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BIAMPEROMETRIC TITRATION OF LEAD (II) BY IODIDE IN ACETONE

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ABSTRACT

Biamperometric titration of lead (II) by iodide in acetone was applied. Three end-points were observed, the first one according to the equation: $Pb^{2+} + 2I^- \rightarrow PbI_2\downarrow$ (I), the second-according to the following equation: $PbI_2\downarrow + I^- \rightarrow PbI_3^-$ (II), while, the third-according to the equation: $PbI_3^- + I^- \rightarrow PbI_4^{2-}$ (III). The proposed method was successfully applied, for the first time, for the determination of 1×10^{-4} mol.L^{-1} lead (II) with RSD not more than 2.1 %. The electrochemical behavior of studied couples and ions showed that, $Pb^{2+}/Pb\downarrow$; $PbI_2/PbI_3^-,Pb\downarrow$ and $PbI_3^-/PbI_4^{2-},Pb\downarrow$ were reversibility couples and average values of $K = i_d/C$ for ions Pb^{2+}, PbI_3^- and PbI_4^{2-}, when $\Delta E=175$ mV, has been calculated as the follows: 6.8×10^4, 0.84×10^4 and 0.98×10^4 µA.mol^{-1}.L, respectively.

**Keywords:** Biamperometric Titration, Pb^{2+}, I^-, PbI_3^-, PbI_4^{2-}, Acetone.

INTRODUCTION

The amperometric detection with two polarized indicating electrodes (also named as biamperometic detection) is based on the measurement and the intensity of current passing through the two identical, usually inert, electrodes, to which a small potential difference from few tens to few hundreds millivolts was applied.

The current flowing in the detection cell is observed only, when solution contacting the electrodes contains two forms of reversible redox couple, it means such one for which at the same potential the oxidation of the reduced form or the reduction of oxidized form can occur. This behavior is observed for such couples as Br_2/Br^-; I_2/I^-; Fe^{3+}/Fe^{2+}; Ce^{4+}/Ce^{3+}; Ag^+/Ag; $AgI/Ag,I^-$; $AgBr/Ag,Br^-$; $AgCl/Ag,Cl^-$; quinine/hydroquinine; Cu^{2+}/Cu^+ (in aqueous and nonaqueous media), *etc.*[1-3].

In biamperometric detection, in the presence of an excess of one form of reversible redox couple, the magnitude of the current measured is linearly proportional to the concentration of the second form in the solution as long as concentration over potential is not involved. When the polarizing potential difference applied to the electrodes (ΔE) is increased, an extension of the linear range of response is observed, however, it is associated with possible interference for other redox species present in solution. When the system detected in the solution is irreversible, the oxidation and reduction processes have activation potentials much larger, even up to 1 V. Such a large polarizing potential difference is also applied in biamperometric detection carried out in non-aqueous solvents [4,5].

Automatic biamperometric titration of copper (II) by iodide in non-aqueous media (methanol, ethanol, propanol, butanol and acetonitrile) was applied. In methanol no quantify acceptable curves appeared. In ethanol two end-points were observed, the first one according to the equation:

$$2Cu^{2+} + 4I^- \rightarrow 2CuI\downarrow + I_2 \text{ (1)},$$
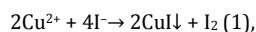
while, the second-according to the following equation:

$$I_2 + I^- \rightarrow I_3^- \text{ (2)}.$$
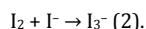
In propanol and butanol two end-points were observed, the first one according to the equation:

$$2Cu^{2+} + 2I^- \rightarrow 2Cu^+ + I_2 \text{ (3)},$$

the second-according to the following equation:

$$Cu^+ + I^- \rightarrow CuI\downarrow \text{ (4)}$$
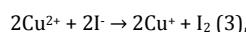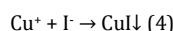
Finally in acetonitrile two end-points were observed, the first one according to the equation (3) and the second according to the equation (2). The proposed method was successfully applied, for the first time, for the determination of 4×10^{-5} mol.L^{-1} copper (II) with RSD not more than 4.2 %. The electrochemical reversibility of Cu^{2+}/Cu^+ and I_2/I_3^- couples and irreversibility of $Cu^+/Cu\downarrow$ is indicated by biamperometry. The behavior of Cu^{2+}, Cu^+, CuI, I_2 and I_3^- has been compared. A comparison with solvents also has been made [6]. Potentiometric titrations of copper(II) in aqueous media were applied [7-10]. In these case get a one end-point only. While in non-aqueous media some titration of Cu(II) were used as the potentiometry (with Pt electrode [11,12], Cu electrode [13] and ion-selective electrode [14]), conductometry and high frequency [15]; where have received some end-points as the equations (1, 2 and 4) and the follows:

$$CuI\downarrow + I^- \rightarrow CuI_2^- \text{ (5)}$$

$$CuI_2^- + 2I^- \rightarrow CuI_4^{3-} \text{ (6)}$$
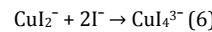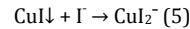
The reactions(1-4) get in alcohols, acetonitrile and acetone [12-24], while the reactions (5 and 6) get in acetone only [13,14]. Potentiometric and differential potentiometric titrations of Pb^{2+} by iodide in acetone using different indicator electrodes: Pb, Cu and Pt were studied. Two end-points were observed, the first one according to the following equation:

$$Pb^{2+} + 2I^- \rightarrow PbI_2\downarrow \text{ (7)}$$
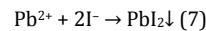
While, the second endpoint according to the following equation:

$$PbI_2\downarrow + I^- \rightarrow PbI_3^- \text{ (8)}$$
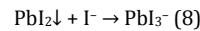
The following complex PbI_3^- is formed in acetone solution, for the first time, a clearly and consistently log K=-21.92 (dissociation constant) is obtained. Solubility product (SP) of the deposit ($PbI_2\downarrow$) is calculated, the values of log SP$_{PbI_2\downarrow}$ were between -18.30 to -18.80. A 103.5 µg of Pb^{2+} was determined with relative standard deviation not to exceed ± 3.1%[25]. In the present paper, the biamperometric titration of lead(II) by iodide in acetone using Pb (two wire) indicator electrode was carried out.

MATERIALS AND METHODS

Instruments and apparatus

An automatic potentiometer and biamperometre (702 SM Titrino, Metrohm), automatic burette (806 Exchange Unit, Metrohm), indicator electrode (two polarized wire indicating electrodes) type Pt(6.0338.100) galvanized by lead, Metrohm, magnetic stirrer (728 stirrer, metrohm), sensitive balance (0.01 mg, sartorius-2474). The

dilute pipette model DIP-1 (Shimadzu), having 100 µ L sample syringe and five continuously adjustable pipettes covering a volume range from 20 to 5000 µL (model Piptman P. Gilson) were used. A ultrasonic processor model POWERSONIC 405 was used to sonicate the sample solutions.
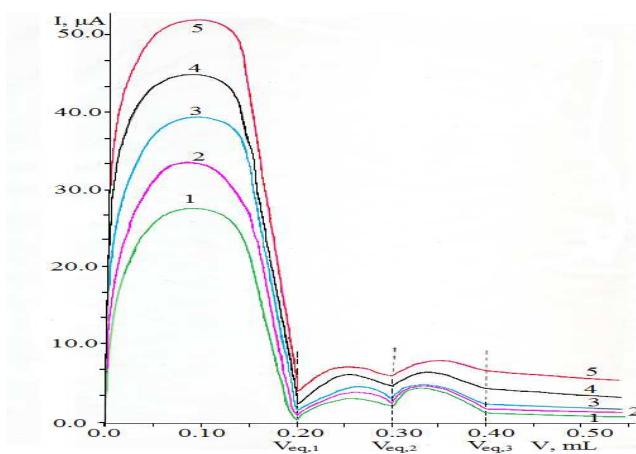

Fig. 1: Biamperometric titration 10 mL of 1x10⁻³ mol.L⁻¹ of Pb(II) by iodide (0.100 mol.L⁻¹) in acetone using Pt (two wire galvanized by lead) as indicator electrode with different ΔE: 1- 150 mV; 2- 175 mV; 3- 200 mV; 4- 225 mV; 5- 250 mV..

Reagents

All solutions are prepared with acetone (extra pure, Merck) with analytical-reagent grade chemicals as the following: 0.01 M $Pb(ClO_4)_2 \cdot 3H_2O$ (pure, Fluka Chemika- Switzerland, the purity 98.0%) was prepared by dissolving of 0.4694 g in acetone, then transferred into volumetric flask volume of 100 mL and finally complete the volume to 100 mL using acetone. 0.100 M KI was prepared by dissolving of 1.660 g in 1.0 mL deionized water, added to 60 mL of acetone, then transferred into volumetric flask volume of 100 mL and the final volume was completed to 100 mL using same solvent. All dilutions of the solutions were made with acetone. The appropriate volume of the standard solution of Pb(II) is putting into volumetric flask volume of 10 mL, added acetone until the volume 10 mL, transferred solution to analytical cell and then titrated by iodide.

RESULTS AND DISCUSSION

Biamperometric titration

Biamperometric titrations of Pb^{2+} by iodide in acetone were studied as the follows:

Three end-points were observed (Fig. 1), the first one according to the equation(I):

$$Pb^{2+} + 2I^- \rightarrow PbI_2\downarrow \text{ (I)},$$

The second-according to the equation(II):

$PbI_2\downarrow + I^- \rightarrow PbI_3^-$ (II),
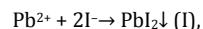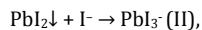
While, the third-according to the equation(III):

$PbI_3^- + I^- \rightarrow PbI_4^{2-}$ (III).
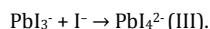
Fig. 1 shows that, the biamperometric titration of 10 mL Pb^{2+} (1×10^{-3} mol.L⁻¹), which contents 10 µmol of Pb^{2+}, by iodide (0.100 mol.L⁻¹) gets the follows:

The first end-point according to titrating 10 µmol of Pb^{2+} with 20 µmol of added iodide to form 10 µmol of $PbI_2\downarrow$, the working electrochemical equation as the follows:

$Pb^{2+} + 2e \rightarrow Pb\downarrow$ (IV)
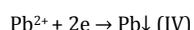
The second end-point according to titration of formed $PbI_2\downarrow$ with 10 µmol of iodide to form 10 µmol of complex PbI_3^-, the working electrochemical equation as the follows:

$3PbI_2\downarrow + 2e \rightarrow 2PbI_3^- + Pb\downarrow$ (V)
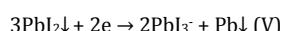
The third end-point according to titration of formed PbI_3^- with 10 µmol of iodide to form 10 µmol of complex PbI_4^{2-}, the working electrochemical equation as the follows:

$4PbI_3^- + 2e \rightarrow 3PbI_4^{2-} + Pb\downarrow$ (VI)
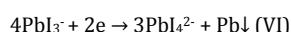
After third end-point the working electrochemical equation as the follows:

$PbI_4^{2-} + 2e \rightarrow 4I^- + Pb\downarrow$ (VII)
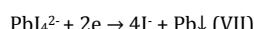
The effect of the polarizing potential (ΔE) between electrodes was studied, it was found that the better value was 175 mV, see Figure 1.

The optimum parameters established for biamperometric titration of Pb^{2+} by iodide in acetone using Pt (two wire galvanized by lead) as indicator electrode were included in Table 1.

Table 1: The optimum parameters established for biamperometric titration of lead(II) by iodide in acetone using pt (two wire galvanized by lead) as indicator electrode.

Optimum parameters	
Indicator electrode	Pt two wire, type Pt(6.0338.100), galvanized by lead.
Non-aqueous solvent	Acetone
Temperature of solution	30°± 1°C
Better end-point	First end-point
Volume of sample, mL	10
Volume increment (V. step), mL	0.002-0.005
Titr. Rate, mL.min⁻¹	max
Signal drift, s	off
Equilibr. time, s	26
Start volume (start V)	off
Filling rate, mL.min⁻¹	max
Meas. impute	[U(pol)]
ΔE, mV	175
$K_{Pb^{2+}}$, µ A.mol⁻¹.L	6.8×10^4
$K_{PbI_3^-}$, µ A.mol⁻¹.L	0.84×10^4
$K_{PbI_4^{2-}}$, µ A.mol⁻¹.L	0.98×10^4
Redox couple $Pb^{2+}/Pb\downarrow$	Reversible
Redox couple $PbI_2/PbI_3^-,Pb\downarrow$	Reversible
Redox couple $PbI_3^-/PbI_4^{2-},Pb\downarrow$	Reversible
Range of concentration	$1 \times 10^{-4} – 5 \times 10^{-3}$ mol.L⁻¹
RSD	2.1%

Table 2: Biamperometric titration 10 mL of Pb(II) by iodide in acetone using Pt (two wire galvanized by lead) as indicator electrode (ΔE=175 mV).

| X_i, mmol.L^{-1} (taken)	End-point (used)	$\overline{x}$ *, mmol.L^{-1} (found)	SD, mmol.L^{-1}	$\dfrac{SD}{\sqrt{n}}$, mmol.L^{-1}	$\overline{x} \pm \dfrac{t.SD}{\sqrt{n}}$ mmol.L^{-1}	RSD %
0.100	I	0.102	0.002	0.0009	0.102±0.0027	2.1
	II	0.097	0.004	0.0018	0.095±0.0051	4.2
	III	Not determined	-	-	-	-
0.200	I	0.202	0.004	0.0018	0.202±0.005	2.0
	II	0.200	0.007	0.0030	0.200±0.008	3.4
	III	0.098	0.004	0.0017	0.098±0.005	4.0
0.350	I	0.351	0.007	0.0031	0.351±0.009	2.0
	II	0.351	0.011	0.0050	0.351±0.014	3.2
	III	0.348	0.013	0.0059	0.348±0.016	3.8
0.400	I	0.401	0.008	0.0036	0.401±0.010	2.0
	II	0.402	0.012	0.0056	0.402±0.015	3.1
	III	0.397	0.015	0.0067	0.397±0.019	3.8
0.600	I	0.602	0.011	0.0051	0.602±0.014	1.9
	II	0.601	0.019	0.0083	0.601±0.023	3.1
	III	0.598	0.022	0.0099	0.598±0.027	3.7
0.800	I	0.802	0.016	0.0071	0.802±0.020	1.9
	II	0.800	0.025	0.011	0.800±0.030	3.1
	III	0.798	0.029	0.013	0.798±0.037	3.7
1.00	I	1.00	0.018	0.0080	1.00±0.022	1.8
	II	1.01	0.031	0.014	1.01±0.039	3.1
	III	0.99	0.037	0.016	0.99±0.045	3.7
2.00	I	2.01	0.036	0.016	2.01±0.045	1.8
	II	2.01	0.060	0.027	2.01±0.075	3.0
	III	1.98	0.071	0.032	1.98±0.088	3.6
3.00	I	3.02	0.051	0.023	3.02±0.064	1.7
	II	2.99	0.089	0.040	2.99±0.111	3.0
	III	2.99	0.108	0.048	2.99±0.134	3.6
4.00	I	4.03	0.068	0.031	4.03±0.085	1.7
	II	4.01	0.120	0.054	4.01±0.149	3.0
	III	3.96	0.142	0.064	3.96±0.177	3.6
5.00	I	5.02	0.085	0.038	5.02±0.106	1.7
	II	4.99	0.150	0.067	4.99±0.186	3.0
	III	4.98	0.189	0.085	4.98±0.235	3.8

* n=5, t=2.776.

Biamperometric titrations of Pb^{2+} by iodide in acetone using Pt (two wire galvanized by lead) as indicated electrode showed that, the redox couples Pb^{2+}/Pb↓; PbI$_2$/PbI$_3^-$,Pb↓ and PbI$_3^-$/PbI$_4^{2-}$,Pb↓ are reversible. The saturated diffusion constant K = i_d/C (where; i_d saturated diffusion current and C concentration of ion, mol.L^{-1}) for studied ions (Pb^{2+}, PbI$_3^-$ and PbI$_4^{2-}$), when ΔE=175 mV, has been calculated by biamperometry as the follows: 6.8x10^4, 0.84x10^4 and 0.98x10^4 μA.mol^{-1}.L, respectively. It was found that, the third end-point was disappeared when concentration of Pb(II) < 2x10^{-4} mol.L^{-1}, the second and the first end-points were disappeared when $C_{Pb(II)}$<1x10^{-4} mol.L^{-1}, see Figure 2.

Analytical results

Concentrations of Pb^{2+} (from 1x10^{-4} to 5x10^{-3} mol.L^{-1}) using biamperometric titration by iodide in acetone at Pt (two wire galvanized by lead) as indicator electrode were determined. It was found that, the results were better when the first end-point is used (where $C_{Pb(II)}$ ≥ 1x10^{-4} mol.L^{-1}), then by used the second end-point (where $C_{Pb(II)}$ ≥1x10^{-4} mol.L^{-1}) and the finally by used the third end-point (where $C_{Pb(II)}$ ≥2x10^{-4} mol.L^{-1}).

The proposed method was successfully applied, for the first time, to the determination 1x10^{-4} mol.L^{-1} of Pb(II) with RSD not more than 2.1% using first end-point, see Table 2.
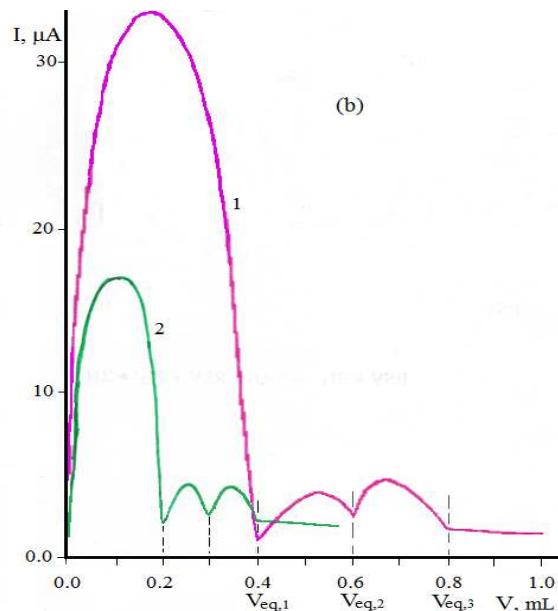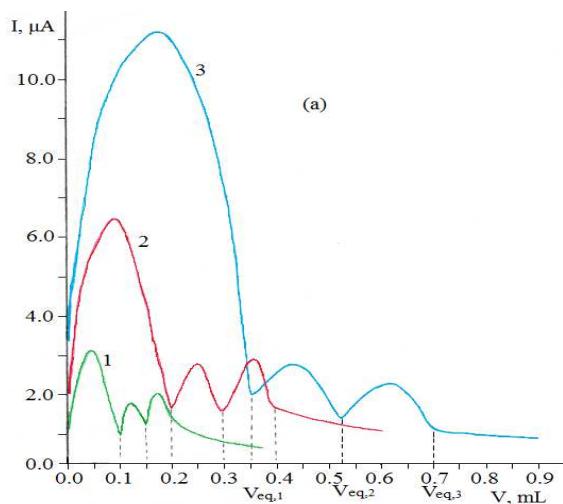
Fig. 2: Biamperometric titration 10 mL of Pb(II) by iodide in acetone using Pt (two wire galvanized by lead) as indicator electrode (ΔE=175 mV):

a) 1- $C_{Pb(II)}$=1x10^{-4} mol.L^{-1}; 2- $C_{Pb(II)}$=2x10^{-4} mol.L^{-1}; 3- $C_{Pb(II)}$=3.5x10^{-4} mol.L^{-1} (C_L=0.020 mol.L^{-1});

b) 1- $C_{Pb(II)}$=1x10^{-3} mol.L^{-1} and 2- $C_{Pb(II)}$=0.5x10^{-3} mol.L^{-1} (C_L=0.050 mol.L^{-1}).

CONCLUSION

Biamperometric titration of lead (II) by iodide in acetone at Pt (two wire galvanized by lead) as indicator electrode was applied. Three end-points were observed, the first one according to the equation: $Pb^{2+} + 2I^- \rightarrow PbI_2\downarrow$ (I), the second-according to the equation: $PbI_2\downarrow + I^- \rightarrow PbI_3^-$(II), while, the third-according to the equation: $PbI_3^- + I^- \rightarrow PbI_4^{2-}$ (III). The proposed method was successfully applied, for the first time, for the determination 1×10^{-4} mol.L^{-1} of lead (II) with RSD not more than 2.1 %. The electrochemical behavior of studied couples and ions showed that, $Pb^{2+}/Pb\downarrow$; PbI_2/PbI_3^-,$Pb\downarrow$ and PbI_3^-/PbI_4^{2-},$Pb\downarrow$ were reversibility couples and average values of K = i_d/C (where; i_d saturated diffusion current and C concentration of ion, mol.L^{-1}) for ions Pb^{2+}, PbI_3^- and PbI_4^{2-}, when ΔE=175 mV, has been calculated as the follows: 6.8x10^4, 0.84x10^4 and 0.98x10^4 μ A.mol^{-1}. L, respectively.

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