

Formation and Solubility of Lead(II) Compounds at Various pH Values in Aqueous Suspensions Containing Acetate Ions

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Received July 31, 1978

When aqueous suspensions containing NaOH and $\text{Pb}(\text{OAc})_2$ in various mol ratios were subjected to aging at 25, 50, and 80°C, formation of $\text{Pb}(\text{OAc})_2 \cdot 2\text{Pb}(\text{OH})_2$, $\text{PbO} \cdot 2/5\text{H}_2\text{O}$, orthorhombic PbO, or tetragonal PbO took place, depending on the pH, temperature, and acetate ion concentration. Their solubilities in the suspension media with various pH values at 25°C were determined.

INTRODUCTION

We found in the previous study that when aqueous suspensions of gelatinous precipitates, prepared by mixing solutions of PbCl_2 and NaOH in various mol ratios ($4 < \text{pH} < 14$), are subjected to aging at temperatures 25, 50, and 80°C, one of $\text{Pb}(\text{OH})\text{Cl}$, $\text{PbCl}_2 \cdot 3\text{PbO} \cdot 2/3\text{H}_2\text{O}$, $\text{PbCl}_2 \cdot 6\text{PbO} \cdot 2\text{H}_2\text{O}$, or a mixture of the two out of these three is formed depending mainly on the pH of the suspension. Their solubilities at 25°C in the suspension media with various pH values have been reported.¹⁾

In one of the subsequent studies on the hydrolysis of lead (II) ions, we clarified the chemical compositions and crystal structures of lead compounds obtained by aging at temperatures 25, 50, and 80°C of aqueous suspensions containing NaOH and $\text{Pb}(\text{OAc})_2$ in various mol ratios. The experimental results on the products and their solubilities at various pH values of suspension media will be reported.

EXPERIMENTAL

The starting suspensions of gelatinous and whitish precipitates were prepared as follows: 0.1 ml of $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ (analytical grade) was dissolved in 100 ml of water to form a solution. To this an aqueous solution of NaOH was added in required amounts. Each suspension was diluted with water to 200 ml in a polyethylene bottle. A number of such suspensions (0.5 M $\text{Pb}(\text{OAc})_2$) of various mol ratios expressed by $2\text{NaOH}/\text{Pb}(\text{OAc})_2 (=R)$ from 0.1 to 5.0 were subjected to aging at 25, 50, and 80°C for a period of 50 to 300 h until the reaction reached equilibrium where no change in the pH values occurred with a time lapse as measured at 25°C by an electrode pH meter. The experimental procedures in the present study are substantially the same as those previously described.²⁾

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RESULTS AND DISCUSSION

The pH values at 25°C of the suspensions, containing 0.5 M $\text{Pb}(\text{OAc})_2$, which were subjected to aging at 25 (○) and 50°C (●) are plotted against the R values in Fig. 1.

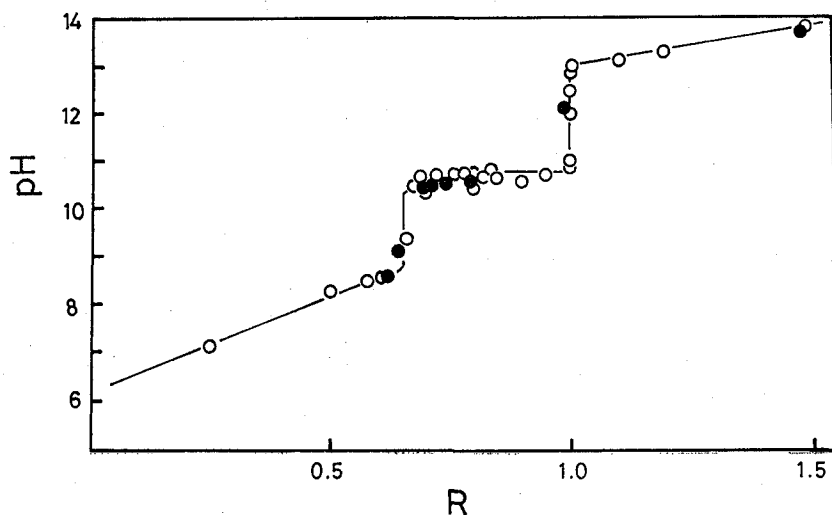


Fig. 1. The pH values of suspensions with various R values subjected to aging at 25 (○) and 50°C (●).

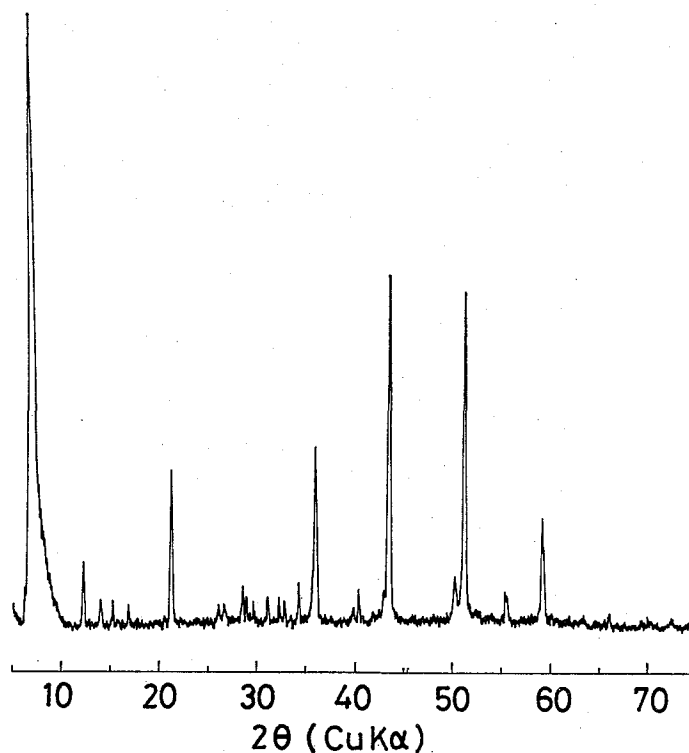


Fig. 2. X-ray diffraction pattern of $\text{Pb}(\text{OAc})_2 \cdot 2\text{Pb}(\text{OH})_2$ (=phase A).

X-ray analysis using $\text{FeK}\alpha$ or $\text{CuK}\alpha$ radiation has verified that the products, obtained by aging at 25°C for $0.5 \leq R \leq 5.0$, consist of one of phase A (Fig. 2), B, C, D, or a mixture of the two out of these four, the formation of which depending on the R values. The products of phase B are whitish, their X-ray diffraction data were identical with those of $\text{PbO} \cdot 2/3\text{H}_2\text{O}$ ³⁾ and $\text{PbO} \cdot 2/5\text{H}_2\text{O}$.⁴⁾ The products of phase C are greenish, having

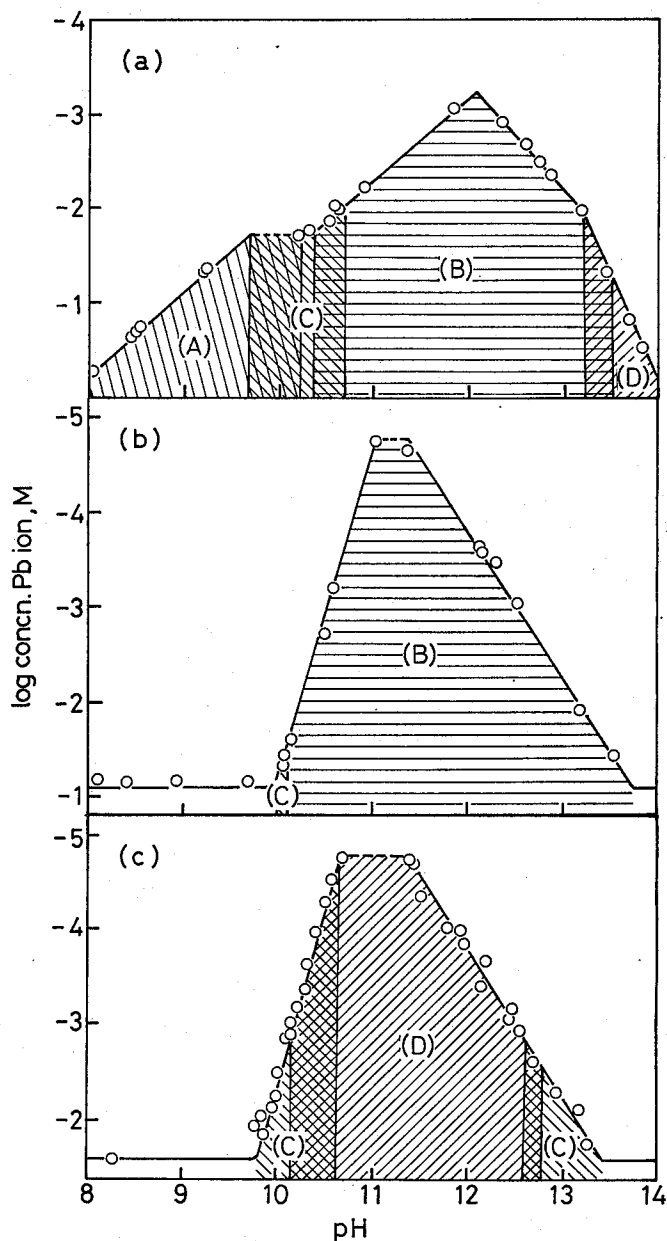


Fig. 3. Solubilities of lead compounds (A= $\text{Pb}(\text{OAc})_2 \cdot 2\text{Pb}(\text{OH})_2$, B= $\text{PbO} \cdot 2/5\text{H}_2\text{O}$, C=orthorhombic PbO , D=tetragonal PbO) at various pH values of the suspensions with 0.5(a), 0.008(b) and 0.025M $\text{Pb}(\text{OAc})_2$ (c) subjected to aging at 25°C .

the same crystal structure as that of orthorhombic PbO .⁵⁾ The products of phase D are red, having the same crystal structure as tetragonal PbO .⁶⁾ The R range for the formation of phase D became wider as the aging temperature was increased from 25 to 50 and from 50 to 80°C. The aging products, obtained at 80°C for $R=0.7$, consisted only of phase D, whereas all products, obtained at 25–80°C for $R \leq 0.5$, were white and amorphous on X-ray analysis.

Whitish samples, each consisting only of phase A or B with particles of size 5 μm or greater, were selected from the products and subjected to the usual chemical analysis. The sample of phase A was found to be $\text{Pb}(\text{OAc})_2 \cdot 2\text{Pb}(\text{OH})_2$, whereas the samples of phase B were $\text{PbO} \cdot 2/5\text{H}_2\text{O}$, not $\text{PbO} \cdot 2/3\text{H}_2\text{O}$.

In order to study the effect of the acetate ion concentration on the products, similar experiments were carried out at 25°C using a number of suspensions containing one of 0.2, 0.08, or 0.025 M $\text{Pb}(\text{OAc})_2$ and NaOH in the range $0.2 \leq R \leq 5.0$. No precipitation took place for $R \leq 0.5$ (where $\text{Pb}(\text{OAc})_2 \cdot 2\text{Pb}(\text{OH})_2$ is formed in the above experiments), because of small Pb ion concentration. Formation of phase C was observed for 0.2 and 0.08 M $\text{Pb}(\text{OAc})_2$ with $R=0.9$. In the range $1.0 \leq R \leq 5.0$, the products were found to consist of $\text{PbO} \cdot 2/5\text{H}_2\text{O}$ (phase B) for both of 0.2 and 0.08 M $\text{Pb}(\text{OAc})_2$, and of one of orthorhombic, tetragonal PbO or a mixture of the two for 0.025 M $\text{Pb}(\text{OAc})_2$.

The concentrations of Pb ions in the filtrates obtained by aging at 25°C of the suspensions containing 0.5, 0.08, and 0.025 M $\text{Pb}(\text{OAc})_2$ were determined at 25°C and are shown at various pH values of the suspensions in Figs. 3 (a), (b), and (c), together with products. As seen in Fig. 3(a) ($=0.5 M$ $\text{Pb}(\text{OAc})_2$), the points for phases A and B are on straight lines with the slope 1 and some points for phase B are on a straight line with the slope -1.5 . The points for phase D are on a straight line with the slope -2 . When the acetate ion concentration is decreased to 0.08–0.025 M the points are on the straight lines with slopes 3 and -2 , and both the pH value for minimizing the solubility of Pb ions and the minimum solubility become smaller.

ACKNOWLEDGMENT

The authors are indebted to Mr. K. Murakami for his help in the experiments.

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