# Electrophoretic Mobility Studies of Colloidal Particles in Aqueous Solutions of Various Phosphates

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## Abstract

Electrophoretic mobilities of carbon black, titanium dioxide, ferric oxide and bentonite particles have been systematically measured in solutions of a series of sodium polyphosphates and metaphosphates. The mobilities of those particles carrying negative charge in phosphate solutions are relatively high as compared with those in solutions of various electrolytes other than phosphates. This would be indicative of strong adsorption of phosphate ions onto the surface of the particle. In polyphosphate ($Na_{n+2}P_nO_{3n+1}$) solutions the mobility increases with increasing n in the region of $n \leq 3$ and then becomes constant at $n > 3$, while in metaphosphate ($Na_nP_nO_{3n}$) solutions the mobility is nearly constant independent of n except the case with n of 3. The electrophoretic behavior of the particles is highly dependent on the pH of the solutions—the higher the pH of the solution, the greater the mobility of the particle. However, the mobilities in phosphate solutions are in general much higher than those expected from the pH of the solutions. The electrophoretic data in solutions of acid and neutral phosphates have also been included.

## Introduction

Condensed phosphates have been used for many years in colloidal systems and much has been learned about such properties as dispersion, deflocculation and peptization (1–5). These properties are thought to have some relation with the electrophoretic mobility or zeta potential of colloidal particles suspended in dilute solutions of the phosphates. However, systematic studies of the electrophoretic behavior of colloidal particles in solutions of various types of phosphates have scarcely been made in spite of their wide applicability in industry.

When dispersions having electrical double layers are placed in an electrical field, the particles can be observed to migrate toward one of the electrodes. If the fixed portion of the double layer is negative at the slipping plane, migration to the positive electrode is observed. Surface charge and zeta potentials of colloidal particles are not easily measurable but are reflected in the experimentally derivable electrophoretic mobilities.

In the present work, the effects of a series of polyphosphates and metaphosphates on the electrophoretic mobilities of colloidal particles in solutions have been studied in relation to their numbers of phosphorus atoms per molecule and to the pH of their aqueous solutions. The particles examined were carbon black, titanium dioxide, ferric oxide and bentonite clay. The results have been discussed in comparison with the mobilities of these particles in solutions of other types of electrolytes such as sodium chloride, sulfate, carbonate, silicate and borate.

## Experimental Procedures

### Materials

Two different types of phosphates, $Na_{n+2}P_nO_{3n+1}$ and $Na_nP_nO_{3n}$, where n is the number of phosphorous atoms per molecule, and phosphates in which one or two sodium atoms are substituted by a hydrogen atom or atoms were used in the present experiment.

Orthophosphates ($Na_3PO_4$, $Na_2HPO_4$ and $NaH_2PO_4$), pyrophosphates ($Na_4P_2O_7$ and $Na_2H_2P_2O_7$) and tripolyphosphate ($Na_5P_3O_{10}$) were of reagent grade, obtained from Wako Pure Chemicals Co. Other two polyphosphates were specially prepared commercial products having $Na_2O/P_2O_5$ ratios of 1.50 and 1.40. Paper chromatographic analyses were made for these polyphosphates, according to the method of Karl-Kroupa (6–8). The sample having a $Na_2O/P_2O_5$ ratio of 1.50 gave only one zone on the paper chromatogram, the $R_f$-value of which corresponds to tetrapolyphosphate (6). The sample having a $Na_2O/P_2O_5$ ratio of 1.40, on the other hand, gave one large zone corresponding to pentapolyphosphate (6) and two very small zones on the upper and lower sides of the large zone. From the $Na_2O/P_2O_5$ ratio, paper chromatography and end group titration (9), it could be established that these polyphosphates were sodium tetrapolyphosphate ($Na_6P_4O_{13}$), and mainly pentapolyphosphate ($Na_7P_5O_{16}$) but contained small amounts of tetrapolyphosphate and polyphosphates higher than pentapolyphosphate.

The metaphosphates used, where $Na_2O/P_2O_5$ is unity, were tri-, tetra-, penta- and hexametaphosphates which were obtained from Taihei Chemicals Co. or Phosphorus Chemical Co. According to the analytical data by the manufacturer, these phosphates have average numbers of three, four, five and six phosphorus atoms per molecule, respectively. Characterization of these samples was also made by paper chromatography (8,10,11). The chromatogram showed tri- and tetrametaphosphates were free of higher and lower homologues. These two phosphates were in crystalline form. Penta- and hexametaphosphates gave almost the same $R_f$ values as those reported by Van Wazer (10) and, therefore, the main constituents could be estimated to be metaphosphates having five and six phosphorus atoms per molecule, respectively. From the $R_f$ values of these phosphates in acid and basic solvents, they are considered to be metaphosphates and not polyphosphate glasses. Although the two higher metaphosphates described here are not necessarily pure substances, they will be called simply as penta- and hexametaphosphates, respectively, in this paper.

All electrolytes other than the phosphates, such as sodium chloride, carbonate, etc., were of reagent grade.

Carbon black (Channel No. 100) was obtained from Mitsubishi Kasei Co. and was dried in an oven at 150 C for at least three hours before use. Titanium dioxide (R-820, rutile type) was supplied by Ishihara Industries, Inc., and its purity was stated to be more than 99%, to be used without further purification.

TABLE I

Mobilities of Carbon Black, Titanium Dioxide, Ferric Oxide and Bentonite Particles in Phosphate Solutions of a Constant Concentration of 1.7 × $10^{-3}$ M as $P_2O_5$ or 3.0 × $10^{-2}$% by Weight

| n Values for Phosphates | Sample No. | Mobility × $10^4$, cm²/V·sec | | | | | |
|---|---|---|---|---|---|---|---|
| | | In 1.7 × $10^{-3}$M Solution | | | | In 3.0 × $10^{-2}$% Solution | |
| | | Carbon | $TiO_2$ | $Fe_2O_3$ | Bentonite | Carbon | $TiO_2$ |
| ($Na_{n+2}P_nO_{3n+1}$) | | | | | | | |
| 1 | 1 | −3.25 | −3.86 | −3.82 | −3.00 | −3.40 | −3.89 |
| 2 | 2 | −3.69 | −4.50 | −4.35 | −3.36 | −3.84 | −4.60 |
| 3 | 3 | −3.78 | −4.69 | −4.49 | −3.52 | −3.91 | −4.80 |
| 4 | 4 | −3.80 | −4.70 | −4.47 | −3.58 | −3.93 | −4.80 |
| 5 | 5 | −3.85 | −4.75 | −4.39 | −3.60 | −3.85 | −4.75 |
| ($Na_nP_nO_{3n}$) | | | | | | | |
| 3 | 6 | −3.30 | −4.44 | −4.04 | −3.35 | −3.32 | −4.27 |
| 4 | 7 | −3.90 | −4.77 | −4.48 | −3.76 | −3.91 | −4.65 |
| 5 | 8 | −3.87 | −4.85 | −4.43 | −3.80 | −3.94 | −4.75 |
| 6 | 9 | −3.95 | −4.75 | −4.45 | −3.79 | −4.01 | −4.70 |

Ferric oxide (Toda rouge 120-R) and bentonite clay were obtained from Toda Industries, Inc., and Wako Pure Chemical Co., respectively. These samples were thoroughly washed with water and dried in vacuum before use.

**Electrophoresis**

Electrophoretic mobility measurements were made at 25 C with a Zeta Meter (Zeta Meter Inc., New York), in which the mobility is observed in a cylindrical microelectrophoresis cell fitted with two platinum electrodes (12,13). This apparatus was calibrated by determining the mobilities of amorphous silica in water and titanium dioxide in 0.02% hexametaphosphate solution. The results agreed with the data of Kane, et al. (13) and Hattori (14) obtained with the same type of an apparatus.

The suspension for mobility measurement was prepared by mixing approximately 1.0 mg of the sample with 100 ml of the electrolyte solution in a 150 ml beaker with a magnetic stirrer at a fixed high speed or with an ultrasonic mixer for 3 min. In some cases, the pH of the suspension was adjusted to the desired value by using dilute sodium hydroxide or hydrochloric solution over stirring. The suspension was then allowed to stand for 30 min. On the upper part of the suspension containing relatively small particles, electrophoretic mobility determinations were made in accordance with the direction in the Zeta Meter manual, with special care being taken to avoid bubble formation and turbulence in the cell.

## Results

Table I summarizes the electrophoretic mobilities of carbon black, titanium dioxide, ferric oxide and bentonite particles suspended in aqueous solutions of various phosphates, their concentration being kept constant at 1.7 × $10^{-3}$ M on the basis of mole of $P_2O_5$, or 3.0 × $10^{-2}$% by weight. The mobilities of these particles, especially titanium dioxide and ferric oxide particles, in phosphate solutions are high as compared with those in other electrolyte solutions, as will be described later.

The mobilities of these particles depend on the concentrations of phosphates. A typical result for the effect of phosphate concentration on the mobility is shown in Figure 1 where the mobility of a titanium dioxide particle is plotted against the concentration of sodium tripolyphosphate. For comparison, the similar relation for the titanium dioxide particle in sodium carbonate solutions of different concentrations is included in Figure 1. The mobility in sodium tripolyphosphate solution is much higher than that in sodium carbonate solution at any concentration, and there appears a maximum around a concentration of 0.03%.

Table II (A) gives the mobilities of titanium dioxide particles in solutions of various electrolytes other than phosphates, together with the pH of the solutions, to compare the roles of phosphates in the electrophoretic behavior with those of other electrolytes. The mobilities in these solutions, in general, are lower than those in phosphate solutions.

Table II (B) also shows the mobilities of titanium dioxide particles in solutions of acid or neutral phosphates in which one or two sodium atoms are substituted by a hydrogen atom or atoms; in Table II, the mobilities in solutions of the normally alkaline salts are also included for comparison.

## Discussion

The electrophoretic mobility of a colloidal particle can be related to its zeta potential ($\zeta$) and surface charge by the equations derived by Smolukowski, Henry or others (15). 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

TABLE II

Mobilities of Titanium Dioxide Particles in Solutions of Various Electrolytes at a Constant Concentration of 0.03 % (A), and in Solutions of Acid and Neutral Phosphates at a Constant Concentration of 1.7 × $10^{-3}$ M as $P_2O_5$ (B)

| A | | | | B | | | |
|---|---|---|---|---|---|---|---|
| Electrolyte | Sample No. | pH | Mobility × $10^4$ cm²/V·sec | Phosphates | | pH | Mobility × $10^4$ cm²/V·sec |
| NaCl | 10 | 6.1 | −3.12 | Ortho- | $Na_3PO_4$ | 11.4 | −3.86 |
| $Na_2CO_3$ | 11 | 10.6 | −3.91 | | $Na_2HPO_4$ | 8.0 | −3.69 |
| $Na_2SO_4$ | 12 | 6.2 | −2.89 | | $NaH_2PO_4$ | 5.3 | −3.53 |
| $Al_2(SO_4)_3$ | 13 | 3.8 | +1.05[a] | Pyro- | $Na_4P_2O_7$ | 9.5 | −4.50 |
| $K_2Al_2(SO_4)_4$ | 14 | 3.9 | +1.11[a] | | $Na_2H_2P_2O_7$ | 4.8 | −3.58 |
| $NaBO_2$ | 15 | 10.0 | −3.75 | Trimeta- | $Na_3P_3O_9$ | 6.9 | −4.04 |
| $Na_4B_2O_7$ | 16 | 9.1 | −3.69 | | $Na_2HP_3O_9$ | 3.0 | −3.34 |
| $Na_2O\cdot0.5SiO_2$ | 17 | 11.3 | −3.80 | Hexameta- | $Na_6P_6O_{18}$ | 6.6 | −4.75 |
| $Na_2O\cdot1.0SiO_2$ | 18 | 11.1 | −3.80 | | $Na_3H_3P_6O_{18}$ | 3.2 | −4.11 |
| $Na_2O\cdot2.5SiO_2$ | 19 | 10.2 | −4.08 | | | | |

[a] Some particles were precipitated during measurement.

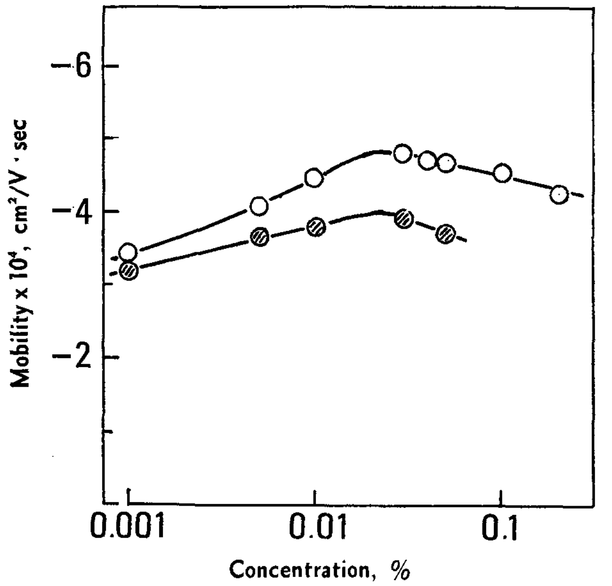

FIG. 1. Effect of concentration of sodium tripolyphosphate (○) or sodium carbonate (◍) on mobility of titanium dioxide particle at 25 C.

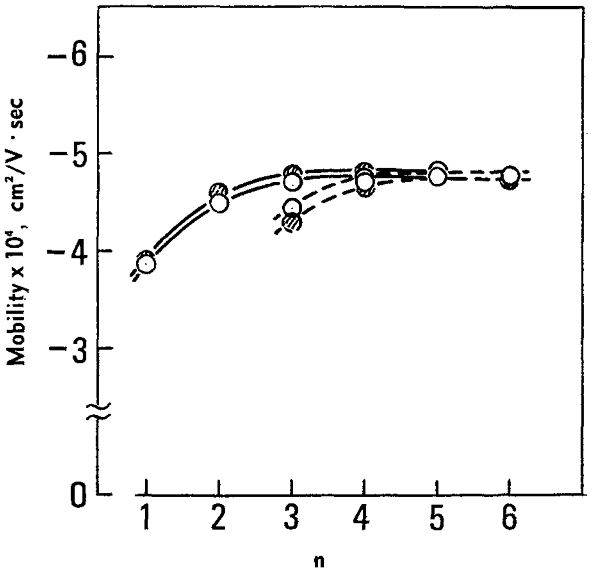

FIG. 2. Mobility of titanium dioxide particle in phosphate solutions of a constant concentration (○, $1.7 \times 10^{-3}$ M as $P_2O_5$, and ◍, $3.0 \times 10^{-2}$ wt %) as a function of n at 25 C: ——, in $Na_{n+2}P_nO_{3n+1}$ solution; – – –, in $Na_nP_nO_{3n}$ solution.

of the liquid. In the present case, the following simple equation may be used for calculation in $\zeta$ since $\kappa a$ is estimated to be >250 (16,17), where $\kappa$ is the Debye-Hückel parameter and a is the radius of the particle.

$$\zeta = (4\pi\eta/D)v \qquad [1]$$

where $v$ is the mobility of the particle, $\eta$ and D are the viscosity and dielectric constant of the medium, respectively. Thus, since to a first approximation the zeta potential of the particle is proportional to the electrophoretic velocity, as described in Equation 1, we have elected to express electrophoretic data simply as mobility.

The velocity of migration of a colloidal particle for a given electric field is affected primarily by the nature and extent of the particle charge. Therefore, any factor affecting the zeta potential will influence the velocity of migration. With addition of electrolytes, the charge effect and zeta potential are determined by adsorption and hence the mobility is also determined by adsorption (2).

### The Effect of the Chain Length of Phosphates on the Mobilities of Particles

As is seen in Table I, the mobilities of titanium dioxide and ferric oxide particles in phosphate solutions are higher than those of carbon black and bentonite particles when they are compared at a given value of n. This could be explained by the different chemical nature of the surface involved and different adsorption of phosphate ions by the surface of the particle. The mobility of titanium dioxide particles in solutions of polyphosphates and metaphosphates is plotted against the number of n in Figure 2, in which the hydrolysis of phosphates is not taken into account. Similar relations are obtained for other particles if the mobility is plotted against n. It is known that condensed phosphates hydrolyze in aqueous solutions to yield less condensed phosphates and ultimately pure orthophosphate. The rate of hydrolysis is dependent upon the temperature, pH, concentration of phosphate and ionic environment (18,19). However, the rate of hydrolysis or degradation would be extremely slow under such a condition as that in the present experiment, and thus the hydrolysis during the preparation and mobility measurement of samples is not significant.

The mobility of titanium dioxide particles in polyphosphate solutions increases with increasing n until n reaches 3 and then becomes constant at $n > 3$, while the mobility in metaphosphate solutions is nearly constant independent of n except for the phosphate with n of 3. The reason for these results is not clear at this stage, but the following explanation seems plausible. If the same extent of phosphate ions is adsorbed onto the surface of the particle, then phosphates with higher values of n increase the surface charge density of the particle more efficiently (2), which leads to increased mobility. This may be the case for polyphosphates with n values of 1, 2 and 3. For polyphosphates and metaphosphates with $n \geqq 4$, on the other hand, it would be explained that smaller amounts of phosphate ions are adsorbed with increasing value of n probably because of the entropy effect (20,21), but retaining the same extent of surface charge.

### The Effect of the pH of Solutions on the Mobilities of Particles

Figure 3 shows the relation between the mobility of titanium dioxide particles and the pH of phosphate solutions of a constant concentration of 0.03%. Similar relations are obtained for other particles although they are not illustrated here. The number attached to each point in the Figure refers to the sample number given in Table I. The solid curve indicates the mobility vs. pH relation in the absence of phosphate salts, in which the pH of the solution was adjusted only with hydrochloric acid or sodium hydroxide; higher mobility values in the alkaline region result from adsorption of $OH^-$ ions by the particles (5). As seen in Figure 3, in all cases the mobilities in phosphate solutions are located higher than the solid curve except those in orthophosphate solution. In Figure 4 the mobility of titanium dioxide particle obtained in tripolyphosphate solutions of different concentrations is plotted against the pH of the solutions. The solid curve also shows the mobility vs. pH relation in the absence of tripolyphosphate.

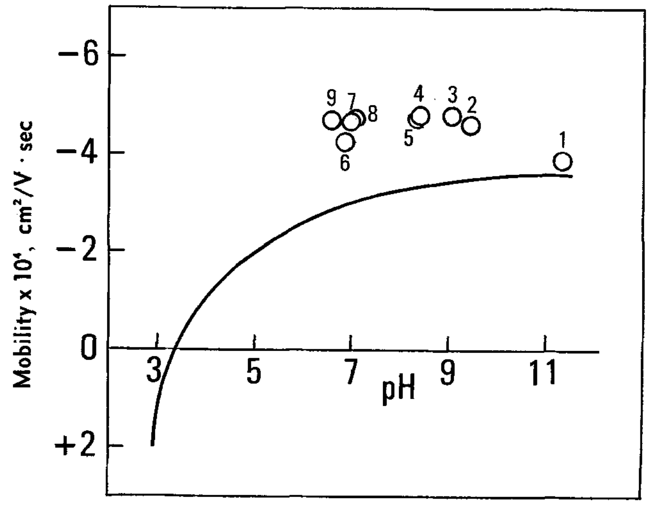

FIG. 3. Relation between mobility of titanium dioxide particle and pH of 0.03% phosphate solutions at 25 C. (Number attached to each point refers to sample number given in Table I, and solid curve indicates mobility vs. pH relation in the absence of phosphate salts.)

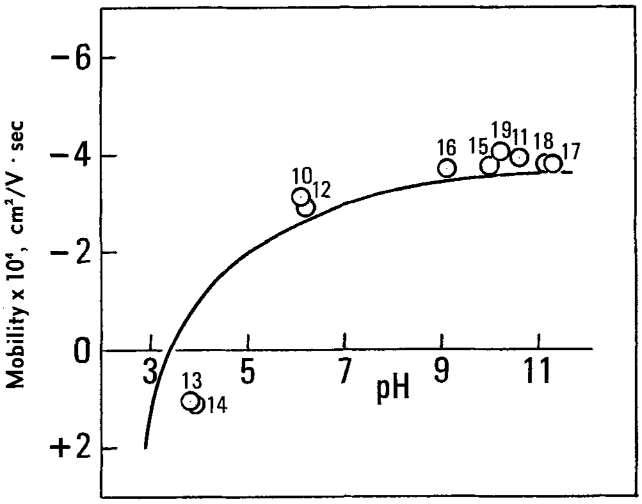

FIG. 5. Relation between mobility of titanium dioxide particle and pH of various electrolyte solutions at a concentration of 0.03% at 25 C. (Number attached to each point refers to sample number given in Table II [A]).

At any concentrations examined, addition of tripolyphosphate makes the mobility increase more than the value shown by the solid curve. It is of interest to compare these results with those shown in Figure 5 where the mobilities in the solutions of various electrolytes other than phosphates are given as a function of the pH of the solutions. Most of the points lie near to the solid curve. This suggests that these electrolytes are less adsorbed and therefore influence the mobility of the particle less. Higher mobilities in phosphate solutions relative to those in other electrolyte solutions would be accounted for by the preferential adsorption of phosphate ions onto the surface of the particle. It is known that phosphate ions are adsorbed to a greater extent than simpler ions like chloride and sulfate and their adsorption extends into the alkaline region (17).

The mobility vs. concentration curve for titanium dioxide particles in tripolyphosphate solution shows increasing mobility at low electrolyte concentrations, reaching a maximum, then decreasing at elevated concentrations. The rising portion of the curve is attributed to increasing charge density, while the maximum and decreasing portion are attributed to double layer compression from increasing gegenion concentration (22). This trend was also found in carbonate solutions as seen in Figure 1. However, the values of mobility in tripolyphosphate solutions are much higher than those in carbonate solutions. It is considered that polyvalent tripolyphosphate anions are preferentially adsorbed to give a higher surface charge relative to that from $CO_3^{2-}$ or $OH^-$ ions or both. The curve shown in Figure 6, i.e., the mobility vs. concentration curve at a constant pH, supports the above consideration. The difference between the mobilities at zero concentration and at a given concentration of tripolyphosphate could correspond to an increase in mobility by adsorption of the phosphate anions, since the pH effect of the solution is eliminated in this case. In carbonate solution, competitive adsorption would occur between $CO_3^{2-}$ and $OH^-$ ions, probably $CO_3^{2-}$ anions being less adsorbed than $OH^-$ ions as may be understood from Figure 4.

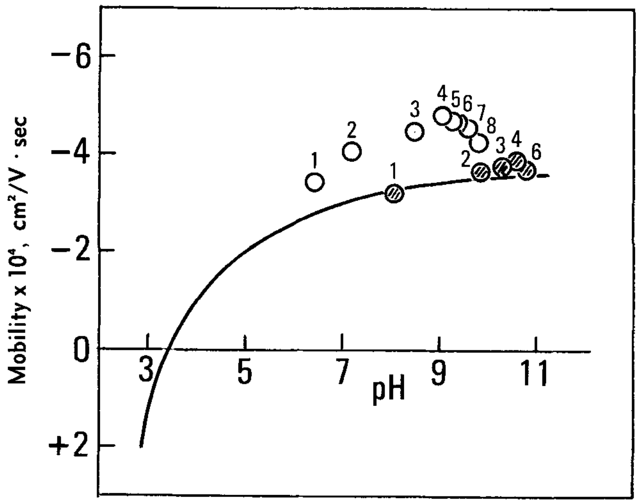

FIG. 4. Relation between mobility of titanium dioxide particle and the pH of sodium tripolyphosphate (○) or sodium carbonate (▨) solutions of different concentrations at 25 C: 1, 0.001%; 2, 0.005%; 3, 0.010%; 4, 0.030%; 5, 0.041%; 6, 0.050%; 7, 0.10%; 8, 0.20%.

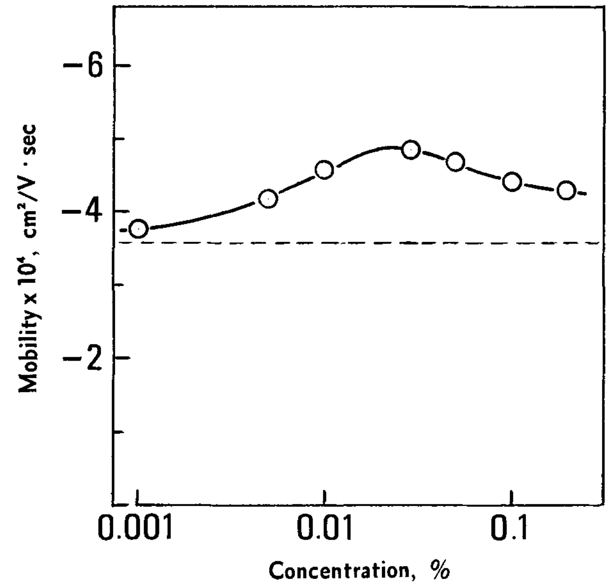

FIG. 6. Effect of concentration of sodium tripolyphosphate on mobility of titanium dioxide particle at a constant pH of 10.5. (Dashed line indicates mobility in the absence of phosphate at pH 10.5.)

### The Mobilities of Particles in Solutions of Acid and Neutral Polyphosphates

Partial substitution of one or two sodium atoms in the phosphate molecule by a hydrogen atom or atoms makes the mobility of titanium dioxide particle lower. As is shown in Table II (B), however, the extent of the decrease in mobility is relatively small if one takes into account depression of pH of the solution by this substitution. For example, the mobility of titanium dioxide particles in acid pyrophosphate solution is $-3.58$ $cm^2/V \cdot sec$ at pH 4.8, whereas the mobility in hydrochloric acid solution at this pH without the phosphate is $-1.80$. This indicates that even the acid or neutral phosphates in small concentrations greatly affect suspensions of colloidal particles.

From the above discussion, whatever the detailed mechanism may be, we can understand that poly- and metaphosphates have an effect in raising the mobility of a colloidal particle, which would be attributable to strong adsorption of poly- and metaphosphate anions onto the surface of the particle. The results presented will be discussed more fully in a forthcoming paper in connection with the dispersing action and builder effect of these phosphates.

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