Int. J. Electrochem. Sci., 7 **(2012)** 11558 - 11563

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Electrochemical Study on Adsorptive Wave of Tin-PMHP Complex

Liying Xu[1,2], *Ning Li*[1,*], *Jiamin Li*[3]

[1] School of Chemical Engineering and Technology, Harbin Institute of Technology, No.92,Western Dazhi Road, Nangang, District. Harbin 150001,China
[2] School of Science, Harbin University, Harbin 150086, China
[3] College of Science, Northeast Forestry University, Harbin 150040, China
[*]E-mail: Lining1957@126.com

Received: 28 September 2012 / *Accepted:* 19 October 2012 / *Published:* 1 November 2012

In the medium of HAc-NaAc（pH 4.0），Sn（II）reacts with HPMHP(1-phenyl-3-methyl-4-heptanoyl -pyrazalone-5) to form a complex and there is a sharp and sensitive polarographic wave at –0.66V（vs SCE). The peak height is linear with the concentration of Sn (II) in the range of 0.002～10μg·L^{-1} Many electrochemical methods were used to study the properties of the polargraphic wave and the mechanism of electrode reaction and it was proved that the polargraphic wave at –0.66V is an adsorptive wave of the complex. The peak current is produced by reduction of the ion Sn（II）.The molar ration of the complex is Sn (II): HPMHP =1:2,and the conditional formation constant was found to be 4.05×10^{7}.

Keywords: Tin; Acylpyrazolone; Adsorptive wave; Electrochemistry

1. INTRODUCTION

Acylpyrazolones are an interesting class of *β*-diketones, containing a pyrazole fused to a chelating arm. These ligands have played a key role in coordination compounds that have found wide application in several areas, such as metal extraction agents. HPMHP is a kind of β-diketo compound. The neutral of the matter may exist with several possible tautomeric forms as reported[1]. The enol form OH is weakly acidic, as a surfactant, which makes it suitable for electrochemical analysis, and has practical significance in polarographic determination of trace metals, Various methods for the detection of Tin have been reported[2-7] ,However, there are fewer studies about the acylpyrazolones applied to detect tin, In this article, HPMHP was used firstly in determination tin, This work aims to investigate the electrochemical behavior of Tin on the electrode. The results show good selectivity, high sensitivity, and a low detection limit with Tin. It is a good electrochemical method for the quantitative determination of Tin in metal samples.

2.EXPERIMENTAL

2.1.Apparatus and Reagents

All electrochemical experiments were carried out at a CHI-660A electrochemical workstation (Shanghai CH Instruments, China) with a conventional three electrode system. A dropping mercury electrode working electrode, a platinum wire counter electrode, a saturated calomel reference electrode, and a 10mL cell were used for electrochemical measurements.

HPMHP was firstly synthesized according to the method proposed by Jensen [8](yield 71%, mp 363.5–364.3 K) with further purification, and standard solution of HPMHP was prepared from anhydrous ethanol solution. Tin was obtained from the Shanghai Reagent Company, and a stock standard solution of tin(II) was prepared from concentrated H_2SO_4 solution and stored in a refrigerator until used. Buffer solution of pH 4.0 was prepared from $2mol\cdot L^{-1}$ HAc and NaAc. Other chemicals were of analytical grade. All solutions were prepared with redistilled water.

2.2.Experiment Measurements

Electrochemical determination of tin was carried out in a cell with 10mL supporting electrolyte solution. Standard stock Tin solution was added according to the requirement. Before the single-sweep polarography scanning, high purity N_2 was used to remove oxygen. The scanning from potential of -0.80 to -0.4V were recorded after a 6-s quiescence period. All electrochemical experiments were carried out at ambient temperature (298±2 K).

3.RESULTS AND DISCUSSION

3.1.Single-sweep polarography scanning of tin

The experiment was performed in the buffer solution (pH 4.0), with Single sweep oscillopolarogram sweeps in the potential range of -0.8 to -0.4V at a scan rate of 100mV/ s. As shown in Fig. 1a,b, no peaks of buffer solution and HPMHP were found. But in Fig. 1c, that one oxidation peak of tin (-0.62V) in buffer solution was observed; As the HPMHP is added in the Sn(II)-HAc-NaAc solusion ,the peak potential(-0.66V) shifted to the negative direction, the shape of the peak turned sharper, and the peak current increased significantly. The enhancement effect may be due to the HPMHP reaction with tin promoting the electron transfer on the electrode. It can be seen from Fig. 1d and Fig. 1e , along with the increased quantum of tin(II), that the oxidation peak current gradually increases. This indicates that electrode reaction process is controlled by adsorption .The enhancement effect may be due to the HPMHP coordination with tin and promoting the electron transfer of tin on the electrode.[9]

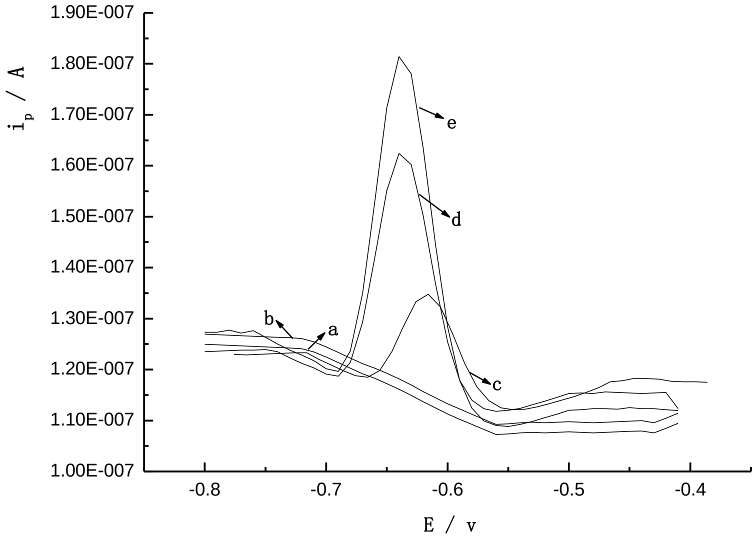

Figure 1. Single sweep oscillopolarogram on complex of Sn^{2+} and HPMHP (a. HAc-NaAc, b. a+ HPMHP c. a+0.400ugSn (II), d. b+0.400ugSn (II), e. d+0.400ugSn (II))

3.2.Effect of Solution pH

The effect of solution pH on the peak current and peak potential of tin-HPMHP was investigated . pH was adjusted from3 to 5.5 with 0.1 mol·L^{-1} NaOH or HCl. It was found that at pH>5.5, no peak of tin was observed in buffer solution; at pH<5.5, with the increasing pH value, the peak potential shifted negatively and the peak current increased firstly then decreased gradually, which indicated that protons are directly involved in the oxidation of Tin.

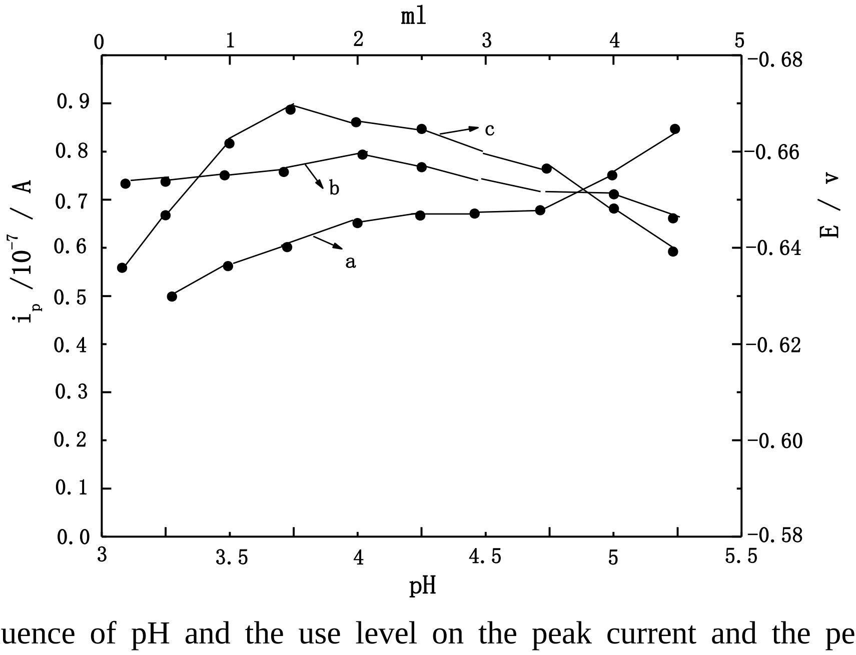

Figure 2. Influence of pH and the use level on the peak current and the peak height (a. i_p～pH curve,1.00ug Sn (II), b. E_p～pH curve,1.00ug Sn (II), c. i_p～the Amount of HPMHP,1.00ugSn (II))

As shown in Fig. 2, at pH range from 3 to 5.5, the oxidation peak was stable; therefore, we chose a pH of 4.0 for the analytical experiments. The pH dependence of oxidation peak potential obeyed the equation, Ep (V)=0.368-0.064 pH (r=0.995). The slope of 64mV pH^{-1} also indicated that two protons took part in the rate-determining step.[10] This result was in good agreement with the electro-oxidation mechanism reported in the literature.[11,12]

3.3.Effect of sweep rate

The peaks' current are found to increase with the square root of the scan rates from 0.025 to $0.15V\cdot s^{-1}$, and to deviate from Randle-Sevcik equation(shown in Fig.3).The result indicates that electrode reaction was a adsorption-controlled process[13].

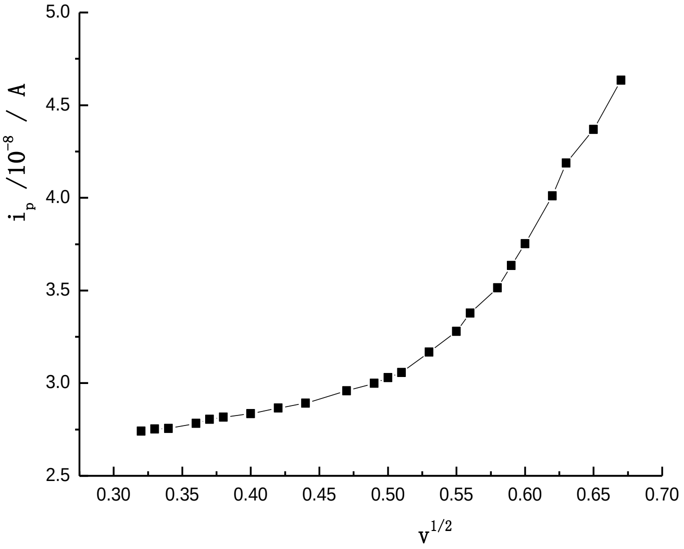

Figure 3. The curve of $i_p \sim v^{1/2}$

3.4.Determination of Tin

With increasing concentration of tin, the peak current increased. Linear concentration range was found from 0.002 to 0.005, 0.005 to 0.007μmol·L^{-1}, with the linear regression equations： I_{Pa}(μA)=0.2615c+0.2635(μmol·L^{-1}) (r=0.9986), I_{Pa}(μA)=0.1763c+0.2345 (μmol·L^{-1}) (r=0.9995), The detection limit is 0.02μg·L^{-1}. This detection limit was lower and the sensitivities were higher than high performance liquid chromatography method reported in the literature [14].

3.5.Interferences

Prior to the application of proposed method on samples, it was vital to investigate the effect of the interfering ions on the recovery percentage of tin. The effects of some ions such as Ni^{2+}、Co^{2+}、Zr^{4+}、Ce^{3+}600, Cr^{3+} 500, Al^{3+}、Zn^{2+}300, Ag^{+}250, In^{3+}、Mn^{2+}80, Cd^{2+}60, Cu^{2+}50； SO_4^{2-}、NO_3^{-}

were examined. The tolerance limit was defined as the maximum concentration of the interfering, substance that caused an error less than ±5% for determination of tin. The results showed that these ions have no influence on the determination of Tin and the proposed method has good selectivity for the determination of tin.

3.6.Mechanism of coordination

From all the experiment results , the polarographic wave is coordination adsorptive wave, the reaction is not reversible process, the mechanisms as follows:

$$Sn^{2+}+2PMHP^{-}=[Sn\text{-}2PMHP]$$

$$[Sn\text{-}2PMHP] = [Sn\text{-}2PMHP]_{ads}$$

$$[Sn\text{-}2PMHP]_{ads}+2H^{+}+2e=Sn（Hg）+2HPMHP$$

4.CONCLUSIONS

HPMHP had been used to investigate the electrochemical behaviors of tin , It was a diffusion controlled irreversible process with two electrons and two protons. This, electrode exhibited high electrocatalytic activities towards the oxidation of tin by significantly decreasing their oxidation over potentials and enhancing the peak currents. This electrochemical sensor showed excellent selectivity and high sensitivity. Also, the proposed method has potential application in the determination of tin in metal samples with satisfactory results.

ACKNOWLEDGMENT
This work was supported by grants from Scientific Research Foundation of the Education Department of Heilongjiang, Province People's Republic of China (No.12513059), Youth Foundation of Harbin University (No. HXKQ200610) and the Fundamental Research Funds for the Central Universities (No. DL11BB28).

References

1. 1.. Marchetti F, Pettinari C, Pettinari R ,*Coord Chem Rev*,249 (2005) 2909
2. J.Z. Li, G.. Li ,W.J. Yu. *J. Rare Earths*, 18 (2000)233
3. S. Wang, Y.M. He , *Anal. Laboratory*, 16 (1997)22
4. C.P. Tian, *Anal. Laboratory*,21 (2012)19
5. Z. Zhang, J.S. Wang,L.J. Zhang, *Anal. Laboratory* ,19 (2005)71
6. Reza Ojani, Jahan-Bakhsh Raoof, Banafsheh Norouzi， *Int. J. Electrochem. Sci*., 7(2012)1852
7. X.L. Li, Y. Lu， Z.L. Zhou， M.L. Zeng, *Anal. Chem*, 8(2000)652
8. B.S. Jensen, *Acta .Chem.* 13(1959)1668
9. L.Y Xu, J.Z Li, *Chin. J. Inorg. Chem.* 21(2005)1614
10 S.Yun, J.Z.Li, *J. Instru Sci & Tech*,39(2011)261
11 Goyal, R. N.; Chatterjee, S.; Bishnoi, S. *Electroanal*,21(2009) 1369
12 R. Zhang, G. D.Jin, X.Y.Hu, *J. Solid State Electro*,13 (2009)1545

13 W. Sun, Y. Z. Li, H.W.Gao, *Microchim. Acta*,165(2009)313
14 X.P.Wang, H.Y.Jin,L.G.Chen, *Anal chem,* 11(2007) 116