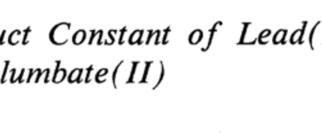
The Composition and the Solubility Product Constant of Lead(II) Ethylenediaminetetraacetatoplumbate(II)

By Nobuyuki TANAKA, Minoru KAMADA and Gen SATÔ

(Received October 13, 1960)

Although most metal-ethylenediaminetetraacetate (EDTA) complexes are very soluble in water, a few metal-EDTA complexes which are insoluble or slightly soluble have been reported$^{1-4)}$. Schwarzenbach$^{1)}$ obtained two kinds of slightly soluble compounds when he oxidized cobalt(II)-EDTA complexes with lead dioxide. He concluded from the results of chemical analysis that those compounds had compositions represented by $\mathrm{Pb[CoY]_2 \cdot 7H_2O}$ and $\mathrm{Co[CoY]_2 \cdot 10H_2O}$. Schmid and Reilley$^{2)}$ reported that when a mercury electrode was immersed in solutions containing mercury(II)-EDTA complexes, slightly water-soluble materials, such as $\mathrm{Hg[HgY]}$ and $\mathrm{Hg_2[HgY]}$, were deposited on its surface. Moreover, there have been two reports concerning slightly soluble compounds which are composed of lead(II) and EDTA. One was given by Tanaka, Kato and Tamamushi$^{3)}$, who suggested, from their preliminary study of the solubility product constant, that the compound was represented as lead(II) ethylenediaminetetraacetatoplumbate(II). The other report was made by Brintzinger, Thiele and Müller$^{4)}$, who assumed their slightly soluble lead(II)-EDTA compound to be of the formula,



$$\begin{array}{ll}\mathrm{CH_2{-}N}\left\langle\begin{array}{l}\mathrm{CH_2COO}\\ \mathrm{CH_2COO}\end{array}\right\rangle\mathrm{Pb} & \\ \quad | & \cdot\mathrm{H_2O}\\ \mathrm{CH_2{-}N}\left\langle\begin{array}{l}\mathrm{CH_2COO}\\ \mathrm{CH_2COO}\end{array}\right\rangle\mathrm{Pb} & \end{array}$$

Because of the discrepancy between these two reports, the present authors are concerned in this communication with the reinvestigation on the composition and the solubility product constant of the slightly soluble white crystals which precipitate from the solution containing lead(II) and EDTA.

---

1) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

2) R. W. Schmid and C. N. Reilley, *J. Am. Chem. Soc.*, **78**, 5513 (1956).

3) N. Tanaka, K. Kato and R. Tamamushi, This Bulletin, **31**, 283 (1958).

4) H. Brintzinger, H. Thiele and U. Müller, *Z. anorg. allgem. Chem.*, **251**, 285 (1943).

Experimental

Reagents.—A stock solution of lead(II) nitrate was prepared by dissolving an appropriate amount of lead(II) nitrate of guaranteed reagent grade in distilled water and standardized with the authentic EDTA solution by amperometric titration, using a dropping mercury electrode as an indicator electrode5). The EDTA solution was prepared from disodium ethylenediaminetetraacetate (DOTITE 2NA) and standardized amperometrically5) against the standard copper(II) nitrate solution. A solution of lead(II)-EDTA complex was obtained by mixing lead(II) nitrate and an equivalent EDTA solution. The pH of the solution was adjusted to be 4.8 by addition of sodium carbonate solution. Acetic acid-sodium acetate buffers were prepared with acetic acid and sodium carbonate of guaranteed reagent grade. All the other chemicals used were of guaranteed reagent grade.

The slightly soluble crystals of lead(II) ethylenediaminetetraacetatoplumbate(II) were obtained by following procedure. The lead(II) solution and the lead(II)-EDTA solution were mixed in acetate buffers (0.05 M acetate) of appropriate pH and ionic strength 0.2, when white crystalline compounds appeared in the solution. The solution with the crystals was shaken on the shaker in a thermostat of a given temperature. After being shaken for a week, the crystals were filtered with the aid of suction, and then washed several times with cold water. The crystals were kept in a desiccator at room temperature (15°C).

Apparatus.—A manual apparatus similar to that of Kolthoff and Lingane6) was used for the precise measurement of current-voltage curves. A dropping mercury electrode used as an indicator electrode had an m value of 2.57 mg./sec. and a drop time τ of 3.52 sec., being measured in a de-aerated acetate buffer solution of pH 4.7 containing 0.1 M potassium nitrate, 0.1 M sodium acetate and 0.01% gelatin at 25°C with open circuit. A saturated calomel electrode (SCE) was used as a reference electrode, which was connected to the electrolytic solution through a Hume and Harris' type salt bridge7). The pH of the solution was measured with a Hitachi Model EHP-1 pH meter with glass electrode within the accuracy of 0.02 pH unit.

Determination of the Concentrations of Pb^{2+} and PbY^{2-} Ions in the Solution.—Since preliminary experiments showed that when the crystals were dissolved in water all the lead(II) existed partly as Pb^{2+} ions and partly as PbY^{2-} ions, the method for determining these two species in the solution was examined and established.

The current-voltage curves of the mixture of Pb^{2+} and PbY^{2-} ions were obtained in the acetate buffers of pH 4.8 and of ionic strength 0.2 containing acetate ions of 0.05 M to 0.10 M and 0.01% gelatin. In this supporting electrolyte, PbY^{2-} ions do not dissociate appreciably and therefore the diffusion current measured at -0.60 volt vs. SCE must correspond only to the concentration of Pb(II) ions which are not complexed with EDTA. On the other hand, PbY^{2-} ions are thought to dissociate completely in 1 M nitric acid solution. After measuring the current-voltage curves of the mixture of Pb^{2+} and PbY^{2-} ions in 50 ml. solution of the above-mentioned supporting electrolyte of pH 4.8, 5 ml. of 11 M nitric acid was added to the solution drop by drop and the current-voltage curves were measured again. The diffusion current at -0.60 volt vs. SCE corresponds to the concentration of the total concentration of lead(II). The concentration of the PbY^{2-} ions present in the original solution can be obtained from the difference of these two measurements.

A linear relation was obtained between the concentration of Pb^{2+} ions and the diffusion current in the supporting electrolyte of pH 4.8 in the absence

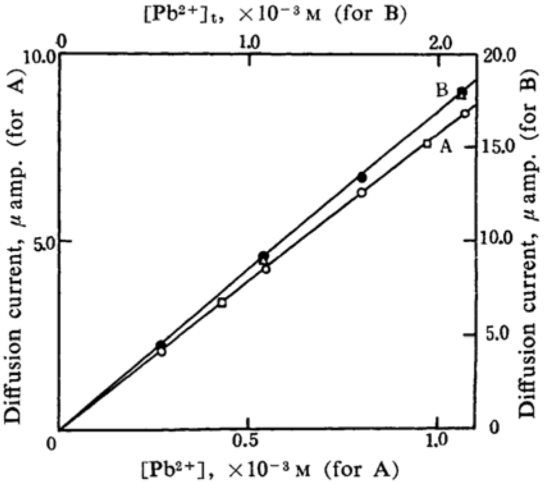


Fig. 1. Relation between the diffusion currents and the concentration of lead(II) ions at 25°C and ionic strength 0.2 before (A) and after (B) the addition of nitric acid: (A) In acetate buffer of pH 4.85 containing 0.08 M acetate without (○) and with 1.177×10^{-3} M PbY^{2-} (□); (B) In 1 M nitric acid containing 0.16 M acetic acid without (●) and with 0.970×10^{-3} M EDTA (△).

TABLE I. POLAROGRAPHIC DETERMINATIONS OF $[Pb^{2+}]$ AND $[PbY^{2-}]$

Species	Concentration added $\times10^3$ mol./l.	Concentration found $\times10^3$ mol./l.	Error %
$[Pb^{2+}]$	0.801	0.795	-0.7
$[PbY^{2-}]$	0.810	0.814*	$+0.5$
$[Pb^{2+}]_t$	1.611*	1.609	-0.1
$[Pb^{2+}]$	0.494	0.495	$+0.2$
$[PbY^{2-}]$	0.499	0.499*	0.0
$[Pb^{2+}]_t$	0.993*	0.994	$+0.1$

* Values calculated with the equation, $[Pb^{2+}]_t=[Pb^{2+}]+[PbY^{2-}]$.

---

5) N. Tanaka, M. Kodama, M. Sasaki and M. Sugino, *Japan Analyst* (*Bunseki Kagaku*), 6, 86 (1957).

6) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, New York (1952), p. 297.

7) D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **15**, 465 (1943).

and the presence of PbY^{2-} ions. This is indicated in Fig. 1. In Fig. 1 is also shown a linear relation between the lead concentration and the diffusion current which was obtained in 1 M nitric acid solution containing 0.16 M acetic acid in the absence and the presence of EDTA. These relations clearly indicate that the procedure can be used for the determination of the concentrations of Pb^{2+} and PbY^{2-} ions present in the solution. Two of the examples in which $[Pb^{2+}]$ and $[Pb^{2+}]_t$ were determined in the acetate buffers and in the 1 M nitric acid solution respectively are given in Table I with the $[PbY^{2-}]$ calculated from the $[Pb^{2+}]_t$ and $[Pb^{2+}]$.

Results

Composition of the Compounds.—The slightly soluble white crystals which were prepared in the solution of pH 4.50 were dissolved in the above-mentioned acetate buffers of pH 4.8 and the concentrations of Pb^{2+} and PbY^{2-} ions present in the solution were determined by the polarographic method. From the results shown in Table II, the molar ratio of Pb^{2+} to PbY^{2-} ions in the solution was determined as one to one. This suggested that the crystals might contain Pb^{2+} and PbY^{2-} ions at the ratio of one to one. The same molar ratio of Pb^{2+} to PbY^{2-} ions was obtained with the crystals prepared at pH 3.53. This excluded any possibility of the existence of such related species as $Pb[PbHY]_2$

TABLE II. THE MOLAR RATIO OF PbY^{2-} TO Pb^{2+} IN THE CRYTALS*

	$[Pb^{2+}]\times 10^3$ mol./l.	$[PbY^{2-}]\times 10^3$ mol./l.	$[PbY^{2-}]/[Pb^{2+}]$
A	0.922	0.931	1.01
	0.891	0.893	1.00
	0.502	0.509	1.01
B	0.786	0.793	1.01
	0.304	0.306	1.01

* The crystals were prepared at 25°C in the solutions of ionic strength 0.2 and pH 4.50 (A) and pH 3.53 (B) containing 0.05 M acetate ions.

The crystals dried at 15°C lost 3.22% of the water when being kept at 160°C in the air oven. Since the theoretical value of water content for monohydrate of lead(II) ethylenediaminetetraacetatoplumbate(II) is 2.56%, the crystals were considered to be of the monohydrate. The discrepancy between the theoretical and the experimental values may be attributed to the small amount of hygroscopic water contained in the crystals.

Solubility Product Constant of Pb[PbY].—In aqueous solution, the lead(II) ethylenediaminetetraacetatoplumbate(II), Pb[PbY], is in equilibrium according to the equation,

$$Pb[PbY] \rightleftarrows Pb^{2+} + PbY^{2-} \qquad (1)$$

As Pb[PbY] is slightly soluble in water, its solubility product constant (K_{sp}) is represented as,

$$K_{sp} = [Pb^{2+}][PbY^{2-}] \qquad (2)$$

In the acetate buffers of pH 4.6 containing acetate ions of 0.02 M to 0.08 M the concentrations of Pb^{2+} and PbY^{2-} ions which are determined polarographically are apparent concentrations[8], $[Pb^{2+}]_{app}$ and $[PbY^{2-}]_{app}$, respectively which are represented by the equations,

$$[Pb^{2+}]_{app} = [Pb^{2+}] + [PbOAc^+] + [Pb(OAc)_2] \qquad (3)$$

$$[PbY^{2-}]_{app} = [PbY^{2-}] + [PbHY^-] \qquad (4)$$

Consequently, the solubility product constant calculated with these concentrations is considered to be the apparent constant, $K_{sp,app}$, which is given by the equation,

$$K_{sp,app} = [Pb^{2+}]_{app}[PbY^{2-}]_{app} \qquad (5)$$

Using the overall formation constants of acetatolead(II) complexes $K_{Pb(OAc)_n}$ and the equilibrium constant, K^{H}_{PbHY}, Eqs. 3 and 4 are rewritten as

$$[Pb^{2+}]_{app} = [Pb^{2+}]\{1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n\} \qquad (6)$$

$$[PbY^{2-}]_{app} = [PbY^{2-}]\{1+K^{H}_{PbHY}[H^+]\} \qquad (7)$$

where

$$K_{Pb(OAc)_n} = \frac{[Pb(OAc)_n{}^{(2-n)+}]}{[Pb^{2+}][OAc^-]^n} \qquad (8)$$

$$K^{H}_{PbHY} = \frac{[PbHY^-]}{[PbY^{2-}][H^+]} \qquad (9)$$

With Eqs. 2, 6 and 7, the apparent solubility product constant $K_{sp,app}$ given by Eq. 5 is expressed as

$$K_{sp,app} = K_{sp}\{1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n\} \times\{1+K^{H}_{PbHY}[H^+]\} \qquad (10)$$

The apparent solubility product constants were obtained at pH 4.6 and ionic strength 0.2 but at various acetate concentrations. The relation between the $K_{sp,app}$ and the acetate concentration is shown in Fig. 2. The solubility product constant (K_{sp}) at ionic strength 0.2 was calculated with Eq. 10 from the apparent solubility product constants observed at various acetate concentrations. The results obtained at 25°C are exemplified in Table III. A satisfactory agreement in the K_{sp}'s obtained at various acetate concentrations clearly indicates

---

[8] N. Tanaka and K. Kato, This Bulletin, 33, 417 (1960).

TABLE III. $K_{sp,app}$ AND K_{sp} ($\mu=0.2$) OBTAINED AT VARIOUS ACETATE CONCENTRATIONS AT 25°C

$[OAc^-]$ mol./l.	$[Pb^{2+}]_{app}\times10^3$ mol./l.	$[PbY^{2-}]_{app}\times10^3$ mol./l.	$K_{sp,app}\times10^5$ (mol./l.)^2	α*	$K_{sp}\times10^6$ (mol./l)^2
0.0621	6.07	7.69	4.67	10.54	4.37
0.0564	5.74	7.20	4.13	9.56	4.27
0.0452	4.08	8.42	3.44	7.66	4.43
0.0443	5.04	6.68	3.37	7.51	4.43
0.0434	6.64	4.73	3.14	7.34	4.23
0.0248	4.04	4.84	1.96	4.45	4.34

* $\alpha=1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n$

TABLE IV. $K_{sp,app}$ AND K_{sp} ($\mu=0.2$) OBTAINED AT DIFFERENT pH'S*

pH	$\dfrac{K_{sp,app}}{1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n}$ (mol./l.)^2	$1+K^{H}_{PbHY}[H^+]$	K_{sp} (mol./l.)^2
3.50	4.15×10^{-6}	1.16	3.58×10^{-6}
4.67	3.63×10^{-6}	1.01	3.59×10^{-6}

* The measurements were made at 15°C in the solution containing 0.035 M acetate ions.

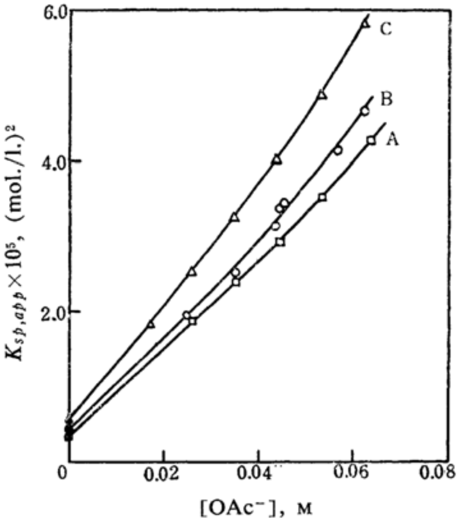


Fig. 2. Relation between the apparent solubility product constant $K_{sp,app}$ and the concentration of acetate ions, determined at pH approximately 4.6, ionic strength 0.2 and at (A) 15°, (B) 25° and (C) 35°C. ■, ● and ▲ indicate the values of K_{sp} calculated with Eq. 10.

the validity of Eq. 10 as well as of the treatment presented in this paper. The validily is further confirmed by the fact that the solubility product constant which was calculated from the $K_{sp,app}$ obtained at pH 3.5 is in satisfactory agreement with the K_{sp} obtained at pH 4.6. One of the examples is shown in Table IV. The formation constants, K_{PbOAc} and $K_{Pb(OAc)_2}$, used in these calculations were those reported by Tanaka and Kato[8]. For the equilibrium constant, K^{H}_{PbHY}, the value given by Schwarzenbach, Gut and Anderegg[9] was used after correction for ionic strength[3]. The activity coefficient of hydrogen ion was estimated to be 0.80 at ionic strength 0.2.

In Table V are given the solubility product constants of lead(II) ethylenediaminetetraacetatoplumbate(II) at 15, 25 and 35°C.

TABLE V. THE SOLUBILITY PRODUCT CONSTANT AT IONIC STRENGTH 0.2

Temp., °C	K_{sp}, (mol./l.)^2
15	3.54×10^{-6}
25	4.34×10^{-6}
35	5.72×10^{-6}

Discussion

The slightly soluble crystals which contain lead(II) and EDTA at molar ratio of two to one were prepared by Brintzinger, Thiele and Müller[4] by adding an excessive amount of lead(II) nitrate to the EDTA solution. They reported that when the crystals were dissolved in water, the solution reacted with hydrogen sulfide, sulfuric acid, potassium dichromate and potassium iodide in the same fashion as the solution containing only hydrated lead(II) ions did. From this observation, they concluded that all lead(II) present in the solution had characteristics of hydrated lead(II) ions, but not those of lead(II)-EDTA complexes.

---

[9] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, 37, 937 (1954).

However, if a suitable condition is chosen(10), PbY^{2-} ions give precipitates by the reaction with hydrogen sulfide, although they give no precipitate generally by that reaction. Furthermore, lead sulfate can be formed when PbY^{2-} ions react with sulfuric acid, because PbY^{2-} ions dissociate to a considerable extent in a strong acid solution(11). Therefore, the formation of the precipitate is no longer a guarantee that lead(II) ions exist in the form of hydrated lead(II) ions.

Some qualitative observations were made also in the present study. When a sufficient amount of potassium dichromate solution was added to the solution which was obtained by dissolving the crystals prepared at pH 4.50, yellow precipitates were observed. After the precipitates were filtered off, sulfuric acid was added to the filtrate when white precipitates appeared in the solution. The yellow precipitates were lead chromate that was formed from the hydrated lead(II) ions present in the solution. The white precipitates, on the other hand, were identified to be lead sulfate which was formed with the lead(II) ions resulting from the dissociation of PbY^{2-} ions in the solution. It should be noted here that lead chromate did not precipitate when potassium dichromate was added to the solution which contained only PbY^{2-} ions. These observations and considerations contradict the conclusion given by Brintzinger et al., but support the interpretation that the solution of the crystals in question contains both Pb^{2+} and PbY^{2-} ions. Consequently, it may be reasonable to conclude that the crystals in question also contain both Pb^{2+} and PbY^{2-} ions. The solubility product constants obtained and the analysis of the composition support the idea that the crystals are lead(II) ethylenediaminetetraacetatoplumbate(II) monohydrate.

Summary

The slightly soluble white crystals which form when lead(II) nitrate is added to the lead(II) ethylenediaminetetraacetate complexes in acetate buffer solution have been investigated. From the chemical analysis, it was found that the crystals have the composition of lead(II) ethylenediaminetetraacetatoplumbate(II) monohydrate. The solubility product constant,

$$K_{sp} = [Pb^{2+}][PbY^{2-}]$$

where Y^{4-} means an ethylenediaminetetraacetate anion was determined at ionic strength 0.2 as $3.54\times10^{-6}(\text{mol./l.})^2$ at 15°C, 4.34×10^{-6} $(\text{mol./l.})^2$ at 25°C and 5.72×10^{-6} $(\text{mol./l.})^2$ at 35°C.

The authors are grateful to the Ministry of Education for the financial support grated for this research.

Department of Chemistry
Faculty of Science
Tohoku University
Katahira-cho, Sendai

---

10) R. Pribil, *Collection Czechoslov. Chem. Communs.*, **16**, 86 (1951).

11) C. N. Reilley and R. W. Schmid, *Anal. Chem.*, **30**, 947 (1958).