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Dispersibility of Magnetic and Nonmagnetic Iron(III) Oxides in 2-Butanone

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The dispersion stability of needlelike and octahedral iron(III) oxides of magnetic or nonmagnetic particles in 2-butanone was studied. Two kinds of copolymers of poly(vinyl acetate-vinyl chloride-maleic acid) (VAVCCOOH) and poly(vinyl acetate-vinyl chloride-vinyl alcohol) (VAVCOH) were used as dispersants. The sedimentation of dispersions, the adsorption of copolymer dispersants on the particles and zeta potentials were measured. By polymer adsorption, the dispersion of nonmagnetic needlelike iron(III) oxide was stabilized and the dispersions of magnetic needlelike iron(III) oxides were somewhat stabilized, but the dispersions of magnetic octahedral iron(III) oxides were only slightly stabilized. This characteristic behavior of the sedimentation experiment was discussed in relation to the amount of polymer adsorption and zeta potential and was correlated with the observations by an electron microscope. The magnetic attractive force operating between the two magnetic particles was calculated to illustrate the dispersibility of magnetic oxides. It was suggested from the calculation that the strength of the magnetization and the volume of a particle are the main factors affecting the flocculation of the magnetic particles.

The dispersions of the magnetic particles in polar organic media have been used as a paint for magnetic tapes. Good dispersibility is necessary to improve the properties of the magnetic tapes. However, the fundamental studies on dispersibility are very few, though some rheological studies have been done.[1–3)]

Many data on the stability of colloidal dispersions in nonpolar organic media as well as in water have been accumulated. The stability of colloidal dispersions in water has been discussed by the well-known DLVO theory,[4)] and this theory has been extended to that in nonpolar organic media.[5–9)] Recently, synthetic polymers have drawn attention as dispersants and the effect of adsorbed polymer layers on the stability of pigment dispersions has been reported.[10–16)] The double layer interaction between the particles indicated by the DLVO theory and the steric stabilization by the adsorbed polymers must both be considered in order to illustrate the stabilization of pigment dispersions in nonpolar organic media.[17)]

However, few studies on the stability in polar organic media such as alcohols and ketones have been done.[18)]

In this paper, as fundamental study of magnetic paints, the dispersions of needlelike and octahedral iron(III) oxides of the magnetic or nonmagnetic particles were prepared in 2-butanone. The sedimentation of dispersed particles, the adsorption of copolymer dispersants on the particles and zeta potentials were measured. The characteristic behavior of the sedimentation experiment is compared with the observation by an electron microscope.

Experimental

Material. Five kinds of iron(III) oxides were prepared according to the references.[19–21)] Each property of these iron(III) oxides is shown in Table 1. They were washed with 2-butanone in a Soxhlet apparatus for 16 h and then with hot distilled water in order to remove inorganic salts. This procedure was followed by drying in vacuum for 16 h at 100 °C; the materials were stored in a desiccator before use.

Two kinds of copolymers of poly(vinyl acetate-vinyl chloride-maleic acid) (abbreviated as VAVCCOOH) and poly (vinyl acetate-vinyl chloride-vinyl alcohol) (VAVCOH) were prepared[22–24)] and used as dispersants. Their molecular weights and chemical compositions, determined by the gel permeation chromatographic method (GPC), are shown in Table 2. These copolymers were extracted with methanol in a Soxhlet apparatus for 16 h and dried in vacuum for 16 h at 60 °C.

The 2-butanone used as a solvent was purified as follows: It was shaken four times with saturated potassium carbonate solutions and kept over potassium carbonate anhydride for a day. It was then distilled and dried with Molecular Sieve 4A to remove any trace of water.

Preparation of Dispersions. The dispersion of the particle content of 0.2 wt% and fixed concentration of a dispersant** (VAVCCOOH or VAVCOH) was prepared by mixing the particles and the solution under irradiation with an ultrasonic apparatus (Kaijo Denki Co. Model TA-4015, Power Supply 150 W, 20 kHz) for 5 mins. No precipitation was observed

Table 1. Properties of iron (III) oxides

Particle No.	Shape	Class	Specific surface area / m^2 g^{-1}	Saturation magnetization / emu g^{-1}	Size / Å	Density / g cm^{-3}
1	Needle	γ-Fe_2O_3	37.6	68	1470×160	4.3
2	Needle	α-Fe_2O_3	108	1	1610×142	3.9
3	Needle	α-Fe_2O_3	33.1	33[a)]	1400×178	4.0
4	Octahedron	γ-Fe_2O_3	9.3	62	1820	4.5
5	Octahedron	α-Fe_2O_3	8.6	29[a)]	1820	4.6

a) α-Fe_2O_3 keeps its magnetization.

** The viscosity of the dispersant solution was approximately equal to that of the solvent.

TABLE 2. GPC MOLECULAR WEIGHT DATA OF DISPERSANTS[a)]

Sample	$M_n \times 10^4$	$M_w \times 10^4$	M_w/M_n	Chemical component
VAVCCOOH	2.54	6.19	2.44	VA : VC : COOH=13 : 86 : 1
VAVCOH	3.29	6.95	2.11	VA : VC : OH=3 : 91.5 : 5.5

a) Apparatus: Water associates GPC-244, column: TSK-GEL, solvent: THF 2.0 ml/min 25 °C, sample: 0.5 w/v% 500 μl. Molecular weights were computed from the polystyrene calibration curve.

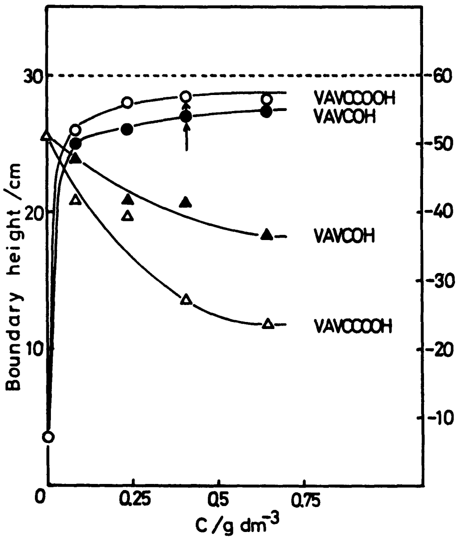

Fig. 1. Relation of the boundary height and ζ-potential with polymer concentration for No. 2 sample. Particle concentration=0.2 wt%. ○, ●: Boundary height, △,▲: zeta potential.

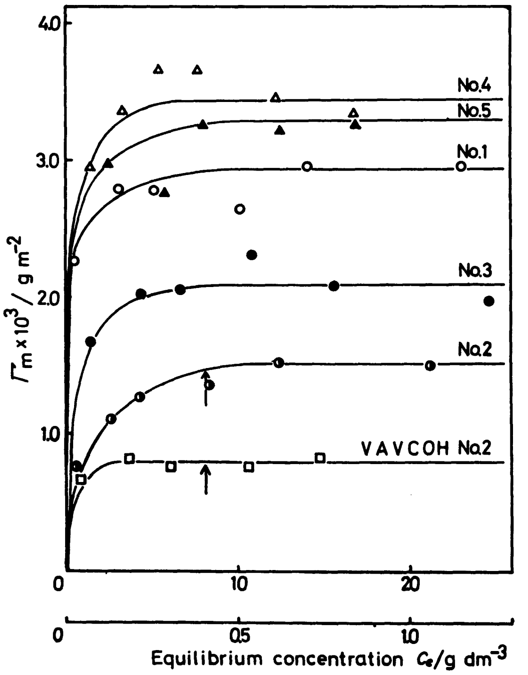

Fig. 2. Adsorption Isotherms.
Particle concentration=4 wt%. The lower scale correspond to the particle concentration of 0.2 wt%. Arrows correspond with the arrows in Fig. 1.

immediately after this procedure.

Estimation of Dispersion Stability. The stability of dispersion was estimated by the sedimentation experiment. The dispersion prepared by the above method was again shaken in a flask for 16 h at 30 °C and then transferred in a sedimentation tube. The dispersion had a height of 30 cm in each tube. The movement of the sharp boundary between supernatant and sediment was recorded with time after the material was introduced the tube and shaken at 30±0.1 °C.

A state of flocs of particles which formed in the medium after 24 h was directly observed by an electron microscope (JEM-100B). The sample was prepared as follows: Collodion solution was evaporated to obtain cellulose trinitrate. A small quantity of this cellulose trinitrate was dissolved (1.5 wt%) in the dispersion used for the sedimentation experiment. A small amount of the dispersion was dropped on the water (30 °C) and the film formed was stretched on the mesh used for an electron microscope.

The electron microscope observation showed that the states of flocs of particles were similar in all of the meshes for the same dispersion. No effect of collodion addition on the dispersibility was observed.

Adsorption and Zeta Potential Measurement. The amount of the polymer adsorbed on iron(III) oxides was determined as follows: The polymer solution of the known concentration involving a fixed amount of an iron(III) oxide (4 wt%) was shaken for a given period of time at 30±0.1 °C until adsorption equilibrium was reached. The adsorption equilibrium was reached after about 16 h for each system. The iron(III) oxides was then separated by centrifugation and a known amount of the supernatant was taken to determine the equilibrium polymer concentration. The quantity of polymer adsorbed was determined by direct weighting of the polymer which had been dried up by evacuated evaporation of the solvent from the supernatant.

Electrophoretic mobility was measured by microelectrophoresis with Laser Zee TM Model 500 (PEN KEM CO.) to which was attached externally a constant voltage power supply (BIO SCIENCE MODEL PS-30); here a rectangular quartz cell was used to prevent the leakage of electric current along the wall. Particles were illuminated by He–Ne laser (2 mW, 6328 Å). Zeta potential was calculated with use of the Hückel equation. The dispersion used for the microelectrophoresis was about 0.01 wt% diluent of the supernatant in the sedimentation experiment.

Results and Discussion

Effect of Polymer Concentration. All of the particles, especially the needlelike ones, were stabilized by the addition of polymer, as exemplified in Fig. 1. In order to examine the effect of the polymer concentration on the dispersibility and zeta potential, the sedimentation experiment and zeta potential measurement were carried out for the nonmagnetic needlelike particle (No. 2). The dependence of the height of the boundary in the sedimentation tube at 24 h after the shaking and zeta potential on the polymer concentration is indicated in Fig. 1. The dispersion stability was markedly improved by addition of a small amount of both kinds of polymers and the zeta potential decreased gradually

Table 3. Results of each measurement for VAVCCOOH and VAVCOH systems

Particle No.	VAVCCOOH			VAVCOH	
	Initial velocity mm min^{-1}	ζ-Potential mV	$\Gamma_m \times 10^3$ g m^{-2}	ζ-Potential mV	$\Gamma_m \times 10^3$ g m^{-2}
1	0.65	−46.9	2.95	−32.4	1.54
2	0.014	−29.2	1.57	−41.4	0.84
3	0.017	−32.2	2.00	−35.4	0.86
4	10	−24.9	3.40	−24.9	1.59
5	7.5	−23.8	3.37	−48.7	0.85

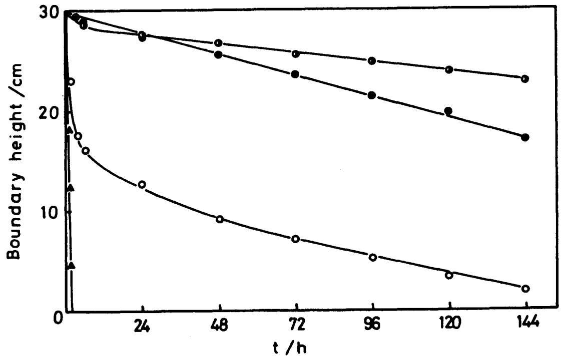

Fig. 3. Plots of boundary height *vs.* time.
○: No. 1, ●: No. 2, ◑: No. 3, ▲: No. 4, 5. [VAVCCOOH]=25 wt% per particles constant.

with increase of the polymer concentration. The decrease would be due to the shift of the slipping plane from the particle surface caused by the polymer adsorption.[15] The fact that the zeta potential of the VAVCOH system is higher than that of the VAVCCOOH system results from the difference of the adsorbed amount of polymer; this assertion will be depicted in Fig. 2.

The measurement of polymer adsorption was done in order to investigate the effect of polymer. The adsorption isotherms of VAVCCOOH for five kinds of iron(III) oxides (4 wt%) in 2-butanone are shown in Fig. 2. All isotherms were of the Langmuir type. Their Langmuir plots, $C/\Gamma \approx C$ curves, were linear in all cases. This same relationship was also obtained for the VAVCOH systems. One of them (No. 2) is shown in Fig. 2. The saturation values of adsorption (Γ_m) for the VAVCCOOH and VAVCOH were obtained from these Langmuir plots. The results are listed in Table 3. The saturation values of the adsorption for the VAVCCOOH system are larger than that for the VAVCOH system, as seen in Table 3. Such results would be due to the effect of functional groups in the interaction of the polymers with iron(III) oxides. It is known that carboxyl group interacts more strongly with oxide surfaces than does the hydroxyl group.[25–27]

The dispersibility was improved by addition of polymer, as pointed out in Fig. 1 of the sedimentation experiment. The polymer concentration shown by the arrow in Fig. 2, where the adsorption reaches approximately the saturation, coincides roughly with the concentration of the attainment of the stabilization shown by the arrows in Fig. 1. The effect of adsorbed polymer on the dispersibility of the nonmagnetic No. 2 sample can be illustrated from this correspondence.

Comparison of the Dispersibility of Five Kinds of Iron(III) Oxides. The sedimentation experiment was carried out for each sample to compare the dispersibilities of five kinds of iron(III) oxides. The change of the boundary height in the tube is shown as a function of time for five samples in Fig. 3. Here VAVCCOOH of 25 wt% per particles was used as a dispersant and the particle concentration was 0.2 wt%. The effect of the polymer on the stabilization of dispersions was marked in the system of the needlelike nonmagnetic iron(III) oxide (No. 2), as shown in Figs. 1 and 3. The dispersibility of No. 3, the needlelike magnetic iron(III) oxides, was considerably improved by the addition of the polymer, as shown in Fig. 3, though that of No. 1, needlelike and highly magnetic iron(III) oxide, was not much improved compared with Nos. 2 and 3. On the other hand, the dispersibility of the octahedral magnetic iron(III) oxides (Nos. 4 and 5) was scarcely improved at all. The improvement of the dispersibility of the five samples by VAVCOH was similar to that in the VAVCCOOH systems.

The initial velocity of the sedimentation curves, that is, the initial slope of the curves in Fig. 2, is listed in Table 3 to allow us to estimate the dispersibility. Table 3 shows that the order of the magnitude of sedimentation velocity is as follows:

$$\text{No. } 4 \gtrsim \text{No. } 5 \gg \text{No. } 1 > \text{No. } 3 > \text{No. } 2. \qquad \text{(A)}$$

The electron microscope photographs of typical states of the flocs for each particle are shown in Fig. 4. These electron microscope observations show that the state of the flocs of particles is similar in all of the meshes for each particle. Figure 4 shows that the order of the size of the flocs is approximately as follows:

$$\text{No. } 4 > \text{No. } 1 > \text{No. } 5 > \text{No. } 3 > \text{No. } 2. \qquad \text{(B)}$$

The particles of No. 2 do not form the flocs. The result of (B) agrees with the result of (A) except for the ordering between Nos. 1 and 5. The difference in (A) and (B) appearing between Nos. 1 and 5 can probably be ascribed to the difference in the density of the flocs.

Table 3 shows that there are no great differences among the zeta potentials of each particle, and the values do not agree with the flocs' size or with the sedimentation velocity. Moreover, the order of the saturation amount of adsorbed polymer (Γ_m) does not agree with that of the flocs' size.

The electric repulsion and the steric repulsion of the adsorbed polymer layer, therefore, are not the determinative factors of the formation of the flocs and the

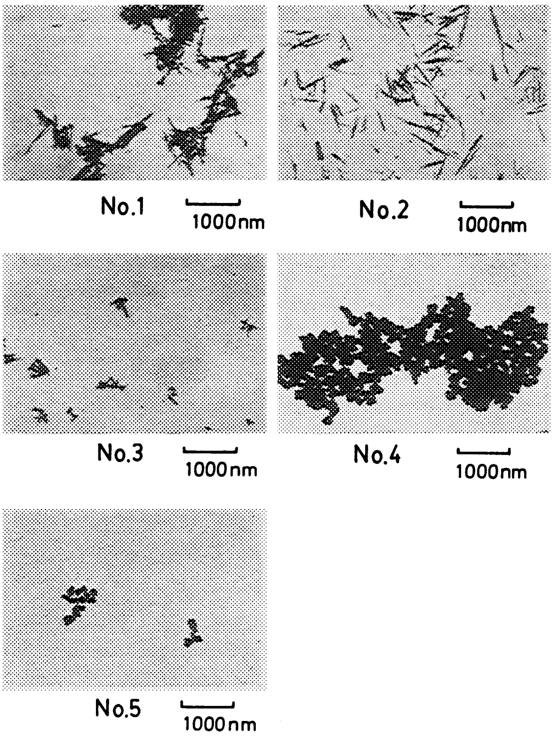

Fig. 4. Photographs of the electron microscope for each particle. Magnification: × 15000.

dispersibility of the five kinds of particles.

Here the magnetic attractive force has to be considered. The magnetic potential energy between two magnetic particles is expressed as follows:[28]

$$V_A^M = -K\left(\frac{M}{4\pi}\right)^2 \frac{V^2}{r^3},$$

where M is the strength of the saturation magnetization (Gauss), V is the volume of a particle, r is the distance between two particles and K is a constant ($K=2$ for the octahedral particles and head-tail interaction of the needlelike particles and $K=1$ for parallel interaction of the needlelike particles). The calculated values of V_A^M, at a constant distance r using the values of M in Table 1, are listed in Table 4. The order of the magnitudes of V_A^M agreed qualitatively with the results of (A) and (B).

Table 4. MAGNETIC ATTRACTIVE FORCE OF EACH PARTICLE

Particle No.	V_A^M/J
1	-8.0×10^{19}k[a)]
2	-8.9×10^{15}k
3	-2.3×10^{19}k
4	-7.7×10^{23}k
5	-1.8×10^{23}k

a, k$=K/r^3$ (unit : m^{-3}).

The strength of the magnetization and the volume of a particle are, therefore, the main factors which control flocculation of the magnetic particles and the size of the flocs.

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