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Apparent Viscosities of Ferric Oxide–Water Suspensions

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The effects of various types of anionic surfactants and inorganic phosphates on the apparent viscosities of ferric oxide–water suspensions of high pigment concentrations are examined. The additions of surfactants or inorganic phosphates to the suspensions cause depressions in their apparent viscosities from values of more than 10000 centipoise (cP) to about 10 cP. The concentration of the surfactants or the inorganic phosphates required to depress the apparent viscosity, which is designated as C_0, is highly dependent upon the alkyl-chain length of the 1-1-type surfactants, the degree of the polymerization of the surfactants of the type of the vinyl copolymers and the degree of the condensation of the surfactants of the type of the formalin condensates or inorganic phosphates. With the 1-1-type surfactants, the values of the C_0 decrease with the increases in the alkyl-chain length, and the surfactants with much shorter alkyl-chain lengths, such as Na octyl sulfate, linear-chain Na hexylbenzene sulfonate, and Na butyl-naphthalene sulfonate, have no marked viscosity depression effects. With the formalin condensates and the inorganic phosphates, the values of C_0 decrease with the degree of condensation. With the vinyl copolymers, the C_0 show smallest values at the appropriate degree of polymerization, *e.g.*, about 10—40 for the Na salt of polyacrylic acid. Both the absolute value of the zeta potential and the amount of adsorption increase remarkably in the concentration regions showing marked viscosity depressions. The viscosity depressions of the suspensions upon the additions of the surfactants or inorganic phosphates can be qualitatively explained by taking into account the contributions of the zeta potential values and concentrations to the dispersion-coagulation of the pigment particles.

It has been well known that the additions of surfactants or electrolytes to pigment–water suspensions with high pigment concentrations and with apparent viscosities of more than 10000 centipoise (cP) show the apparent viscosities to be depressed to about 10 cP.[1–9] The viscosity depressions caused by the additions of surfactants or electrolytes have been widely used as a measure of the dispersibility of surfactants.[5,10]

Many studies of the pigment–water suspensions of high pigment concentrations have been reported from the view-point of viscometric behavior,[6–9] but these few studies have been from the view point of surface chemistry, such as zeta potential and adsorption. Marked viscosity depressions have been observed in the aqueous suspensions of various sorts of inorganic pigments, such as ferric oxide, titanium dioxide, zinc oxide, and carbon black. In the present paper, ferric oxide was used as the inorganic pigment, which had no special meaning.

The present paper will describe the effects of the alkyl-chain length of 1-1-type anionic surfactants, the degree of the polymerization of vinyl copolymers, and the degree of the condensation of formalin condensates or inorganic polyphosphates on the apparent viscosities of 50 wt% ferric oxide suspensions, and will discuss these effects in relation to the zeta potential, adsorption, and the pH data.

Experimental

Materials. All the surfactants used were prepared according to a procedure described earlier.[11] Their chemical compositions, degrees of polymerization or condensation, and abbreviations are listed in Table 1. The orthophosphates (NaH_2PO_4 and Na_3PO_4), pyrophosphates ($Na_2H_2P_2O_7$ and $Na_4P_2O_7$), and tripolyphosphate ($Na_5P_3O_{10}$) were of a reagent grade. The tetrapolyphosphate ($Na_6P_4O_{13}$) was a specially prepared commercial product. The phosphates were obtained from the Wako Pure Chemicals Co. Most of the surfactants and inorganic phosphates described above are known to have dispersing power and are used widely.[10]

Pigments. Ferric Oxide (Toda Color 130R) obtained from the Toda Industries Co., which had not been treated, was washed with water until there was no change in the conductivity of the filtrate. The surface area, as determined by the B.E.T. method using nitrogen at −195 °C, was 7.0 m^2/g. The average particle radius, calculated from electron microscopic observation, was 0.2 μm. The particles have a sphere-like form. The isoelectric point of ferric oxide, determined according to the method of Parks *et al.*,[12] is 5.5.

Apparent Viscosity Measurements. Aqueous solutions of the materials, which refer to the surfactants or inorganic phosphates, were prepared by dissolving the desired quantities of the materials in distilled water of 500 ml. Into a beaker with a 750-ml capacity, a 400-ml portion of the material solutions thus prepared was poured, and maintained at 25± 0.1 °C in a water bath. The desired quantities of ferric oxide were then added to the material solutions. After the above ferric oxide–material solution suspensions had been stirred with a Homomixer, TK type (Tokushu Kiki Industries Co.), for five minutes, the apparent viscosities were determined using a Viscometer (Tokyo Kiki Manuf. Co. Type BM, rotor 60 rpm).

Sedimentation Velocity Measurements. Suspensions containing 1 wt% ferric oxide were prepared by the dilution of the desired quantities of the same suspensions used for the apparent viscosity measurements in supernatant solutions of their suspensions obtained by removing the ferric oxide particles with a refrigerated-automatic Ultracentrifuge, Serval Model RC-2B. Into graduated test cylinders with a 30-ml, capacity and 30 cm in height, 30 ml portions of the suspension thus prepared were poured, and the mixtures were maintained at 25 °C in the thermostat. The cylinders were turned end-over-end ten times and then allowed to stand. By the sedimentation of the pigment particles, a sedimentation boundary was formed between the material solution and the suspension. The positions, h, of the sedimentation boundaries were read periodically and were plotted *vs.* the standing time, t. The time (designated as the sedimenting time, $T_{1/2}$) during which h falls from a 30-cm height to a 15-cm height is calculated from the h *vs.* t curves and used as a measure of the sedimentation velocity.

Sedimentation Volume Measurements. Suspensions containing 5 wt% ferric oxide were prepared by the dilution of

Table 1. Chemical composition, average molecular weight and abbreviation of surfactants

Type	Chemical composition	Degree of condensation or polymerization	Abbreviation
1-1 type anionic surfactants	Na octyl sulfate		C_8S
	Na decyl sulfate		$C_{10}S$
	Na decyl sulfate		$C_{12}S$
	Na tetradecyl sulfate		$C_{14}S$
	linear-chain Na hexylbenzene sulfonate		C_6BS
	linear-chain Na octylbenzene sulfonate		C_8BS
	linear-chain Na decylbenzene sulfonate		$C_{10}BS$
	linear-chain Na docdecylbenzene sulfonate		$C_{12}BS$
	linear-chain Na tetradecylbenzene sulfonate		$C_{14}BS$
	Na butylnaphthalene sulfonate		C_4NS
Formalin condensate	Na salt of formalin condensate of β-naphthalene sulfonic acid	3.7	NSF-3.7
	Na salt of low formalin condensate of butylnaphthalene sulfonic acid	3.5	C_4NSF-3.5
	Na salt of high formalin condensate of butylnaphthalene sulfonic acid	5.1	C_4NSF-5.1
Vinyl copolymer	Na salt of polyacrylic acid	12	PA-12
	Na salt of polyacrylic acid	33	PA-33
	Na salt of polyacrylic acid	64	PA-64
	Na salt of polyacrylic acid	146	PA-146
	Na salt of homopolymer of maleic acid	7.5	PM
	Na salt of copolymer of vinyl acetate and maleic acid	14	VacM
	Na salt of copolymer of styrene and maleic acid	19	SM
	Na salt of copolymer of α-olefine (C_8) and maleic acid	16	OM

the desired quantities of the suspensions used for the apparent viscosity measurements into supernatant solutions of their suspensions obtained by the method described above. Into graduated test cylinders with a 30-ml capacity and 30 cm in height, 30-ml portions of the suspensions thus prepared were poured, and the mixtures were maintained at 25 °C in the thermostat. The test cylinders were turned end-over-end ten times, and then allowed to stand. The positions of the sedimentation boundary between the material solution and the suspension, formed by the sedimentation of ferric oxide particles, were lowered with the standing times. After the rates of their lowerings became almost zero, the positions of the sedimentation boundaries were measured and the sedimentation volumes of ferric oxide particles were calculated from these data.

Average Radius of the Particle Measurements. The average radius of the particle was calculated by means of microscopic observation by the dilution of a quantity of the suspensions used for apparent viscosity measurements into supernatant solutions of their suspensions.

Electrophoretic Mobility Measurements. The mobility measurements of ferric oxide particles were made using a Zeta-Meter (Zeta-Meter, Inc.) by the dilution of a quantity of the suspensions used for the apparent viscosity measurements into supernatant solutions of their suspensions.

Adsorption Measurements. The amounts of the adsorption of the materials onto ferric oxide particles were calculated from measurements of the difference in concentrations of the material solutions before and after preparing the suspensions. The material solutions after preparing the suspensions described above refer to the same supernatant solutions as those used for sedimentation velocity measurements. The concentrations of the surfactants having benzene ring or naphthalene ring in the molecule, among the surfactant solutions, were calculated by measuring the intensity of the absorption band at about 260 nm using a Shimadzu Spectrophotometer, UV-200. On the other hand, those having no benzene ring or naphthalene ring in the molecule were measured with a TOC Meter, Toshiba-Beckman Model 102, which determined the amount of carbon dioxide generated by firing the solutions at 950 °C, using CoO as the catalyst. The concentrations of orthophosphate and polyphosphate solutions were measured according to the directions of Nakahara.[13]

pH Measurements. The pH values of the suspensions used for the apparent viscosity measurements were measured with a pH meter, TOA Electronics, Ltd. The pH values of the suspensions were controlled by adding an aqueous sodium hydroxide solution or an aqueous hydrochloric acid solution to the suspensions.

Results and Discussion

In Fig. 1, the apparent viscosities of ferric oxide–water suspensions containing 30, 50, 60, and 70 wt% ferric oxide are plotted as a function of the concentration of PA-33. Figure 1 shows that the additions of PA-33 to the ferric oxide–water suspensions with apparent viscosities of more than 10000 cP have their viscosities depressed to about 10 cP, and that the concentrations of PA-33 required to depress the vis-

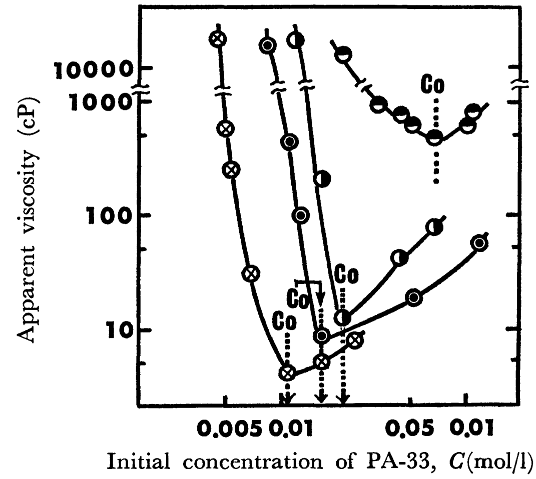

Fig. 1. The effects of the concentrations of PA-33 on the apparent viscosities of ferric oxide-water suspensions containing 30(⊗), 50(⊙), 60(◑) and 70(◓) wt% ferric oxide at 25 °C.
The initial concentrations of PA-33 refer to the mole concentrations expressed per monomer unit.

cosities up to about 10 cP, which are designated as C_0, increase with the increase in the pigment concentrations of the suspensions. As the concentrations of PA-33 approach C_0, the apparent viscosities of the suspensions decrease remarkably, but they increase gradually above C_0. These results suggest that the values of C_0 can be used as a measure of the apparent viscosity depression effects.

The values of C_0 and the apparent viscosities at C_0 for ferric oxide–aqueous-surfactant or inorganic phosphate-solution (weight ratio of 50/50) suspensions are listed in Table 2. Both the values of C_0 and the apparent viscosities at C_0 for 1-1-type anionic surfactants tend to decrease with the increases in the alkyl-chain length of the surfactants. The viscosity depression effects of the surfactants with a short alkyl-chain length, such as C_8S, $C_{10}S$, C_6BS, C_8BS, and C_4NS, are small, as may be seen in Table 2. These results show that the viscosity depression effects of 1-1-type anionic surfactants have a correlation with the critical micelle concentration (CMC) values of the surfactants, and that the surfactants with large CMC values have not marked viscosity depression effects. The values of C_0 for the formalin condensates decrease with the increases in the degree of condensation. The C_0 for PA series becomes smallest at a degree of polymerization of about 33. However, the changes in the degree of the polymerization from 12 to 33 have only a little influence on the values of C_0. As may be seen in Table 2, there exist only small differences in the values of C_0 among the vinyl copolymers except PA-64 and PA-146. These polymers have degrees of polymerization from 7.5 to 33, and the C_0 values are expressed in monomer units. Therefore, it can be concluded that the C_0 values undergo only a little influence by the changes in the chemical composition of the polymers, whereas they are greatly influenced by the changes in the degrees of polymerization. The C_0 values for polyphosphates are small compared with those of the surfactants described above, and tend to lower with the degree of the condensation of polyphosphates. With orthophosphates, on the other hand, no viscosity depression effects can be found.

In Fig. 2, the apparent viscosity, $T_{1/2}$, the sedimentation volume, and the average radius of pigment particles for the suspensions are plotted as functions of the concentration of PA-33, NSF-3.7, and $Na_5P_3O_{10}$ respectively. As may be seen in Fig. 2, a correlation can be found among the apparent viscosity, $T_{1/2}$, the

TABLE 2. VALUES OF THE C_0 AND APPARENT VISCOSITIES AT THE C_0 FOR FERRIC OXIDE–AQUEOUS SURFACTANT OR INORGANIC PHOSPHATE SOLUTION (50/50) SUSPENSIONS

Materials	Values of the C_0 (mol/l)	Apparent viscosities (cP) at the C_0
1-1 type anionic surfactants		
C_8S	—	>1000
$C_{10}S$	0.077	55
$C_{12}S$	0.035	10
$C_{14}S$	0.029	26[b)]
C_6BS	—	1000
C_8BS	0.28	650
$C_{10}BS$	0.042	35
$C_{12}BS$	0.040	30
$C_{14}BS$	0.035	10
C_4NS	—	>1000
Formalin condensates		
NSF-3.7	0.023	9
C_4NSF-3.5	0.020	8
C_4NSF-5.1	0.017	8
Vinyl copolymer		
PA-12	0.018	7
PA-33	0.016	8
PA-64	0.032	25
PA-146	0.053	27
PM	0.014	10
VacM	0.020	11
SM	0.018	9
OM	0.012	10
Orthophosphate		
NaH_2PO_4	—	>1000
Na_3PO_4	—	>1000
Polyphosphate		
$Na_2H_2P_2O_7$	0.0067	10
$Na_4P_2O_7$	0.0042	7
$Na_5P_3O_{10}$	0.0041	8
$Na_6P_4O_{13}$	0.0032	7

a) Concentrations (mol/l) of vinyl copolymers and formalin condensates are expressed in those of monomer unit of them, respectively. b) Measured at 40 °C because of insolubility of $C_{14}S$ at 25 °C.

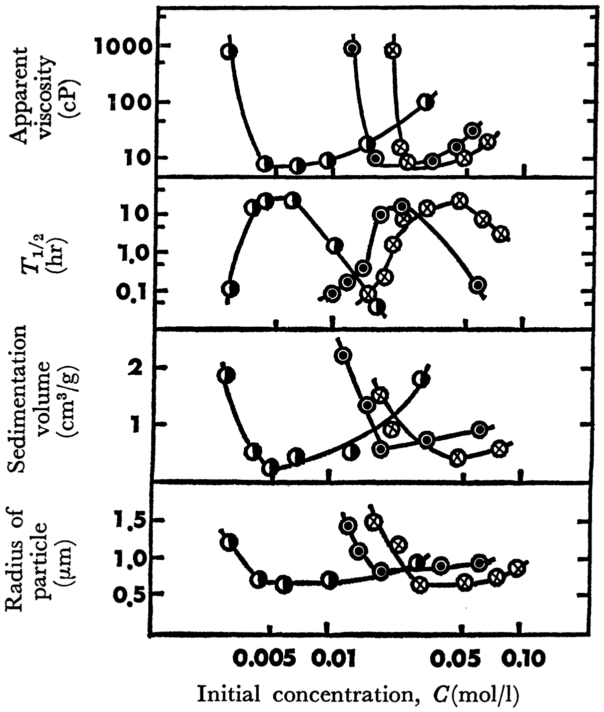

Fig. 2. Apparent viscosity, sedimenting time, $T_{1/2}$, sedimentation volume and average radius of the particle *vs.* initial concentration, C, curves for PA-33 (⊙), NSF-3.7 (⊗) and $Na_5P_3O_{10}$ (◑).
The concentrations of PA-33 and NSF-3.7 refer to the mole concentrations expressed per monomer unit of them.

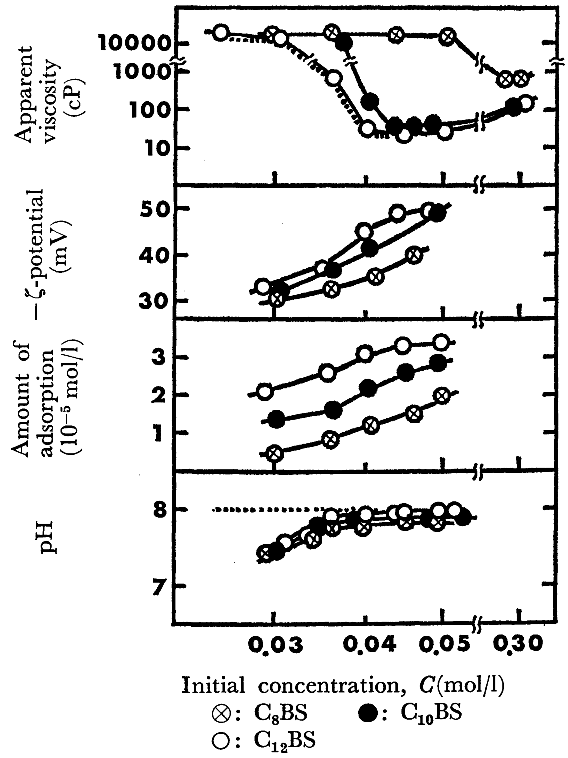

Fig. 3. The effects of the alkyl-chain length of linear-chain Na alkylbenzene sulfonates on the apparent viscosities of 50 wt% ferric oxide suspensions, and their relations with zeta potential, adsorption and pH data.
A dotted line refers to the apparent viscosity *vs.* log concentration, *C*, curve for $C_{12}BS$ at a controlled pH of 8.0.

sedimentation volume, and the average radius of the particle data. These results suggest that the viscosity changes in the suspensions are based upon the dispersion-coagulation of the ferric oxide particles.

Figure 3 shows the effects of the alkyl-chain length of linear-chain Na alkylbenzene sulfonate on the apparent viscosities, and their relations with the zeta potential, the adsorption, and the pH data. The calculation of the zeta potential, ζ, on the basis of the electrophoretic-mobility, u, measurements is done using the Helmholtz-Smoluchwski equation for the systems of $\kappa a \geq 200$,[14] where κ is the reciprocal of the thickness of the double layer, and a, the particle radius:

$$u = \frac{E\zeta\varepsilon}{4\pi\eta} \tag{1}$$

where η and ε are the viscosity and the dielectric constant of the medium respectively, and where E is the applied electric field.

Both the absolute values of the zeta potential and the amounts of adsorption for $C_{10}BS$ and $C_{12}BS$ increase remarkably in the concentration regions showing marked viscosity depressions, as may be seen in Fig. 3. The absolute values of the zeta potential and the amounts of adsorption for C_8S are very small compared with those for $C_{10}S$ and $C_{12}S$ in all the concentrations tested.

The viscosity changes in the suspensions are due to the dispersion-coagulation of the ferric oxide particles, as has been described above. Therefore, the viscosity changes in the suspensions may be explained by taking into account the contributions of the zeta potential values and the thickness of the double layer, $1/\kappa$*, to the dispersion-coagulation of the particles, that is, by applying the DLVO theory.[16] With 1-1-type anionic surfactants, the contributions of the zeta potential and $1/\kappa$ to the dispersion-coagulation of the particles increase with the increases in the zeta potential values, and decrease with the increases in the concentrations of the surfactant ions. As may be seen in Fig. 3, the amount of adsorption is in the order of $C_{12}BS > C_{10}BS > C_8BS$ at the same initial concentration, which shows that the equilibrium concentration at the same initial concentration is in the order of $C_8BS > C_{10}BS > C_{12}BS$. Accordingly, the negative contributions of the concentrations to the viscosity depressions increase in the order $C_8BS > C_{10}BS > C_{12}BS$. The apparent viscosities for C_8BS decrease up to about 600 cP at very high concentrations, as may be seen in Fig. 3. Perhaps this viscosity depression is related to the contribution of the zeta potential. In the high concentrations, however, precise electrophoretic mobility measurements cannot be made, because electrolysis may occur between the anodic and cathodic electrodes. Therefore, the calculation of the zeta potential cannot be made at high concentrations. As may be seen in Fig. 3, the apparent viscosities for $C_{10}BS$ and $C_{12}BS$ show considerable increases at very high concentrations. This may be due to the increase in the negative contribution of the concentration to the viscosity depression.

Generally, the stabilities of lyophobic colloids and the suspensions depend upon the pH of the systems.[17,18,11] Figure 3 shows that the pH values of the suspensions dispersed with each surfactant of C_8BS, $C_{10}BS$, and $C_{12}BS$ become almost the same at the same concentration, and undergo very little changes with an increase in the concentration, except for those in the region of low concentrations. The dotted line in Fig. 3 refers to the viscosity *vs.* concentration curve for $C_{12}BS$ at a controlled pH of 8.0. The dotted line is nearly in accord with the solid line of $C_{12}BS$, for which the pH is not controlled, this shows that the pH changes of the suspensions accompanied by changes in the concentrations have no appreciable influences on the viscosities.

It can be concluded from these results that the viscosity depression data can be explained by the zeta potential and the adsorption data. The weak viscosity depression effects of 1-1-type anionic surfactants with short alkyl chain lengths, such as C_8S and C_6BS, shown in Table 2 may be due to the lack of the amounts of adsorption and their contributions to the zeta potential.

Figure 4 shows the effects of the degree of the condensation of the formalin condensates on the apparent

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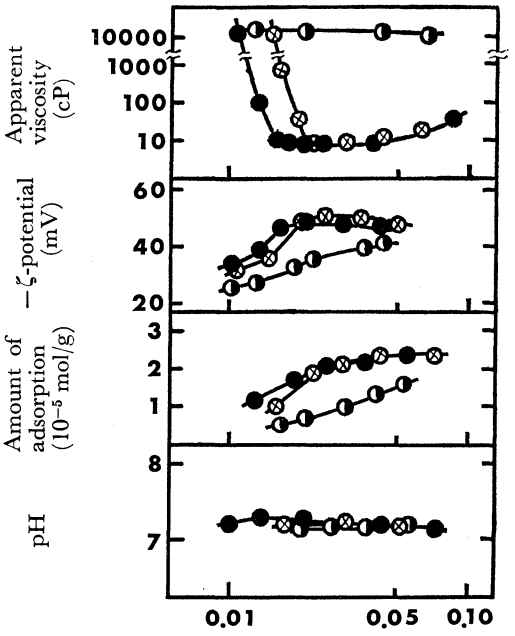
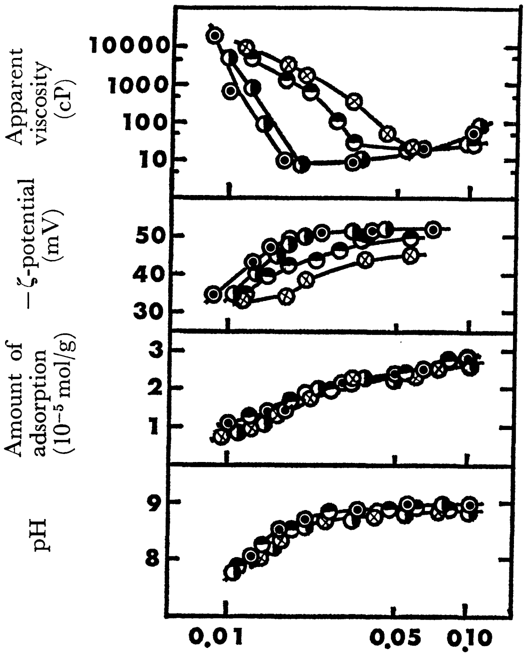
* $$1/\kappa = \left(\frac{\varepsilon KT}{4\pi e^2 \sum n_i Z_i^2}\right)^{1/2}$$

where e is the elementary charge, z_i, the valency, n_i, the number of ions of the species, i, per cubic centimeter, K, Boltzmann's constant, and T, the absolute temperature.[15]



Initial concentration, C(mol/l)
◑: C_4NS ⊗: C_4NSF-3.5
●: C_4NSF-5.1

Fig. 4. The effects of the degree of the condensation of alkylnaphthalene sulfonate formalin condensates on the apparent viscosities of 50 wt% ferric oxide suspensions, and their relations with zeta potential, adsorption and pH data.



Initial concentration, C(mol/l)
◑: PA-12 ⊙: PA-33
◓: PA-64 ⊗: PA-146

Fig. 5. The effects of the degree of the polymerization of Na salt of polyacrylic acid on the apparent viscosities of 50 wt% ferric oxide suspensions, and their relations with zeta potential, adsorption and pH data.

viscosities, and their relations with the zeta potential, the adsorption, and the pH data. With C_4NS, no marked viscosity depression effects are observed. With C_4NSF-3.5 and C_4NSF-5.1, on the other hand, marked viscosity depression effects are observed, and the value of C_0 for C_4NSF-5.1 is smaller than that for C_4NSF-3.5. That is, the viscosity depression effects are highly dependent upon the degree of condensation. As may be seen in Fig. 4, the zeta potential and the adsorption data are closely correlated with the viscosity data. The pH of the suspensions dispersed with each surfactant of C_4NS, C_4NSF-3.5, and C_4NSF-5.1 show almost the same values at the same concentration. These results suggest that the degrees of the condensation of the formalin condensates have great influences on the viscosity depression effects, and that their effects are due to the marked increases in the absolute values of the zeta potential and the amounts of adsorption with the increases in the degree of condensation.

Figure 5 shows the effects of the degree of the polymerization of the Na salt of polyacrylic acid (PA) on the viscosities, and their relations with the zeta potential, the adsorption, and the pH data. Figure 5 shows that PA with low degrees of polymerization, such as PA-12 and PA-33, show marked viscosity depressions in the region of low concentrations, whereas those with high degrees of polymerization, such as PA-64 and PA-146, show small viscosity depressions in the region of low concentrations. The absolute values of the zeta potential for the PA series increase remarkably in the concentration regions showing marked viscosity depressions, and the order of C_0 corresponds to the order of the zeta potential. Similarly, the amounts of adsorption for the PA series increase in the concentration regions showing viscosity depressions. However, no pronounced differences in the amounts of adsorption for the PA series are observed, although the amounts of adsorption may be expected to increase with the degree of polymerization. The absolute values of the zeta potential for high degrees of polymerization are small compared with those for low degrees of polymerization; this suggests that the contributions of the amounts of adsorption to the zeta potentials decrease with the increases in the degree of polymerization. In other words, the concentration of PA on the pigment surface, *i.e.*, the parts of PA which contribute to the zeta potential, decrease with an increase in the degree of polymerization. This may be attributed to the difference in the adsorption conformation among the PA on the pigment surface. Generally, the bridging action of polymers increases with an increase in the degree of polymerization,[19,20)] and serves to promote coagulation. However, in the case of the PA tested the bridging action is negligible, because the degree of polymerization is not large enough to have a large bridging action.

The pH values of the suspensions dispersed with each PA show almost equal values at the same concentration; this shows that the pH's of the suspensions are not dependent upon the degrees of polymerization.

Figure 6 shows the effects of the degree of the condensation of inorganic phosphates on the viscosities, and their relations with the zeta potential, the adsorption, and the pH data. Sodium dihydrogen phosphate

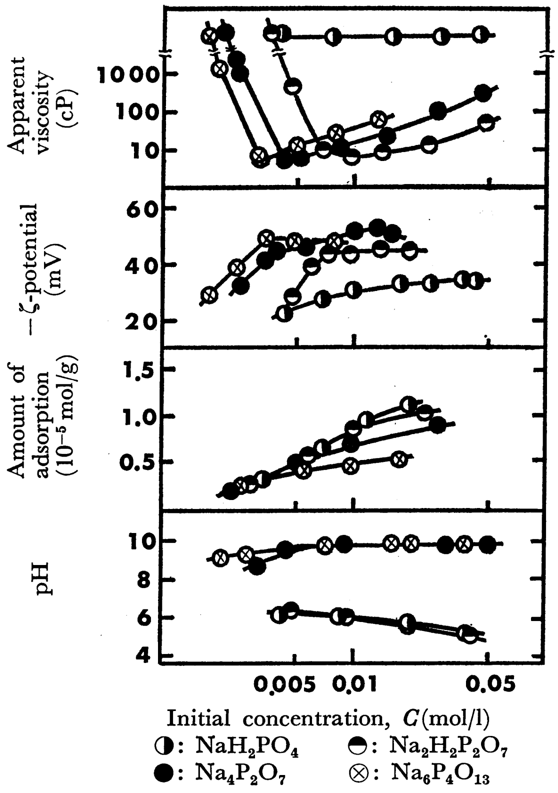


Fig. 6. The effects of the degree of the condensation of inorganic phosphates on the apparent viscosities of 50 wt% ferric oxide suspensions, and their relations with zeta potential, adsorption and pH data.

(NaH$_2$PO$_4$) has no marked viscosity depression effects, whereas acid sodium pyrophosphate (Na$_2$H$_2$P$_2$O$_7$), sodium pyrophosphate (Na$_4$P$_2$O$_7$), and sodium tetrapolyphosphate (Na$_6$P$_4$O$_{13}$) have such effects. The values of C_0 are in the order of Na$_6$P$_4$O$_{13}$<Na$_4$P$_2$O$_7$,< Na$_2$H$_2$P$_2$O$_7$. The zeta potential data are closely related with the viscosity data, whereas the adsorption data are not necessarily related with the viscosity data. The pH's of the suspensions dispersed with each phosphate of NaH$_2$PO$_4$ and Na$_2$H$_2$P$_2$O$_7$ show almost the same values lower than the isoelectric point (pH 5.5) of the ferric oxide particles at very high concentrations. Similarly, the pH's of the suspensions dispersed with each phosphate of Na$_4$P$_2$O$_7$ and Na$_6$P$_4$O$_{13}$ show almost the same values, much higher than the isoelectric point of the particles. In the pH range below the isoelectric point, where the pigment particle has positive charge, the anionic phosphate ion adsorbs on the particle and cancels the charge. On a further increase in adsorption, the particle comes to have a negative charge.[13] The pH's of an aqueous solution of Na$_2$H$_2$P$_2$O$_7$ and NaH$_2$PO$_4$** are lower than the isoelectric point of the particle. Therefore, the phosphate ion may be consumed to cancel the positive charge of the particle in the region of low concentrations. The absolute values of the zeta potential for Na$_2$H$_2$P$_2$O$_7$ are much smaller than those for Na$_4$P$_2$O$_7$ and Na$_6$P$_4$O$_{13}$ in the region of low concentrations, whereas the amounts of adsorption for Na$_2$N$_2$P$_2$O$_7$ and NaH$_2$PO$_4$ are larger than those for Na$_4$P$_2$O$_7$ and Na$_6$P$_4$O$_{13}$. These may be explained in relation to the isoelectric point of the particle described above. The zeta potential and the adsorption data show that the contributions of the amount of adsorption to the zeta-potential values increase with an increase in the valency of the phosphate ions. The pH's of the suspensions dispersed with Na$_2$H$_2$P$_2$O$_7$ and NaH$_2$PO$_4$ show somewhat higher values than the isoelectric point of the pigment particle in the region of low concentrations. This may be because the majority of the phosphate ions are adsorbed upon the particles.

It can be concluded from these results that the viscosity depression effects increase with the increase in the degree of the condensation of the phosphates, and have close relations with the zeta potential, the adsorption, and the pH data, especially the isoelectric point of the pigment particle.

According to the DLVO theory,[16] the total potential energy, V, between the two sphere particles (ferric oxide particles) for a system in which $\kappa a \gg 1$ and $H \ll a$ is given by:

$$V/a = \frac{\varepsilon\zeta^2}{2}\ln(1+e^{-\kappa H}) - \frac{A}{12H} \tag{2}$$

where A is the Hamaker constant, and H, the shortest distance between the two particles.

Using the value of A (4.5×10^{-13}) calculated by Fowkes,[21] the value of V/a can be calculated from Eq. (2). The value of V/a depends upon the absolute value of the zeta potential and the value of $1/\kappa$, *i.e.*, the thickness of the double layer. The thickness of the double layer is inversely proportional to the square of the valency of the material ion and the concentration of the material ion, as has been described above. Accordingly, the value of V/a increases with the absolute value of the zeta potential and decreases with the increase in the concentration and the valency of the material ion.

The values of V/a for aqueous 50 wt% ferric oxide suspensions dispersed with 1-1-type surfactants such as C$_{12}$BS have been calculated from Eq. (2) and plotted as a function of H in Fig. 7. In this figure, the apparent viscosity *vs.* $\log C$ curve is also shown to facilitate examination of the correlation of the V/a data with the apparent viscosity data. The abscissa in Fig. 7 is expressed in terms of the initial concentration of the surfactant. The calculation of V/a is made by using the equilibrium concentration of the surfactant, which was measured for the 50 wt% suspension. The values of V/a become positive over certain ranges of H for the concentrations of the numbers of 2 and 3, showing the suspensions with low apparent viscosity values. In other words, in the suspensions of the numbers of 2 and 3, repulsive forces enough to disturb the coagulation of the particles work between the particles. Therefore, the apparent viscosities of the suspensions may have small values. On the other hand, the values of V/a become negative in all the H values for the concentration of the number of 1, showing suspensions of very high viscosity values. In other words, in this suspension no repulsive force enough to disturb the coagula-

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** The pH's of aqueous solutions of Na$_2$H$_2$P$_2$O$_7$ and NaH$_2$PO$_4$ change from 4.7 at 0.0045 mol/l to 4.18 at 0.45 mol/l, and from 4.98 at 0.0042 mol/l to 4.65 at 0.042 mol/l, respectively.

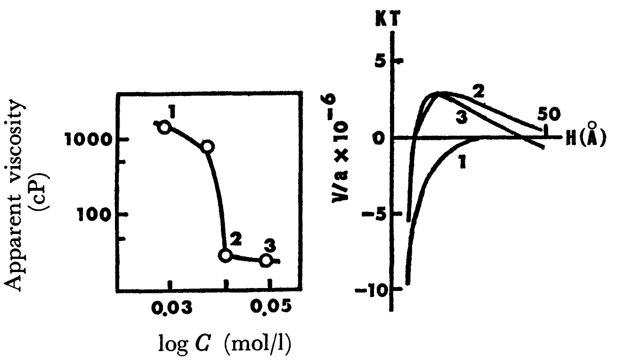

Fig. 7. The relations between V/a and apparent viscosity data for $C_{12}BS$.

1: initial concentration; 0.0287 mol/l
equilibrium concentration; 0.0084 mol/l
ζ-potential; −33 (mV)

2: initial concentration; 0.0402 mol/l
equilibrium concentration; 0.0089 mol/l
ζ-potential; −45 (mV)

3: initial concentration; 0.0489 mol/l
equilibrium concentration; 0.0152 mol/l
ζ-potential; −49 (mV)

tion of the particles works between the particles. Therefore, the particles coagulate, and the apparent viscosity of the suspension may have a large value. A relation similar to that found for the systems of $C_{12}BS$ is also found for the systems of C_8BS and $C_{10}BS$. These results show that the viscosity changes of 50 wt% ferric oxide suspensions upon the addition of surfactants can be explained by taking into account the zeta potential value, the valency, and the concentration of the surfactants, *i.e.*, the application of DLVO theory. Not only the viscosity changes in ferric oxide suspensions, but also the viscosity changes in other pigment suspensions, such as titanium dioxide and zinc oxide, can be explained qualitatively by the DLVO theory. This will be reported in a forthcoming paper.

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References

1) H. V. Olphen, *Discuss. Faraday Soc.*, **11**, 82 (1951)
2) N. Street, *J. Colloid Sci.*, **12**, 1 (1957).
3) D. H. Declerck and G. J. Su, *J. Amer. Ceram. Soc.*, **49**, 252 (1966).
4) A. L. Johnson and F. H. Norton, *ibid.*, **24**, 189 (1941).
5) T. Takeuchi, F. Tokiwa, Y. Tanino, and K. Hattori, *Kogyo Kagaku Zasshi*, **74**, 2239 (1971).
6) H. A. Kersey, *Trans. Instin. Chem. Engrs.*, **40**, 141 (1962).
7) H. Kambe, *Zairyo*, **17**, 459 (1968).
8) H. Kambe, *ibid.*, **15**, 265 (1966).
9) J. Seto, A. Amaya, K. Umeya, *ibid.*, **16**, 537 (1967).
10) K. Hattori, and Y. Komeda., *Yushi*, **17**, 80 (1964), *ibid.*, **17**, 79 (1964).
11) N. Moriyama, *J. Colloid Interface Sci.*, **50**, 80 (1975).
12) G. A. Parks and P. L. De. Bruyn, *J. Phys. Chem.*, **66**, 967 (1962).
13) Y. Nakahara, *Nippon Kagaku Kaishi*, **1972**, 695.
14) J. Th. G. Overbeek, "Colloid Science I," ed. by H. R. Kruyt, Elsevier Co., Amsterdam-Houston-New York-London (1952), pp. 207—212.
15) J. Th. G. Overbeek, *Advan. Colloid Sci.*, **3**, 97 (1950).
16) E. J. W. Verwey, and J. Th. G., Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier Co., Amsterdam-New York (1948).
17) E. Matijević and L. J. Stryker, *J. Colloid Interface Sci.*, **22**, 68 (1966).
18) E. Matijević and G. E. Januer, *ibid.*, **21**, 197 (1966).
19) M. Noda, *Nippon Kagaku Zasshi*, **82**, 1611 (1961).
20) Y. Toyoshima, *ibid*, **82**, 1295, 1297, 1301, (1961).
21) F. M. Fowkes, "Chemistry and Physics of Interfaces," ed. by S. Ross, American Chemical Society Publications Washington, D. C. (1965), p. 7.