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Dispersibility of Magnetic and Nonmagnetic Iron(III) Oxides in Cyclohexane and Effect of Water on the Stability

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The dispersion stability of needlelike and octahedral iron(III) oxides of magnetic or nonmagnetic particles in cyclohexane solutions of sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethanesulfonate (Aerosol OT or AOT) was studied on anhydrous and hydrous systems. The dispersion stability of the anhydrous system was examined for seven kinds of oxides. The sedimentation velocity of dispersions, the histograms of particle distribution, the adsorption of Aerosol OT on the particles and zeta potential were measured. Potential energies of the interaction between a pair of particles were calculated for the anhydrous system. It was suggested from the calculation of potential energies that the magnetic attractive force, which is a function of the strength of the saturation magnetization and the volume of particle, is a main factor affecting the flocculation of the magnetic particles in cyclohexane as well as in 2-butanone reported in the previous papers. The study of the dispersion stability of the hydrous system was done for three kinds of needlelike oxides. The relatively stable region appeared in the lower concentration range of water. The stability decreased at the fixed water concentration followed by marked flocculation ("floc formation" region). It was considered that the appearance of the "floc formation" is caused by the formation of thick hydration layer on the oxide surface and the decrease of zeta potential.

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 discussed in water by the DLVO theory[1] has been extended to that in nonpolar organic media.[2-5] The effect of zeta potential of carbon black and titanium oxides on the dispersibility in nonpolar organic media has been discussed.[4,6,7]

The important role of a small quantity of water had also been indicated in nonpolar media. For example, the effect of water on the dispersion of TiO_2 in surfactant solutions in nonpolar media has been reported by Parfitt *et al.*.[7] The effect of water on the dispersibility and the zeta potential for carbon black particles has been also shown in Aerosol OT/cyclohexane solution.[8,9]

On the other hand, the dispersion stability of pigments in polar organic media has recently drawn much attention as seen in paints used for magnetic tapes in the industrial field. However, the fundamental studies of pigment in polar organic media are very rare.[10] The authors have reported the dispersibility of the magnetic particles by two kinds of copolymer dispersants for the anhydrous and the hydrous systems[11-13] and that of the carbon black particles by Aerosol OT[14] in 2-butanone. Hence it seems to be interesting that the dispersibility of the magnetic particles in nonpolar organic media is compared with that in polar organic media published already.[11-13]

In this paper, the dispersions of needlelike and octahedral iron(III) oxides of the magnetic or nonmagnetic particles are prepared in cyclohexane. The sedimentation experiments of dispersions and measurements of adsorption and zeta potential are carried out to study the dispersibility. The characteristic behavior of the sedimentation experiment in the anhydrous system is compared with the calculated data of the potential energies and with the results of the dispersibility in polar organic media. Further study is mainly focussed the effect of water on the stability. Interesting behavior of the dispersibility is compared with the system of the dispersion of carbon black in cyclohexane in the previous paper.

Experimental

Materials. Seven kinds of iron(III) oxides were prepared according to the references.[15-17] Each property of these iron(III) oxides is shown in Table 1. The oxides of Nos. 1—5 were the same samples as used in the previous papers[11-13] and purified similarly.

Cyclohexane used as a solvent was purified and dried from GR-grade material as usual and treated finally with Molecular Sieve 4A to remove any trace of water. Aerosol OT used as a dispersant was commercial grade and was purified according to the previous method.[18]

Preparation of Dispersions. The dispersion was prepared by mixing the particles (0.2 wt%) and the solution of a fixed concentrations of the dispersant(AOT) and water under irradiation with ultrasonic apparatus (Kaijo Denki Co. Model TA-4015, Power Supply 150 W, 20 kHz) for 5 min. No precipitation was observed immidiately after this procedure.

Estimation of Dispersion Stability. The stability of the dispersion was estimated for the anhydrous and hydrous systems by two kinds of sedimentation experiments stated in the previous papers.[11-13] One was the experiment to obtain the sedimentation velocity in sedimentation tubes of the diameter of 1 cm. The other was done with a sedimentation balance in order to verify the dispersion stability obtained by sedimentation tube. The particles were almost distributed over the range of the diameter 0—1 μm in the particle distribution histograms obtained by the latter. So that the median diameter, which seems to be the most partinent parameter to indicate the dispersion stability, was determined from the histograms.[12]

Measurements of Adsorption of Aerosol OT or Water and Zeta Potential. The dispersions of the oxides involving a fixed amount of AOT and/or water(the molar ratio of water to AOT, R=[water]/[AOT], was fixed; that was R=0.5, 1, 2, 3) were shaken for 16 hr at 30±0.1 °C. The concentration of the oxide was 4 wt% for the adsorption of AOT and 0.2 wt% for that of water. The equilibrium concentrations of AOT and water in the supernatant after centrifugation were determined

TABLE 1. PROPERTIES OF IRON(III) OXIDES

No.	Class	Specific surface area	Saturation magnetization		Size	Density	Volume of a particles
		(m²/g)	(emu/g)	(gauss)	Å	(g/cm³)	(m³)
1	γ-Fe_2O_3	37.6	68	3674	1470×160	4.3	2.96×10^{-23}
2	α-Fe_2O_3	108	1	46.5	1610×142	3.9	2.55×10^{-23}
3	α-Fe_2O_3	33.1	33[a]	1659	1400×178	4.0	3.48×10^{-23}
4	γ-Fe_2O_3	9.3	62	3400	1820	4.5	3.16×10^{-21}
5	α-Fe_2O_3	8.6	29[a]	1674	1820	4.6	3.16×10^{-21}
6	γ-Fe_2O_3	14.8	72	4072	6736×773	4.5	3.16×10^{-21}
7	α-Fe_2O_3	10.3	0.3	14.7	6770×765	3.9	3.11×10^{-21}

a) α-Fe_2O_3 keeps its magnetization.

by an ultraviolet spectrometer (UV-200 S, Shimadzu Co.) and a Karl-Fischer apparatus, respectively, to calculate the amount of adsorption.

Electrophotoretic mobility was measured by microelectrophoresis with Laser Zee TM Model 500 (PEN KEM Co.) as stated in the previous papers.[11,13,14]

Calculation of Potential Energy. Potential energies between particles were calculated in the anhydrous system according to the methods published in previous paper[12] in order to evaluate the result of the dispersibility of seven kinds of oxides. The octahedral and needlelike particles used in this paper were assumed to be spherical and cylindrical, respectively. The parallel interaction was only considered for the needlelike particles, because it is clear from the previous paper that the parallel interaction is more predominant than the head-tail interaction between the needlelike particles.[12]

Four kinds of potential energies of the interaction between a pair of particles were considered: Steric repulsion between adsorbed layers(V_R^{en}), electrostatic double layer repulsion(V_R^{el}), van der Waals attraction (V_A^{δ} or V_A^{L}) and magnetic attraction (V_A^{M}). They are expressed in following equations (1)—(8).

For Octahedral Particles: i) Steric repulsion between adsorbed layers; Here Ottewill-Walker's equation was utilized:[19]

$$V_R^{en} = \frac{4\pi kTC_v^2}{3v_1\rho_2^2}\cdot(\psi_1-\kappa_1)\left(\delta-\frac{H}{2}\right)^2\left(3a+2\delta+\frac{H}{2}\right) \quad (1)$$

where C_v is the concentration of AOT in the adsorbed layer, v_1 is the molecular volume of a solvent, δ is the thickness of an adsorbed layer, ρ_2 is the density of AOT, a is the radius of a particle, H is the shortest distance between the particle surfaces and ψ_1 and κ_1 are entropic and enthalpic parameters of mixing proposed Flory.

ii) Electrostatic double layer repulsion:[20]

$$V_R^{el} = \frac{\varepsilon a^2\zeta^2}{2a+H} \quad (2)$$

where ε is the dielectric constant of a medium and ζ is zeta potential.

iii) Van der Waals attraction; Here Vold's equation was used, considering the effect of adsorbed layer:[21]

$$V_A^{\delta} = -\frac{1}{12}\left\{(\sqrt{A_{22}}-\sqrt{A_{33}})^2\cdot\frac{a+\delta}{H}+(\sqrt{A_{33}}-\sqrt{A_{11}})^2\cdot\frac{a}{H+2\delta}\right.$$
$$\left.+4a(\sqrt{A_{22}}-\sqrt{A_{33}})(\sqrt{A_{33}}-\sqrt{A_{11}})\cdot\frac{a+\delta}{(H+\delta)(2a+\delta)}\right\} \quad (3)$$

where A_{11}, A_{22} and A_{33} are the Hamaker constants of the oxide, a solvent and AOT adsorbed, respectively.

iv) Magnetic attraction:[22]

$$V_A^{M} = -2\left(\frac{\mathrm{M}}{4\pi}\right)^2\frac{v^2}{(2a+\mathrm{H})^3} \quad (4)$$

where M is the saturation magnetization (gauss) and v is the volume of a particle.

For Needlelike Particles: i) Steric repulsion between adsorbed layers:[19]

$$V_R^{en} = \frac{2kTC_v^2}{v_1\rho_2^2}\cdot(\psi_1-\kappa_1)\cdot V \quad (5)$$

where V is the total volume of the overlapping zone of the adsorbed layer.

ii) Electrostatic double layer repulsion:[12]

$$V_R^{el} = \frac{\varepsilon\sqrt{h\kappa}\psi_0^2}{2\pi}\left[\frac{2}{3}\left(\frac{1}{\exp(\kappa H+1)+1}\right)-\frac{1}{\exp(\kappa H)+1}\right)\cdot$$
$$\times\ (1+3\kappa H)+2\left\{\left(\frac{1}{\exp(\kappa H)+1}-\frac{1}{\exp(\kappa H+1)+1}\right)\kappa H\right.$$
$$\left.+\frac{1}{\exp(\kappa H)+1}\right\}+1.142\exp(-\kappa H)-2\exp(-\kappa H-1)\Bigg] \quad (6)$$

where h is the radius of the cylinder of a needlelike particle, H is the shortest distance between the particle surface and κ is the reciprocal Debye length expressed as follows:

$$\kappa = \sqrt{\frac{8\pi nz^2e^2}{\varepsilon kT}} \quad (6')$$

The equation (6) introduced under an assumption of $\kappa h > 1$ in the previous paper[12] was approximately used for the cyclohexane system($\kappa h < 1$). This approximation can be allowed, because the contribution of this repulsion is comparatively small as seen in Table 3-2.

iii) Van der Waals attraction:[1]

$$V_A^{L} = -\frac{A}{48}\left\{\frac{1}{(H/2)^2}+\frac{1}{(H/2+h)^2}-\frac{2}{(H/2+h/2)^2}\right\} \quad (7)$$

where A is the Hamaker constant of the oxide in cyclohexane. Here the effect of adsorbed layer was neglected.

iv) Magnetic attraction:[12]

$$V_A^{M} = -\left(\frac{\mathrm{M}}{4\pi}\right)^2\frac{v^2}{(2h+H)^3} \quad (8)$$

Total potential energy (V_T) of the octahedral and the needlelike particles are calculated by summing the contributions of Eqs. (1)—(4) and Eqs. (5)—(8), respectively.

Results

Effect of AOT on the Stability. The change of the boundary lines between the supernatant and the dispersion (the sediment height) in the sedimentation tube are shown as a function of time for seven kinds of oxides in Fig. 1. Here AOT of 20 mM was used as a dispersant. In the absence of AOT, all of the dispersions sedimented rapider than Nos. 4, 5, 6 in Fig. 1. This shows the effectiveness of AOT on the stability of iron oxides in cyclohexane. The sedimentation velocity, that is, the gradient of the lines in Fig. 1 was used to discussed the dispersion stability.

In order to examine the effect of AOT concentration on the dispersibility and zeta potential, measurements of the sedimentation and zeta potential were carried out for the magnetic needlelike particle (No. 1). The dependence of the sedimentation velocity and zeta potential on the AOT concentration is indicated in Fig. 2. The amount of adsorbed AOT is also shown in Fig. 2. The dispersion stability is markedly improved by the addition of a small amount of AOT (2—3 mM), as seen in Fig. 2. This concentration is the similar order to the critical micellar concentration of AOT in cyclohexane (1.4 mM).23) Moreover, at this concentration of AOT, the adsorption reaches approximately the saturation. This correspondence illustrates the effect of AOT molecules adsorbed on the dispersibility of the oxide.

Comparison of the Dispersibility of Seven Kinds of Oxides in Anhydrous System. The following result is seen from Fig. 1. The effect of AOT on the stabilization of the dispersions is remarkable in the system of the needlelike nonmagnetic oxide(No. 2). The dispersibility of the needlelike and magnetic oxides (Nos. 1 and 3) and needlelike and nonmagnetic oxide (No. 7) is considerably improved by the addition of AOT of 20 mM. On the other hand, the dispersibility of the octahedral oxides(Nos. 4 and 5) and the needlelike and magnetic oxide in which particles have large volume(No. 6) is scarcely improved.

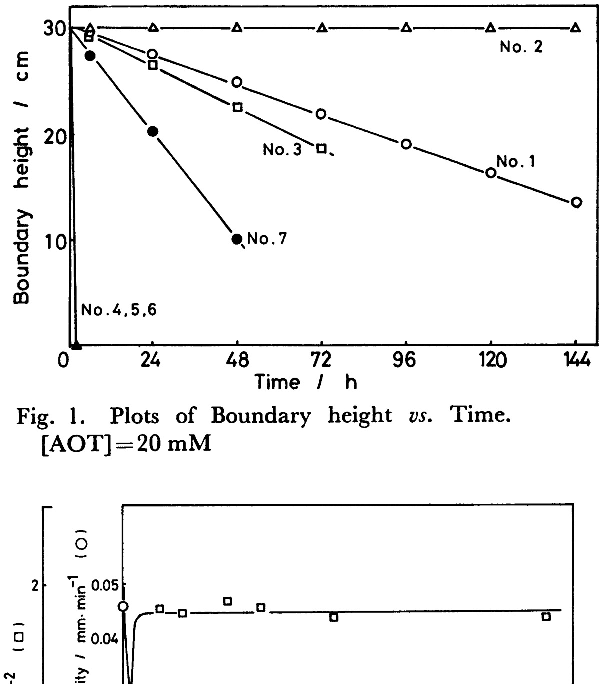

Fig. 1. Plots of Boundary height *vs.* Time. [AOT]=20 mM

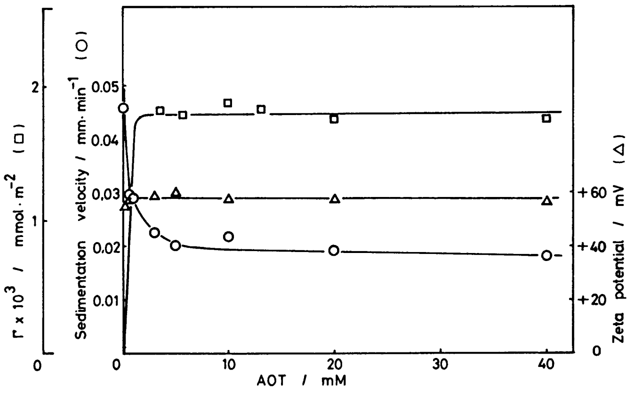

Fig. 2. Relation of the sedimentation velocity (○), zeta potential (△) and amount of adsorbed AOT (□) with Aerosol OT concentration for No. 1 sample.

The result of each measurement for seven kinds of oxides was listed in Table 2 to estimate the dispersibility. Here adsorption isotherms were the Langmuirian type and their Langmuir plots were linear in all cases. The saturation values of adsorption (Γ_m) listed in Table 2 for seven kinds of oxides were obtained from these Langmuir plots. Table 2 shows that the order of the magnitude of the sedimentation velocity is as follows;

$$\text{No. } 6 \simeq 4 > \text{No. } 5 \gg \text{No. } 7 > \text{No. } 3 > \text{No. } 1 > \text{No. } 2 \qquad \text{(A)}$$

The result of (A) agrees with the result of the dispersibility in 2-butanone for Nos. 1—5 oxides stabilized by two kinds of copolymer dispersants,11) except for the order between No. 3 and No. 1, though the difference between them is minor.

The order of the magnitude of the median diameter in Table 2 obtained by the sedimentation balance is as follows;

$$\text{No. } 6 > \text{No. } 4 > \text{No. } 5 > \text{No. } 3 > \text{No. } 7 > \text{No. } 1 > \text{No. } 2 \qquad \text{(B)}$$

The result of (B) agrees with the result of (A) except for the order between No. 3 and No. 7, though the difference between them is minor.

It is seen in Table 2 that there are not so much differences among the zeta potential of each particle, and the order of the value does not agree with that of the sedimentation velocity. Moreover, the order of the saturation amount of adsorbed AOT does not also agree with that of the sedimentation velocity.

Potential Energy in Anhydrous System. The dispersibility of seven kinds of oxides might be evaluated quantitatively from the magnitude of the total potential energy consisting of repulsive (V_R^{en}, V_R^{el}) and attractive (V_A^{δ} or V_A^L, V_A^M) energies between particles which were expressed by Eqs. (1)—(8).

Numerical values used for each equation were as follows: In Eqs. (1) and (5), $\psi_1 - \kappa_1 = 0.1$24), $a=1000$ Å, $\rho_1=$

TABLE 2. RESULTS OF EACH MEASUREMENT OF IRON(III) OXIDES

No.	Sedimentation velocity (mm/min)	ζ-potential (mV)	$\Gamma_m \times 10^3$ (mmol/m²)	D_{med} (μm)
1	0.019	+55.7	1.74	0.898
2	0	+60.0	1.45	0.649
3	0.027	+43.2	1.75	1.65
4	3.00	+40.8	2.06	15.3
5	2.00	+37.5	1.89	9.78
6	3.00	+53.7	1.74	23.5
7	0.068	+57.7	1.44	1.06

1.0 g/cm^3 [25] and C_v was calculated from the following equation for each particle, $C_v = \Gamma_m / \delta \cdot So$, where Γ_m is the saturation amount of adsorbed AOT, δ is the thickness of the adsorbed surfactant molecules(15 Å)[25] and So is the specific surface area of each particle.

In Eqs. (2) and (6), $\varepsilon = 2.02$[26] and ζ was listed in Table 2. $\kappa = 3132\ \mathrm{cm}^{-1}$ was calculated for 20 mM AOT/cyclohexane solution from Eq. (6)′ with the ion concentration(n) obtained by the electric conductivity method described before.[27] In Eqs. (3) and (7), the Hamaker constants were as follows: $A_{11} = 2.1 \times 10^{-19}$ J for particles,[12] $A_{22} = 5.9 \times 10^{-20}$ J for solvent,[12] $A_{33} = 2.5 \times 10^{-20}$ J for adsorbed layer.[24] The value of A, 4.6×10^{-20} J, in Eg. (7) was calculated from the following equation, $A = (\sqrt{A_{11}} - \sqrt{A_{22}})^2$.

TABLE 3-1. THE POTENTIAL ENERGY FOR OCTAHEDRAL PARTICLES (unit: kT)

	H/Å	10	20	100
No. 4	V_A^M	-7.76×10^4	-7.55×10^4	-6.7×10^4
	V_A^δ	-19.5	-14.6	-6.60
	V_R^{el}	4.51	4.49	4.32
	V_R^{en}	265	66.4	0
	V_T	-7.63×10^4	-7.54×10^4	-6.7×10^4
No. 5	V_A^M	-1.86×10^4	-1.83×10^4	-1.63×10^4
	V_A^δ	-19.5	-14.6	-6.60
	V_R^{el}	3.81	3.79	3.65
	V_R^{en}	223	55.8	0
	V_T	-1.84×10^4	-1.83×10^4	-1.63×10^4

TABLE 3-2. THE POTENTIAL ENERGY OF PARALLEL INTERACTION FOR NEEDLELIKE PARTICLES (unit: kT)

	H/Å	10	20	100
No. 1	V_A^M	-3691	-3109	-1032
	V_A^L	-1068	-254	-5.78
	V_R^{el}	0.246	0.246	0.246
	V_R^{en}	499	178	0
	V_T	-4260	-3180	-1040
No. 2	V_A^M	-0.60	-0.50	-0.15
	V_A^L	-1033	-240	-5.04
	V_R^{el}	0.293	0.293	0.292
	V_R^{en}	361	129	0
	V_T	-672	-111	-4.90
No. 3	V_A^M	-769	-658	-238
	V_A^L	-1136	-278	-6.59
	V_R^{el}	0.149	0.149	0.149
	V_R^{en}	506	180	0
	V_T	-1400	-751	-244
No. 6	V_A^M	-5.3×10^5	-5.1×10^5	-3.8×10^5
	V_A^L	-2.41×10^4	-5914	-234
	V_R^{el}	2.30	2.30	2.30
	V_R^{en}	4769	1689	0
	V_T	-5.49×10^5	-5.14×10^5	-3.80×10^5
No. 7	V_A^M	-6.88	-6.62	-4.95
	V_A^L	-2.40×10^4	-5914	-223
	V_R^{el}	2.66	2.66	2.66
	V_R^{en}	3282	1159	0
	V_T	-2.07×10^4	-4760	-225

In Eqs. (4) and (8), the values in Table 1 (gauss) were used for the saturation magnetization(M).

The results of the calculation for the octahedral particles obtained from Eqs. (1)—(4) and for the needlelike Eqs. (5)—(8) are listed in Tables 3-1 and 3-2, respectively. The dispersibility of the seven kinds of oxides can be discussed quantitatively from the results.

As seen in Table 3-1 for the octahedral particles (Nos. 4, 5), the orders of the energy of the magnetic attractive force(V_A^M) are about $-10^4 kT$, though the orders of the energy of steric repulsion(V_R^{en}) and electric repulsion(V_R^{el}) are about 2×10^2—$5\times10 kT$ and below $5kT$, respectively. Therefore, it can be considered that the total potential energies(V_T) are mainly dominated by the magnetic attractive force.

As seen in Table 3-2 for the needlelike particles, the orders of the energy of magnetic attractive force(V_A^M) are about -10^2—$-10^3 kT$ for No. 1 and No. 3 oxides. The energy of van der Waals attractive force(V_A^L) is also high, similarly to the magnetic attractive force in the range of the short distance. But it drastically decreases with increase of the distance. The energies of steric repulsion(V_R^{en}) and electric repulsion(V_R^{el}) are relatively low. Hence the total potential energies(V_T) for the highly magnetic and needlelike particles(Nos. 1, 3 and 6) are dominated by both the energies of magnetic attractive force and those of van der Waals attractive force in the region of the short distance between two particles. But they are only dominated by the energy of the magnetic attractive force in the region of the long distance. Fig. 3 shows the potential energy curves for Nos. 1, 2 and 3 oxides as examples.

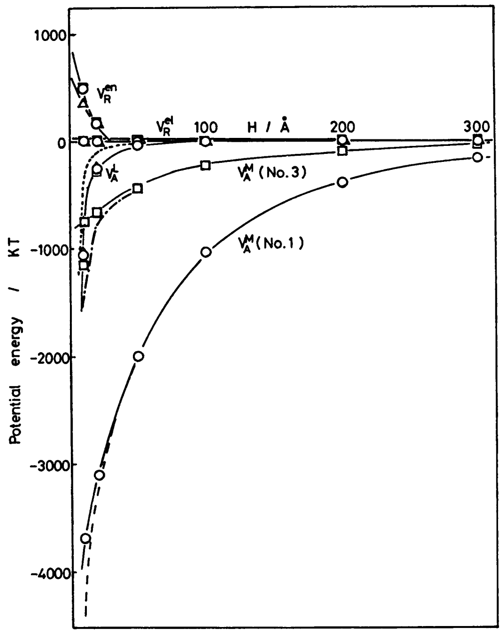

Fig. 3. The potential energy curves of the parallel interaction for three kinds of needlelike particles.

Sample	V_T
○; No. 1	— — — — —
△; No. 2	—— - —— -
□; No. 3	- - - - - - - -

On the other hand, the energy of the magnetic attractive force(V_A^M) for nonmagnetic and needlelike particles(Nos. 2 and 7) is low. So that they are only dominated by the van der Waals attractive force.

Effect of Water on Dispersibility. The effect of water on the stability of dispersions in cyclohexane was investigated in the presence of 20 mM of AOT. The needlelike particles of Nos. 1, 2 and 7 were selected for the study.

The sedimentation velocity, zeta potential and the amount of water adsorbed on the oxide surface are shown as a function of water concentration for Nos. 1, 2 and 7 oxides in Fig. 4. As shown in Fig. 4 the stable region(lower sedimentation velocity) appeared in the lower concentration range of water and the sedimentation velocity suddenly increases in a fixed concentration range. The latter behavior shows the occurrence of rapid flocculation for three kinds of oxides. The concentration region is named the "floc formation" region. Water concentrations of about 60, 100 and 80 mM are the "floc formation" regions for Nos. 1, 2 and 7 oxides, respectively. The similar "floc formation" due to the presence of water was already observed for the hydrophobic carbon black particles [9] and for the iron oxide particles. [13] Zeta potential gradually decreases with increase of the concentration of water.

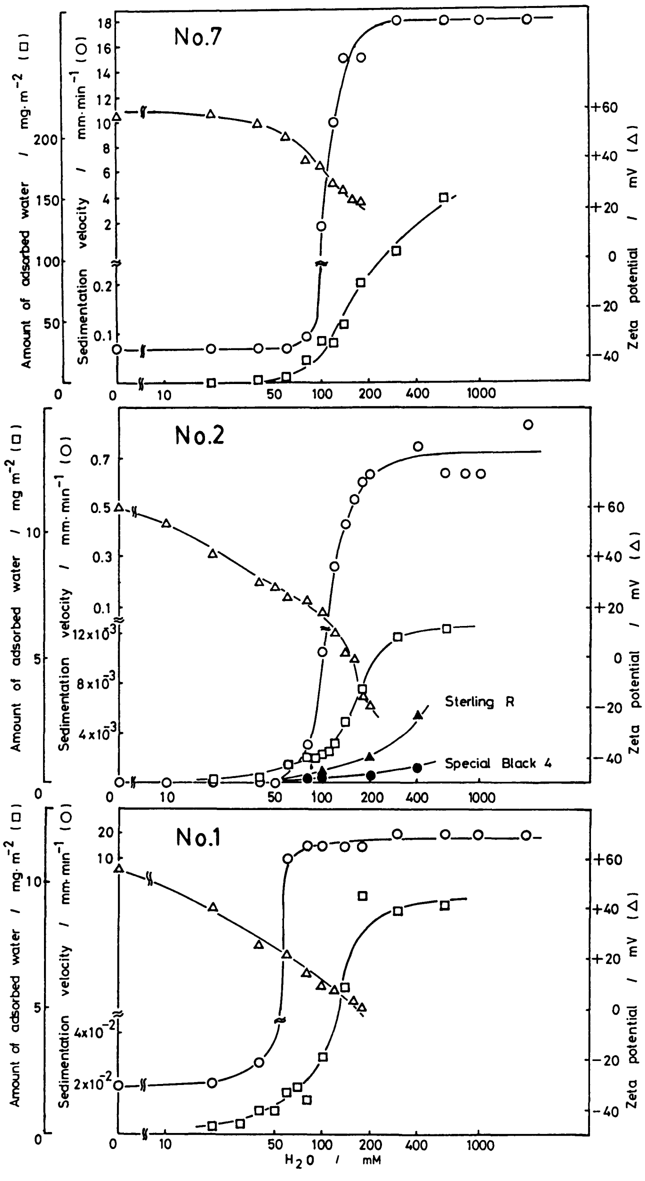

Fig. 4. Change of the sedimentation velocity (○), zeta potential (△) and amount of adsorbed water (□) of Nos. 1,2 and 7 samples with water concentration. [AOT]=20 mM. Fulled mark in the figure is expressing the amount of adsorbed water of carbon black particles (Sterling R and Special Black-4) from Ref. (9). Sterling R: Cabot Co. pH=5.5, Specific surface area=25 m²/g. Special black-4: Degussa Co. pH=2.0, Specific surface area=180 m²/g.

The median diameter(D_{med}), determined from the particle distribution histograms, was shown in Fig. 5 as a function of concentration of water for three kinds of oxides. These results are well correspondent with the results of Fig. 4, though the increase of the median diameter of No. 2 oxide is relatively low.

The amount of adsorbed AOT was shown in Fig. 6 as a function of concentration of water under the constant concentration of AOT(20 mM). The amount of adsorbed AOT gradually decrease with increase of water concentration.

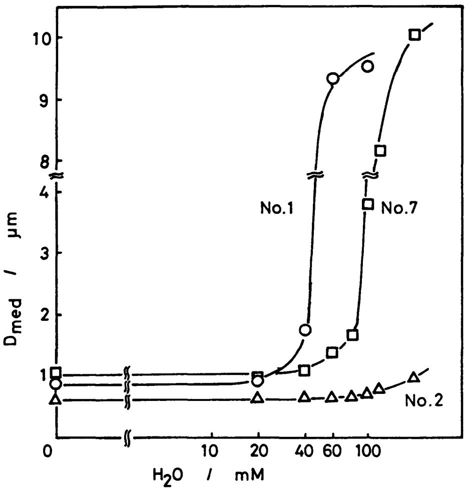

Fig. 5. Change of the median diameter of No. 1, 2 and 7 samples with water concentration.

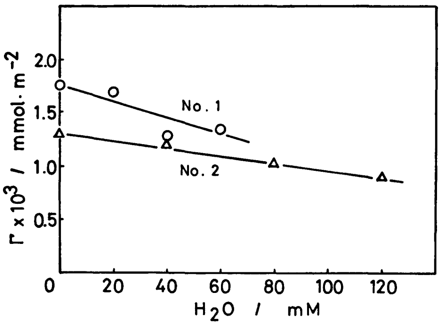

Fig. 6. Change of the amount of adsorbed Aerosol OT for No. 1 and No. 2 samples with water concentration. [AOT]=20 mM.

Discussion

Dispersibility of the Anhydrous Systems. The dispersibility of iron oxides in cyclohexane is stabilized by the addition of AOT as shown in Figs. 1 and 2. However, the difference in the dispersibility of seven kinds of oxides as seen in series (A) or (B) does not correspond with the difference of zeta potential and the amount of adsorbed AOT of each particle in Table 2. This fact was seen in the dispersibility in 2-butanone.[11] It was discussed from the difference in the saturation magnetization and the size of particles. In order to check the applicability of the discussion to this study, the potential energies between the particles were calculate.

The order of the magnitude of the total potential energy, by comparison at the same distance(*i.e.* H=20 Å) in Table 3-1 and 3-2, is as follows:

$$\text{No. } 6 > \text{No. } 4 > \text{No. } 5 > \text{No. } 7 > \text{No. } 1 > \text{No. } 3 > \text{No. } 2 \quad (C)$$

It is clear that this result of (C) agrees with the results of (A) and (B) expressing the order of the dispersibility except for the No. 3 oxide. This fact shows that the magnetic attractive force, which depends on the strength of the magnetization and the volume of particle, is the main factor affecting the dispersibility of the iron oxides in cyclohexane similarly in 2-butanone.[11,12]

Effect of Water on the Dispersibility. The amount of adsorbed water, as shown in Fig. 4, remarkably increased from a fixed concentration range of water which is approximately coincident with the region of the "floc formation". Hence the occurrence of the "floc formation" is discussed as follows: The thickness of water molecules in hydration layer was calculated from Fig. 4, under an assumption that water molecules would be uniformly adsorbed on the particle surface. The thickness was above 6 molecules for all systems in the region of the "floc formation" from the calculation. So that it can be estimated that the water forms thick hydration layer above this region. The hydration layers formed at the oxide surface would work as a binder between the particles by the strong hydrogen bond among water molecules and would cause the "floc formation". The occurrence of the "floc formation" would be also due to the decrease of the energy of the electric repulsive force, because zeta potential decreases with increase of water concentration as shown in Fig. 4.

The mechanism of the effect of water on the dispersibility as seen in Fig. 4 is considered from the following discussion. In the anhydrous system, AOT molecules would be adsorbed on the oxide surface orienting nonpolar group outside and at the same time excess counter ions(Na^+) are prefferentially adsorbed on the oxide surface to cause the zeta potential positive. On the addition of a small amount of water, a part of water molecules would be adsorbed on the oxide surface and the others would be solubilized in AOT micelles in the bulk solution. With increase of the concentration of water, AOT on the oxide surface would be desorbed and transferred to the swollen micelles due to their strong ion-dipole interaction with water molecules as shown in Fig. 6. The counter ions would be also transferred to the water solubilized in reversed micelles to decrease the zeta potential. Further increase of the concentration of water increases the adsorption of water on the particle surface as well as the increase of the water core in reversed micelles. Zeta potential furthermore decreases by the shift of the slipping plane from the particle surface caused by the formation of the thick hydration layer. So that the dispersion is destabilized by the thick hydration layer and the decreased zeta potential to form "floc formation" region.

It is considered that the difference in "floc formation" regions of Nos. 1 and 2 which was seen in Fig. 4 is caused by the difference of the degree of hydrophilicity. It was described in the previous paper that the degree of hydrophilicity of No. 1 particle is higher than No. 2 particle.[13] The formation of the thicker hydration layer on No.1 particle at lower water concentration is also evidently seen in Fig. 4 for cyclohexane system. This hydration layer works as the attractive force between particles. Moreover, it was also described in the previous papers[12,13] that the energy of magnetic attractive force would not be influenced by the kind of solvents. Hence the magnetic attractive force would operate between No. 1 particles in cyclohexane as well as in 2-butanone. So that No. 1 paticle having higher saturation magnetization will be also causes the strong magnetic attractive forces between the particles in cyclohexane as shown in Fig. 3. Therefore, No. 1 particle flocculate at the lower water concentration than No. 2 particle.

It was reported in the previous paper[9] that carbon black particles (Sterling R and Special Black-4) are restabilized in the water concentration of 800—1000 mM by formation of the weak network structure among carbon black particles and AOT microemulsion. This behavior was not observed for the iron oxide particles in this study. This difference would be due to the difference of the amount of the adsorbed water, the density and the size of each particle. The amount of adsorbed water on the oxide surface is much higer than that on carbon black surface as seen in Fig. 4, due to the difference of the hydrophilicity. This may lead restabilization of the iron oxide difficult.

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