# The Electrokinetic Potential of Lead(II) Sulfate

By Tetsuo MORIMOTO, Yutaka HIRATA and Shigeharu KITTAKA

(Received July 30, 1964)

It was reported in a previous paper that the signs of the electrokinetic potentials of sparingly soluble salts in water generally agree with those of the excess ions used when the salts are prepared. Lead(II) sulfate, however, was observed to be an exception.[1] Samples of lead sulfate which were prepared using either excess lead or sulfate ions both had positive charges. Buchanan and Heymann[2] observed that lead sulfate possesses a positive charge in a saturated solution. In the present paper, further studies of the electrokinetic behaviors of lead sulfate have been carried out in order to determine the origin of its positive electrokinetic potential. The electrokinetic potentials have been determined by applying the streaming potential method to samples prepared by different methods and treated at various temperatures, and the surface acidities of the samples have been investigated by the dye-adsorption method.

## Experimental

**Materials.** — Two solutions containing 0.005 M lead nitrate and 0.005 M sodium sulfate were mixed at room temperature in a large flask. In mixing, one reagent was used in a 5% excess over the other. The precipitations occurred after the solutions had been vigorously mixed for one minute or less. The pH values of the supernatant liquids were in the range from 4.60 to 4.74. The precipitates formed were washed with conductivity water by decantation and filtration until the pH values and the conductivities of the supernatant liquids attained limiting values. After these procedures the final pH values were 6.10—6.20 at 25°C. Finally, the samples were dried at 110°C for three hours. Parts of each sample were treated at 300, 500 and 700°C in an electric oven for an hour each.

**Electrokinetic Measurements.** — The streaming potential method was used for the determination of the electrokinetic potentials ($\zeta$-potentials). For the measurement of the streaming potentials, an apparatus and techniques similar to those described in previous papers[1,3] were employed. The specific conductivity of the cell packed with the powdered sample was obtained by using the conductometer made by the Toa Dempa Co. The streaming potentials produced on the electrodes placed at the ends of the diaphragm were read by a precision potentiometer and were plotted against the pressure applied on the liquids flowing through the diaphragm. The linear relation obtained between them made possible the calculation of the $\zeta$-potentials by using the Helmholtz-Smoluchowski equation. All the measurements were carried out at 15—20°C.

**Surface Acidity.**—In order to test the surface acidities, the dye-adsorption method was employed. 0.3 g. samples of the powders were shaken with 4 cc. of an isooctane solution containing 0.01% of methyl red.[4] After the adsorption of the dye molecules, the powders were separated and dried in air. The color of the adsorbed molecules on the surface of the powders was analyzed against magnesia as a reference by means of a Shimadzu spectrophotometer.

## Results and Discussion

The $\zeta$-potentials obtained in water are summarized, together with those of the samples used, in preliminary experiments, in Table I. These values are equilibrium values obtained after a long streaming of water.

It may be seen from Table I that all the values of the $\zeta$-potential of lead sulfate have a positive sign, irrespective of the kinds of reagents used, of the excess ions, and of the pH values of the solutions. It was found in a previous paper that the surfaces of lead(II) chromate, barium sulfate and barium chromate have charges of the same sign as that of the excess ion used in the preparation.[1] This suggests that the lattice ions extensively occupy the lattice points on the surface and that it is very difficult to remove them by washing. However, this is not true for lead sulfate.

The $\zeta$-potentials, obtained from measurements on the samples at intervals of about one hour, of lead sulfate, treated at different temperatures, vary slowly with time to an equilibrium value which is positive, as is shown in Figs. 1 and 2. The equilibrium $\zeta$-potentials are plotted against the treatment temperatures in Fig. 3. The $\zeta$-values decrease

---

[1] T. Morimoto, This Bulletin, 37, 386 (1964).

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

[3] T. Morimoto and M. Sakamoto, This Bulletin, 37, 719 (1964).

[4] K. Tanabe and M. Katayama, *J. Res. Inst. Catalysis, Hokkaido Univ.*, 7, 106 (1956); C. Walling, *J. Am. Chem. Soc.*, 72, 1164 (1950).

TABLE I. ζ-POTENTIALS OF LEAD SULFATE IN WATER

| Sample | Reagent | | pH of solution | ζ-Potential |
|---|---|---|---|---|
| 1 | 0.005 M $Na_2SO_4$<br>1900 ml. | 0.005 M $Pb(NO_3)_2$<br>2000 ml. | 4.60 | +31.0 |
| 2 | 0.005 M $Na_2SO_4$<br>2000 ml. | 0.005 M $Pb(NO_3)_2$<br>1900 ml. | 4.74 | +28.6 |
| 3 | 1 M $Na_2SO_4$<br>200 ml. | 1 M $Pb(NO_3)_2$<br>180 ml. | 2.65 | +23.6 |
| 4 | 1 M $Na_2SO_4$<br>200 ml. | 1 M $Pb(NO_3)_2$<br>180 ml. | 1.04* | +21.2 |
| 5 | 1 M $Na_2SO_4$<br>180 ml. | 1 M $Pb(NO_3)_2$<br>200 ml. | 2.50 | +32.9 |
| 6 | 1 M $Na_2SO_4$<br>200 ml. | 1 M $PbAc_2$<br>180 ml. | 6.70 | +12.5 |
| 7 | 1 M $Na_2SO_4$<br>180 ml. | 1 M $PbAc_2$<br>200 ml. | 6.53 | +13.1 |

* Nitric acid was added to the lead nitrate solution prior to the preparation of the precipitate.

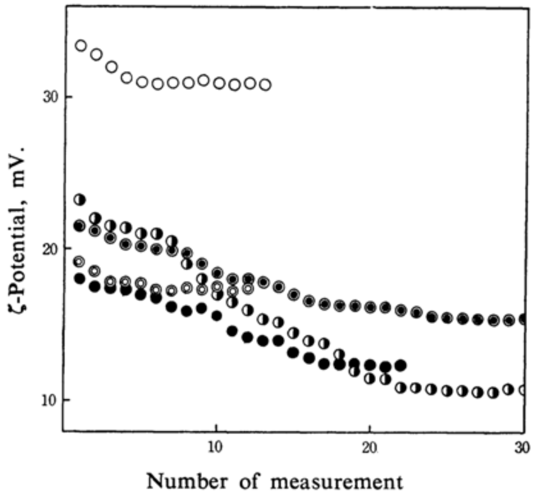

Fig. 1. ζ-Potentials of lead sulfate prepared from excess lead ions and treated at: ○ no heat treatment, ◎ 100°C, ⊙ 300°C, ◑ 500°C, ● 700°C.

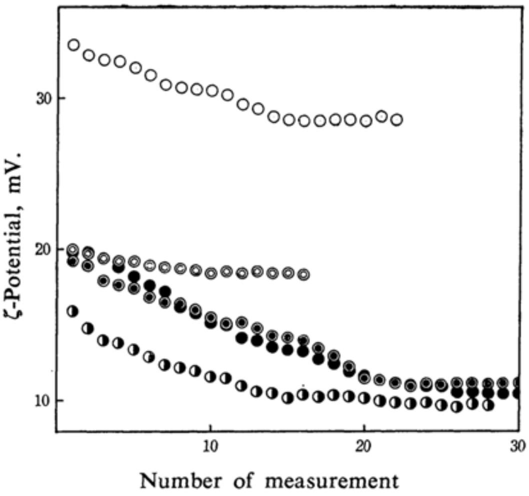

Fig. 2. ζ-Potentials of lead sulfate prepared from excess sulfate ions and treated at: ○ no heat treatment, ◎ 100°C, ⊙ 300°C, ◑ 500°C, ● 700°C.

initially to an almost constant value, irrespective of the kinds of excess ions used in the preparation of the samples.

Figure 4 shows the reflectance spectrum of lead sulfate, which adsorbed the molecules of methyl red. The yellow colors of the samples treated at higher temperatures indicate a decrease in the surface acidities with a rise in the treatment temperature. The same tendency has been seen in samples prepared from both excess lead ions and excess sulfate ions.

When the samples treated at higher temperatures were exposed to water vapor, the surfaces of the samples recovered their original acidities. It may be seen from Fig. 5 that the longer the time of exposure to water vapor, the deeper the red color of the adsorbed dye molecules, and, therefore, the stronger the acidity of the surface.

If lead sulfate is hydrolyzed in an aqueous solution, the following relations will hold in equilibrium at 25°C:

$$[Pb^{2+}]\,[SO_4{}^{2-}]=K_S{}^{5)}=1.58\times10^{-8} \qquad (1)$$

$$[Pb^{2+}]\,[OH^-]^2=K_B{}^{6)}=3\times10^{-20} \qquad (2)$$

$$[H^+]\,[OH^-]=K_W=10^{-14} \qquad (3)$$

$$2[Pb^{2+}]+[H^+]=2[SO_4{}^{2-}]+[OH^-] \qquad (4)$$

The hydrogen ion concentration which can satisfy these four equations is $10^{-6.2}$ at 25°C. The pH value of the saturated solution of

---

5) J. A. Cowperthwaite and V. K. LaMer, ibid., **53**, 4342 (1931).

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

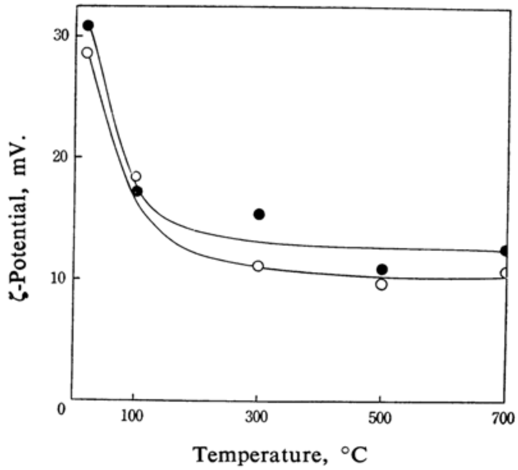

Fig. 3. Dependence of the ζ-potential of lead sulfate on the pretreatment temperature.
● lead ion excess, ○ sulfate ion excess

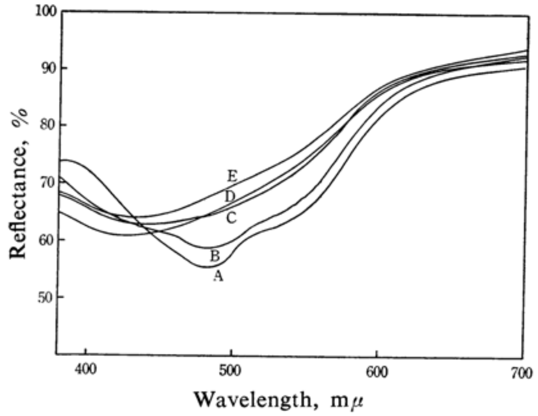

Fig. 4. Reflection spectra of methyl red adsorbed on lead sulfate treated at: A, no treatment; B, 100°C; C, 300°C; D, 500°C; E, 700°C.

lead sulfate should, therefore, be 6.2. The experimental pH values of the saturated solution of lead sulfate were 6.10—6.20, in good agreement with the calculated value. This suggests that the surface hydrolysis of lead sulfate leaves lead hydroxide on its surface although the saturated solution becomes acidic. From these considerations, it seems plausible that the lead sulfate produced from an aqueous phase and dried at lower temperatures has an acidic surface due to surface hydrolysis in the presence of adsorbed water. If the sample is treated at higher temperatures, the sulfuric acid will be removed, a solid surface being a basic characteristic of adsorbed dye molecules. The inversion of the surface acidity of the sample by water adsorption or by immersion in water can probably be explained by additional hydrolysis on the surface. In the measurement of the ζ-potentials on such hydrolyzed samples of lead sulfate, the solid surface may largely act like lead hydroxide.

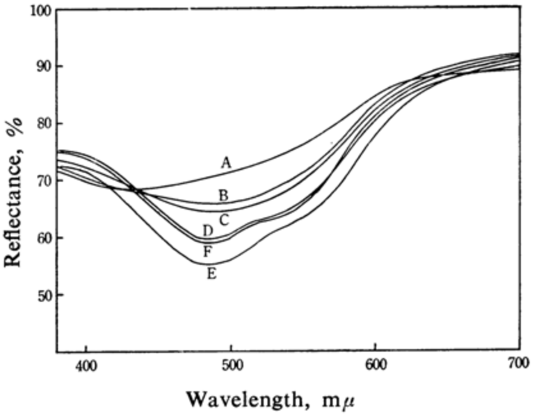

Fig. 5. Reflection spectra of methyl red adsorbed on lead sulfate treated at 700°C (A) and then exposed to saturated water vapor at 22°C for 1 hr. (B), 3 hr. (C), 24 hr. (D), 30 hr. (E). Sample F was immersed in water for 3 days and after that dried at 110°C for 1 hr.

In order to test the ζ-potential of lead hydroxide, a sample was prepared in the following way: in order to produce lead oxide pure lead oxalate was decomposed in an electric oven held at 600°C for an hour. The ζ-potential of this sample was found to be +10.1 mV. in water. Lead oxide can be hydrated to form surface hydroxyl groups in water. The fact that the surface of lead oxide has a positive charge is probably the result of the dissociation of surface hydroxyl groups thus formed:

$$-\mathrm{PbOH} \rightarrow -\mathrm{Pb}^{+} + \mathrm{OH}^{-}$$

These considerations appear to indicate why the ζ-potential of lead sulfate is always positive in water. In this case, the preferential adsorption of hydrogen ions produced by surface hydrolysis may more or less contribute to the surface charge of lead sulfate. By progressive treatment at higher temperatures, the ζ-potentials decrease to a constant value, probably because the lead oxide produced by heat treatment by the condensation of surface hydroxyl groups, or by the decomposition of lead sulfate, can not be easily rehydrated on immersion in water, resulting in a decrease in the charge density on the surface.

## Summary

The ζ-potential of lead sulfate has been studied by applying the streaming potential

method to samples obtained by various preparative methods and subjected to various temperature treatments. All the ζ-potentials measured have a positive sign, irrespective of such conditions as the kinds of reagents and excess ions used in the preparation or the pH value of the reacting solution. It has been postulated that the surface of lead sulfate is hydrolysed to produce lead hydroxide, whose ζ-potential is explicit in the measurement of the streaming potential of lead sulfate. This is supported by the pH value of the saturated solution of lead sulfate. The surface behavior of lead sulfate in relation to the dye adsorption can also be explained in this way.

*Department of Chemistry*
*Faculty of Science*
*Okayama University*
*Tsushima, Okayama*