Effects of Surfactants and Inorganic Phosphates upon Apparent Viscosities of Pigment-Water (50-50) Suspensions

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ABSTRACT

The effects of various types of surfactants and inorganic phosphates upon the apparent viscosities of pigment-water (50/50) suspensions are examined. The additions of surfactants or inorganic phosphates to the pigment-water suspensions depress the apparent viscosities from the values of more than 10,000 centipoise to those of ca. 10 centipoise. The concentration of surfactants or inorganic phosphates required to depress the apparent viscosity depends upon the chemical composition and the mol wt of surfactants or inorganic phosphates. The effects are correlated with zeta potential, adsorption, and pH data.

INTRODUCTION

Additions of surfactants or inorganic phosphates to the pigment-water suspensions having apparent viscosities of more than 10,000 centipoise (cp) have their apparent viscosities depressed to ca. 10 cp (1-11). Previous investigations of the viscosity depression have dealt almost exclusively with viscometric behaviors (1-10). In a preceding paper (12), a detailed investigation on the marked depressions of the apparent viscosities in ferric oxide-water suspensions containing 50 wt % ferric oxide, and its correlation with zeta potential, adsorption, and pH has been reported. The present paper describes effects of various types of surfactants and inorganic phosphates upon the apparent viscosities of aqueous suspensions of several inorganic pigments containing 50 wt % pigment and correlates the effects on zeta potential, adsorption, and pH.

TABLE I

Chemical Composition and Average Mol Wt of Surfactants

Type	Chemical composition	Average mol wt
Vinyl copolymers	Na salt of polyacrylic acid	3100
	Na salt of homopolymer of maleic acid	1200
	Na salt of copolymer of vinyl acetate and maleic acid	3500
	Na salt of copolymer of styrene and maleic acid	4500
	Na salt of copolymer of α-olefine (C_8) and maleic acid	4100
Formalin condensates	Na salt of formalin condensate of β-naphthalene sulfonic acid	900
	Na salt of formalin condensate of alkyl (C_4) naphthalene sulfonic acid	1100
General surfactants	Sodium dodecyl sulfate	288
	Sodium dodecyl benzene sulfonate	348
	Sodium alkyl (C_4) naphthalene sulfonate	286

EXPERIMENTAL PROCEDURES

Materials

All surfactants used were prepared according to the procedure described before (13). Their chemical compositions and average mol wt are listed in Table I. Orthophosphate (NaH_2PO_4), pyrophosphate ($Na_2H_2P_2O_7$ and $Na_4P_2O_7$), and tripolyphosphate ($Na_5P_3O_{10}$) were of reagent grade. These surfactants and inorganic phosphates are known to have dispersing power and are used widely (14).

Pigment

Zinc oxide, chrome yellow, aluminum hydroxide, kaolin, clay, and carbon black were used as inorganic pigments. Various physical properties of these pigments are listed in Table II. Specific surface areas were determined by the Brunauer-Emmet-Teller method, using nitrogen at -195 C. Isoelectric points were determined according to the directions of Parks, et al. (15). Average radii of primary particles were calculated from electron microscopic observation.

Apparent Viscosity Measurements

Aqueous solutions of surfactants and inorganic phosphates were prepared by dissolving the desired quantities in 500 ml distilled water. In 750 ml beaker, 400 ml solutions thus prepared were poured and maintained at 25 ± 0.1 C in a water bath. Into the solutions, 400 g pigment was added. After the pigment-solution suspensions were stirred with homomizer, TK type (Tokushu Kiki Industries Co., Osaka, Japan), for 5 min apparent viscosities were determined with a Viscometer.

Electrophoretic Mobility Measurements

Mobility measurements of pigment particles were made with a Zeta meter (Zeta Meter, Inc., New York, N.Y.) by diluting a quantity of the same suspensions used for apparent viscosity measurements into the supernatant solutions of their suspensions obtained by removing the particles with refrigerated automatic ultracentrifuge, Serval model RC2-B.

TABLE II

Various Physical Properties of Inorganic Pigments

Pigment	Specific surface areas (m^2/g)	Average particle size (μ)	Isoelectric point	Maker
Zinc oxide	4.0	0.3	8.4	Hakusui Chemicals Co. (Special grade)
Chrome yellow	3.5	0.5	—	Kikusui Dyes Co. (ODG)
Aluminium hydroxide	3.2	0.6	9.7	Showa Denko KK (Higilite H-42)
Clay	1.2	0.5	—	Nozaki Clay Co. (SSW)
Kaolin	2.0	0.6	—	Tsutiya Kaolin Co. (ASP 170)
Carbon black	110	0.03	—	Mitsu Bishi Kasei Co. (Channel black 100)

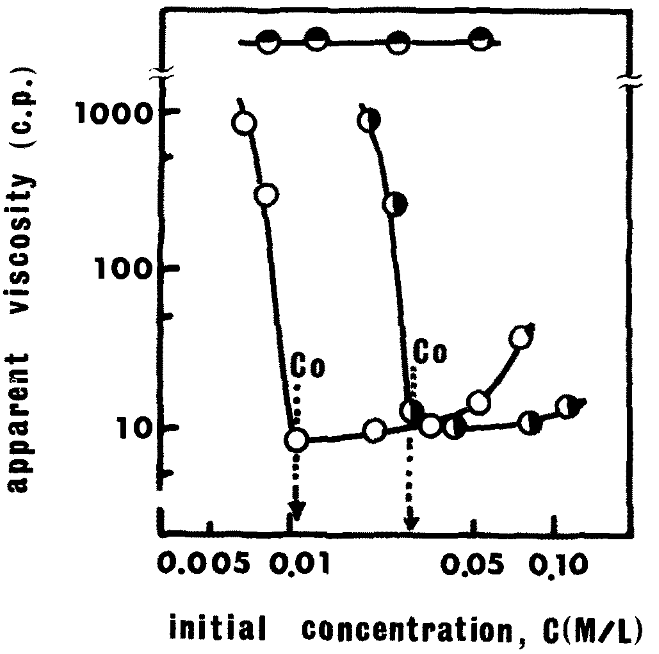

FIG. 1. The effects of the concentrations of Na salt of polyacrylic acid (PA) (○), Na salt of formalin condensate of β-naphthalene sulfonic acid (NSF) (◑) and sodium tripolyphosphate (◓) upon the apparent viscosities of zinc oxide-water (50/50) suspensions. The initial concentrations of PA and NSF refer to the mole concentrations expressed/monomer unit of them. cp = Centipoise and C(M/L) = initial mole concentration of surfactant and polyphosphate.

Adsorption Measurements

The quantities of surfactants and inorganic phosphates absorbed onto the pigment particles were calculated from measurements of the difference in concentrations of solutes in the solutions before and after preparing the suspensions. The solutions after preparing the suspensions described above are the same supernatant solutions as those used for electrophoretic mobility measurements. Concentrations of the surfactants having a benzene ring or naphthalene ring in the molecule were calculated by measuring the intensity of the adsorption band at ca. 260 mμ using Shimadzu spectrophotometer UV-200. On the other hand, surfactants 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 catalyst. The concentrations of orthophosphate and polyphosphate solutions were measured according to the method of Nakahara (16).

pH Measurements

pH values of the same suspensions used for the apparent viscosity measurements were measured with a pH meter, Toa Electronics, Tokyo, Japan. pH values of the suspensions were controlled by adding aqueous sodium hydroxide solution or aqueous hydrochloric acid solution.

RESULTS AND DISCUSSION

In Figure 1, apparent viscosities of zinc oxide-water suspensions containing 50 wt % zinc oxide are plotted as a function of the concentration of Na salt of polyacrylic acid (PA). Na salt of formalin condensate of β-naphthalene sulfonic acid (NSF), and sodium tripolyphosphate (STP), respectively. Figure 1 shows that additions of PA and NSF to the zinc oxide-water suspensions having apparent viscosities more than 10,000 cp depress the viscosities to ca. 10 cp, whereas additions of STP do not depress their viscosities. In the region of low concentration, apparent viscosities decrease with increasing concentration and reach almost constant values at a certain concentration, which is designated as C_0. In the present paper, the values of C_0 and the apparent viscosities at C_0 are used as a measure of apparent viscosity depression effects.

TABLE III

Values of C_0 and Apparent Viscosities at C_0 for Zinc Oxide-Aqueous Surfactant or Inorganic Phosphate Solution (50/50)Suspensions

Material[a]	Value of C_0 (M/L)	Apparent viscosity (centipoise) at C_0
Vinyl copolymer		
PA	0.011	9
PM	0.014	12
VacM	0.045	320
SM	0.0041	11
OM	0.0040	11
Formalin condensate		
NSF	0.029	12
Al-NSF	0.029	13
General surfactant		
SDS	---	>1000
DBS	---	>1000
ANS	---	>1000
Inorganic phosphate		
NaH_2PO_4	---	>1000
$Na_2H_2P_2O_7$	---	>1000
$Na_4P_2O_7$	---	>1000
$Na_5P_3O_{10}$	---	>1000

[a] PA = Na salt of polyacrylic acid, PM = Na salt of homopolymer

Values of C_0 and apparent viscosities at C_0 for zinc oxide-aqueous surfactant or inorganic phosphate solution (wt ratio of 50/50) suspensions are listed in Table III. With the surfactants of the type of vinyl copolymers, values of C_0 tend to be lowered with increase in their hydrophobic properties, except Na salt of copolymer of vinyl acetate and maleic acid (VacM) which has comparatively little effect. With the surfactants of the type of formalin condensates, values of C_0 are somewhat large compared with those of the surfactants of the type of vinyl copolymers. General surfacts, e.g. sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (DBS), etc., and inorganic phosphate, e.g. NaH_2PO_4, $Na_2H_2P_2O_7$, $Na_4P_2O_7$, etc., do not depress the viscosity, as shown in Table III. (Note: in this paper, the surfactants and inorganic phosphates which depress the apparent viscosities to the values of below 1000 cp are regarded as having the appreciable viscosity depression effects, because the systems having the viscosity values of more than 1000 cp have large errors of measurements.)

In Figure 2, the apparent viscosity, the zeta potential, the amount of adsorption, and pH are plotted as a function of the concentration of PA, NSF, and STP, respectively.

The calculation of zeta potention, ζ, from electrophoretic mobility, u, measurements is simple only when κa is very large (>>100) or very small (<<0.1) (17), where κ is the reciprocal of the thickness of the double layer and a the particle radius. As we treat the systems of $\kappa a \geq 200$, Helmholtz-Smoluchowski's equation can be employed in the form:

$$u = \frac{E\zeta\epsilon}{4\pi\eta}, \qquad (I)$$

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

With PA and NSF, the absolute values of zeta potential show considerable increase with the increase in their concentrations, particularly remarkable increase in the neighborhood of C_0, and become almost constant in the region of high concentration. With STP, on the other hand, they show slight increase with the concentrations and are small compared with those for PA and NSF, except in the region

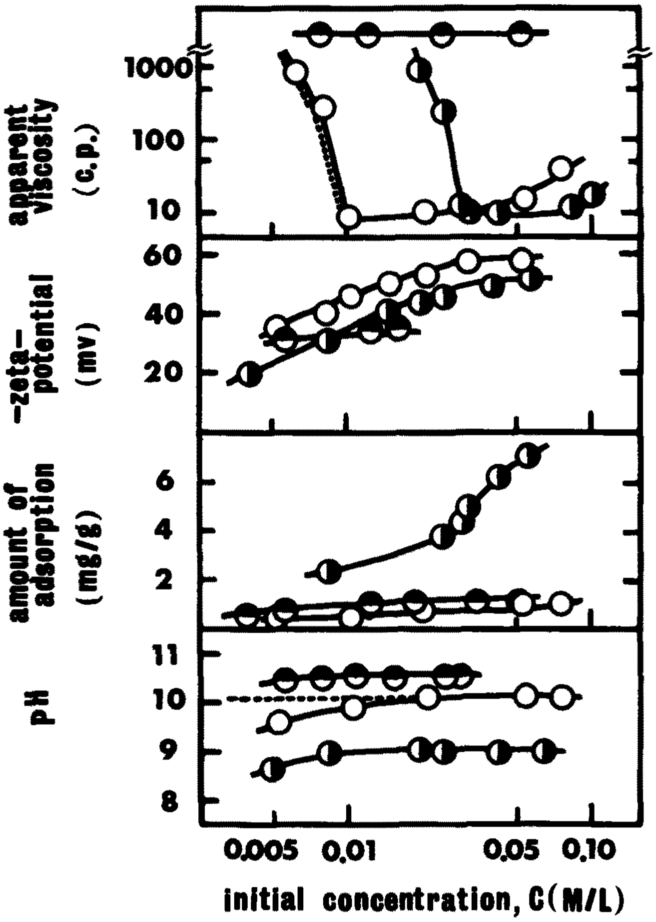

FIG. 2. Apparent viscosity, zeta potential, amount of adsorption, and pH in zinc oxide-water (50/50) suspensions vs initial concentration, c, curves for Na salt of polyacrylic acid (PA) (○), Na salt of formalin condensate of β-naphthalene sulfonate acid (NSF) (◐), and sodium tripolyphosphate (⊙). The initial concentrations of PA and NSF refer to the mole concentrations expressed/monomer unit of them. A dotted line refers to the apparent viscosity vs c curve for PA at a controlled pH of 10.1. cp = Centipoise and C(M/L) = initial mole concentration of surfactant and polyphosphate.

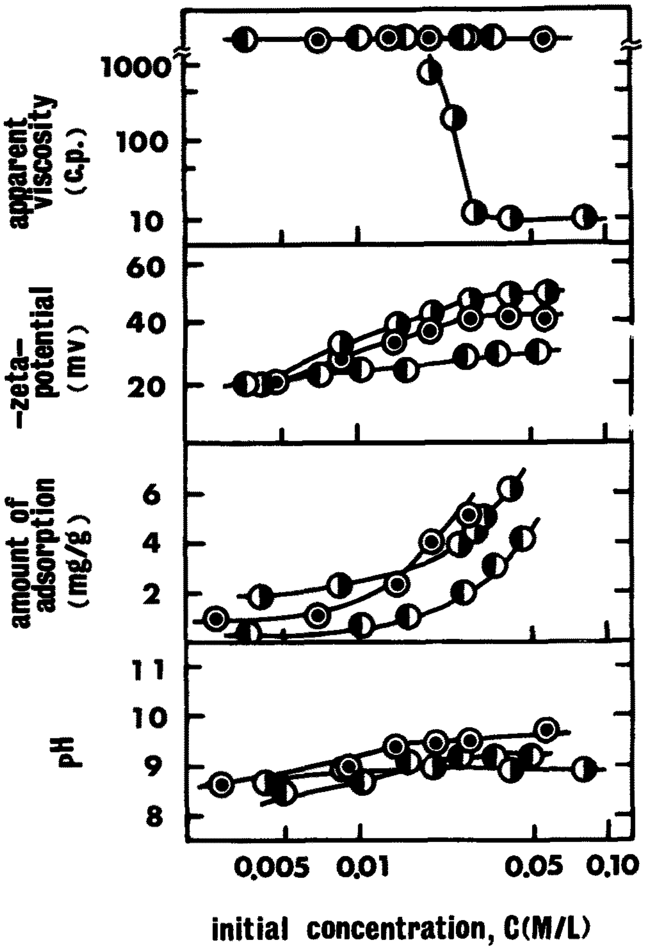

FIG. 3. Apparent viscosity, zeta potential, amount of adsorption, and pH in zinc oxide-water (50/50) suspensions vs initial concentration, c, curves for Na salt of formalin condensate of alkyl (C_4) naphthalene sulfonic acid (Al-NSF) (◑), sodium alkyl (C_4) naphthalene sulfonate (◐), and sodium dodecyl benzene solfonate (◎). The initial concentrations of Al-NSF refer to the mole concentrations expressed/monomer unit. cp = Centipoise and C(M/L) = initial mole concentration of surfactant.

of much low concentration. At the same concentration, the absolute values of zeta potential for PA are large compared with those for NSF over all concentration ranges tested.

According to Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (18), the repulsive potential energy V_R between two spherical particles for a system which $\kappa a >> 1$, is given by:

$$V_R = \frac{\epsilon a \zeta^2}{2} \ln (1 + e^{-\kappa H}), \qquad \text{(II)}$$

where H is the shortest distance between the particles.

Equation II shows that the value of V_R increases with the increase in the absolute value of zeta potential and decreases with the increase in value of κ, i.e. concentration of surfactants and valency of surfactant ions:

$$\kappa = \left(\frac{4\pi e^2 \Sigma n_i z_i^2}{\epsilon KT}\right)^{1/2},$$

where e is the elementary charge; z_i, the valency; n_i, the number of ions of species i/cubic centimeter; K, Boltzmann's constant; and T, the absolute value (19). On the other hand, the value of attractive potential energy V_A does not depend upon the absolute value of zeta potential and the value of κ (18). Accordingly, the total potential energy V between two sphere particles depends upon the value of V_R, which depends upon positive contribution of zeta potential and negative contribution of κ value.

In a preceding paper (12), it has been reported that the marked viscosity depressions of 50 wt % ferric oxide suspensions by additions of 1-1 type surfactants can be qualitatively explained by the application of the DLVO theory. The present systems also may be explained by the same theory, although the strict explanation may be impossible on account of polyvalency of PA and NSF ions.

As described above, STP has not appreciable viscosity depression effect. This finding suggests that zeta potential needs the absolute value more than a certain value, which is dependent upon the value of κ, to depress the viscosity. The value of C_0 for PA is smaller than that for NSF, perhaps because the zeta potential for PA is larger than that for NSF.

With NSF, the amounts of adsorption show remarkable increases in the concentration ranges showing marked viscosity depression. With PA and STP, they show much gradual increases and are much smaller compared with that for NSF. These results show that the absolute values of the amount of adsorption are not necessarily in direct relation with the absolute values of zeta potential, and the contributions of the amount of adsorption to the zeta potential may be different by the sort of surfactants.

Figure 2 shows that pH values of the suspensions dispersed with PA, NSF, and STP undergo little changes with increase in their concentrations, except those in the region of low concentrations. In the region of low concentrations, pH of the suspensions dispersed with PA undergo the largest changes among the surfactants described above. A dotted line shown in Figure 2 refers to the apparent viscosity vs concentration curves for PA at a controlled pH

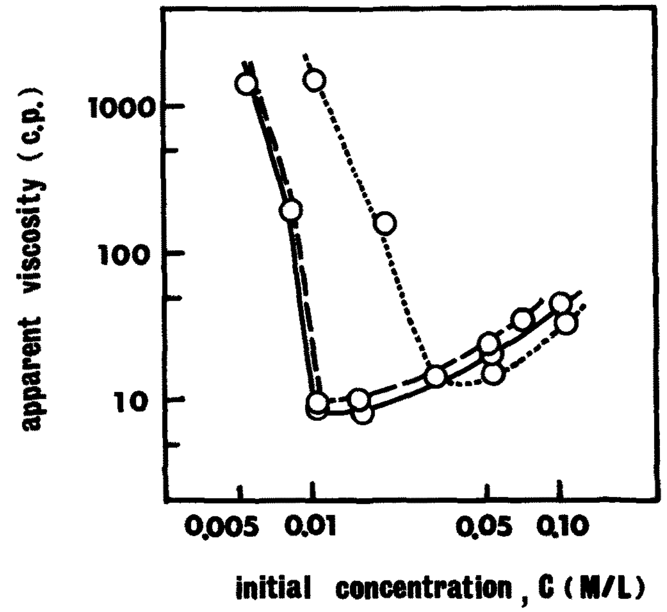

FIG. 4. Apparent viscosity in zinc oxide-water (50/50) suspensions vs initial concentration, c, curves for Na salt of polyacrylic acid (PA) at constant pH of 8 (· · · ·), 9 (- - - -), and 12 (——), respectively. cp = Centipoise and C(M/L) = initial mole concentration of PA expressed/monomer unit.

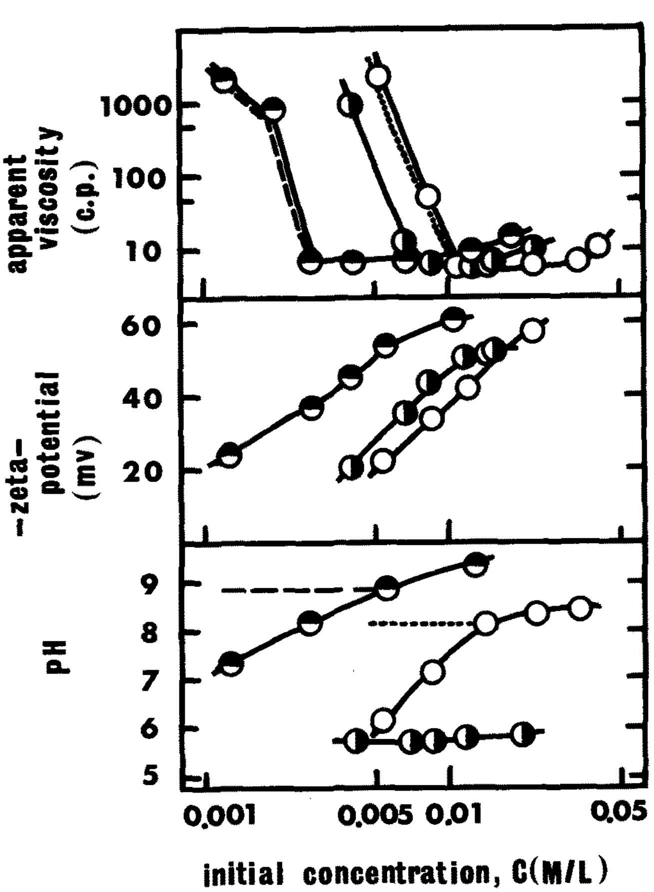

FIG. 5. Apparent viscosity, zeta potential and pH in chrome yellow-water (50/50) suspensions vs initial concentration, c, curves for Na salt of polyacrylic acid (PA) (○), Na salt of formalin condensate of β-naphthalene sulfonic acid (NSF) (◐), and sodium tripolyphosphate (STP) (●). The initial concentrations of PA and NSF refer to the mole concentrations expressed/monomer unit of them. Dotted and broken lines refer to the apparent viscosity vs c curves for PA and STP at controlled pH of 8.1 and 8.9, respectively. cp = Centipoise and C(M/L) = initial mole concentration of surfactant and polyphosphate.

10.1. A dotted line is nearly in accord with a solid line of PA which pH is not controlled. These results show that apparent viscosities in these suspensions are influenced very little by the pH change which acocmpanies increase in surfactant concentration.

It may be concluded from these results that the viscosity depressions are highly dependent upon the absolute values of zeta potential.

In Figure 3, the apparent viscosity, the zeta potential, the amount of adsorption, and pH are plotted as a function of the concentrations of Na salt of formalin condensate of alkyl (C_4) naphthalene sulfonic acid (Al-NSF), sodium alkyl (C_4) naphthalene sulfone (ANS), and DBS, respectively. Al-NSF is a formalin condensate of ANS. The number of condensations of Al-NSF calculated from the average mol wt shown in Table I is 3.7. As seen in Figure 3, Al-NSF depresses viscosity, wherease ANS does not. Both the absolute value of zeta potential and the amount of adsorption for Al-NSF are much larger than those for ANS over all the concentration ranges tested. pH of aqueous Al-NSF solutions containing 50 wt % zinc oxide shows almost equal values with those of ANS containing 50 wt % zinc oxide. These results show that the adsorbabilities of the surfactants increase with mol wt, and the viscosity depressions are highly dependent upon the adsorbabilities of surfactants and their contributions to the zeta potentials. DBS does not appreciably depress viscosity. The zeta potentials for DBS show almost intermediate values between those for Al-NSF and those for ANS. The amounts of adsorption for DBS are smaller than those for Al-NSF at low concentration, whereas the former are larger than the latter at high concentration. DBS has relatively high zeta potential (ca. -40 mV) and large amount of adsorption in the region of high concentration. In these concentrations, however, the negative

TABLE IV

Values of C_0 and Apparent Viscosities at C_0 for Inorganic Pigment-Aqueous Surfactant or Inorganic Phosphate Solution (50/50) Suspensions

	Chrome yellow		Aluminum hydroxide		Kaolin		Clay		Carbon black	
Material[a]	Value of C_0	Apparent viscosity at C_0	Value of C_0	Apparent viscosity at C_0	Value of C_0	Apparent viscosity at C_0	Value of C_0	Apparent viscosity at C_0	Value of C_0	Apparent viscosity at C_0
PA	0.011	6 c.p.	0.011	320 c.p.	0.016	12 c.p.	0.010	13 c.p.	---	>1000 c.p.
PM	0.014	7	0.036	280	0.022	37	0.036	10	---	>1000
VacM	0.013	7	0.013	14	0.0089	57	0.018	20	0.13	16
SM	0.0083	7	0.0083	35	0.012	18	0.0083	11	0.083	220
OM	0.028	11	0.0040	12	0.0080	11	0.0060	9	0.024	10
NSF	0.0083	7	0.025	80	0.017	10	0.042	29	0.042	10
STP	0.0027	7	---	>1000	0.0054	15	0.0054	13	---	>1000

[a] PA = Na salt of polyacrylic acid, PM = Na salt of homopolymer of maleic acid, VacM = Na salt of capolymer of vinyl acetate and maleic acid, SM = Na salt of capolymer of styrene and maleic acid, OM = Na salt of copolymer of α-olefine (C_8) and maleic acid, NSF = Na salt of formalin condensate of β-naphthalene sulfonic acid, STP = sodium tripolyphosphate.

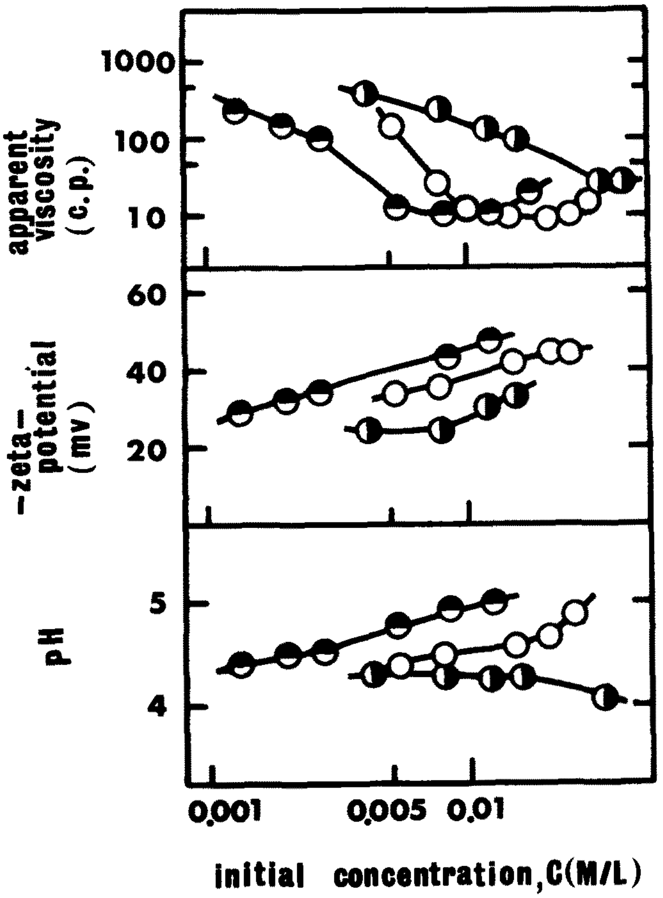

FIG. 6. Apparent viscosity, zeta potential and pH in clay-water (50/50) suspensions vs initial concentration, c, curves for Na salt of polyacrylic acid (PA) (○), Na salt of formalin condensate of β-naphthalene sulfonic acid (NSF) (◑) and sodium tripolyphosphate (◓). The initial concentrations of PA and NSF refer to the mole concentrations expressed/monomer unit of them. cp = Centipoise and C(M/L) = initial mole concentration of surfactant and polyphosphate.

contributions of κ to the viscosity depressions also increase. Therefore, the viscosity depression may not be found. pH of DBS solution containing 50 wt % zinc oxide hardly is influenced with the concentration.

Figure 4 shows the apparent viscosity vs log concentration curves for PA at controlled pHs of 8, 9, and 12, respectively. As seen in Figure 4, the viscosity vs log concentration curves are shifted to the low concentration with increase in pH, i.e. viscosity depressions by additions of PA increase with increase in pH of the systems. pH change from 8 to 9 has an especially large influence on the viscosity. These may occur because of the pH dependencies of surface charge and degree of the dissociation of PA.

In Table IV, the value of C_0 and the apparent viscosity at C_0 for various pigment-aqueous surfactant and inorganic phosphate solution (50/50) suspensions are lised.

PA and Na salt of homopolymer of maleic acid (PM) which have strong hydrophilic properties show the marked viscosity depressions for the suspensions, except that of carbon black, which has hydrophobic properties. Na salt of copolymer of α-olefine (C_8) and maleic acid (OM), Na salt of copolymer of styrene and maleic acid (SM), NSF, and VacM, which have moderate hydrophilic hydrophobic properties show the marked viscosity depressions for every suspension. The viscosity depressions of STP are varied with the kind of pigment. For example, STP does not appreciably depress viscosity for the suspensions of aluminium hydroxide and carbon black.

Similar relations as those found between the viscosity depression data and the zeta potential data in zinc oxide suspensions also can be found in chrome yellow and clay suspensions, as shown in Figures 5 and 6.

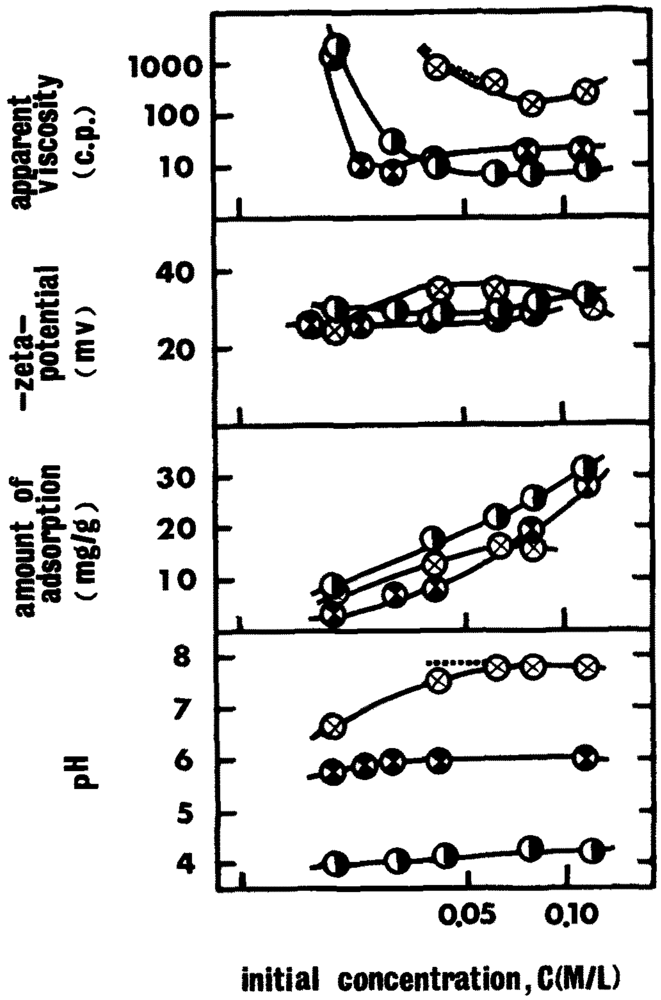

FIG. 7. Apparent viscosity, zeta potential, amount of adsorption, and pH in carbon black-water (20/80) suspensions vs initial concentration (vs pigment), c, curves for Na salt of formalin condensate of β-naphthalene sulfonic acid (NSF) (◑), Na salt of copolymer of styrene and maleic acid (SM) (⊗), and Na salt of copolymer of α-olefine (C_8) and maleic acid (OM) (⊛). The initial concentrations of NSF, SM, and OM refer to the mole concentrations expressed/monomer unit of them. A dotted line refers to the apparent viscosity vs c curve for SM at controlled pH of 7.9. cp = Centipoise and C(M/L) = initial mole concentration of surfactant.

These figures show that the absolute values of zeta potential increase remarkably in the neighborhood of C_0 and suggest that a correlation exists between the viscosity depression data and the zeta potential data.

In Figure 7, the apparent viscosity, the zeta potential, the amount of adsorption, and pH in 20 wt % carbon black suspensions are plotted vs log concentration for NSF, OM, and SM. The zeta potentials show slight increases with the concentrations, and the absolute values are small compared with those of other suspensions. A correlation between the viscosity depression data and the zeta potential data cannot be found in these suspensions. The amount of adsorption show almost linear increases with surfactant concentrations. pH of the suspensions are much different with the kind of surfactant. The concentration dependence of the pH may be negligible, as seen in Figure 7.

Carbon black has the most hydrophobic properties among the inorganic pigments tested, and shows behavior similar to hydrocarbon oil and polyethylene wax (20). From these results, it can be estimated that the repulsive force arising from the adsorbed layer, as well as the electrical repulsive force, may contribute to the viscosity depression effects in carbon black suspensions.

It may be concluded that the viscosity depressions in inorganic pigment suspensions, except for carbon black suspension, are related closely to the zeta potential, i.e. electrical repulsive force.

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