

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Tin Ions Behavior on a Stationary Mercury Microelectrodes in the Presence of Polyacrylamide.

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ABSTRACT

The article presents the results of the study of electroreduction of tin (II) ions on a mercury dropping electrode in solution 4,0M NaOH when the concentration of polymer $0,2 \cdot 10^{-2}$ - $6,0 \cdot 10^{-2}$ % mass.

Keywords: tin ions, stationary mercury microelectrodes, polyacrylamide (PAA), polarography ABC-1.1.

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INTRODUCTION

Study of the effect of surface-active organic substances of different nature on the kinetics of electrode processes carried out mainly on amalgam and mercury dripping electrodes, because even the leakage of mercury allows the flow of electrochemical reactions on the continuously updated surface [1].

Surface-active substances (SAS) are widely used in technological processes of metals electrodeposition in electroplating and hydrometallurgy. Suppressed most of the electrolytes used in electroplating, contain certain organic additives, which improving the structure of physical and chemical, corrosive and other properties of the electrodeposited coating and give the surface specific properties (gloss, adhesion with the surface, and others) [2,3].

Adsorbed on the phase boundary metal-solution, SAS have a significant influence on the proceeding electrochemical reactions.

In some works, on the basis of the conducted research summarizes some regularities of influence of pH, temperature, nature of the anion of the background and other factors on the effectiveness of SAS in the electrodeposition of metals [4-11]. For example, when studying the influence of adsorption processes on the cathode emissions of cadmium and lead on the electrodes of different nature is revealed that a dramatic inhibition of the electroreduction processes, which manifested in the appearance of a low current limit and high polarization, associated with the formation on the electrodes dense adsorption layer, collapsing at high negative potentials. The authors pay attention to the small magnitude of overvoltage during electroreduction of lead (II) on a solid electrode, which is associated with a high rate of discharge of ions of lead (II) [4-8].

The majority of research devoted to studying the electrochemical behaviour of some metals [1] or adsorption of SAS on gallium electrode [2,3]. And study the kinetics of electrode processes under the influence of surfactant organic nature have been conducted primarily on mercury and amalgam dripping electrodes, because even the leakage of mercury provides the flow of electrochemical reactions at constant changing surface. And only a small part of the work is devoted to the study of the electroreduction on the same solid electrodes in the presence of various inhibitors. It is very effective inhibitors of the discharge of metal ions was substituted ammonium and other nitrogen-containing compounds, which the electrodes are formed, as a rule, positively charged layers [9-11].

MATERIALS AND METHODS

Study of the effect of high-molecular SAS polyacrylamide (PAA) on the discharge and ionization of tin (II) on a mercury dropping electrode was carried out in solution 4,0M NaOH when the concentration of the polymer $0,2 \cdot 10^{-2}$ - $6,0 \cdot 10^{-2}$, mass %.

Research conducted on polarography ABC-1.1 three-electrode mode.

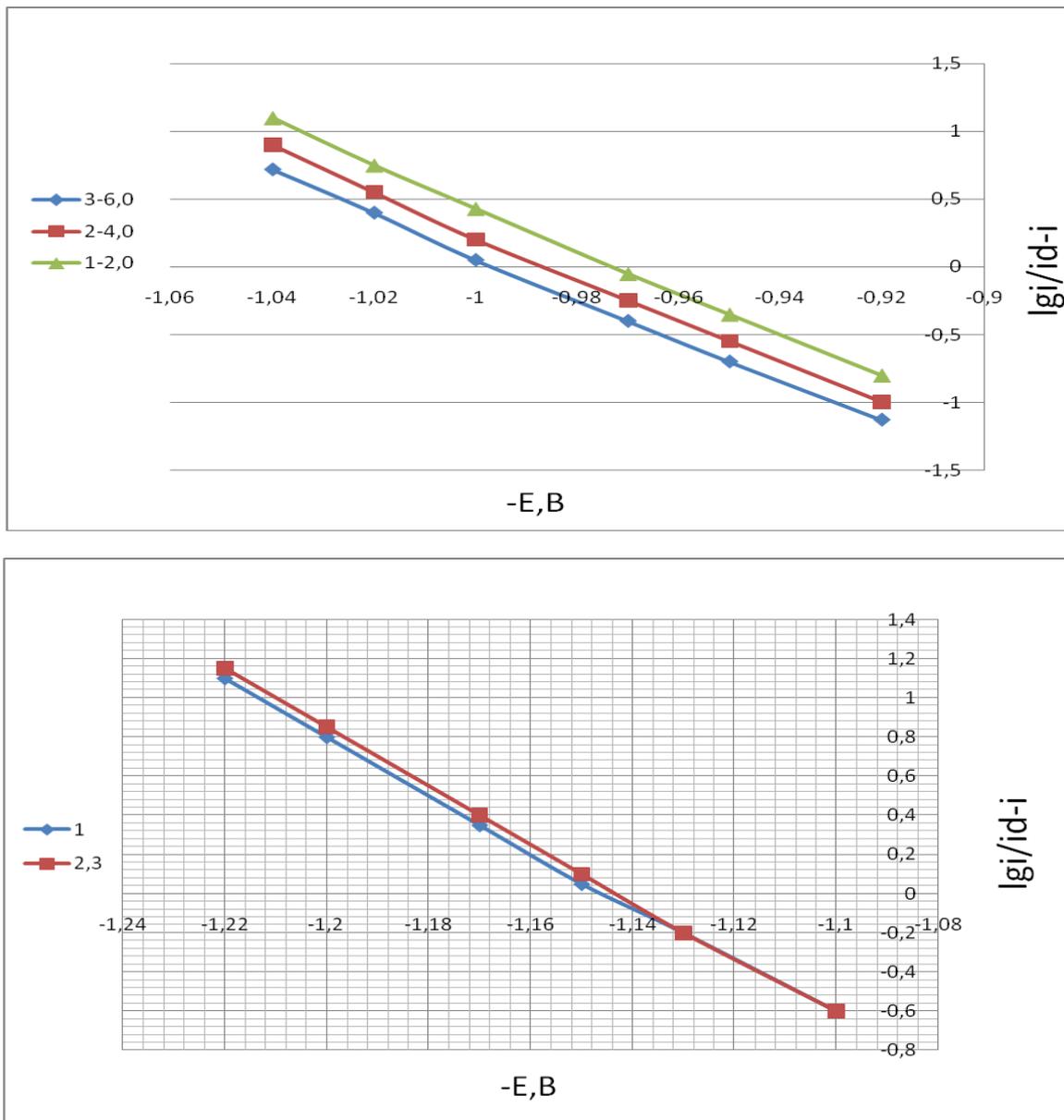
As a working electrode were used mercury electrode with the surface $S=2,2 \cdot 10^{-2}$ Q.cm. As the reference electrode used saturated silver chloride electrode, the auxiliary electrode was a rod spectral pure graphite.

As surface-active substances (SAS) used polyacrylamide (PAA), discharge and ionization of tin (II) on a mercury dropping electrode was carried out in solution 4,0 M NaOH when the polymers concentration $0,2 \cdot 10^{-2}$ - $6,0 \cdot 10^{-2}$ % mass.

RESULTS

On the figure 1 presented according $\lg i/i_d - i$ from E the process of discharge of tin (II) ions in the presence of SAS additives. As can be seen from figure, with the introduction of polarographically solution additives PAA has a split wave of this process. Semi-logarithmic dependence straightforward, the offset of the starting potential slightly.

The calculated value α in presence of PAA increases to $0,40 \pm 0,03$ for I and II waves. For calculate the kinetic parameters of tin (II) ions discharge process in absence and presence of PAA was applied the method of Tanaka-Tamamushi.



**Figure 1: Semi-logarithmic dependence $lg(i_d-i)$ to E process of tin ions discharge in presence of PAA.
Electrolyte composition: $0,002\text{ M Sn}^{2+} + 4\text{ M NaOH}$
 $C_{SAS} \cdot 10^{-2}$, mass. %: 1-2,0; 2-4,0; 3-6,0.**

Built by the $E - 0,059/n \lg(i_d-i)$ to i , mka which is shown in figure 2. From these dependencies found value $E_{1/2}^r$ table 1.

Table 1: The value of $E_{1/2}^r$ discharge process of tin(II) ions in a solution of 4 M NaOH in presence of PAA, for I and II waves.

| $C_{PAA} \cdot 10^{-2}, \%$ | 0 | 2,0 | 4,0 | 6,0 |
|-----------------------------|-------|-------|-------|-------|
| PAA I wave | -0,96 | -0,95 | -0,96 | -0,95 |
| PAA II wave | -0,96 | -1,12 | -1,11 | -1,13 |

As can be seen from table of values $E_{1/2}^r$ the discharge process of tin (II) ions for 1 wave with the introduction of surfactant shifted to positive values, and II waves in negative values. As well as determined the kinetic parameter of tin (II) ions, in which the further used for calculation k_s .

$\log i_d - i/i = \log(1,13) + \frac{anF}{2,3RT}(E - E_{1/2}^r)$, here is
 $\log Z = \log i_d - i/i - \frac{nF(E - E_{1/2}^r)}{2,3RT}$
 $\log(Z-1) = \log 1,13 - (-1) \cdot \frac{nF(E - E_{1/2}^r)}{2,3RT}$
 Built according to $\lg(Z-1)$ or $(E - E_{1/2}^r)$, Fig.2.

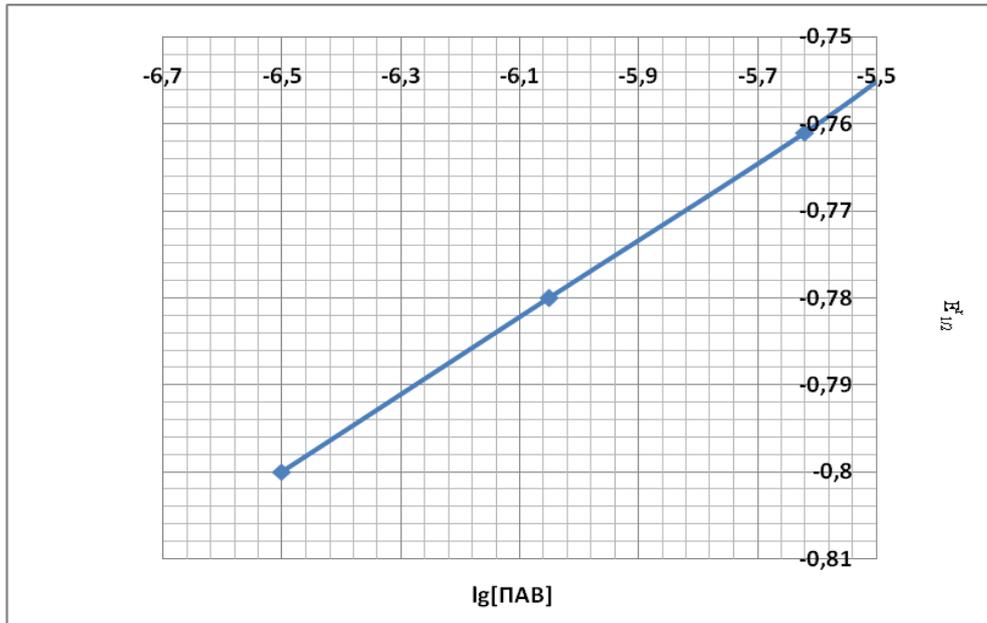
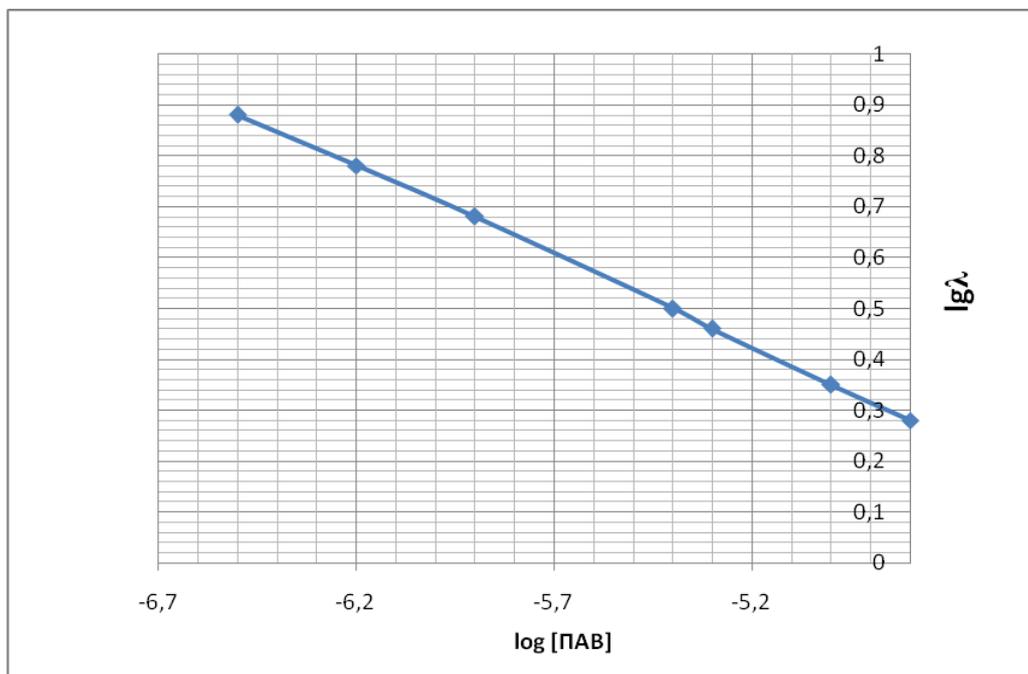


Figure 2



The segment on axis y And is $\log 1,13$. Hence, the calculated values showne in table 2.

Table 2: Values of discharge tin (II) ions in solution of 4 M NaOH in presence of PAA.

| $C_{SAS} \cdot 10^{-2}, \%$ | 0 | 2,0 | 4,0 | 6,0 |
|-----------------------------|------|------|------|------|
| PAA I wave | 0,28 | 0,45 | 0,89 | 0,15 |
| PAA II wave | 0,28 | 0,22 | 0,22 | 0,28 |

Our calculated values of D_{ox} from the equation of Ilkovich $I_d = 607n C_0 D^{1/2} m^{2/3} t c^{1/6}$, wave 3.

Table 3: Values of diffusion coefficients for discharge tin (II) ions in solution of 4 M NaOH in the presence of PAA, T=298 K.

| $C_{SAS} \cdot 10^{-2}, \%$ | 0 | 2,0 | 4,0 | 6,0 |
|-----------------------------|-----|-----|-----|-----|
| PAA I wave | 5,3 | 1,9 | 1,8 | 1,3 |
| PAA II wave | 5,3 | 2,3 | 2,2 | 2,3 |

In table 4. the values of rate constants discharge process of tin (II) ions at a mercury electrode in solution of 4 M NaOH and in presence of PAA, T=298 K.

Table 4: Values of diffusion coefficients for discharge tin (II) ions in solution of 4 M NaOH in the presence of PAA, T=298 K.

| $C_{SAS} \cdot 10^{-2}, \%$ | 0 | 2,0 | 4,0 | 6,0 |
|-----------------------------|-----|-----|-----|-----|
| PAA I wave | 7,3 | 8,9 | 1,8 | 1,7 |
| PAA II wave | 7,3 | 4,4 | 4,3 | 4,0 |

The analysis tables show, that in presence of PAA values rate process constants reduced, that indicating a braking discharge process of tin (II) ions in presence of PAA.

Thus, the obtained experimental data and the kinetic parameters indicate formation of polymer additives connections to discharge the particle compounds, which lead to splitting of reduction wave tin (II) in the presence of PAA.

DISCUSSION

We studied the effect of surfactants PAA on the electrochemical reduction of tin (II) ions at 298K. On basis of temperature and kinetic studies have shown that the recovery process tin (II) ions at mercury electrode is under diffusion control, as evidenced by the independence of the values of the activation energy of the process from the polarization. Inhibition of the electrochemical reaction of surfactants is due to the formation of layer adsorption dense, which required additional energy to transfer through the double electric layer. Adding PAA reduces the efficiency of inhibition reactions by increasing the total energy and thus increasing values of current ions exchange discharge but, however, the offset of the effective entropy of activation allows to conclude about, in presence of surfactant retained inhibitory effect.

Thus, we can conclude that we studied as SAS of PAA affect the electrochemical behavior of tin (II) ions on a mercury dropping electrode.

Kinetic studies show that the inhibition of process is maintained in presence of PAA. We can conclude that the investigated surfactants can be recommended, as inhibitors of ion electroreduction of tin (II) in the studied concentration range.

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