Suspension Stability of Solid Particles in the Presence of Various Types of Electrolytes

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Abstract

Stabilities of titanium dioxide and ferric oxide suspensions in the presence of various types of electrolytes have been studied by measuring their sedimentation volume, rate of sedimentation and optical absorption as a measure of the degree of suspension. The stabilizing ability in suspensions with condensed phosphates is relatively high as compared with that with electrolytes other than the phosphates. This would indicate strong adsorption of phosphate ions onto the surface of the particle. A correlation is found between the extent of stability of a suspension and the electrophoretic mobility of the particle suspended in electrolyte solution, except with silicates. With polyphosphates ($Na_{n+2}P_nO_{3n+1}$) the stabilizing effect is noticeable at $n \geqq 2$, while with metaphosphates ($Na_nP_nO_{3n}$) it becomes noticeable and constant at $n \geqq 4$. The stabilities of titanium dioxide and ferric oxide suspensions containing silicates are high in spite of low electrophoretic mobilities of their suspended particles, which are comparable with the stability operated by tripolyphosphate or a typical dispersing agent. The suspension stability data of acid and neutral condensed phosphates and of the electrolytes used commonly as builders in the presence of a surfactant have also been included.

Introduction

The previous work, studying the electrophoretic mobilities of solid particles suspended in aqueous solutions of various types of electrolytes, has shown that the mobilities of the particles in phosphate solutions are relatively high as compared with those in other electrolyte solutions (1). The electrophoretic mobility or zeta potential of colloid particles is thought to have a close relationship with their stability in suspension, since the stability is primarily governed by the solid/liquid interfacial potential and electrical repulsive potential between charged particles (2,3). Therefore, it is important to investigate the stability of solid particle suspensions from the point of view of the electrical nature of the suspended particles by the help of the electrophoretic data previously reported.

In the present work, the effects of a series of condensed phosphates and other types of electrolytes on the stabilities of titanium dioxide and ferric oxide suspensions have been studied. As a measure of suspending ability the sedimentation volume, the rate of sedimentation and the optical absorption of these suspensions have been determined. The suspending abilities of condensed phosphates were compared with those of other types of electrolytes than the phosphates and discussed in connection with the electrophoretic mobilities of the suspended particles. The results will also be discussed more fully in a forthcoming paper in relation to the builder effect of these phosphates in detergent systems.

Experimental Procedures

Materials

Polyphosphates and metaphosphates used were the same samples as those described in a previous paper (1). Inorganic electrolytes other than the phosphates and the trisodium salt of nitrilotriacetic acid, which were obtained from Wako Pure Chemicals Co., were of reagent grade and used without further purification. The sodium salt of β-naphthalene sulfonic acid-formalin condensate (abbreviated as β-NSF), which is a commonly used dispersing agent, was a sample prepared in the laboratory. Sodium alkylbenzene sulfonate was prepared from alkylbenzene, the average alkyl chain of which was C_{12}, by sulfonation according to the ordinary method (4) and purified by a procedure similar to that for sodium dodecyl polyoxyethylene sulfates, described elsewhere (5). Titanium dioxide (R-820, rutile type, 99+% pure) was supplied by Ishihara Industries Inc., and it was used without further purification. Ferric oxide (Toda rouge 120-R, Toda Industries Inc.) was thoroughly washed with water and dried at 100 C in vacuum before use.

Sedimentation Measurements

Suspensions for sedimentation measurements were prepared as follows. In a graduated glass-stoppered test tube of 30 ml capacity and 32 cm height, 1.0 g of titanium dioxide or ferric oxide and 10 ml of distilled water were added and shaken vigorously by hand for 1 min. A requisite volume of a 0.3% electrolyte solution, diluted with distilled water to a volume of 30 ml, was then added to the shaken suspension. Mixing after electrolyte addition was continued at a fixed speed with an automatic shaker for 5 min. The tube stood overnight at 25 C. After standing, the tube was shaken again 100 times before measurement. Usually it took several days to attain a definite sedimentation volume of the suspension. The reading of the sedimentation volume was taken when such an equilibrium had been attained.

The rates of sedimentation of the above suspensions were also measured. The displacement of the boundary set up by the sedimentation of particles was measured periodically. The rate of sedimentation

TABLE I

Relative Sedimentation Volumes (Sv_{rel}), Sedimentation Rates (Sr) or Absorbances (As) of TiO_2 and Fe_2O_3 Suspensions in the Presence of Condensed Phosphates at a Concentration of 3.0 × 10^{-2} % by Weight

Phosphates	TiO_2 Suspension		Fe_2O_3 Suspension	
	Sv_{rel}	Sr(×10^2 cm/hr)	Sv_{rel}	As[a]
$Na_{n+2}P_nO_{3n+1}$				
n = 1	0.89	[b]	0.81	0.65
2	0.36	2.6	0.31	0.82
3	0.34	2.3	0.25	0.83
4	0.32	2.1	0.28	0.82
5	0.32	2.1	0.28	0.80
$Na_nP_nO_{3n}$				
n = 3	0.57	[b]	0.42	0.58
4	0.33	2.4	0.28	0.75
5	0.33	2.4	0.27	0.78
6	0.31	2.2	0.28	0.80

[a] Values after standing 2 hr.
[b] Particles sedimented rapidly as flocs.

TABLE II

Relative Sedimentation Volumes of TiO_2 Suspensions and Absorbancies of Fe_2O_3 Suspensions in the Presence of Various Electrolytes at a Concentration of 3.0×10^{-2} % by Weight (A) and in the Presence of Acid and Neutral Phosphates at a Concentration of 1.7×10^{-3} M as P_2O_5 (B)

A			B			
Electrolytes	Sv_{rel} of TiO_2 Suspension	As[a] of Fe_2O_3 Suspension	Phosphates		Sv_{rel} of TiO_2 Suspension	As[a] of Fe_2O_3 Suspension
NaCl	0.82	0.05	Ortho-	Na_3PO_4	0.89	0.65
Na_2CO_3	0.84	0.50		Na_2HPO_4	0.88	0.63
Na_2SO_4	0.94	0.05		NaH_2PO_4	0.92	0.61
$Al_2(SO_4)_3$	1.04	......	Pyro-	$Na_4P_2O_7$	0.38	0.81
$K_2Al_2(SO_4)_4$	0.99	......		$Na_2H_2P_2O_7$	0.41	0.74
$NaBO_2$	0.89	0.54	Trimeta-	$Na_3P_3O_9$	0.57	0.56
$Na_2B_4O_7$	0.97	0.45		$Na_2HP_3O_9$	0.63	0.52
$Na_2O \cdot 1.0\ SiO_2$	0.39	0.71	Hexameta-	$Na_6P_6O_{18}$	0.33	0.78
$Na_2O \cdot 2.5\ SiO_2$	0.38	0.74		$Na_3H_3P_6O_{18}$	0.39	0.70
$Na_2O \cdot 3.3\ SiO_2$	0.36	0.74				
β-NSF	0.35	0.79				

[a] Values after standing 2 hr.

was obtained from the change of position of the boundary with time. In polydisperse systems, broadening of the boundary was observed and it made the reading less accurate. The sedimentation velocity measurement was carried out only for the titanium dioxide suspensions shown in Table I.

Optical Absorption Measurements

The absorbance of ferric oxide suspensions was measured as an indication of suspending ability. The suspension was prepared by mixing 0.5 g of ferric oxide and 100 ml of electrolyte solution (in some cases, containing a surfactant) of a desired concentration in a 200 ml beaker with a homogenizer for 2 min and with an ultrasonic mixer for 3 min. The thoroughly mixed suspension was then poured into a graduated cylinder of 50 ml capacity and 2.3 cm diameter. After 2 or 24 hr at 25 C, 1.0 ml of the sample was taken from 5 cm below the surface and diluted with 50 volumes of distilled water. The absorbance at 510 mμ was measured immediately after dilution by a Shimadzu Model AQV-50 spectrophotometer.

Results

Table I summarizes relative sedimentation volumes (Sv_{rel}) and rates of sedimentation (Sr) for titanium dioxide suspensions and Sv_{rel} values and absorbances (As) for ferric oxide suspensions in the presence of a series of condensed phosphates, their concentration being kept constant at 3.0×10^{-2} % by weight; Sv_{rel} being a ratio of sedimentation volume of particles in electrolyte solution to that in water. Titanium dioxide and ferric oxide particles form looser sediments in water than in phosphate solutions, the sedimentation volumes of these particles in water being 2.02 and 2.28 ml/g, respectively. A correlation is found between Sv_{rel} and Sr although the Sr value is not so reliable as Sv_{rel} in the present experiment.

TABLE III

Effect of Some Electrolytes on Absorbances of Fe_2O_3 Suspensions in the Presence of Sodium Alkylbenzene Sulfonate

Electrolytes	Absorbances	
	after 2 hr	after 24 hr
Na_3PO_4	0.37	0.18
$Na_5P_3O_{10}$	0.85	0.63
$Na_2O \cdot 2.5\ SiO_2$	0.78	0.31
Na_2CO_3	0.18	0.03
Na_2SO_4	0.40	0.20
$Na_2B_4O_7$	0.23	0.04
SNTA	0.57	0.12
β-NSF	0.90	0.44
No added electrolyte	0.47	0.12

The values given in Table I depend on the concentrations of phosphates. A typical result for the effect of phosphate concentration on the Sv_{rel} of titanium dioxide suspension and on the As of ferric oxide suspension is shown in Figure 1 where the value of Sv_{rel} or As is plotted against the concentration of sodium tripolyphosphate. For comparison, the similar relations for sodium nitrilotriacetate (SNTA) recently used as a builder in detergent formulations, are included in Figure 1. The Sv_{rel} value with SNTA is greater than that with tripolyphosphate, and the As value with SNTA is lower than that with tripolyphosphate at any concentration. This is indicative of the greater suspending ability of tripolyphosphate for these particles.

Table II(A) gives the Sv_{rel} and As values for titanium dioxide and ferric oxide suspensions, respectively, in the presence of various electrolytes other than phosphates, to compare the suspending abilities of phosphates with those of other electrolytes. The values with silicates, which are comparable to the values with condensed phosphates, are to be noted. When β-NSF, which is a typical dispersing agent, is used a high degree of stability is achieved and it is also comparable to tripolyphosphate.

Table II(B) gives the Sv_{rel} and As values in the solutions of acid and neutral phosphates in which one or two sodium atoms are substituted by a hydrogen atom or atoms; these values in the solutions of the normally alkaline salts are also included for comparison.

Some of the above electrolytes are commonly employed as builders in detergent formulations. Table III shows the As values of ferric oxide suspensions containing sodium alkylbenzene sulfonate, sodium sulfate and the electrolyte in a ratio of 20:50:30, the total concentration of the additives being kept at 0.2% by weight. The suspending abilities of the electrolytes are affected by addition of the surfactant, as seen in Table III.

Discussion

It is known that sediments of flocculated suspensions are usually much more voluminous than those of stable suspensions of the same concentration. The rate of sedimentation will depend on the effective size of the particle so that a flocculated suspension will settle more rapidly (the entire floc acting as a particle) than a deflocculated one. Because of this effect, flocculated sediments form quickly but are loose and low in density (6).

The relative sedimentation volume Sv_{rel} of titanium dioxide particles in solutions of polyphosphates and

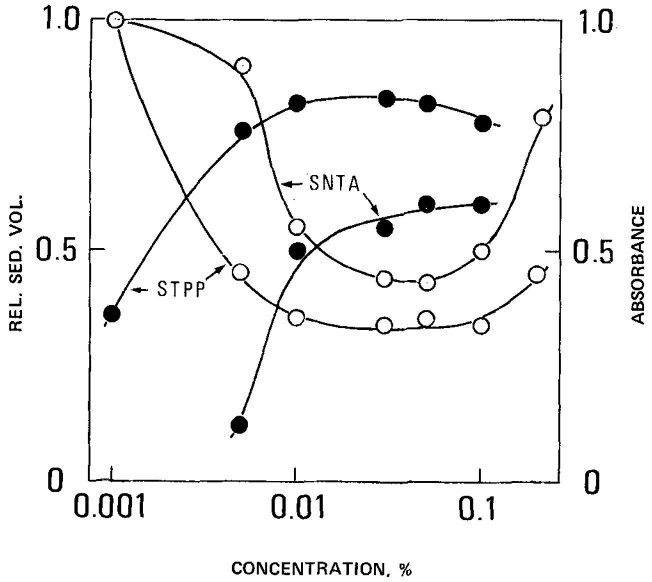

FIG. 1. Effect of the concentration of sodium tripolyphosphate (STPP) or trisodium nitrilotriacetate (SNTA) on the relative sedimentation volume (○) of TiO_2 suspension and absorbance (●) of Fe_2O_3 suspension.

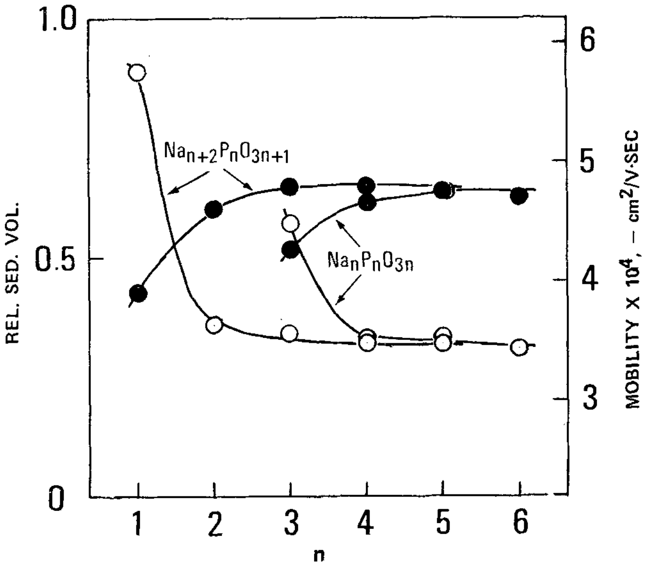

FIG. 2. Relative sedimentation volume (○) of TiO_2 suspension and electrophoretic mobility (●) of its particle in the presence of $Na_{n+2}P_nO_{3n+1}$ or $Na_nP_nO_{3n}$ at a concentration of 3.0×10^{-2} % as a function of n.

metaphosphates is plotted against the number of n in Figure 2, in which the hydrolysis of phosphates is not taken into account. The rate of hydrolysis or degradation would be relatively slow under the conditions of the present experiment, as expected from data of hydrolysis of condensed phosphates reported by Van Wazer et al. (7,8) and Bennet and Liss (9). The similar relation shown in Figure 3 is obtained for ferric oxide particles. In both cases, the Sv_{rel} values in solutions of polyphosphates or metaphosphates decrease with increasing numbers of n and at higher n they reach a nearly constant value.

The stability of the suspension against flocculation is largely conditioned by electrostatic repulsion, and is governed by the height of a potential barrier resulting from superposition of van der Waals attractive forces and the double layer repulsive forces (2). Therefore, the double layer potential, i.e., the zeta potential of the particle may be used as a measure of the suspension stability. Zeta potential is defined as the difference in charge between the immovable liquid layer attached to the surface of a solid phase and the movable part of the diffuse layer in the body of the liquid. The zeta potential of the particle can be related in general to its electrophoretic mobility and, in the present case, is proportional to the mobility since κa is estimated to be >250, where κ is the Debye-Hückel parameter and a is the radius of the particle (10,11). In Figure 2 the electrophoretic mobilities of titanium dioxide particles in solutions of polyphosphates and metaphosphates, are shown, plotted as a function of n for the purpose of comparison with sedimentation data. There is a parallelism between the Sv_{rel} of the suspension and the mobility of the particle, that is, the higher the electrophoretic mobility the smaller the sedimentation volume. This result also indicates that electrical repulsion is one of the important factors which govern the suspension stability. The high Sv_{rel} value in orthophosphate solution, thus, could be explained by the low mobility of the suspended particle. The effect of tripolyphosphate on the values of Sv_{rel} and As shows increasing suspending action at low electrolyte concentrations, reaching a maximum, then decreasing at elevated concentrations. The increase in stability of the suspension is attributed to increasing charge density, while the maximum and decreasing portion are attributed to double layer compression from increasing gegenion concentration (12).

When two suspensions containing an equivalent amount of ferric oxide are compared, a more dispersed suspension will give a greater As value since the sample for absorbance measurement was taken after a definite time from a definite distance from the surface of the suspension. With respect to ferric oxide suspensions in the presence of phosphates, a correlation is found between Sv_{rel} and As, as seen in Figure 3, that is, the greater the As value the smaller the Sv_{rel} value. The tendency of the dependence of Sv_{rel} on n for ferric oxide suspensions is similar to that for titanium dioxide suspensions, although the absolute values of Sv_{rel} are not neces-

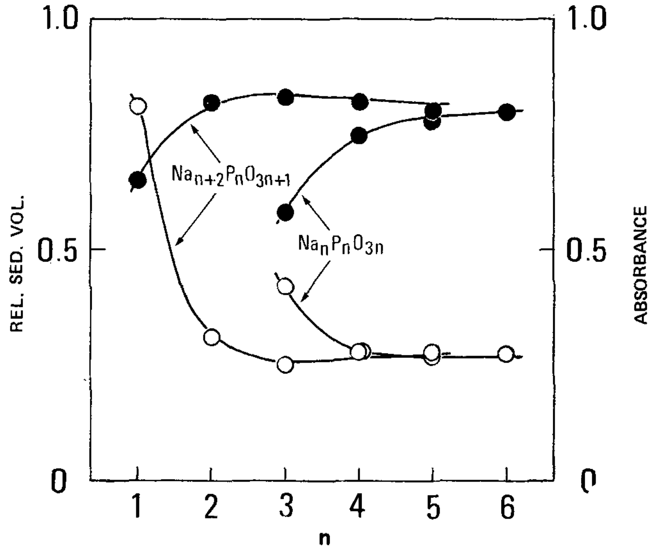

FIG. 3. Relative sedimentation volume (○) and absorbance (●) of Fe_2O_3 suspension in the presence of $Na_{n+2}P_nO_{3n+1}$ or $Na_nP_nO_{3n}$ at a concentration of 3.0×10^{-2} % as a function of n.

sarily in agreement when they are compared at a given number of n. This discrepancy in Sv_{rel} could be explained by difference in the chemical nature of the surface involved and a different degree of adsorption of phosphate ions by the surface of the particle.

It is of interest to compare the sedimentation or absorbance data shown in Table I with those shown in Table II(A). In connection with the mobility data previously obtained (1), these results indicate that the stabilities of particles in solutions of polyphosphates and metaphosphates are greater than those in solutions of other electrolytes except silicates. The effectiveness of phosphates in stabilizing the suspensions may be attributed to strong adsorption of phosphate ions onto the surface of the particle with consequent increase in zeta potential. It has been reported that phosphate ions, especially polyphosphate ions, are adsorbed to a greater extent than simpler ions like chloride, sulfate and carbonate ions (11), and the zeta potential of particles in phosphate solutions is higher than in such electrolyte solutions (1).

It is to be noted that in the presence of silicates the Sv_{rel} value for titanium dioxide suspension is smaller and the As value for ferric oxide suspension is greater than the values in the presence of other electrolytes listed in Table II(A) in spite of the relatively low zeta potentials of the particles (1). The effectiveness of silicates in stabilizing the suspensions is comparable to that of tripolyphosphate and β-NSF. The reason for this result is not clear. However, it is probable that the adsorbed silicates contain OH groups which form hydrogen bonds with the water molecules and thus reduce the rate of sedimentation (13). In addition, it seems that their surface activity and polyelectrolyte character are related to the high suspending power of silicates. Surface tension and interfacial tension, here more pertinent, were found to be lower than for equivalent solutions of other alkalies (14). The polyelectrolyte properties of silicate solutions have been discussed by Schleyer (15).

Partial substitution of one or two sodium atoms in the phosphate molecule by a hydrogen atom or atoms slightly, but not significantly, affects the Sv_{rel} and As values of suspensions, as shown in Table II(B). The result indicates that even the acid or neutral phosphates in low concentrations have strong suspending power for colloidal particles like normally alkaline phosphates. This could be explained by the fact, previously reported, that the particles in acid and neutral phosphate solutions have relatively high zeta potential in spite of the depression of pH of the solutions by this substitution (1).

Most inorganic salts examined here are commonly used as builders in detergent systems. Table III shows some of the results for the effect of electrolytes on the stability of ferric oxide suspensions in the presence of sodium alkylbenzene sulfonate of a constant concentration. The stability in tripolyphosphate or β-NSF solution is high, as observed in the absence of the surfactant, and good suspending action is also found for sodium silicates in the presence of the surfactant. Interpretation of the results for the ferric oxide suspension containing both electrolyte and surfactant is more complex than for the suspension containing electrolyte alone. It is considered that the competitive adsorption of electrolyte ions and surfactant ions will take place in the suspension. However, the adsorption of surfactant ions at the solid-liquid interface may be preferential and the predominant factor in stability (2). On this basis one would expect the addition of electrolyte to promote stability by increasing the adsorption of surfactant ions; this effect will be offset by the reduction in the double layer repulsion produced by increase in electrolyte concentration.

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