

Square-Wave Voltammetry of 1-Benzyl-tetrazole-5-thiol

Blagoja Jordanoski, Valentin Mirčeski, and Kornelija Stojanova

*Institut of Chemistry, Faculty of Sciences, St. Kiril and Metodij University,
Arhimedova 5, Skopje, Macedonia,*

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Basic electrochemical characteristics of 1-benzyl-tetrazole-5-thiol in acid medium were investigated applying classical (DC) polarography, cyclic (CV) and square-wave voltammetry (SWV). During the HMDE life-time, a compound was spontaneously formed between the mercury and thiol and deposited on the HMDE surface. The surface precipitation process results in formation of a multi-layer film on the electrode surface. The SW response of the investigated component mainly depends on the structure of the film.

INTRODUCTION

Some mercaptotetrazoles possess an antituberculosis activity.¹ One of the derivatives is 1-benzyl-tetrazole-5-thiol which hereafter will be referred to as RSH. In the present communication, the basic polarographic characteristics of RSH will be described.

Literature data on electrochemical investigations of organic compounds that contain the mercapto group in many cases contain controversial results.²⁻⁴ This indicates that the redox process of thiols at mercury electrode is very complex. However, the importance of the thiols, from the biological and pharmaceutical viewpoint, makes them a subject of many investigations.

It is well known that the DC polarographic response of compounds containing SH (thiol) group is an anodic wave due to the dissolution process of the mercury combined with the formation of a mercuric mercaptide.⁵⁻¹⁰ In most cases compound formed between the mercury and the thiol is an insoluble salt deposited on the surface of the mercury electrode. With anodic DC, this phenomenon yields waves with many irregularities.

On the other hand, surface precipitation of the insoluble salt formed between the analyte and mercury can be used for analytical purposes. For the compounds that chemically react with mercury to form insoluble salts, such as chloride, bromide, iodide,¹¹⁻¹⁴ sulphide,¹⁵⁻¹⁷ cyanide,¹⁸ selenide,¹⁹ and various thiols,^{3,20-24} the most commonly used method is the cathodic stripping voltammetry (CSV). In all these cases, the CSV methods include both deposition and a stripping process. The deposition process is connected with an electrolytic process, such as formation of the insoluble salt on the electrode surface resulting from the reaction between the analyte and electrochemical oxidized material of the electrode. The film of insoluble salt formed on the electrode surface is stripped under cathodic potential direction.

In the present work, electrochemical behaviour of RSH was investigated during electrolysis by DC polarography, cyclic and square-wave voltammetry. Emphasis will be laid on the results obtained by square-wave voltammetry because it is one of the most advanced electroanalytical techniques²⁵⁻²⁹ with the highest quantitative sensitivity to RSH. The investigations performed indicate that the square-wave voltammetry response of RSH solutions is a result of a cathodic stripping process of the film deposited on the surface of HMDE. The film is formed by chemical reaction between the mercury and the RSH on the surface of HMDE. The total SW response mainly depends on the film structure.

EXPERIMENTAL

An EG&G Princeton Applied Research microprocessor-based polarographic analyzer (PAR Model 384B) equipped with a PAR Model 303A static mercury drop electrode was used to record all voltamograms. The electrode compartment consisted of a static mercury drop (SMDE), silver-silver chloride (saturated KCl) and a platinum wire as its working, reference and auxiliary electrodes, respectively. The solutions were degassed with highly purified nitrogen at start of each experiment and a flow of nitrogen was maintained over the solution during the experiment to prevent oxygen interference. The nitrogen used for purging oxygen from solutions was deoxygenated by passage through acidic vanadium (II) chloride solutions. The purging time was 8 minutes. All experiments were performed at room temperature.

All chemicals used were of analytical reagent grade. RSH was synthesized at the Farm. Fak. Univ. Karlovy, Hradec Kralove, Czech by K. Waisser *et al.*¹ Britton-Robinson buffers with pH values from 2 to 10 were used as a supporting electrolyte. The Britton-Robinson buffers with constant ionic strength of 0.10 mol dm^{-3} were prepared from $0.04 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$, H_3PO_4 and H_3BO_3 and $0.20 \text{ mol dm}^{-3} \text{ NaOH}$. Redistilled water was used.

The square-wave and cyclic voltamograms were recorded at the hanging mercury drop electrode (HMDE), while the DC polarograms were recorded at the dropping mercury electrode (DME).

The most commonly used experimental conditions were: potential range from 0.10 V to -0.70 V, scan increment 6 mV, SW frequency 100 Hz and SW amplitude 20 mV. The scan rate for cyclic voltammetry was 600 mV/s. The parameters of the experiments carried out under other conditions are given in the figure captions.

The starting potential was used as a deposition potential.

RESULTS AND DISCUSSION

The polarographic studies of 5×10^{-4} mol dm $^{-3}$ RSH solution in Britton-Robinson buffers, in the pH range from 2 to 10, have shown that anodic polarographic waves can be obtained across the whole pH range. The position and the shape of the waves are affected by the pH of the medium (Figure 1). With positive potentials of more than 0.05 V, abnormalities occur in the plateau of the waves especially in the medium with pH > 7. In such media, there is a tendency of increasing the limiting current, followed by irregularity along the rising portion of the waves (Figure 1). The analysis of the dependency of $E - \log(i_l/i_l - i)$ shows that the slope of the straight line depends on many factors, such as the pH of the medium, concentration of the investigated component, drop-step time, *etc.* (Table I). Also, variations of the pH of the medium and the concentration of the investigated component affect the half-wave potential of the waves (Table II). It is obvious from Table II that by increasing the pH and the thiol concentration, the anodic waves are shifted towards more negative potentials. All these results indicate that the redox reaction is irreversible or quasireversible.

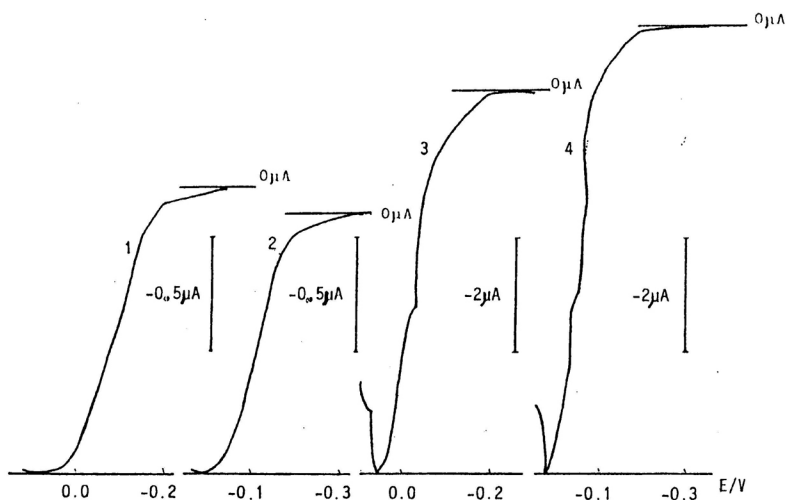


Figure 1. DC polarography waves of 5×10^{-4} mol dm $^{-3}$ RSH at various pH of the medium: pH = 3 (1), 5 (2), 7 (3) and 10 (4); drop-step time 1 s; scan increment 4 mV.

TABLE I

Analysis of the reversibility of the DC waves as a function of the drop-step time and pH of the medium.

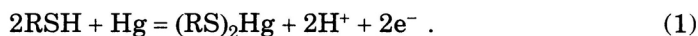
pH = 3		Drop-step time: 1 s	
Drop-step time/s	$\Delta E/mV$	pH	$\Delta E/mV$
0.5	69	2	84
1	79	3	79
2	60	4	94

TABLE II

Dependence of the $E_{1/2}$ of the anodic DC waves on the pH of the medium and the concentration of investigated thiol

pH	$E_{1/2}/V$	$\frac{C \times 10^{-3}}{\text{mol dm}^{-3}}$	$E_{1/2}/V$
2	-0.09	0.5	-0.12
3	-0.07	1	-0.125
4	-0.11	2	-0.14
5	-0.12	3	-0.15
6	-0.12	4	-0.16

According to the available literature data⁵⁻¹⁰ on the polarographic investigation of thiols, the most probable reaction that can describe the redox reaction of thiol at the mercury electrode is:



The electrode process is complicated by the presence of the film of insoluble salt on the electrode surface, formed between the thiol and the mercury.

It can be seen from Figure 1 that the anodic dissolving of the mercury combined with formation of the insoluble salt is more intensive in the medium with $\text{pH} > 7$. Thus, the film formed at the electrode surface causes inhibition of the redox reaction. As a consequence, polarographic maxima and certain irregularities appear in the rising portion of the waves (Figure 1, curves 3,4). Also, the diffusion coefficient of the thiol through the deposited film is different than in the solution, which causes the wave to break in two slightly separated waves. For the same reasons, the increase of the drop lifetime decreases the height of the waves.

The fact that the half-wave potentials become more negative with the increasing pH of the medium can be explained by the thiol group ability dissociation. This is an expected result and it was also found in investigations of other thiols.⁶

The electrochemical behaviour of RSH using HMDE as a working electrode was investigated by the application of cyclic and square-wave voltammetry.

From Figure 2 it can be seen that, at pH = 3 and 5×10^{-4} mol dm⁻³ concentration of RSH, a well-defined SW peak can be obtained. Cyclic voltammetry measurement under the same conditions reveals that the SW peak is a result of the reduction process. The shape of the SW peak and its analogous counterpart in the cathodic part of the cyclic voltamogram is typical of stripping peaks.

The analysis of cyclic voltamograms recorded at various scan rates has shown that the cathodic peak current depends linearly on the scan rate. In the anodic part of the cyclic voltamogram an anodic wave can be seen as a result of reoxidation of the product of cathodic reaction. The anodic peak in-

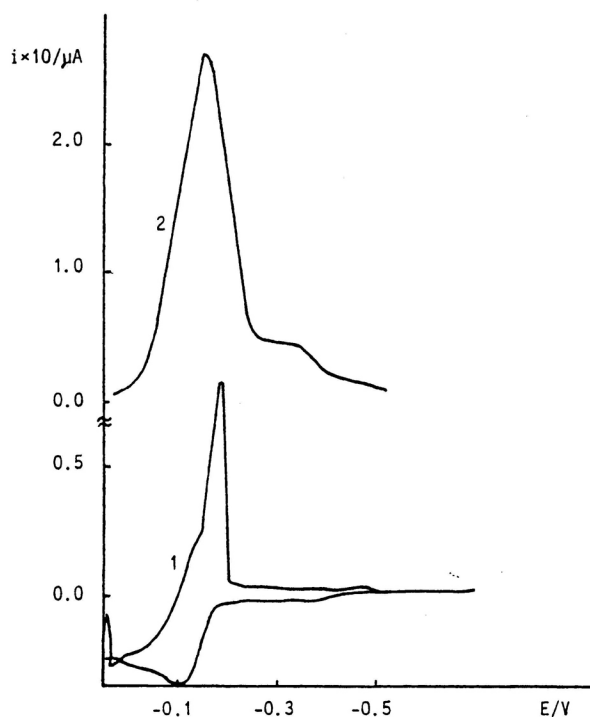


Figure 2. Cyclic (1) and square-wave voltamogram (2) of 5×10^{-4} mol dm⁻³ RSH at pH = 3; deposition time 0 s (unstirred solutions).

creases proportionally to the square root of the scan rate, which indicates that the oxidation process is diffusion controlled. The presence of the peak in the anodic part of the cyclic voltammogram confirmed that the redox reaction is not totally irreversible.

The investigation performed gives a global view of the electrode process during electrolysis by the square-wave voltammetry in the cathodic potential direction. This is a mechanism of the cathodic stripping process and can be described by the formation process of the mercuric mercaptide film on the electrode surface at the starting potential and stripping of the formed film in the cathodic potential direction.

According to this mechanism, the total SW response depends on the formation and dissolving kinetics of the mercuric mercaptide film on the HMDE surface, as well as on the structure and characteristics of the film. The investigations have shown that the characteristics of the film are mainly effected by the concentration of the RSH, deposition time and pH of the medium.

Figure 3 shows the dependence of SW peaks on the deposition time. Under 5×10^{-6} mol dm⁻³ concentration of RSH and deposition time of 30 s, there is only one SW peak that proportionally increases with the enhancement of the deposition time. Increasing of the peak is mainly a result of progressive coating of the HMDE surface by mercuric mercaptide film. At a deposition time of 150 s, the HMDE surface is totally covered, and any further increase of the film is followed by formation of subsequent layers of the film. This phenomenon results in the splitting of the peak, and a new peak as a result of the reduction of subsequent layers, appears at a more positive potential. At a longer deposition time, only the new peak increases while the

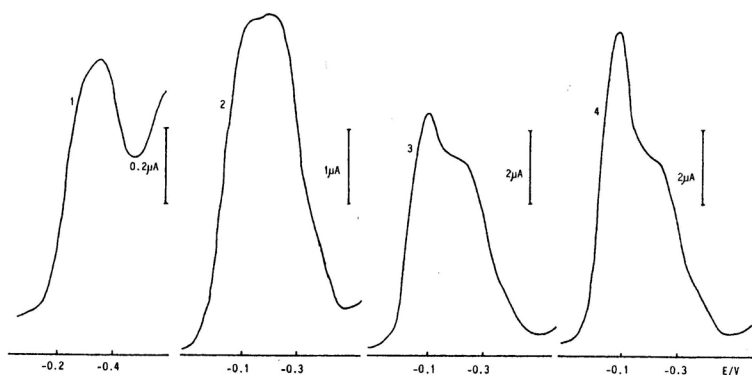


Figure 3. Effect of the deposition time on the SW response of RSH. Deposition time: 30 s (1), 150 s (2), 200 s (3) and 250 s (4) (unstirred solutions); concentration of RSH = 5×10^{-6} mol dm⁻³; pH = 3; frequency 100 Hz; amplitude 20 mV; scan increment 6 mV.

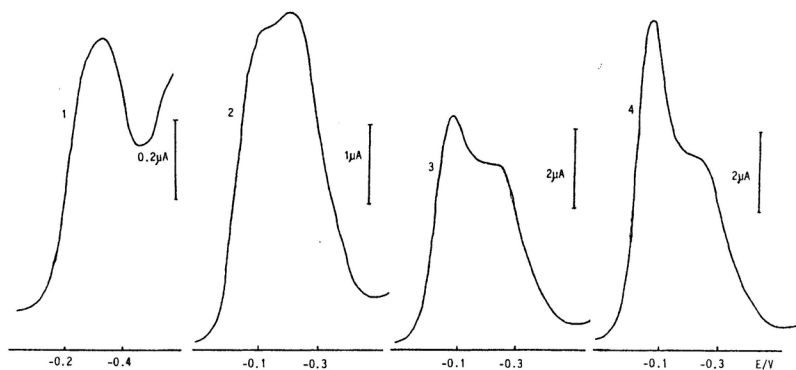


Figure 4. Dependence of the SW peaks on various concentrations of RSH: 5×10^{-6} (1), 1×10^{-5} (2), 1.5×10^{-5} (3) and 2×10^{-5} mol dm $^{-3}$ (4); deposition time 30 s. All other parameters as in Figure 3.

peak at a more negative potential is not affected by the deposition time. It is obvious that the peak at a more negative potential is being affected by deposition time until the surface of the electrode is totally covered. Figure 4 shows the effect of the RSH concentration at a constant deposition time of 30 s on the SW response. From Figure 4 it is obvious that the increasing concentration of the thiol has the same effect on the SW response as the increasing deposition time. All these results indicate that the SW response is directly dependent on the thickness and the structure of the film.

The thickness of the film is a function of the deposition potential. During a constant concentration of the investigated component and a constant deposition time, application of a more positive deposition potential results in more intensive dissolving of the mercury and an increase in the amount of the mercury mercaptide formed on the electrode surface. Hence, shifting of the deposition potential to more positive potentials has the same effect on the SW response as an increase of the deposition time or RSH concentration in the solution.

The oxidation process of mercury in the presence of RSH was investigated by recording SW voltammograms in the positive potential direction, where the potential of 0.70 V was chosen for the starting potential. From Figure 5, it can be seen that the oxidation process results in two SW peaks, which are independent on the deposition time. These peaks correspond to the formation of the first and subsequent layers of the film deposited on the electrode surface. The SW response of RSH in the positive potential direction is independent of the deposition time. Therefore, there is no adsorption of the RSH species on the surface of HMDE.

Finally, it has to be mentioned that the cathodic dissolving process of the film deposited on the surface of HMDE also depends on the excitation

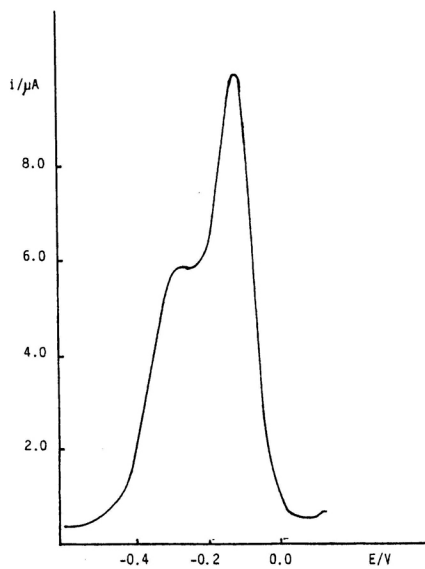


Figure 5. SW response of $5 \times 10^{-4} \text{ mol dm}^{-3}$ RSH recorded in the positive potential direction. Deposition time was increased from 0 to 15 s. All other parameters as in Figure 3.

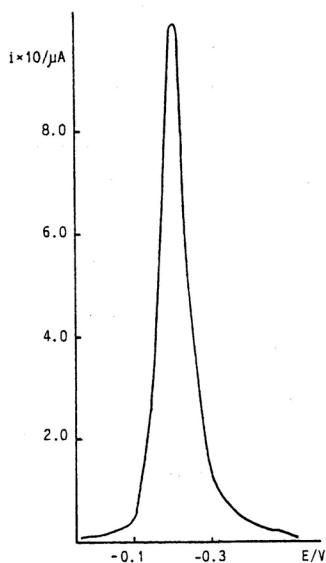


Figure 6. SW response of $5 \times 10^{-4} \text{ mol dm}^{-3}$ RSH at pH = 2; frequency 60 Hz; amplitude 100 mV; scan increment 6 mV; deposition time 5 s.

signal parameters. In other words, the SW response of RSH in the cathodic potential direction depends on the applied SW frequency, SW amplitude and scan increment. Such investigations were performed with a solution of $5 \times 10^{-4} \text{ mol dm}^{-3}$ concentration of RSH, in a medium with $\text{pH} = 2$ (Figure 6). In these experimental conditions, the SW response of RSH consists of a single SW peak, located at about -0.20 V . The existence of a single peak indicates that the complexity of the electrode process is avoided.

In Figure 7, the interdependence of peak currents and SW frequency is presented. It is obvious that the increasing of frequency in the range from 20 to 120 Hz is followed by a proportional increase of the peak currents. The SW frequency variation also affects the peak potentials. Thus, an increase in frequency causes shifting of the SW peaks of RSH towards more positive potentials.

On the other hand, variation of the SW amplitude in the range from 2 to 100 mV effects only peak currents and the half-width of the peaks. Thus, the peak currents increase with the increasing SW amplitude, but the interdependence of the peak currents and the SW amplitude is nonlinear and very complex. The increasing of the SW amplitude also causes an increase of the half-width of the peaks. This tendency is present in the range of SW amplitude from 2 to 20 mV. Above these values, the half-width of the RSH peaks is almost constant and independent of the SW amplitude.

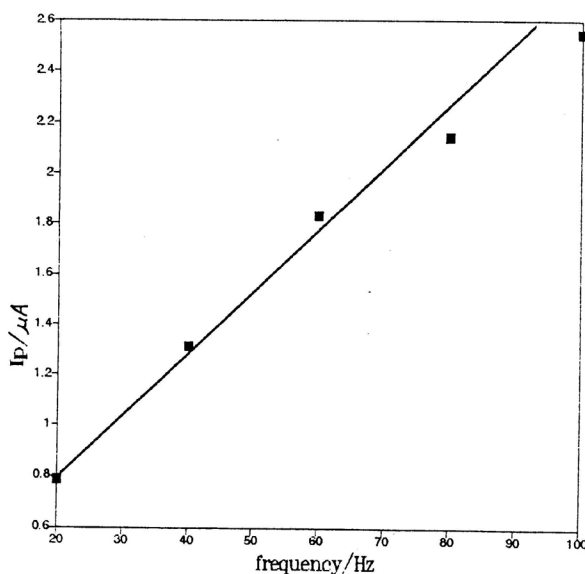


Figure 7. Dependence of SW peak currents on SW frequency. Concentration of RSH: $5 \times 10^{-4} \text{ mol dm}^{-3}$; amplitude 20 mV; scan increment 6 mV; deposition time 5 s (unstirred solution).

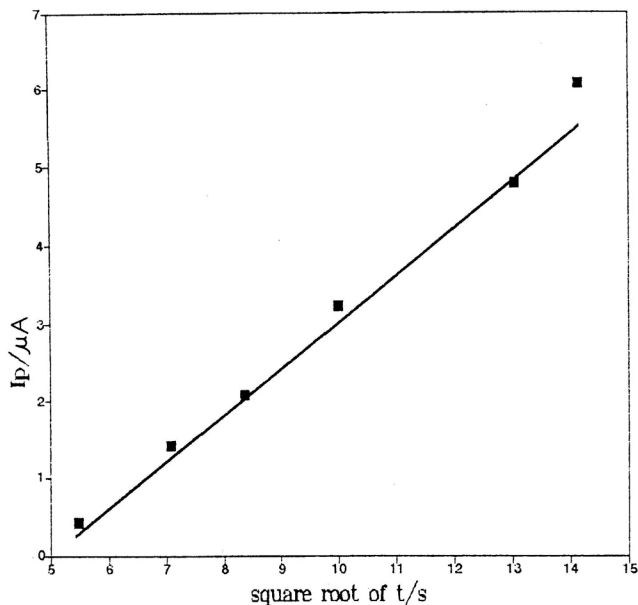


Figure 8. Dependence of SW peak currents on the square root of the deposition time; frequency 60 Hz. All other parameters as in Figure 7.

The experiment performed at various scan increment values confirmed that the peak currents decrease with increasing scan increment. On the other hand, the increase of scan increment has the opposite effect on the half-width of the peaks. The peak potentials are almost independent of scan increment.

The SW peak of RSH presented in the Figure 6 was also investigated as a function of deposition time. The peak currents increase proportionally to the square root of the deposition time (Figure 8). Under this experimental conditions, increasing of the peak is not followed by a splitting of the SW peak.

All this results can be successfully used for further development of the cathodic stripping square-wave voltammetric method for quantitative determination of investigated thiol.

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SAŽETAK

Pravokutna voltametrija 1-benziltetrazol-5-tiola

Blagoja Jordanoski, Valentin Mirčeski i Kornelija Stojanova

Temeljne elektrokemijske značajke 1-benziltetrazol-5-tiola u kiselom mediju istraživane su metodama klasične (DC) polarografije, cikličke (CV) i pravokutnovalne voltametrije (SWV). Za vrijeme života viseće živine kapi na površini žive spontano nastaje spoj žive i tiola. Procesom taloženja na površini nastaje višeslojni film na površini elektrode. SW odziv proučavanog sastojka poglavito ovisi o strukturi filma.