

SQUARE-WAVE VOLTAMMETRY OF 1-ISOBUTYL-TETRAZOLE-5-THIOL

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Abstract

Basic electrochemical characteristics of 1-isobutyl-tetrazole-5-thiol in the acid medium, in the course of electrolysis by square-wave voltammetry at the hanging mercury drop electrode (HMDE) are reported. In the life-time of the HMDE a compound between the mercury and thiol was spontaneously formed and adsorbed on the HMDE surface. The process of adsorption is related with formation of a multilayer adsorbed film. As the consequence, two kinds of square-wave (SW) voltammetry peaks appear. The first one is as a result of reduction of the monomolecular layer, while the second peak (at more positive potential) is as a result of the reduction process of the subsequent layers distinguished by lower adsorption energy. The results of square-wave voltammetry of 1-isobutyl-tetrazole-5-thiol successfully correlate with theoretical prediction for the SW voltammetry of an adsorbed reactant.

Keywords: *Square-wave voltammetry, 1-Isobutyl-tetrazole-5-thiol*

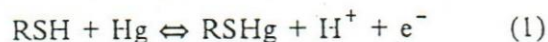
Introduction

Some mercaptotetrazoles have an antituberculosis activity. One of these derivatives is 1-isobutyl-tetrazole-5-thiol [1] (which further will be referred to as RSH).

It is well known that *dc* polarographic response of compounds which contain SH (thiol) group is an anodic wave because of the dissolution process of the mercury, combined with the formation of a mercuric mercaptide [2-7]. In the most cases the formed compound between the mercury and the thiol has electrocapillary properties and adsorbs on the surface of mercury electrode. This phenomenon is followed by appearance of few anodic *dc* waves with many irregularities on them [2,3].

The performed electrochemical investigations of the RSH have shown that the *dc* polarography response is well defined anodic waves, which are as a result of the oxidation process de-

scribed by eqn. [8] :



The product of the oxidation strongly adsorbs on the dropping mercury electrode (DME). Thus, the reversibility of the electrode process depends on many factors such as concentration of RSH in the solutions, drop life-time, medium pH, etc.

On the other side, the adsorption of the electroactive species on the surface of the working electrode can be used as preconcentration step in electroanalytical methods for their quantitative determination [9]. The accumulation can be combined with different voltammetry techniques such as linear scan [10, 11], altering current [12, 13], pulse [14-18], differential pulse [18-20] and square-wave voltammetry [21-25].

In the present paper the basic polarographic characteristics of RSH will be described. The em-

phasis will be on the results obtained by square-wave voltammetry because it is one of the most advanced electroanalytical techniques with the highest quantitative sensitivity to RSH, and because several interesting effects arising from the adsorption of RSH on the HMDE surface have been observed [26,27].

The study of electrochemical behaviour of RSH during the electrolysis by square-wave voltammetry is of great importance for the future development of a complete electroanalytical method for its quantitative determination.

Experimental

An EG&G (USA) Princeton Applied Research microprocessor-based polarographic analyser (PAR Model 384B) equipped with PAR, Model 303A static mercury drop electrode (SMDE) and a PAR Model 305 stirrer were used to record all SW voltammograms. The electrode compartment is consisted of a static mercury drop electrode, silver-silver chloride (saturated KCl) and a platinum wire as a working, reference and auxiliary electrode, respectively. The solutions were degassed with highly purified nitrogen at the start of each experiment and a flow of nitrogen was maintained over the solution during the experiment to prevent oxygen interference. All experiments were performed at a room temperature.

The all chemicals used were of analytical reagent grade. Bidistilled water is used.

The nitrogen used for purging oxygen from solutions was deoxygenated by passing through acidic vanadium (II) chloride solutions. The purging time was 8 min.

RSH was synthesized by K. Waisser et al. from Pharm. Fak. Univ. Karlovy, Hradec Kralove, Chech. Fundamental experiments were carried out in 1×10^{-4} mol/dm³ ethanol solutions of RSH in *Briton-Robinson* buffers with pH values from 2 to 9. The *Briton-Robinson* buffers with constant ionic strength of 0.10 mol/dm³ were prepared from 0.04 mol/dm³ CH₃COOH, H₃PO₄ and H₃BO₃ and 0.20 mol/dm³ NaOH.

The square-wave and cyclic voltammograms

were recorded at hanging mercury drop electrode (HMDE), while the *dc* polarograms were recorded on dropping mercury electrode (DME).

The used experimental conditions were as follows: potential range from 0.05 to -0.70 V, scan increment 6 mV, SW frequency 100 Hz and SW amplitude 20 mV. The parameters of the experiments which were carried out under other conditions are presented in the titles of the Figs. 1-4.

The starting potential was used as an accumulation potential.

Results and Discussion

The polarographic studies of RSH solutions with 5×10^{-4} mol/dm³ concentration of *Briton-Robinson* and acetate buffers in the pH range from 2 to 9 have shown that anodic polarographic waves can be obtained across the whole pH range [8]. The position and the shape of the waves are affected by the nature of the buffers and pH of the medium. At more positive potential than 0.05 V abnormalities occur in both buffers [8]. The oxidation product strongly adsorbs on the DME surface and changes the oxidation rate on the covered surface. With increasing of the drop life-time, the height of *dc* anodic waves decreases (Fig.1). Hence, total *dc* polarography

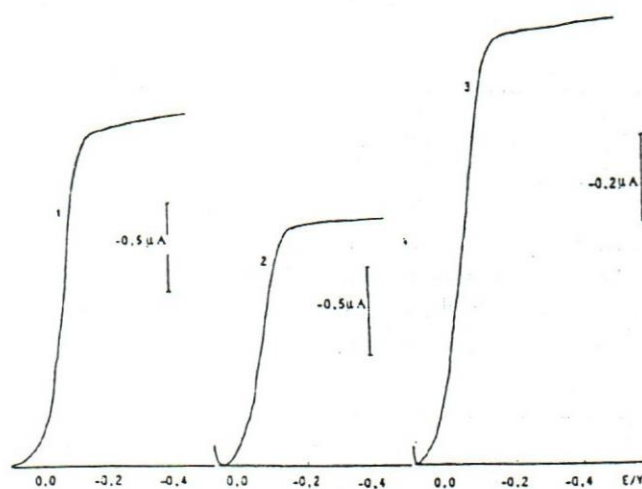


Fig.1. The effect of the drop step time on the *dc* polarograms of 5×10^{-4} mol/dm³ RSH solutions: 1) drop-step time 0.5 s; 2) drop-step time 1 s; 3) drop-step time 2 s; pH=3; scan increment 6 mV;

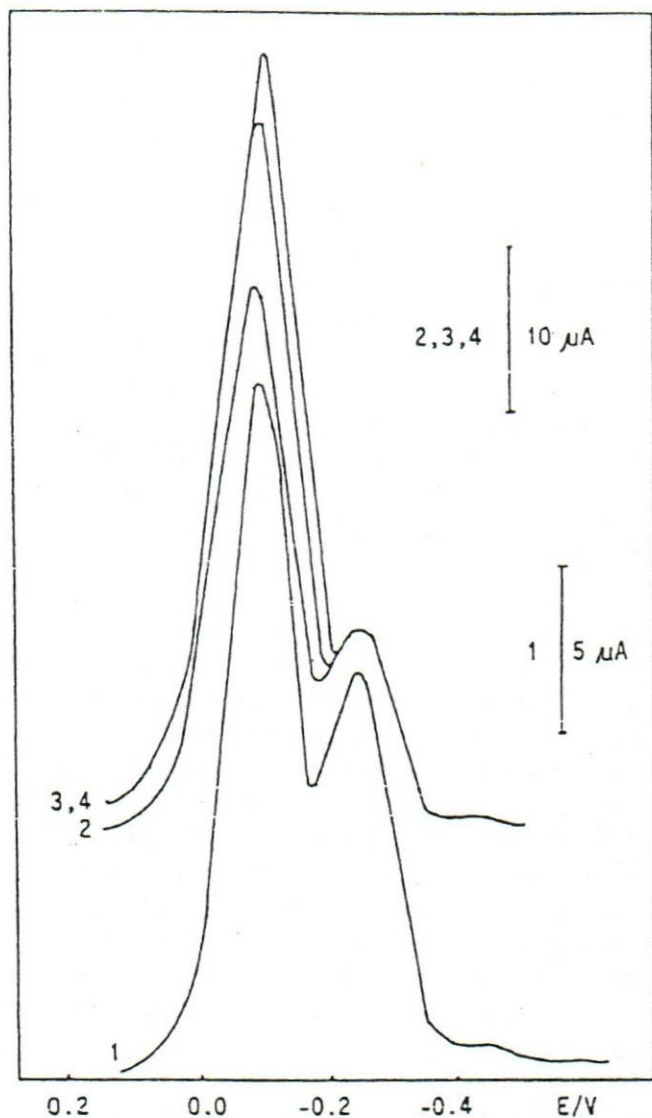


Fig.2. Influence of the accumulation time on the SW peaks of RSH.

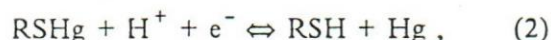
1) accumulation time 0 s; 2) accumulation time 1 s; 3) accumulation time 3 s; 4) accumulation time 5 s. Concentration of RSH 5×10^{-4} mol/dm³; frequency 100 Hz; amplitude 20 mV; scan increment 6 mV.

response depends on a drop life-time and reactant concentration. If both these variables are small, the oxidation of the free electrode surface prevails, while if these variables are large, the reaction on the DME surface, totally covered by the adsorbed product dominates.

Square-wave voltammetric measurements of

RSH solutions with 5×10^{-4} mol/dm³ concentration of Britton-Robinson buffer (pH 3), with negative potential direction (same direction as in *dc* polarography) have shown that SW response are two SW peaks (Fig.2.1). For detail examination of electrode reaction, the RSH solutions were recorded with cyclic voltammetry, under the same experimental conditions. It was concluded that at negative potential direction the reduction process occurs followed by reoxydation process at positive potential direction. The interpretation of cyclic voltammograms shows that the electrode process is irreversible under these experimental conditions.

Electrochemical activity of the RSH during electrolysis by square-wave voltammetry at negative potential direction, can be described by following electrode reaction:



where: RSHg species is spontaneously formed in the bulk of the solutions, during the life of the hanging mercury drop electrode and adsorbed on its surface.

This assumption is in accordance to the electrochemical behaviour of the other organic compounds which also contain SH group [28-30].

From Fig.2 it can be seen that with the increase of the accumulation time from 1 to 5 s the relationship between the height of SW peaks is changed. Namely, the peak current of the SW peak at about -0.25 V is almost constant, while the peak at about -0.10 V increases proportionally by the increasing of the accumulation time. This SW response can be explained by assumption of a formation of a multilayer adsorbed film of mercuric mercaptide on the HMDE surface [29]. The SW peak at more negative potential, which is independent of the accumulation time, appears as a result of a reduction process of monomolecular layer of RSHg species on the HMDE surface. The subsequent layers distinguish themselves by lower adsorption energy. Thus, the reduction of these layers of adsorbed film occurs at more positive potential. The

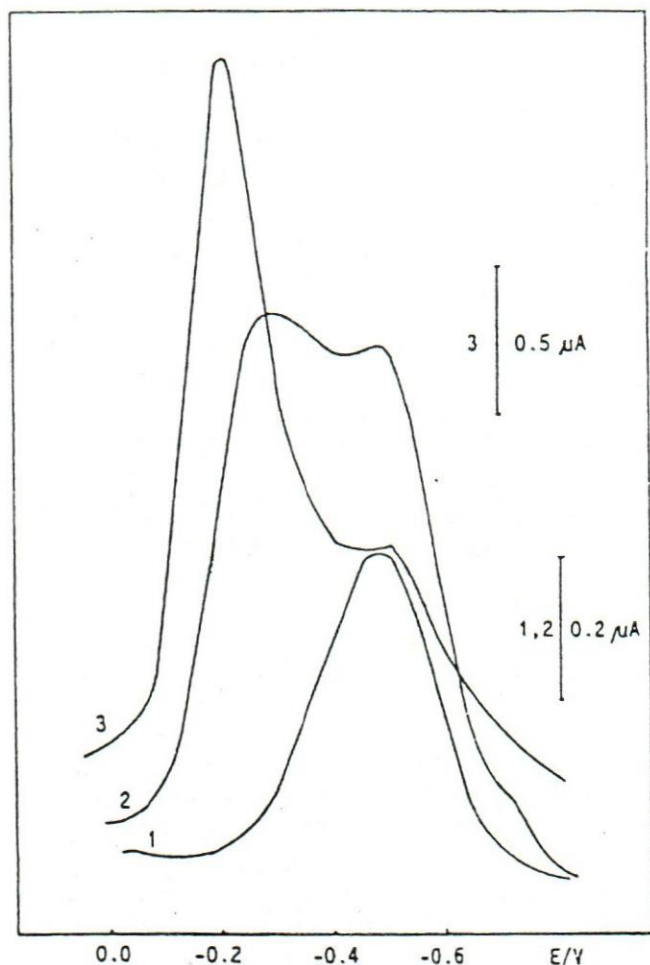


Fig.3. Influence of the accumulation time on the SW peaks of RSH.

1) accumulation time 15 s; 2) accumulation time 60 s; 3) accumulation time 120 s. Concentration of RSH 5×10^{-6} mol/dm³; all other parameters as in Fig.2.

longer accumulation time yields to thicker adsorbed film which results with peak increase at more positive potential.

At lower concentration of RSH in the solutions (5×10^{-6} mol/dm³) and accumulation time of 15 s, only one SW peak arises (Fig.3). With increasing of the accumulation time the SW peak starts to grow. At 60 s accumulation time the SW peak splits and the new peak at more positive potential appears. After 60 s accumulation time only the second peak increases. From Fig.3 it can be concluded that at 5×10^{-6} mol/dm³ RSH concentration and 30 s accumulation time only

monomolecular layer of mercuric mercaptide on the HMDE surface is present. At longer accumulation time the amount of the mercury mercaptide, which is spontaneously formed in the bulk of the solution, is enough for the formation of higher layers of the adsorbed film.

The thickness of the adsorbed film is also a function of the accumulation potential. At the constant concentration of investigated component and constant accumulation time, positivity of the accumulation potential affects by intensive dissolving of the mercury and increasing the amount of the formed mercury mercaptide in the solution. Hence, the shift of the accumulation potential to the more positive one has the same effect on the SW response such as the accumulation time increase or the increase of the RSH concentration in the solution.

The analysis of the cyclic voltammograms recorded at various values of the scan rate confirms that the electrode reaction at negative potential direction takes place from the adsorbed state of the reactant. Such analysis has shown that there is a linear dependence between the height of the cathodic peak current and the magnitude of the scan rate. On the other hand, the dependence of the peak current and concentration of the investigated component is nonlinear. These results are in good agreement with the theoretical prediction for electrode reaction of an adsorbed reactant [31].

From the anodic part of the cyclic voltammograms two anodic peaks can be seen. The height and position of the anodic peaks are not affected by the accumulation time and accumulation potential. They depend only on the RSH concentration in the solution and pH of the medium.

Investigations of the oxidation process were performed by recording SW voltammograms at positive potential direction where potential of -0.70 V was chosen as a starting potential. It can be seen (Fig.4) that oxidation process of RSH results within two SW peaks, independently of accumulation time. The first anodic peak on the SW voltammograms and the analog one on the cyclic voltammograms, are as a result of the adsorption of the anodic oxidation product. The

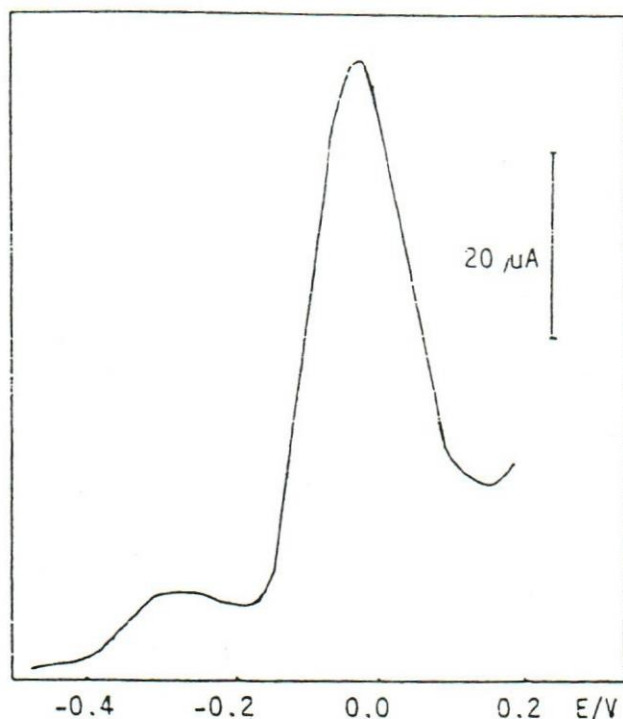
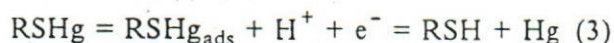


Fig.4. SW peaks of RSH at accumulation time from 0 to 15 s under positive potential direction. Concentration of RSH 5×10^{-4} mol/dm³. All other parameters as in Fig.2.

second peak illustrates the oxidation process of RSH to RSHg. The SW response with positive potential direction clearly indicates that RSH species does not adsorb at the HMDE surface.

The performed investigations of adsorption properties of RSH and RSHg species enable us to define the electrode process of reduction of RSHg by SW voltammetry as follows:



Hence, the total electrode mechanism of the

RSH includes the chemical reaction before the faradic process, and adsorption of the chemical reaction product on HMDE surface, which results in formation of multilayer adsorbed film under suitable conditions. This is a very complex electrode mechanism and until now there is not a theoretical model for this type of reaction.

M. Lovric et al. [32] have developed a theory of square-wave voltammetry of the electrode reaction where the adsorption of the reactant plays an important role. The theoretical model of Lovric et al. assumed that the adsorption of the reactant follows the law of linear isotherm. The electrode mechanism of RSH is more complex than the mechanism that was theoretically analysed by Lovric et al. However, the following results indicate that qualitative comparison between the experimental and theoretical results is possible.

According to the theory of irreversible electrode reaction where only the reactant is adsorbed on the HDME surface (in our case this is the RSHg species), the functional dependence between the peak current i_p and t_o , f , a , ΔE , and c , (where t_o is the accumulation time, f is the frequency, a is the amplitude, ΔE is the scan increment, α is transfer coefficient and c is the concentration of the investigated component), is presented by equation:

$$i_p = \text{const } c \alpha n^2 \Delta E f a^x t_o^{1/2}, \quad (x < 1) \quad (4)$$

On the Figs.5 and 6 is presented the dependence between the i_p and parameters of the SW signal for the SW peak at -0.10 V. It can be seen (Fig.5.1) that there is a linear dependence between the i_p and the square root of accumulation time. The increase of the SW frequency causes

Table 1. Influence of the pH on the SW peaks of RSH. Concentration of RSH 5×10^{-4} mol/dm³; frequency 100 Hz; amplitude 20 mV; scan increment 6 mV.

| pH | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| $i_p \cdot 10^4$ (nA) | 2.075 | 2.188 | 1.801 | 1.792 | 1.113 | 4.716 | 4.339 | 4.339 |
| E_p (V) | -0.096 | -0.096 | -0.096 | -0.096 | -0.090 | -0.018 | -0.036 | -0.036 |
| $i_p \cdot 10^4$ (nA) | 1.300 | 1.300 | 1.300 | 1.300 | 1.300 | 1.300 | - | - |
| E_p (V) | -0.240 | -0.252 | -0.252 | -0.246 | -0.240 | -0.240 | - | - |

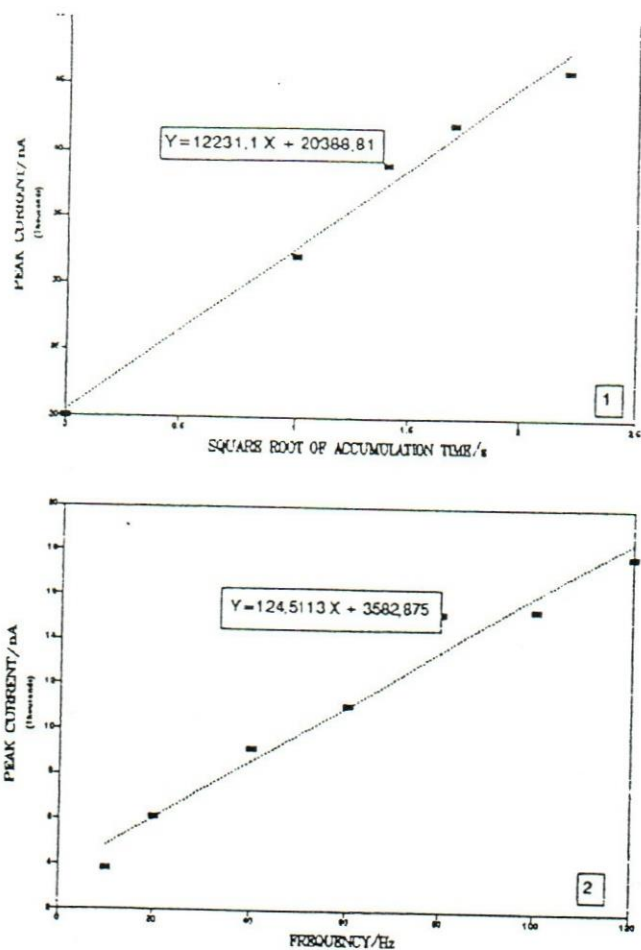


Fig.5. 1) Effect of the accumulation time and 2) SW frequency on the SW peak currents. All other parameters as in Fig.2.

the linear enhancement of the SW peaks of RSH (Fig.5.2). These results are in a good agreement with the above equation.

The dependence between the i_p and SW amplitude is nonlinear (Fig.6.1.) and almost linear between the i_p and the scan increment (Fig.6.2) that also is in compliance with the theoretical prediction.

The presented results have shown that the theory of the SW voltammetry of an adsorbed reactant can be successfully applied for qualitative description of the properties of more complex electrode mechanism, such as the reduction process of the subsequent layers of the adsorbed film of the RSHg species on the HMDE surface.

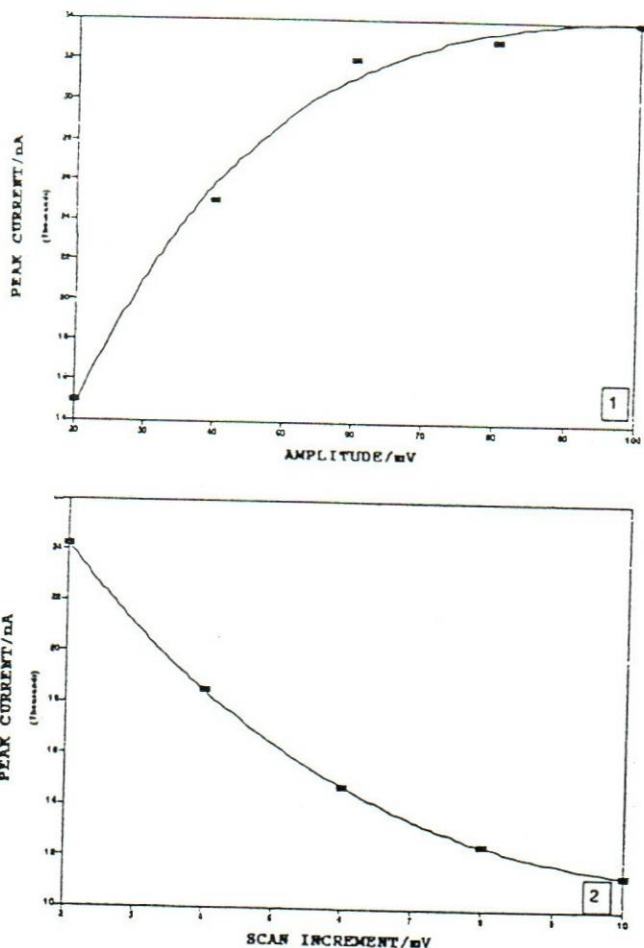


Fig.6. Dependence of SW peak currents on 1) amplitude and 2) scan increments of applied SW signal. All other parameters as in Fig.2.

At last, the SW peaks are investigated as a function of the pH of the medium. It is obvious (Table 1) that there is a tendency of an increase of the peak current for the peak at about -0.10 V with the increase of the pH values. There is a rapid increase of the peak current at $\text{pH} > 7$. If the dissociation of the thiol group has been taken into consideration, this result is expected, too. Namely, in the medium of $\text{pH} > 7$, it is reasonable to predict that the equilibrium of reaction 1 is shifted to the right side. Hence, the amount of the formed mercuric mercaptide in the solution rises and causes the higher SW peak.

The peak current at about -0.25 V across all pH range is constant, because it depends on the

RSH concentration into solutions and on the magnitude of the mercury surface.

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Received: Jan. 13, 1994

Accepted: Aug. 30, 1994