CHEMISTRY LETTERS, pp. 23-28, 1976. Published by the Chemical Society of Japan

FORMATION AND SOLUBILITY OF BASIC LEAD CHLORIDES AT DIFFERENT PH VALUES

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Suspensions prepared by mixing solutions of NaOH and $PbCl_2$ in various mol ratios were subjected to aging at 25, 50 and 80°C. Formation of three kinds of basic lead chlorides takes place, depending mainly on the pH. Their solubilities in the suspension media with various pH values at 25°C were determined.

It is difficult to make a direct study of the behavior in solution of the ions of metals such as Pb(II), Zn(II) and W(VI) which have no incomplete d electron shell. In order to clarify the mechanism of the precipitation of these ions, it is necessary to investigate the conditions for formation of the precipitates. The experimental results on lead(II) ions are given in the following.

Lead(II) ions and amorphous hydroxide in solution form crystalline precipitates on hydrolysis. Their crystal structure and composition change with reaction conditions. Formation of lead oxide, oxyhydroxide and basic nitrates takes place in the suspensions prepared by mixing solutions of lead nitrate and sodium hydroxide, depending on the pH, temperature and presence of silica.[1] Lead oxyhydroxide is also known to be formed by reaction of lead acetate solution and excess NaOH.[2] On the other hand, basic lead perchlorates are obtained by varying the formation conditions.[3]

When the suspensions prepared by mixing solutions of Lead(II) chloride and sodium hydroxide in various mol ratios were subjected to aging at 25, 50 and 80°C, three basic chlorides are formed, according to different pH. The composition and crystal structure of each precipitate and its solubility at different pH values of suspension media will be reported.

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Experimental

In order to remove dissolved CO_2, nitrogen was bubbled into conductivity water at boiling point for 30 min. The starting suspensions were prepared in a box under nitrogen atmosphere and subjected to aging at three different temperatures in order to prevent carbonation. $PbCl_2$ solutions were prepared in 600 ml cylindrical bottles of glass and polyethylene by dissolving 0.010 mol of an analytical grade $PbCl_2$ in 450 ml water. The required amount of 0.2M or 5.0M-NaOH was added to the $PbCl_2$ solution corresponding to the mol ratios of $2NaOH/PbCl_2$(=R), the total volume of the suspension being made 500 ml with water. The narrow inlet neck of the bottle was closed with a polyethylene stopper and covered with a polyethylene cap. In order to accelerate hydrolysis, three sets of bottles each containing the suspension with R values 0.10-10.0 were fixed to a rotating drum in a water bath and slowly turned, being kept at 25°C for 48 hr, 50 and 80 °C for 24 hr. After aging, the pH of suspensions(or filtrates) was determined with a Horiba-Hitachi electrode pH meter at 25$\pm$ 1 °C. The aging products were separated from the solution by filtration through filter paper, washed with water and dried in a desiccator. All the procedure was carried out in nitrogen atmosphere.

The powdery samples were examined by means of X-ray powder diffraction using FeKα radiation. The amounts of Pb^{2+}, Cl^- and Na^+ ions in the solid samples were determined by means of EDTA titration, the Volhard method, and atomic absorption, respectively, after the samples had been dissolved in HNO_3 solution. The amount of Pb ion in the filtrate which was found to be less than 5×10^{-6}M-Pb ion by the EDTA titration method was determined by atomic absorption spectrometry.

Results and Discussion

When NaOH solution is added to a $PbCl_2$ solution, a white precipitate is formed, the pH of suspension increasing as shown in Fig. 1. The titration curve was obtained by adding 0.5M-NaOH at a rate of 1.8 ml/hr to 100.0 ml of 0.02M-$PbCl_2$ in nitrogen at 25°C under stirring. There are two inflection points at R values of 0.5 and 0.75. When titration was carried out at 50 and 80°C, similar curves, with two inflection points at 0.5 and 0.75 in R, were obtained. The presence of these points indicates that precipitates with different compositions were formed according to R values. In order to find the relation between the composition of precipitate and R value, the suspensions were subjected to aging at 25°C. The pH values of the suspensions

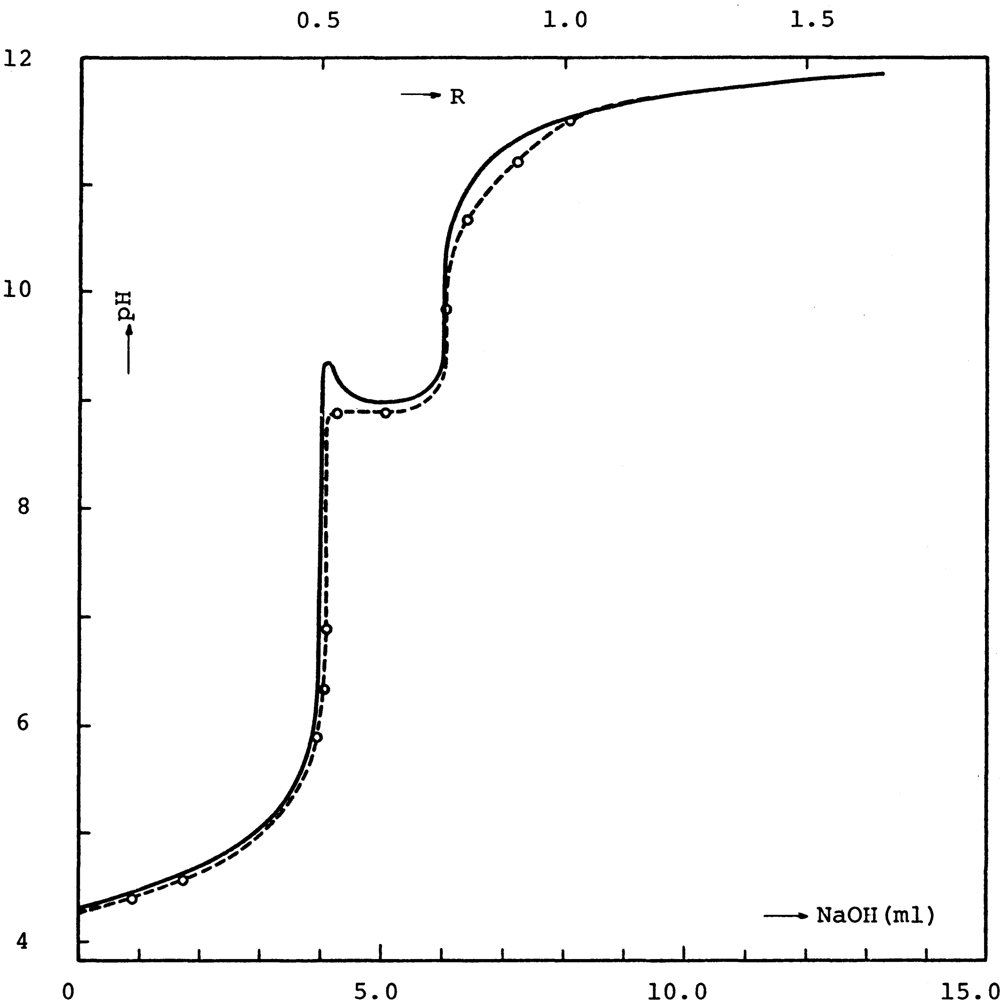

Fig. 1. Potential titration of 0.02M-$PbCl_2$ with 0.5M-NaOH in nitrogen at 25°C.

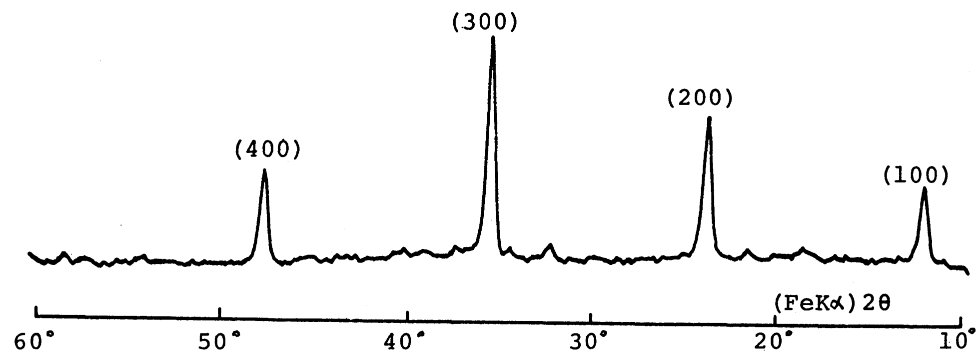

Fig. 2. X-ray diffraction pattern of $6PbO \cdot PbCl_2 2H_2O$.

subjected to aging are also plotted against the R values(dotted curve, Fig. 1). A slight difference in pH between the two curves is seen in the range $0.5<R<1.0$. When the precipitate is in equilibrium with the suspension medium, the solid curve seems to coincide with the dotted curve.

X-ray analysis indicates that the aging products consist of one of three phases, A, B and C, or mixtures of two of them, depending on the R values. The products consisting of A, B and C only were formed in the ranges $R\leq 0.5$, $R=0.75$ and $R\geq 0.9$, respectively. The products consisting of A+B, and of B+C were formed in the R ranges 0.5-0.75, and 0.75-0.9, respectively. Phase A has an orthorombic crystal structure with a= 7.11, b= 9.7 and c= 4.06Å, the chemical formula being PbOHCl.[4] The X-ray diffraction data of phase B correspond to those of $3PbO\ PbCl_2nH_2O$ or $Pb_4O_3Cl_2nH_2O$,[5] and of $Pb_2Cl(O\cdot OH)_{2-x}$.[6] The pattern of phase C(Fig. 2) indicates that it has a cubic crystal structure with a= 9.67Å.

The suspensions were also subjected to aging at 50 and 80°C. Phases A and B were formed in the same range of R values as above, irrespective of the kind of bottle and temperature. When polyethylene bottles were used, phase C was formed in the range $R>0.9$, whereas when glass ones were used, a silicate was formed at 80°C besides phase C.

In order to study the effect of Pb ion concentration on the products, similar experiments were carried out at 25°C with two suspensions, one with Pb content 0.01M and the other 0.002M. The results show that the pH range where each phase is formed is independent of the Pb ion concentration.

Five samples each consisting of one phase with particles of size 5-10 μm were selected from the products and subjected to chemical analysis. Since the samples were found to contain less than 0.1 wt% of Na^+ ion, their chemical formulas were determined from the contents of Pb^{2+} and Cl^- ions assuming that H_2O(wt%)= 100-($PbO + PbCl_2$). The results given in Table indicate that the composition of phase A or C does not strongly depend on the concentration of excess $PbCl_2$ or NaOH.

The pH of suspensions differed from that of their filtrates only in the range $0.5<R<0.75$, with the latter being 6-7. The concentration of Pb^{2+} ions in the filtrates obtained at 25°C by aging of the suspensions containing 0.02M total Pb ions at 25°C in the bottles of glass(△) and polyethylene(o), and at 50°C in the polyethylene bottles(●) are shown at various pH values of the suspensions in Fig. 3, together with the kind of solid phase. The points for pH 4.4-8.3(where only PbOHCl

Table 1. Contents of Pb^{2+} and Cl^- ions in the samples corresponding to various R values.

R	Pb^{2+} (wt%)	Cl^-	Chemical formula
0.25	79.61	13.43	PbOHCl
0.50	80.06	13.34	
0.75	86.25	6.66	$3PbO \cdot PbCl_2 2/3H_2O$
0.90	87.70	4.14	$6PbO \cdot PbCl_2 2H_2O$
5.0	86.76	3.93	

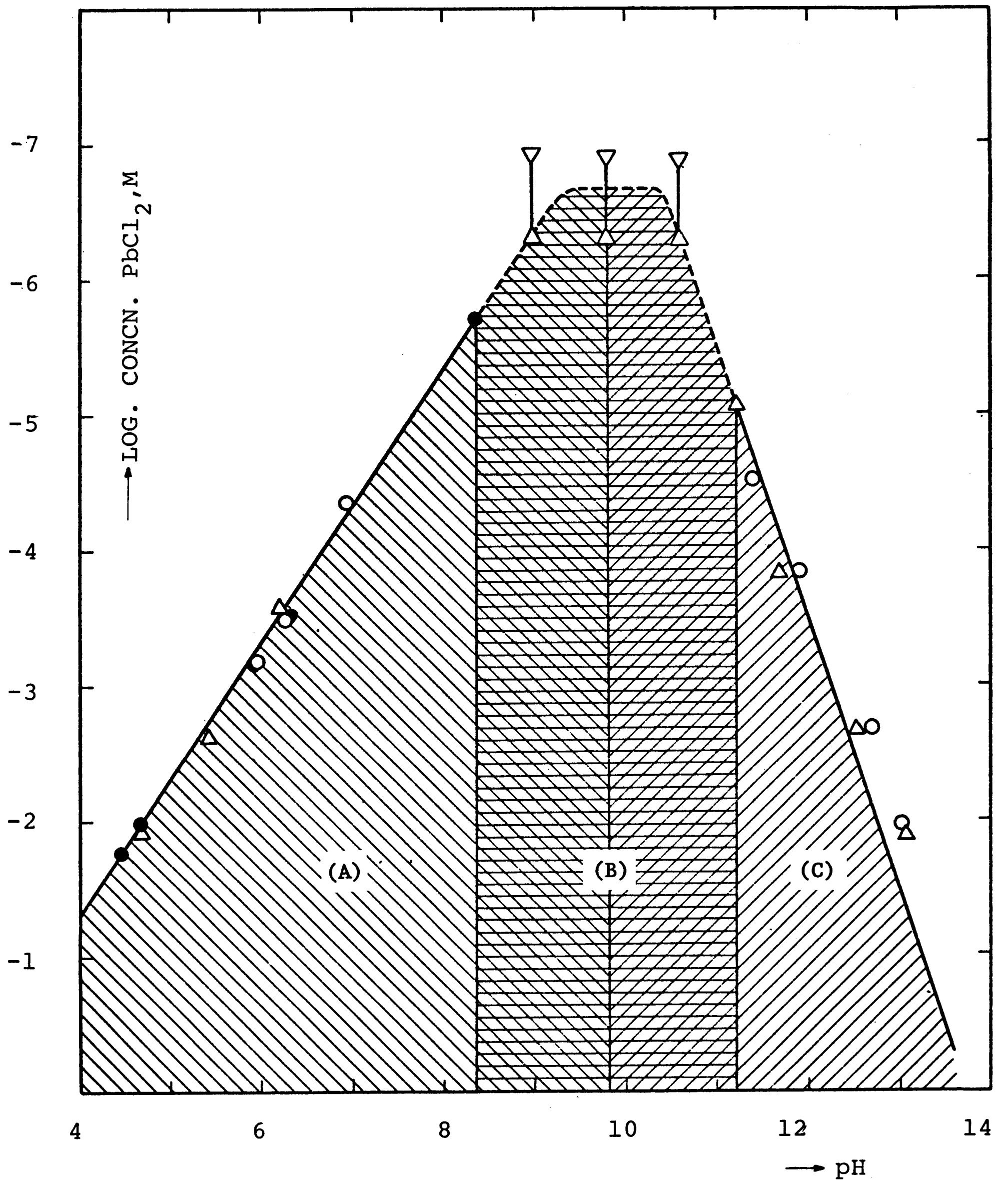

Fig. 3. Solubilities of lead basic chlorides at various pH values. A=PbOHCl, B=$3PbO \cdot PbCl_2 2/3H_2O$, C=$6PbO \cdot PbCl_2 2H_2O$.

exists as a solid phase) are on a straight line with slope 1, whereas those for pH>11.2 (where only $6PbO \cdot PbCl_2 2H_2O$ exists) are on a straight line with a slope approximately -2. The solubility becomes minimum in the range where $3PbO\ PbCl_2$-$2/3H_2O$ exists with or without another phase, the value being 1.5-4.5×10^{-7}.

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(Received November 1, 1975)