective magnetic moment (μ_{eff}) for all Fe ions with time in the solution containing 10.0 mM Fe^{3+} ions, 5.00 mM Fe^{2+} ions, and 200 mM PVA at pH 10.5 in a sealed state. The μ_{eff} value increases with time, but levels off after 24 h, where the μ_{eff} value is much higher than the spin-only μ_{eff} value of 5.9 B.M. for free Fe^{3+} ions. This indicates that Fe^{3+} and Fe^{2+} ions in the solutions aggregate to form some ferromagnetic substance. Actually this

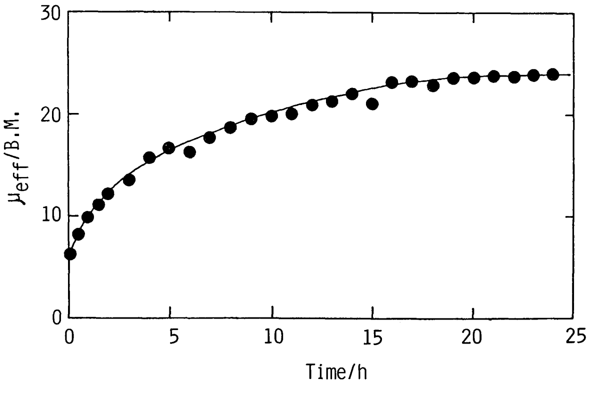

Fig. 1. Time dependence of μ_{eff} at 20.0 °C for the solution containing 10.0 mM Fe^{3+} ions, 5.50 mM Fe^{2+} ions, and 200 mM PVA at the initial pH of 10.5 (1 M=1 mol dm^{-3}).

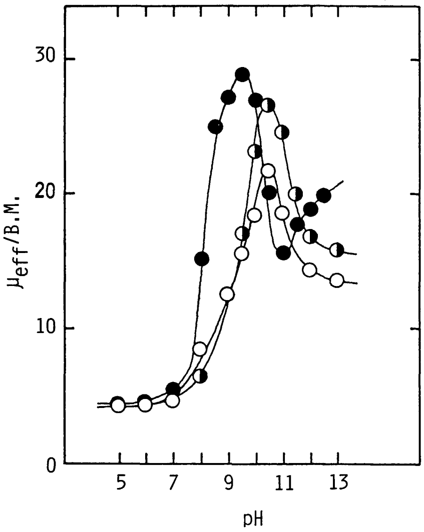

Fig. 2. pH dependence of μ_{eff} for the solutions containing 10.0 mM Fe^{3+} ions, 200 mM PVA, and Fe^{2+} ions in the following conditions after standing at 20.0 °C for 24 h: ○, 5.0 mM Fe^{2+} ions, in a sealed state; ◑, 5.50 mM Fe^{2+} ions, in a sealed state; ●, 5.0 mM Fe^{2+} ions, under N_2 atmosphere.

ferromagnetic substance is magnetite, as will be described later. In conclusion, it takes about 24 h to produce magnetite in a highest yield by this procedure. On the other hand, Fig. 2 shows the pH dependence of μ_{eff} for similar solutions after standing at room temperature for 24 h. Interestingly, it has been found for the first time that there is an optimal pH for the formation of magnetite at room temperature; in other words, its yield decreases remarkably at high pH values above the optimum. Furthermore, the yield becomes higher, as the solution is held more completely under anaerobic conditions. Since the Fe^{2+} ions added are gradually oxidized in the solution, the yield is improved by adding in advance a slight excess of Fe^{2+} ion stoichiometrically.

The sample solution becomes darker with an increase in the yield of magnetite. When the darkened solution is exposed to air, the surface solution readily changes to the same reddish-brown color as in the complex of Fe^{3+} ions with PVA at pH$\gtrsim$3,[14] owing to the air-oxidation of Fe^{2+} ions in the solution. Figure 3 shows ultraviolet and visible absorption spectra of the solutions at pH 5.0, 8.0, and 10.5 after standing at room temperature in a sealed state for 24 h. These spectra are similar in line shape to each other, but a remarkable raise of the base line is observed for the spectrum at the last pH which is most suitable for the yield of magnetite. This is reasonably considered to be due to light scattering by colloidal particles formed in this solution.

It is important to determine the total yield of magnetite in the colloidal solutions at pH 10.5, although it is not always easy to do so. In this work, we tried this according to two methods using the magnetite-PVA composite powder which was isolated by pouring the colloidal solutions to acetone. One method is to compare the magnetization between the above sample powder and a simple mixture of commercial PVA and magnetite powders, using a magnetometer of a sample-vibration type. Another method is to utilize Mössbauer spectroscopy for the sample powder. Both methods have revealed that magnetite in the slutions is produced in a 90% or higher yield. Detailed experimental data on these powder samples will be reported elsewhere.[15]

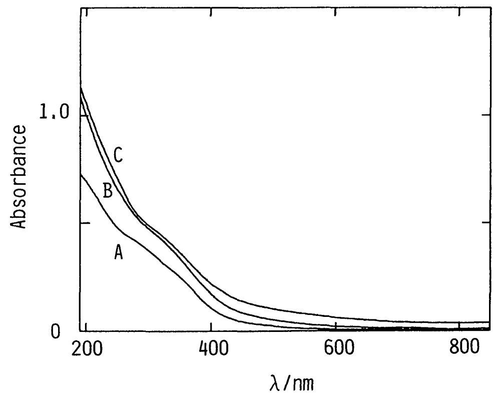

Fig. 3. Absorption spectra of the solutions containing 10.0 mM Fe^{3+} ions, 5.50 mM Fe^{2+} ions, and 200 mM PVA after standing in a sealed state at room temperature for 24 h (0.1 mm quartz cell): A, pH 5.0; B, pH 8.0; C, pH 10.5.

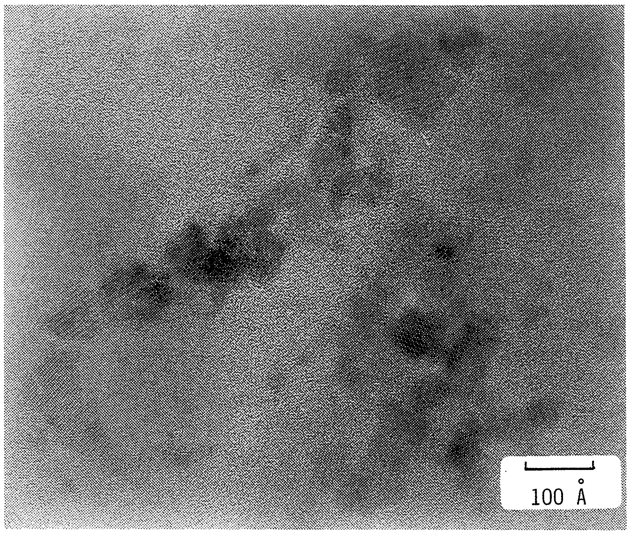

Fig. 4. TEM photograph of the solution containing 5.00 mM Fe^{3+} ions, 3.00 mM Fe^{2+} ions, and 100 mM PVA at pH 10.5 after standing in a sealed state at room temperature for 24 h.

Transmission Electron Microscopic (TEM) Examination. All the TEM photographs taken for the cast films of the present colloidal dispersions demonstrate that particles with diameters of 40—100 Å form either chain-like or cluster-like agglomerates, as

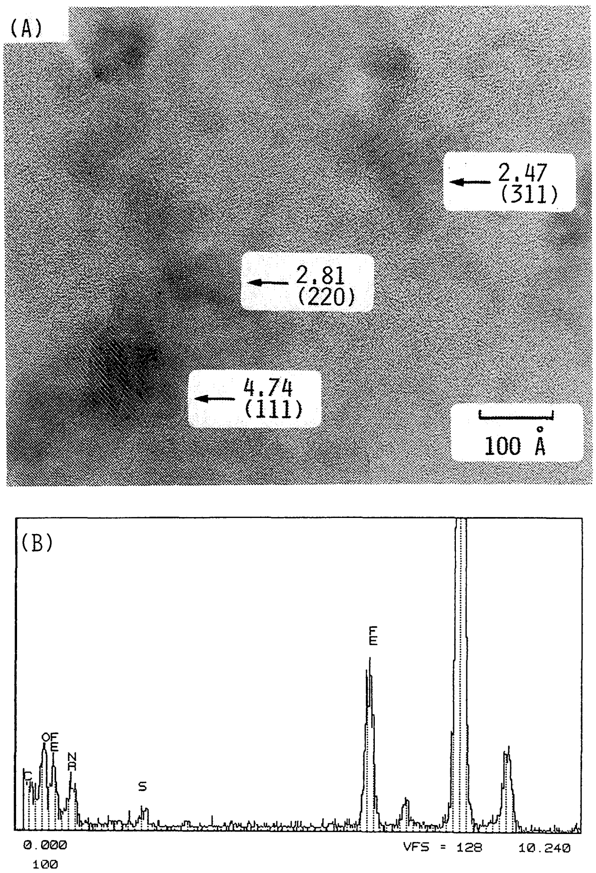

Fig. 5. TEM photograph (A) and X-ray energy dispersive analysis (B) of the same solution as in Fig. 4. In (A), the numbers express the spacings of lattice plane in units of Å for the crystalline particles shown by arrows, while the numbers in parentheses are the Miller indices corresponding to those spacings.

exemplified by Fig. 4. In general, this type of agglomeration is characteristic of magnetic particles. Interestingly, crystal lattice structures can be observed for many of the particles, although their images are not clear. We tried to improve the resolution to a much higher degree than that in Fig. 4, but the trial was unsuccessful. This is probably due to the presence of PVA which thickly coats every magnetite particle. In this study, unfortunately, we could not obtain any information on the manner in which PVA coats the particles, namely, on the interaction mode between PVA and the particles, although this problem is most interesting for us. The electron diffraction patterns observed for the particles which are not shown here were typical of the cubic crystal system, to which magnetite crystals belong. Figure 5 (A) shows another TEM photograph in which crystal lattice structures of some particles are in comparatively clear focus. Spacings of the lattice planes for some crystal lattice structures could be directly measured from the enlarged photograph, and the corresponding Miller indices of the magnetite crystals were assigned, as shown in Fig. 5 (A).[16] This, together with the electron diffraction result mentioned above, leads to a conclusion that the present colloidal particles are unquestionably ultrafine magnetite crystals. The elemental analysis performed for the cast film of the sample in the field of vision of Fig. 5 (A) by an energy dispersive X-ray microanalyzer attached to the TEM gave the result shown in Fig. 5 (B). This is consistent with the entity of magnetite and PVA with some impurities such as Na_2SO_4 and NaOH.

In this paper, we have demonstrated that an extremely stable colloidal dispersion of magnetite crystals with diameters of 40—100 Å is easily formed in the presence of PVA at room temperature under anaerobic conditions. Compared with this colloid, any of the magnetite colloids so far prepared by the conventional methods[7,8] are not stable. Furthermore, these colloids have been reported to consist of aggregates of somewhat larger particles of about 100 Å in diameter, although this seems to be an objective of re-examination by advanced techniques.

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