

Potentiometric Titration of Lead(II) by Iodide in Acetone and Formation of Complex PbI_3^-

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Potentiometric and differential potentiometric titrations of Pb^{2+} by iodide in acetone using different indicator electrodes: Pb, Cu and Pt were studied. Two end-points were observed, the first one according to the following equation: $\text{Pb}^{2+} + 2\text{I}^- \rightarrow \text{PbI}_2\downarrow$. While, the second end-point according to the following equation: $\text{PbI}_2\downarrow + \text{I}^- \rightarrow \text{PbI}_3^-$. The following complex PbI_3^- is formed in acetone solution, for the first time, a clearly and consistently $\log \bar{K} = -21.92$ (dissociation constant) is obtained. Solubility product (SP) of the deposit ($\text{PbI}_2\downarrow$) is calculated, the values of $\log \text{SP}_{\text{PbI}_2\downarrow}$ were between -18.30 to -18.80. A 103.5 μg of Pb^{2+} was determined with relative standard deviation not to exceed $\pm 3.1\%$.

Key Words: Potentiometric titration, Lead(II), Iodide, Acetone, Complex PbI_3^- .

INTRODUCTION

One of the most widely used applications of electrochemistry is to determine the end point of titrations. Advantages of electrochemical methods over other methods (*e.g.*, visual methods) include greater sensitivity, as well as increasing accuracy and precision. These electrochemical methods are based on simple techniques. Inexpensive motorized pipettes as well as stopper motor-controlled miniature syringe pumps can facilitate titrations in small volumes, both for research and teaching purposes¹. A number of different titrations are commonly used. These are reviewed in instrumental analysis and quantitative analysis textbooks²⁻⁴. Potentiometric titrations are the most important electrochemical titrations. The basis of potentiometric titration is the Nernst equation, which relates the concentration of electroactive species at the surface of an electrode (Cs) to the potential of that electrode (E); *i.e.*, for the reaction:



$$E = E^\circ_{\text{Ox/Red}} + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]} = E^\circ_{\text{Ox/Red}} + \frac{\theta}{n} \log \frac{[\text{Ox}]}{[\text{Red}]} \quad (\text{I})$$

$\theta = 2.303RT/F = 0.0001983T = 0.0591 + 0.0002 (t-25 \text{ }^\circ\text{C})$; (*e.g.*, at 30 $^\circ\text{C}$, $\theta = 0.0601 \approx 0.06$), where E° is the formal redox potential of the electron transfer reaction between the indicator electrode and the reference electrode (typically the saturated calomel or the silver/silver chloride electrode), *i.e.*, standard potential^{1,5,6}.

Potentiometric titration of Pb^{2+} by iodide in some alcohols, dimethylformamide and acetonitrile using Pt electrode⁷⁻⁹ were studied. It was found that, one end-point of the titration was observed according to the following equation:



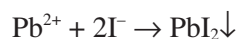
Potentiometric titration of Pb^{2+} by iodide in some alcohols, dimethylformamide and acetonitrile using lead ion-selective electrode^{10,11} were studied. It was found that, two clear end-points of the titration in methanol and ethanol were observed, the first one according to the following equation:



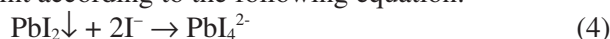
where, the second end-point according to the following equation:



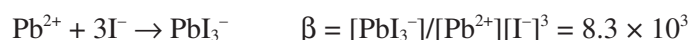
In acetonitrile also, two clear end-points of the titration were observed, the first one according to the following equation:



While, the second end-point according to the following equation:



The complex $[\text{PbI}_3]^-$ unstable in aqueous solutions¹²:



but found in crystal forms, such as: $\{(\text{C}_4\text{H}_{12}\text{N})_2[\text{PbI}_3]\text{I} \cdot 2\text{H}_2\text{O}\}_n$ ¹³, $(\text{Pr}_4\text{N})[\text{PbI}_3^-]$ and $[\text{Mg}(\text{dmf})_6][\text{PbI}_3]_2$ ¹⁴.

EXPERIMENTAL

In the present measurements study of potentiometric titration of lead(II) by iodide in acetone and formation of complex PbI_3^- using Pb, Cu and Pt electrodes were carried out.

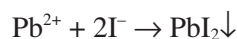
An automatic potentiometer (702 SM Titrino, Metrohm), automatic burette (806 Exchange Unit, Metrohm), rotating electrode (DI-65-14 with controvit unit-Tacussel), reference electrode (REF 421, Metrohm), magnetic stirrer (728 Stirrer, Metrohm) and sensitive balance (0.01 mg, Sartorius-2474) were used.

Solutions preparation: All solutions are prepared with acetone (extra pure, Merck) with analytical-reagent grade chemicals as the following: 0.01 M $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ was prepared by dissolving of 0.46014 g in acetone, then transferred into volumetric flask volume of 100 mL and the final volume was completed to 100 mL using acetone. 0.1 M KI was prepared by dissolving of 1.66010 g in 0.1 mL deionized water, added 60 mL of acetone, then transferred into volumetric flask volume of 100 mL and the final volume was completed to 100 mL using acetone. All dilutions of the solutions were made with acetone.

Procedures: The appropriate volume of the standard solution of lead is putting in analytical cell, added acetone until the volume 10 mL and then titrated by iodide.

RESULTS AND DISCUSSION

Potentiometric titrations $\{E = f(V)\}$ of Pb^{2+} by iodide in acetone were studied. Two end-points were observed, Fig. 1, the first one according to the following equation:



where, the second end-point according to the following equation:

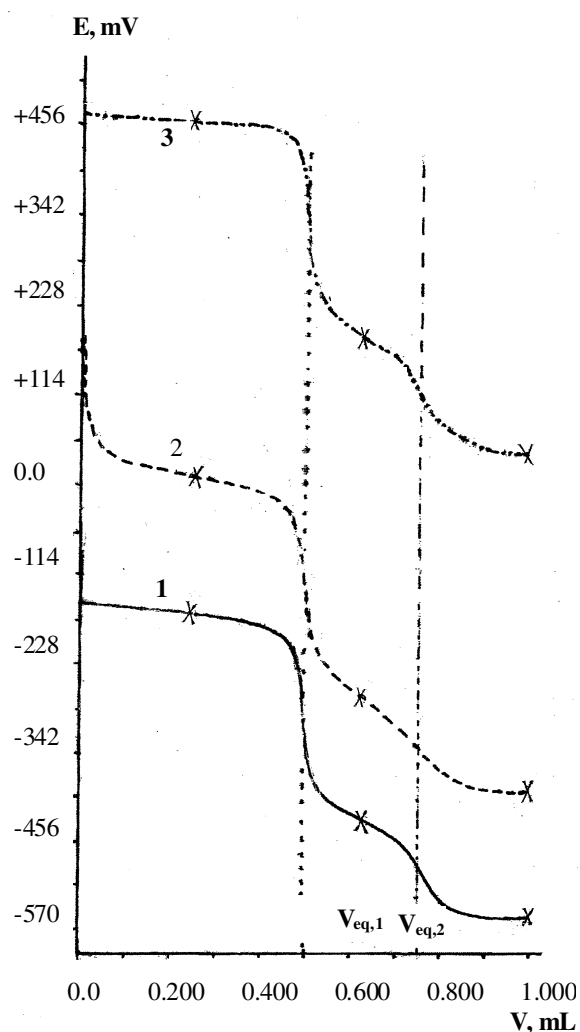


Fig. 1. Curves for the potentiometric titration of 10 mL of 0.0015 M Pb^{2+} by 0.060 M iodide using different types of indicator electrode (Pb, Cu and Pt): (1) Pb, (2) Cu and (3) Pt (reference electrode Ag/AgCl)

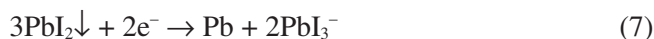
Fig. 1 shows that, the first end-point according to titrating 15 μmol of lead(II) with 30 μmol of added iodide to form 15 μmol of low solubility salt $\text{PbI}_2\downarrow$. The second end-point according to dissolution of $\text{PbI}_2\downarrow$ after addition of 15 μmol of other iodide to form 15 μmol of complex PbI_3^- is formed. This can be illustrated as follows:

To the first end-point of titration: The chemical reaction (3) is expressed as follows:



$$E_1 = E^\circ_{\text{Pb}^{2+}/\text{Pb}} + 1/2 \theta \log [\text{Pb}^{2+}] = E^\circ_1 + 1/2 \theta \log [\text{Pb}^{2+}]; E^\circ_1 = E^\circ_{\text{Pb}^{2+}/\text{Pb}} \quad (\text{II})$$

Between the first and second end-point of titration: The chemical reaction 5 is expressed as follows:



$$\begin{aligned} E_2 &= E^\circ_{\text{PbI}_2/\text{Pb}, \text{PbI}_3^-} - 1/2 \theta \log [\text{PbI}_3^-]^2 \\ &= E^\circ_1 + 1/2 \theta \log \text{SP}_{\text{PbI}_2} - \theta \log [\text{PbI}_3^-] \\ &= E^\circ_2 - \theta \log [\text{PbI}_3^-] \end{aligned} \quad (\text{III})$$

$$E^\circ_2 = E^\circ_1 + 1/2 \theta \log \text{SP}_{\text{PbI}_2} \quad (\text{IV})$$

$$\text{SP}_{\text{PbI}_2} = [\text{Pb}^{2+}][\text{I}^-]^2 \quad (\text{V})$$

After the second end-point of titration: A surplus of iodide is expressed as follows:



$$\begin{aligned} E_3 &= E^\circ_{\text{PbI}_3^-/\text{Pb}, \text{I}^-} + 1/2 \theta \log [\text{PbI}_3^-] - 1/2 \theta \log [\text{I}^-]^3 \\ &= E^\circ_1 + 1/2 \log K + 1/2 \theta \log [\text{PbI}_3^-] - 3/2 \theta \log [\text{I}^-] \\ &= E^\circ_3 + 1/2 \theta \log [\text{PbI}_3^-] - 3/2 \theta \log [\text{I}^-] \end{aligned} \quad (\text{VI})$$

$$E^\circ_3 = E^\circ_1 + 1/2 \theta \log K \quad (\text{VII})$$

$$K = [\text{Pb}^{2+}][\text{I}^-]^3/[\text{PbI}_3^-] \quad (\text{VIII})$$

Calculation of standard potential: Fig. 1 shows that the type of indicator electrodes (Pb, Cu and Pt) affect to very large changes in titration curves and thus standard potentials (Table-1) and the potential bound be more pronounced when Pb electrode is used.

Calculation of solubility product: Solubility product (SP) of the deposit ($\text{PbI}_2\downarrow$) is calculated according to the equation (IV) using different types of indicator electrodes (Pb, Cu and Pt). It was found that the values of $\log \text{SP}_{\text{PbI}_2}$ were between -18.30 to -18.80 (Table-2).

Calculation of dissociation constant of PbI_3^- : Dissociation constant (K) of the complex (PbI_3^-) is calculated according to the equation (VII) using different types of indicator electrodes (Pb, Cu and Pt). It was found that the values of $\log K_{\text{PbI}_3^-}$ were between -21.87 to -21.97 (Table-3).

Differential potentiometric titrations $\{dE/dV = f(V)\}$ of Pb^{2+} by iodide in acetone using different types of indicator electrodes: Pb, Cu and Pt (reference electrode Ag/AgCl) were studied. It was also found that, two end-points were observed (Fig. 2).

TABLE-1
VALUES OF STANDARD POTENTIALS FOR THE POTENTIOMETRIC TITRATION OF Pb^{2+} BY IODIDE USING DIFFERENT TYPES OF INDICATOR ELECTRODES: Pb, Cu AND Pt (REFERENCE ELECTRODE Ag/AgCl)

Electrode	E° , V	\bar{X}^* , V	RSD (%)	$\bar{X}^* \pm SD$, V
Pb	$E_1^{\circ} = E_{Pb^{2+}/Pb}^{\circ}$	-0.123	2.6	-0.123 ± 0.003
	$E_2^{\circ} = E_1^{\circ} + 1/2 \theta \log SP_{PbI_2}$	-0.672	3.1	-0.672 ± 0.021
	$E_3^{\circ} = E_1^{\circ} + 1/2 \theta \log K$	-0.781	3.3	-0.777 ± 0.026
Cu	$E_1^{\circ} = E_{Pb^{2+}/Pb}^{\circ}$	+0.054	4.1	$+0.054 \pm 0.002$
	$E_2^{\circ} = E_1^{\circ} + 1/2 \theta \log SP_{PbI_2}$	-0.510	4.5	-0.510 ± 0.023
	$E_3^{\circ} = E_1^{\circ} + 1/2 \theta \log K$	-0.605	4.8	-0.605 ± 0.029
Pt	$E_1^{\circ} = E_{Pb^{2+}/Pb}^{\circ}$	+0.504	2.9	$+0.504 \pm 0.015$
	$E_2^{\circ} = E_1^{\circ} + 1/2 \theta \log SP_{PbI_2}$	-0.050	3.5	-0.050 ± 0.002
	$E_3^{\circ} = E_1^{\circ} + 1/2 \theta \log K$	-0.152	3.6	-0.152 ± 0.005

*: Average of five measurements.

TABLE- 2
VALUES OF SOLUBILITY PRODUCT (SP) OF THE DEPOSIT ($PbI_2 \downarrow$) FOR THE POTENTIOMETRIC TITRATION OF Pb^{2+} BY IODIDE USING DIFFERENT TYPES OF INDICATOR ELECTRODES: Pb, Cu AND Pt (REFERENCE ELECTRODE Ag/AgCl)

Electrode	Log SP_{PbI_2}		
	\bar{X}^*	RSD (%)	$\bar{X}^* \pm SD$
Pb	-18.30	2.8	-18.30 ± 0.51
Cu	-18.80	4.3	-18.80 ± 0.81
Pt	-18.47	3.0	-18.47 ± 0.55

*: Average of five measurements.

TABLE- 3
VALUES OF DISSOCIATION CONSTANT (K) OF THE COMPLEX (PbI_3^-) FOR THE POTENTIOMETRIC TITRATION OF Pb^{2+} BY IODIDE USING DIFFERENT TYPES OF INDICATOR ELECTRODES: Pb, Cu AND Pt (REFERENCE ELECTRODE Ag/AgCl)

Electrode	log $K_{PbI_3^-}$		
	\bar{X}^*	RSD (%)	$\bar{X}^* \pm SD$
Pb	-21.93	2.4	-21.93 ± 0.52
Cu	-21.97	3.8	-21.97 ± 0.83
Pt	-21.87	2.6	-21.87 ± 0.57

*: Average of five measurements.

Analytical results: Concentrations of Pb^{2+} between 0.5×10^{-4} to 5.0×10^{-3} M using potentiometric titration $\{E = f(V)\}$ and differential potentiometric titration $\{dE/dV = f(V)\}$ by iodide in acetone at different types of indicator electrode (Pb, Cu and Pt) were determined. It was found that the results were better when the first end-point is used in all cases, especially when using the lead electrode (Table-4).

TABLE- 4
 POTENTIOMETRIC TITRATION {E = f(V)} AND DIFFERENTIAL POTENTIOMETRIC
 TITRATION {dE/dV = f(V)} OF Pb²⁺ BY IODIDE IN ACETONE AT DIFFERENT TYPES OF
 INDICATOR ELECTRODE: Pb, Cu AND Pt (REFERENCE ELECTRODE Ag/AgCl, V=10 mL)

C _{Pb²⁺ Taken} × 10 ⁴ , M	Indicator electrode	C _{Pb²⁺ found} × 10 ⁴ , M							
		E = f(V)				dE/dV = f(V)			
		First end-point		Second end-point		First end-point		Second end-point	
		\bar{X}^*	RSD (%)	\bar{X}^*	RSD (%)	\bar{X}^*	RSD (%)	\bar{X}^*	RSD (%)
0.50	Pb	0.49	4.2	–	–	0.50	3.1	–	–
	Cu	–	–	–	–	–	–	–	–
	Pt	0.51	4.9	–	–	0.51	4.0	–	–
0.75	Pb	0.74	4.1	–	–	0.75	3.0	0.73	4.8
	Cu	0.72	7.4	–	–	0.77	7.0	–	–
	Pt	0.74	4.7	–	–	0.76	4.0	0.72	5.6
1.00	Pb	1.02	3.9	0.98	5.3	1.02	3.0	0.97	4.7
	Cu	0.97	7.3	–	–	0.98	6.8	–	–
	Pt	1.01	4.5	0.97	7.1	1.02	3.9	0.98	5.4
2.00	Pb	1.99	3.8	2.02	4.9	2.00	2.9	2.01	4.5
	Cu	1.98	5.0	2.04	6.7	1.99	4.6	2.02	5.3
	Pt	2.01	4.3	1.98	5.8	2.00	3.8	1.98	5.1
4.00	Pb	4.00	3.4	4.01	3.8	4.02	2.8	3.99	4.2
	Cu	3.97	4.8	4.02	5.2	3.98	4.3	4.02	4.8
	Pt	4.01	3.9	3.99	4.8	4.00	3.6	3.99	4.6
6.00	Pb	5.98	3.0	6.01	3.4	5.99	2.6	6.02	3.9
	Cu	6.04	4.5	5.97	4.9	6.02	4.0	5.99	4.4
	Pt	6.02	3.6	5.98	4.3	6.01	3.4	6.00	4.2
8.00	Pb	8.00	2.6	8.01	3.1	7.99	2.5	8.02	3.5
	Cu	8.02	3.4	7.99	4.7	8.01	3.2	8.00	4.2
	Pt	7.99	3.3	8.01	4.1	8.00	3.0	8.01	4.0
10.00	Pb	10.03	2.3	9.99	2.8	10.00	2.2	10.01	3.2
	Cu	9.97	3.3	10.02	4.6	9.98	3.1	10.01	4.1
	Pt	10.00	3.0	9.99	3.9	10.01	2.7	10.00	3.8
15.00	Pb	14.98	2.1	15.01	2.7	15.00	2.0	14.98	3.1
	Cu	15.04	3.2	14.97	4.5	14.98	3.0	15.02	4.0
	Pt	15.02	2.8	14.91	3.7	15.01	2.5	15.00	3.7
20.00	Pb	20.00	2.0	20.02	2.6	20.01	1.9	19.98	3.0
	Cu	19.96	3.2	20.03	4.4	19.98	2.8	20.02	3.8
	Pt	20.01	2.6	20.00	3.5	20.00	2.3	20.02	3.5

*: Average of five measurements.

Conclusion

Potentiometric titrations and differential potentiometric titrations of Pb²⁺ by iodide in acetone using different indicator electrode: Pb, Cu and Pt were studied. Two end-points were observed, the first one according to the following equation: Pb²⁺ + 2I⁻ → PbI₂↓. And the second end-point is according to the following equation: PbI₂↓ + I⁻ → PbI₃⁻; where the complex PbI₃⁻ is formed, for the first time, clearly and consistently log \bar{K} = -21.92 (dissociation constant). A 103.5 μg of Pb²⁺ was determined with relative standard deviation is did not exceed ± 3.1 %.

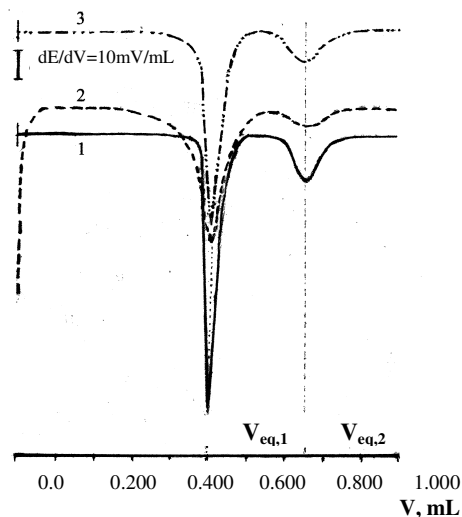


Fig. 2. Curves for the differential potentiometric titration $\{dE/dV = f(V)\}$ of 10 mL of Pb^{2+} 0.0015 M by iodide 0.060 M using different types of indicator electrode: (1) Pb, (2) Cu and (3) Pt (reference electrode Ag/AgCl)

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