

Anodic stripping determination of Pt(IV) based on the anodic oxidation of Hg and Cd from electrochemically deposited Hg–Pt and Hg–Cd alloy phases

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Received: 9 February 2012 / Revised: 20 February 2012 / Accepted: 26 February 2012 / Published online: 8 March 2012
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Abstract An anodic stripping voltammetric determination of Pt(IV) is described which is based on depositing intermetallic mercury–platinum and cadmium–platinum alloy phase on the surface graphite electrode, and recording the oxidation peak of mercury and cadmium from these phases with the help of linear scan voltammetry. Three alloy phases are formed in the case of mercury–platinum, whereas only one phase appears in the case of cadmium–platinum.

Keywords Mercury · Platinum · Cadmium · Intermetallic phase · Stripping voltammetry

Introduction

In a previous paper [1], we have shown that it is possible to determine Pt(IV) by recording the anodic stripping

voltammograms of indium oxidation from deposited InPt alloy phases. The determination of platinum is carried out by means of anodic stripping voltammetric methods [2]. They allow determining microamounts of various metals with great accuracy and sensitivity. Although platinum is reduced at the electrode surface, it does not give an electrooxidation peak in the voltammograms. The possibility to determine platinum by anodic stripping voltammetry using mercury and cadmium as co-deposited metals is presented below.

The goal of this paper is to describe the method of calculating the anodic peak potentials of the co-deposited metal by applying Pauling's correlation equation to the systems Hg–Pt and Cd–Pt. For this purpose it was necessary to study the electrochemical behavior of different Hg–Pt and Cd–Pt phases. These studies form the basis for the development of analytical methods for the determination of platinum in the mineral raw materials, which is an important and demanding task.

Experimental part

Reagents and chemicals

All chemicals used were of analytical or pharmaceutical grade, and solutions were prepared with deionized water. Platinum, mercury, cadmium, and hydrochloric acid were supplied by Merck.

Electrochemical measurements

Voltammetric measurements were carried out with the analyzer TA-4 ("Tom'analit," Tomsk). A conventional three-electrode system was used and special quartz beakers of $V=20$ mL as voltammetric vessels. A polyethylene-impregnated

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graphite electrode produced according to [3] was used as working electrode. A saturated silver/silver chloride electrode served as reference, and another silver/silver chloride electrode served a counter electrode. Platinum(IV), mercury(II), and cadmium(II) were deposited from solutions containing chlorides of these metals at the potential of -1.0 V. The graphite electrode was electrochemically cleaned by keeping it at 1.05 V for 60 s.

Results and discussion

The mercury–platinum system Figure 1 shows the voltammogram of the electrochemical oxidation of mercury–platinum alloys from a graphite electrode surface. The peak at $+0.15$ V is caused by the anodic oxidation of pure mercury which has been deposited on the graphite electrode, whereas the peak at $+0.33$ V (potentials of the peaks are automatically detected by the device) depends on both the platinum(IV) and mercury(II)-ion concentrations in the solution. With increasing platinum(IV) concentration, the voltammograms change and an anodic peak occurs at potential more positive than 0.40 V (Fig. 2).

When the Hg(II) and Pt(IV) concentrations are varied, the individual peak currents (and charges underneath) of the individual intermetallic phases also vary; however, the peak potentials of these peaks remain constant. This is a strong indication of the invariant composition of these intermetallic phases (constancy of composition). It can be expected that the electrochemical oxidation of mercury from different Hg–Pt phases (intermetallic compounds) will occur at anodic peaks at different potentials.

X-ray diffraction [4] of electrolytically prepared mercury–platinum alloys (same conditions as given in Fig. 2)

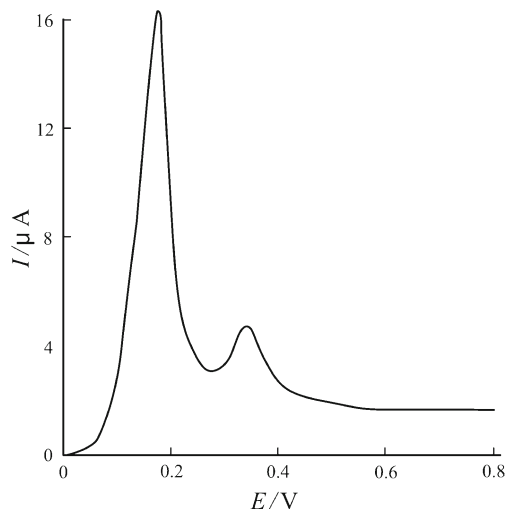


Fig. 1 Voltammogram of the electrochemical oxidation of Hg–Pt alloys. Experiment conditions: 1 mol L^{-1} hydrochloride acid solution, deposition time $t_c = 100$ s, scan rate $v = 80 \text{ mV s}^{-1}$; 0.1 mg L^{-1} Hg(II); 0.01 mg L^{-1} Pt(IV)

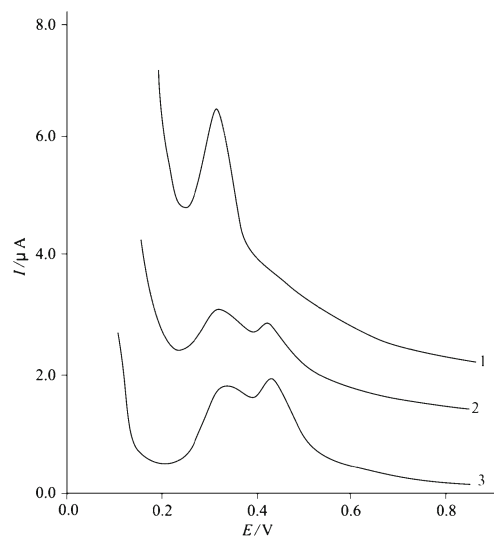


Fig. 2 Voltammograms of the electrochemical oxidation of Hg–Pt alloys. Experiment conditions: 1 mol L^{-1} hydrochloride acid solution, 0.1 mg L^{-1} Hg(II); 0.01 mg L^{-1} Pt(IV) (1), 0.04 mg L^{-1} Pt(IV) (2); 0.08 mg L^{-1} Pt(IV) (3)

revealed that the deposited phase is PtHg_4 . When the deposit was exposed to $+1.0$ V, only pure platinum remained at the electrode surface. This proves that all mercury of the PtHg_4 phase was oxidized, while platinum remains on the electrode. No other intermetallic phases could be detected in the mercury–platinum system by X-ray diffraction. Possibly, if such phases have been formed, they are X-ray amorphous.

According to the Hg–Pt phase diagram [5, 6], three intermetallic phases exist: PtHg_2 , PtHg_4 , and PtHg . The shift of the anodic peak potentials can be described by the following equation [1]:

$$\Delta E_{\text{pa}} = E_{\text{pa}} - E_{\text{pa}}^{\text{m}} = \frac{RT}{zF} \ln X_i - \frac{(1 - X_i)^2}{zF} \varepsilon_{\text{m}} \quad (1)$$

where ΔE_{pa} is the anodic peak potential of pure mercury, E_{pa}^{m} is the anodic peak potential of oxidation of mercury from the Hg–Pt alloys, ε_{m} is the integral mixing heat of the compounds forming the intermetallic phases, and X_i is the mole fraction of Hg. The mixing heats of formation of the alloys can be calculated with Pauling's correlating equation [7]:

$$\varepsilon_{\text{m}} = \frac{1}{2} (\varepsilon_{\text{A-A}} + \varepsilon_{\text{B-B}}) + 100(\chi_{\text{A}} - \chi_{\text{B}})^2 - 6,5(\chi_{\text{A}} - \chi_{\text{B}})^4, \quad (2)$$

where $\varepsilon_{\text{A-A}}$ and $\varepsilon_{\text{B-B}}$ are the energies of formation of the metallic bonds between the components A and B, respectively, and χ_{A} and χ_{B} are their electronegativities. The energies of the formation of metallic bonds and the electronegativity values of elements are taken from the published data [8]. The mixing heat of mercury and platinum calculated from these data is $85.63 \text{ kJ mol}^{-1}$.

Table 1 Calculated and experimental determined values of anodic peak potentials of mercury from Hg–Pt phases

	Potential an anodic peak of mercury	Composition of intermetallic phases Pt–Hg		
		PtHg ₂ ($X_i=0.66$)	PtHg ₄ ($X_i=0.8$)	PtHg ($X_i=0.5$)
X_i mole fraction of mercury in intermetallic phases with platinum	E_{calc} (V)	0.4	0.31	0.48
	E_{exp} (V)	0.43	0.33	No

The calculated peak potentials can be used to identify the order of peaks in the voltammograms (Fig. 2), and thus, it can be concluded what the intermetallic phase is oxidized at the individual peaks. We did not observe the intermetallic phases of PtHg (at 0.48 V) as in the studies using small platinum content, and this peak appears at a high platinum content of about 10 mg L⁻¹.

The calculated and experimental determined values of the anodic peak potentials of mercury from Hg–Pt phases are given in Table 1. The obtained data show that—regardless of the possible formation of three intermetallic phases—in reality only two phases are formed. The electrochemical oxidation of mercury from every Hg–Pt phase occurs at different potentials.

The cadmium–platinum system The application of stripping voltammetry method to this phase system was first mentioned in the article by Kolpakova et al. [9]. However, the above-mentioned authors did not calculate the anodic peak cadmium from the Cd–Pt alloy (Fig. 3).

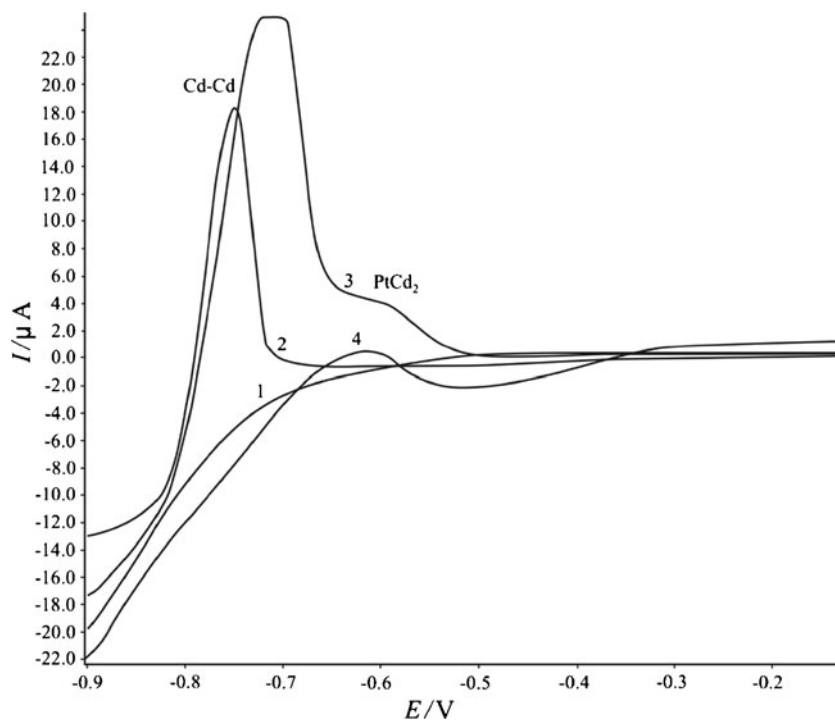
The peak at -0.75 V is due to the anodic oxidation of pure cadmium (phase peak of cadmium), and it depends on

the Cd²⁺-ion concentration. The Cd–Pt phase exhibits an anodic peak with the peak potential of -0.62 V.

The cadmium peak current increases as platinum deposited on the electrode provides active centers in which cadmium is deposited. With further increase of platinum, decreases and the further disappearance of the peak current of cadmium are spent on forming intermetallic phase Cd–Pt.

As already described for the Hg–Pt system, the shift of the anodic peak potential of the Cd–Pt alloy was calculated according to equations analogue to Eqs. 1 and 2. All values for the calculations were taken from reference sources [8]. Calculations based on this reference data show that the integral mixing heat of cadmium and platinum components equals 185.2 kJ mol⁻¹. With that mixing heat, the calculated anodic peak potential is -0.67 V, a value which is rather near to the experimental value -0.62 V. According to the phase diagram [5, 6], cadmium and platinum form only one intermetallic phase PtCd₂, which is in complete agreement with the voltammograms which always show one peak only. The calculated and experimental values of the anodic peak potentials of the Hg–Pt and Cd–Pt intermetallic phases confirm the formation of the known intermetallic phases.

Fig. 3 Voltammogram of the electrochemical oxidation of the cadmium–platinum alloy. Experiment conditions: 1 mol L⁻¹ hydrochloride acid solution (1), 100 mg L⁻¹ Cd (2), 200 mg L⁻¹ Cd+0.0005 mg L⁻¹ Pt (3); 300 mg L⁻¹ Cd+0.001 mg L⁻¹ Pt (4)



Conclusion

The results presented here show that it is possible to determine Pt(IV) in solutions by stripping voltammetry using mercury or cadmium as co-depositing metals. This work is a further proof that Pauling's correlation equation is applicable for the calculation of the anodic peak potentials of dissolution of the co-deposited metals from the respective platinum alloys. With the use of Hg as co-deposited metal appropriately than Cd as for the system Hg–Pt linear dependence on the content of platinum and for Cd–Pt, there is no linear dependence. In the case of the In–Pt system [1], several intermetallic phases are formed that reduce the range of the concentration of platinum. For the Hg–Pt system, the concentration range of platinum order of magnitude is greater.

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