The Electrokinetic Potential of Sparingly Soluble Salts

By Tetsuo MORIMOTO

(Received August 16, 1963)

Investigations concerning the dispersion of particles have been made in this laboratory by measuring the sedimentation volume of sparingly soluble salts in electrolyte solutions.[1] Actually the sedimentation volume of precipitated salts changes widely upon the addition of ions to water in which the particles are suspended. This fact suggests that the preferential adsorption of ions on the solid-liquid interface may result in the variation of charge density on it. The electrical charge on solid particles is the only cause of the repulsive force between them,[2] having been also the essential factor for interpreting the stability of hydrophobic colloids. The origin of the surface charge is, however, still obscure. In order to clarify, therefore, the surface charge or the electrokinetic potential and the origin of ionogenic substances, the present work has been carried out for barium sulfate, barium chromate, lead sulfate and lead chromate. For these purposes, two different samples of each salt were prepared, in each of which one of the two component ions of the precipitated salts were used in excess.

Also, the effects of the lattice ions and some non-lattice ions on the electrokinetic potential of the precipitated salts have been examined. Experiments have been carried out along lines analogous to this study by Reyerson et al.[3] and Buchanan and Heymann,[4] who investigated principally the charge of barium sulfate. Reyerson et al. report a negative charge on barium sulfate in water, while the result of Buchanan and Heymann is the reverse. It is, however, found in the present work that most of the precipitated salts tested may represent either a positive or negative charge in water according to the method of preparing the sample. Furthermore, a few measurements were carried out on the electrokinetic potential of the crystal surfaces in a solution containing two electrolytes, giving some information about the preferential adsorption of ions. It is also noticeable that some phosphates have a serious effect on the charge of the solid surface, as a citrate does.

Experimental

Materials.—All the materials used in this experiment were prepared by means of precipitation reaction; e. g., barium sulfate was prepared by allowing 1M barium chloride and 1M sodium sulfate to mix while being vigorously stirred in water heated at 80°C. The other materials were precipitated in the same manner except for different temperatures: barium chromate was prepared from barium chloride and potassium chromate at 60°C, lead sulfate from lead nitrate and sodium sulfate at 30°C, and lead chromate from lead nitrate and potassium chromate at 30°C. The precipitated salts were washed with water by repeating the decantation and filtration for a few months, until the electrical conductivity of the supernatant liquid attained a lower limiting value. Finally, the salts were washed with pure ethanol and dried at 110°C for several hours. Two different samples of each salt were provided in which either component ion was used in a 5% excess over the other when the salts were prepared.

Electrokinetic Measurements.—To determine the electrokinetic potential, the streaming potential method was used. The cells for the streaming potential measurement were almost the same as those described by Gortner[5] and by Reyerson et al.[3] In order to prevent the polarization of electrodes, the perforated platinum electrodes were substituted for by a reversible electrode, Ag-AgCl.[6] This device made it possible to develop the stable streaming potential between the electrodes. The precipitates were packed directly between the electrodes.

To develop a streaming potential, the solution was forced to flow through the diaphragm under a given pressure from one reservoir to the other. The nitrogen was used to maintain the pressure needed for the streaming potential measurement. The streaming potentials developed were measured by the vacuum-tube potentiometer with a highly sensitive galvanometer attached. Besides the measurement of the streaming potential, it was necessary to measure the specific conductance of the solution in the pores of the diaphragm. A sensitive conductance bridge was used satisfactorily for this purpose, and the cell constant was determined in each packed diaphragm by using a 0.01M

---

[1] T. Morimoto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 236 (1960).

[2] E. J. W. Verwey, *Kolloid-Z.*, **13**, 46 (1954).

[3] L. H. Reyerson, I. M. Kolthoff and K. Coad, *J. Phys. & Colloid Chem.*, **51**, 321 (1947).

[4] A. S. Buchanan and E. Heymann, *J. Colloid Sci.*, **4**, 137 (1949).

[5] R. A. Gortner, *Trans. Faraday Soc.*, **36**, 63 (1940).

[6] A. S. Brown, *J. Am. Chem. Soc.*, **56**, 646 (1934).

potassium chloride solution. From the measurement of the streaming potential developed, the specific conductance of the liquid in the diaphragm, and the pressure applied to force the liquid to flow, it was possible to calculate the electrokinetic potential (ζ-potential) from Helmholtz-Smoluchowski's equation:

$$\zeta=\frac{4\pi\eta\kappa E}{DP} \tag{1}$$

where E is the streaming potential; κ, the specific conductance of a liquid in the diaphragm; P, the pressure driving the liquid; η, the viscosity of the streaming liquid, and D, the dielectric constant of the liquid. In any given run the linear relationship between E and P was checked, because the leakage of precipitated substances from a diaphragm might cause a deviation from linearity. Practically, the gradient of the straight line obtained by plotting E against P, was used for calculating the electrokinetic potential. It is shown by Eq. 1 that the greater the specific conductance of a solution, the less the streaming potential develops and, accordingly, the greater the experimental error, in a system consisting of one solid and one liquid. At a higher concentration of an electrolyte, therefore, the streaming potential measurement is difficult. In the present work the upper limit of the electrolyte concentration capable of the measurement was about 0.02N.

Results and Discussion

Electrokinetic Potentials in Water.—The ζ-potentials obtained on sparingly soluble salts in water are presented in Table I. Most samples studied have a charge of the same sign as that of the lattice ions used in excess when the sample was prepared; e. g., the ζ-potential of barium sulfate prepared from excess barium ions is 11.2 mV., while that of the sample prepared from excess sulfate ions is −6.10 mV. It is often described how the ζ-potential of such ionogenic substances as silver iodide is greatly affected by the adsorption of ions, especially that of lattice ions.⁷⁾ Accordingly, it is plausible that, if the one component ions of the substance are present in excess when the substance is formed, the surface lattice points occupied by the ions will be increased in number compared to those occupied by the other component ions. The present results not only prove the above statement to be valid, but also establish the great persistence of the ions against washing. Therefore, we may generally conclude that the surface of an ionogenic substance has a charge of the same sign as that of the ions used in excess on its preparation.

TABLE I. ζ-POTENTIALS OF SPARINGLY SOLUBLE SALTS IN WATER

Substance	Reactant used in excess	mV.
$BaSO_4$	$BaCl_2$	+11.2
	Na_2SO_4	− 6.10
$BaCrO_4$	$BaCl_2$	+10.2
	K_2CrO_4	− 7.75
$PbSO_4$	$Pb(NO_3)_2$	+16.0
	Na_2SO_4	+ 7.00
$PbCrO_4$	$Pb(NO_3)_2$	+25.7
	K_2CrO_4	−15.1

Lead sulfate is an exception. In the case of lead sulfate, the two samples have a positive charge irrespective of the method of preparing them; the ζ-potential is 16.0 mV. on the sample prepared from excess lead ions and 7.00 mV. on the sample prepared from excess sulfate ions. According to the experiments carried out in more detail in our laboratory,⁸⁾ the charge of lead sulfate appears to be always positive in water, regardless of such conditions of preparation as the kind of reagents and the pH value of the reacting solutions.

In Table II the solubilities of all the samples studied in this experiment are presented.⁹⁾ The solubility of lead sulfate is the greatest of those of the four salts, while that of lead chromate is the least. Because of this relatively larger solubility of lead sulfate and the extremely small solubility of lead hydroxide,¹⁰⁾ it is conceivable that the surface of lead sulfate crystals is hydrolyzed partially in water to produce lead hydroxide. Considering the fact that most metal hydroxides have a positive charge in water,¹¹⁾ one can understand the fact that the surface of lead sulfate crystals has a positive charge. This, however, does not occur on the surface of a lead salt with so small a solubility as lead chromate.

TABLE II. SOLUBILITIES OF SPARINGLY SOLUBLE SALTS IN WATER (25°C)⁹⁾

Substance	$BaSO_4$	$BaCrO_4$	$PbSO_4$	$PbCrO_4$*
Solubility (mol./l.)	1.25×10^{-5}	1.64×10^{-5}	14.8×10^{-5}	0.053×10^{-5}

* The value obtained at 20°C.

The Electrokinetic Potential in an Electrolyte Solution.—As has been described above, it is seen that the lattice component ions which were used in excess on preparation have a pronounced effect on the surface of ionogenic

---

7) A. E. Alexander and P. Johnson, "Colloid Science," Clarendon Press, Oxford (1949).

8) To be published.

9) Y. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Van Nostrand, New York (1940).

10) P. Deschamps and B. Charreton, *Compt. rend.*, **232**, 162 (1951).

11) J. Sameshima, "Koshitsugaku," Shokabo, Tokyo (1949).

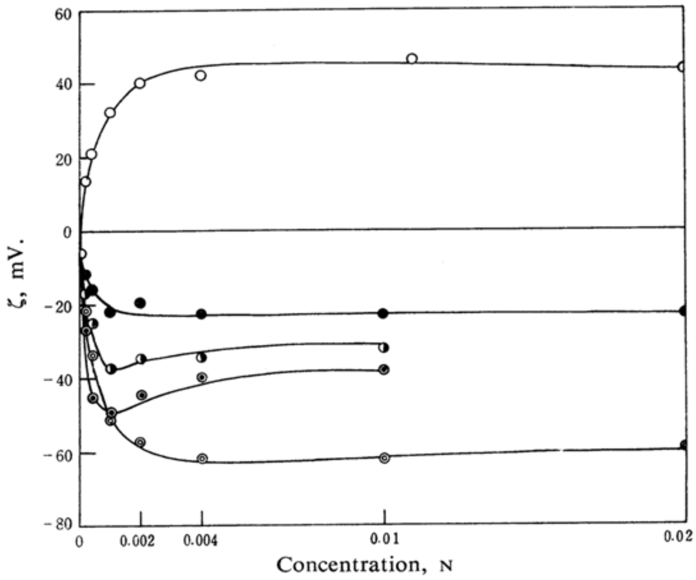

Fig. 1. ζ-Potentials of $BaSO_4$ in solutions of electrolytes.
○ $Ba(NO_3)_2$ ● Na_2SO_4 ⊙ Na_2SO_4 and sodium citrate
◎ Sodium citrate · ◐ $Ba(NO_3)_2$ and sodium citrate.

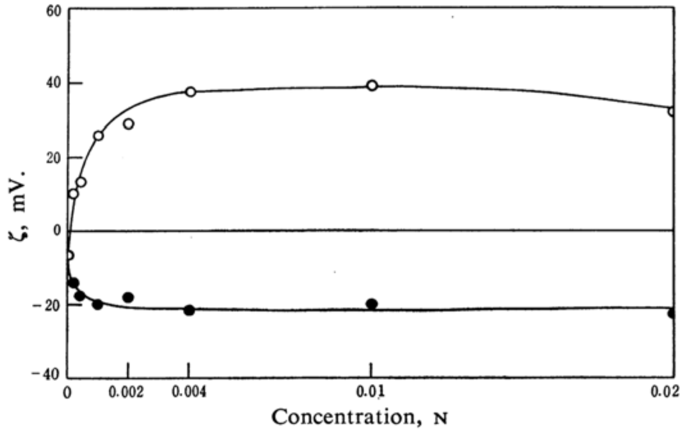

Fig. 2. ζ-Potentials of $BaCrO_4$ in solutions of lattice ions.
○ $Ba(NO_3)_2$ ● K_2CrO_4

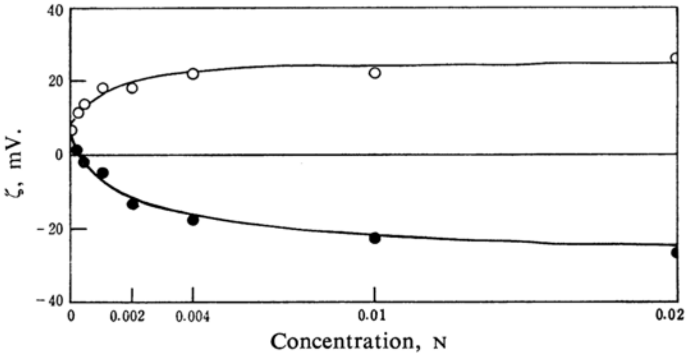

Fig. 3. ζ-Potentials of $PbSO_4$ in solutions of lattice ions.
○ $Pb(NO_3)_2$ ● Na_2SO_4

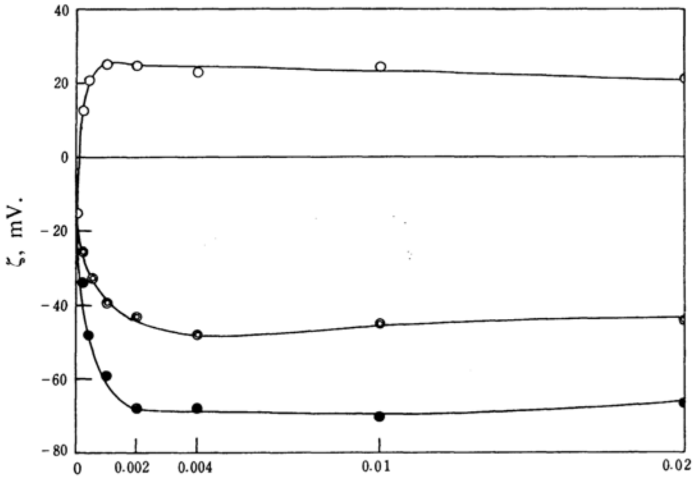

Fig. 4. ζ-Potentials of $PbCrO_4$ in solutions of electrolytes.
○ $Pb(NO_3)_2$ ● K_2CrO_4 ◎ Sodium citrate

substances. Similarly, it is expected that when the lattice ions are added to the water with which the surface of the salt crystals comes in contact, they will have a great influence on the surface charge. In the preliminary experiments, by using samples charged both positively and negatively in water, the effect of barium ions on the ζ-potential of barium sulfate was tested. It was thus found that the ζ-potential curves were nearly parallel to each other, independently of their initial ζ-values. This was the case also with the effect of sulfate ions. Hence, in this series of experiments, one kind of sample for each material was chosen. The results obtained are shown in Figs. 1—4. As expected, it is seen that the lattice ions have a great effect on the surface charge of the precipitated salts. The barium ions, even at an extremely small concentration, charge barium sulfate, which originally has a negative charge, positively. After that the ζ-value increases with the increasing concentration of barium nitrate to a limiting value of 45 mV. Sodium sulfate increases the negative charge of barium sulfate, but the change in ζ-potential caused by sulfate ions is much less than that caused by barium ions.

The results obtained in this work agree well with those of Reyerson et al.(3) and Buchanan and Heymann(4) in that barium ions affect barium sulfate more pronouncedly than sulfate ions, irrespective of the ζ-value in water. Furthermore, Reyerson et al. concluded that barium ions act peptizingly and sulfate ions coagulatingly on barium sulfate. In our laboratory it has been found that the sedimentation volume of barium sulfate decreased steeply in the presence of barium ions, whereas no great changes occurred in the solution of sulfate ions.(1) These phenomena may be explained in terms of the change in ζ-potential.

The behaviors of barium ions and chromate ions for barium chromate are quite similar to those of barium ions and sulfate ions respectively for barium sulfate. On lead sulfate, however, both lead ions and sulfate ions have a very weak effect compared to that of barium ions on barium sulfate. It is, therefore, characteristic that the initial part of ζ-potential curves increases or decreases slowly. Also, the limiting ζ-values are only +20 mV. and −20 mV. respectively. On the contrary, the change in the ζ-potential of lead chromate by lead ions and chromate ions is very large; the ζ-value increases from −15 mV. to +25 mV. in the presence of lead ions and decreases from −15 mV. to −70 mV. in the presence of chromate ions. In this case, the effect of chromate ions is nearly equal to or slightly greater than that of lead ions. The only previous finding concerning the ζ-potential of lead chromate, obtained by Reyerson et al.,(3) shows fairly good agreement with the present finding. Certainly the fact that the sedimentation volume of lead chromate is more decreased in the presence of chromate ions than in the presence of lead ions, must be related closely to the ζ-potential change.

It is strange that, on barium sulfate and barium chromate, the lattice cations, barium ions, have a more serious effect than the anions, while on lead chromate the lattice anions, chromate ions, have the more serious effect. Generally, the adsorbability of ions on a polar solid surface from a solution depends largely upon their hydrating tendency

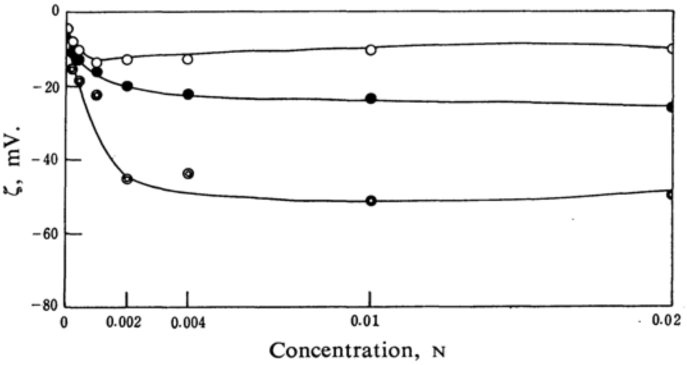

Fig. 5. ζ-Potentials of $BaSO_4$ in Solutions of phosphates and KOH.
○ KOH ● Na_2HPO_4 ◎ $Na_5P_3O_{10}$

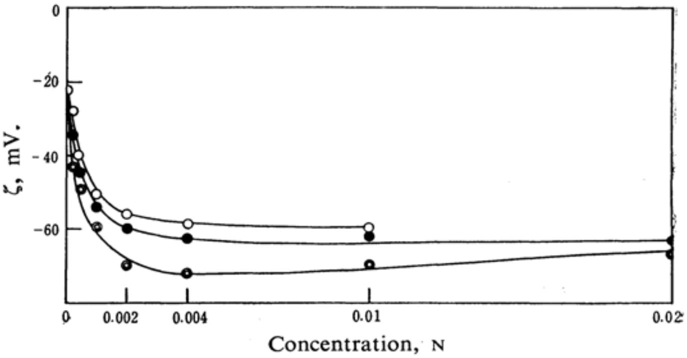

Fig. 6. ζ-Potentials of $PbCrO_4$ in solutions of phosphates and KOH.
○ KOH ● Na_2HPO_4 ◎ $Na_5P_3O_{10}$

and on their valency; the stronger the tendency, the less the adsorbability. However, the solids have also their own problems. As is shown in Table II, there are large differences in solubility among the materials used. The solubility decreases in the order: lead sulfate>barium chromate, barium sulfate>lead chromate. The variation of the potential is, however, just the reverse. Buchanan and Heymann⁴⁾ reported a similar tendency when strontium sulfate, lead sulfate and barium sulfate are used. Thus we may conclude that the smaller the solubility of the ionic crystal, the greater the effect of lattice ions on its surface. Really the variation in the ζ-potentials of lead chromate upon the addition of lead or chromate ions amounts to 50 mV., whereas that of lead sulfate upon the addition of lead or sulfate ions is only 20 mV.

At the surface of a crystal having a smaller solubility, the electrical double layer is possibly constructed more definitely than at the surface of a crystal having a larger solubility. When the solubility of a solid is large, the lattice ions will be diffused in large quantities across the electrical double layer, bringing about the agitation of the double layer; therefore, the fixation of ions on the "fixed layer" occurs only with difficulty. Of course, on such a solid surface the adsorption of indifferent ions also becomes difficult.

The interactions of a salt with its lattice ions, should be considered to cause partially the incorporation of the ions with the solid surface simultaneously with their adsorption on the fixed layer. Lead chromate shows well-defined prism-shaped crystals under an electron microscope.¹⁾ The surface of well-defined crystals will be favorable for producing the streaming potential corresponding to the charge in the diffused layer of an electrical double layer as compared with an irregular surface, because little turbulences occur. The large change in the ζ-value of lead chromate may be partially due to this reason.

The Effect of Foreign Ions.—Sodium citrate has a remarkable effect on the ζ-potential of barium sulfate and lead chromate, as Figs. 1 and 4 show, in accordance with the results of Reyerson et al.³⁾ Apparently, on barium sulfate the effect of sodium citrate is much greater than that of sodium sulfate, whereas on lead chromate it is less than that of potassium chromate. Because of the possibility of forming a complex of citrate ions with barium ions,[12] citrate ions will be adsorbed strongly onto the surface of barium sulfate.

By using sodium citrate and the lattice ions of barium sulfate, the effect of mixed electrolytes on the ζ-potential of barium sulfate was investigated, as is shown in Fig. 1. In these cases, the concentration indicated in abscissa should be read as that of each electrolyte present, so that the equal equivalents of the two electrolytes were dissolved in a solution. The ζ-potential curves of barium sulfate in these two solutions represent an almost identical development over all the range of concentration examined. As has been described above, the effect of sodium citrate on the ζ-potential of the barium sulfate crystal is greater than that of sodium sulfate. In the solution containing these two electrolytes together, the ζ-potential curve of barium sulfate initially goes parallel with the curve obtained in the presence of sodium citrate only, arriving at a limiting value. After that it rises, differing substantially from the effect of sodium citrate only. This means that, because of the stronger adsorption of citrate ions, it excels the adsorption of sulfate ions at smaller concentrations, but at increased concentrations sulfate ions also take part in the adsorption on the fixed layer, together with citrate ions, causing a considerable decrease in the negative ζ-potential of barium sulfate. Even when we use barium nitrate and sodium citrate as mixed electrolytes, the results are almost the same. The resultant ζ-potential rises more steeply after the attainment of the minimum than in the former case, but it does not exceed the isoelectric point. In any case, it is characteristic of the adsorption of ions from a mixed electrolyte solution that the preferential adsorption of the ion affecting more strongly occurs at lower concentrations. The sedimentation volume of barium sulfate measured in these mixed electrolyte solutions decreases initially, attains a minimum, and then rises, corresponding to the change in the ζ-potential.[13] In a solution of sodium citrate only, however, the sedimentation volume of barium sulfate remains almost constant after attaining a limiting value, corresponding to the change in the ζ-potential. This fact is positive evidence that the ζ-potential is responsible for the change in the sedimentation volume of powders. Although one can expect a similar conclusion concerning the ζ-potential of lead chromate in mixed electrolyte solutions, it was impossible to observe this because the extremely small solubility of lead citrate does not permit both lead ions and citrate ions to coexist at the concentrations used here.

Recently studies of the properties of various phosphates which differ in degree of polymerization have been carried out. If they are used on surface phenomena, it may be expected that they will behave as polyelectrolytes. In the present work, phosphates of a lower degree of polymerization were used, along with potassium hydroxide, to investigate the effect on the surface charge of barium sulfate and lead chromate. As shown in Fig. 6, triphosphate, orthophosphate and hydroxyl ions all seriously decrease the ζ-potential of lead chromate. It is peculiar that hydroxyl ions have a large effect in this case, probably because of their greater adsorbability arising from the extremely small solubility of lead hydroxide. For barium sulfate, three kinds of ions affect it differently: the effect of triphosphate is the greatest, as it is for lead chromate, while that of orthophosphate is moderate and that of hydroxyl ions, very small as is shown in Fig. 5. It appears that there are differences between the adsorbabilities of various phosphates corresponding to their polymerization degrees, and that the higher the polymerization degree, the stronger the adsorbability. The detailed observation of the effect of such a series of phosphates on surface properties is a problem for future study.

Summary

1) The ζ-potentials of such sparingly soluble salts as barium sulfate, barium chromate, lead(II) sulfate and lead(II) chromate have been measured in water by means of the streaming potential method. Most samples prepared by using either lattice ion in excess have a charge of the same sign as that of the ion. This suggests that the lattice ions occupy many more lattice points on the surface than do other ones, and that it is difficult to remove them by washing. One exception is lead(II) sulfate, in which the ζ-potentials of the two samples are positive. This seems to depend on the surface hydrolysis of lead(II) sulfate.

2) The ζ-potentials vary widely also when the lattice ions are added to water. The effect of both lattice ions are the greatest on lead(II) chromate and the least on lead(II) sulfate.

---

[12] J. Schubert and J. W. Richter, *J. Am. Chem. Soc.*, **70**, 4259 (1948).

[13] T. Morimoto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 74 (1960).

[14] The solubility of lead citrate is 0.05344 g./100g. (25°C), cf. Ref. 9.

The solubility of the solids is an important factor affecting the variation of ζ-potentials when the lattice ions are added.

3) In order to investigate the effect of the mixed electrolyte solution on the ζ-potential of barium sulfate, sodium citrate, which has a remarkable effect by itself, has been mixed with sodium sulfate or barium nitrate. The resultant ζ-potential curves show a definite minimum, which demonstrates that, although the adsorption of citrate ions excels that of sulfate or barium ions at smaller concentrations, the latter become comparable to the former at larger concentrations.

4) The surface chemical action of triphosphate and orthophosphate ions has been tested. As expected, the higher the polymerization degree of phosphates, the larger the effect on the charge of solid surfaces.

The author wishes to express his deep appreciation to Professor Masaji Miura of Hiroshima University for his valuable advice and encouragement, and to Mr. Masashi Sakamoto for his assistance in this work.

Department of Chemistry
Faculty of Science
Okayama University
Tsushima, Okayama