ELECTROCHEMICAL BEHAVIOUR OF 1-ISOBUTYL-TETRAZOLE-5-THIOLE DURING ELECTROLYSIS BY CLASSICAL AND DIFFERENTIAL PULSE POLAROGRAPHY

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Polarography investigations of 1-isobutyl-tetrazole-5-thiole were carried out by classical (DC) and differential pulse (DP) polarography, in Briton-Robinson and acetate buffers, in pH range from 1.76 to 9.68. DC polarography has shown that electrode reaction can be described by the equation: $RSH + Hg \leftrightarrows RSHg + H^+ + e^-$ *. DP polarography has been used for analytical purposes. The conditions for quantitative determination have been found, in the concentration of component investigated with the range from $4 \cdot 10^{-5}$ to $3,5 \cdot 10^{-4}$ mol dm^{-3}.*

Key words: classical polarography; differential pulse polarography; 1-isobutyl-tetrazole-5-thiole

INTRODUCTION

Some mercaptotetrazoles synthesized by Vanzura and al. [1] have an antituberculosis activity. One of the derivates is 1-isobutyl-tetrazole-5-thiole, which, in the following, will be referred to as *RSH*.

The aim of our work was to study the electrochemical behavior of *RSH* during electrolysis by classical (DC) and differential pulse (DP) polarography, as well as to develop a method for its quantitative determination. There are no written data for the electrochemical behavior of *RSH*.

Investigations performed by Kolthoff and his collaborators on the compounds which also contain mercapto (*SH*) group, (cysteine [2], glutathione [3] etc.) show that electrode reaction can be described by the equation:

$$RSH + Hg \leftrightarrows RSHg + H^+ + e^- .$$

Classical polarography on the *RSH* shows that electrode reaction probably follows the same equation.

DP polarography has been used for analytical purposes. The conditions for quantitative determination have been found in the concentration of the component investigated with the range from $4 \cdot 10^{-5}$ to $3,5 \cdot 10^{-4}$ mol·dm^{-3}. They are similar to those found by Kazandzieva and Nedelcev for 1-methyl-tetrazole-5-thiole [9] .

EXPERIMENTAL

Polarography investigations were carried out by DC and DP polarography. Polarography curves were recorded on POLAROGRAPHIC ANALYZER– MODEL 384B (EG&G PRINCETON APPLIED RESEARCH – USA) with static mercury drop electrode, Ag/AgCl, KCl as a reference electrode, and platinum wire as a third electrode. *RSH* was synthesized on Farm. Fak. Univ. Karlovy, Hradec Kralové, Chech by K. Waisser and al. [1]. Fundamental experiments were carried out on $1 \cdot 10^{-4}$ mol·dm^{-3} aqueous solutions of *RSH* in Briton-Robinson and acetate buffers with different pH values. The Briton-Robinson buffers were prepared from 0.04 mol dm^{-3} CH$_3$COOH,

H$_3$PO$_4$ and H$_3$BO$_3$, and 0.02 mol·dm^{-3} NaOH, and the acetate buffers from 0.1 mol·dm^{-3} CH$_3$COOH and 0.20 mol·dm^{-3} NaOH.

Oxygen was removed from the solutions in the cell with a stream of oxygen-free nitrogen which was purified by bubbling through V$_2$O$_5$ solution and distilled water. All polarograms were obtained at room temperature. The other conditions of experiment were: drop step time 0.5 s, scanning rate 6 mV/s, purge time 240 s, pulse high (for DPP) 0.020 V.

All the glass containers which were used throughout the experiment were previously washed with HNO$_3$ solution (1 : 8) and distilled water.

RESULTS AND DISCUSSION

Polarography studies of *RSH* solutions with $1 \cdot 10^{-4}$ mol·dm^{-3} concentration, in Briton-Robinson and acetate buffers in pH range from 1.76 to 9.68 have shown that polarography waves can be obtained across the whole pH range. The position and shape of waves were found to be affected by the nature of the buffer and pH of the medium (see Fig.1).

At more positive potentials than 0.000 V abnormalities occur in both buffers. From Fig.1 it is obvious that the half-wave potential ($E_{1/2}$) decreases with the increase of the pH values. Diagrams in Fig.2. show the linear dependence of the $E_{1/2}$ vs on pH in acidic media (pH approximately from 1 to 4). Beyond this pH, $E_{1/2}$ remains almost unaltered.
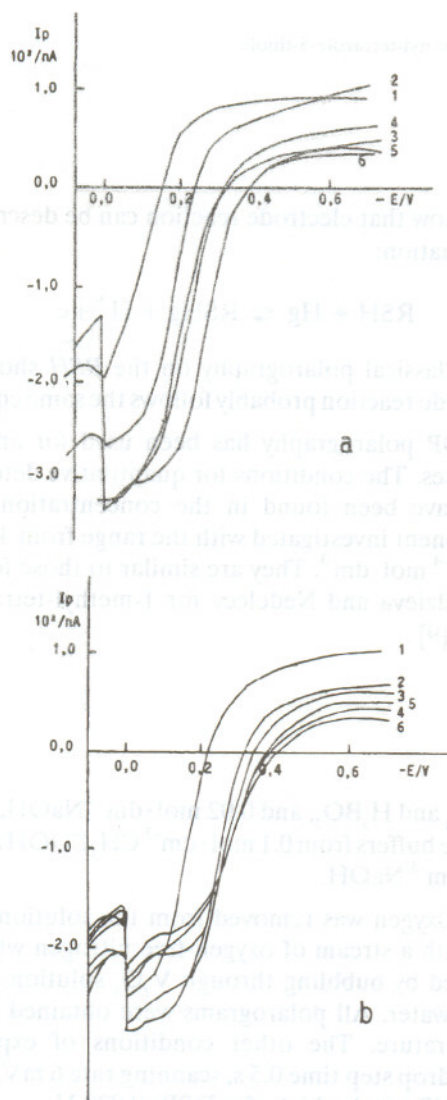
Curves shown in Fig. 1 are cathodic–anodic polarography waves. At a given concentration of *RSH* ($1 \cdot 10^{-4}$ mol·dm^{-3}), the anodic current has the largest part of the total diffusion current.
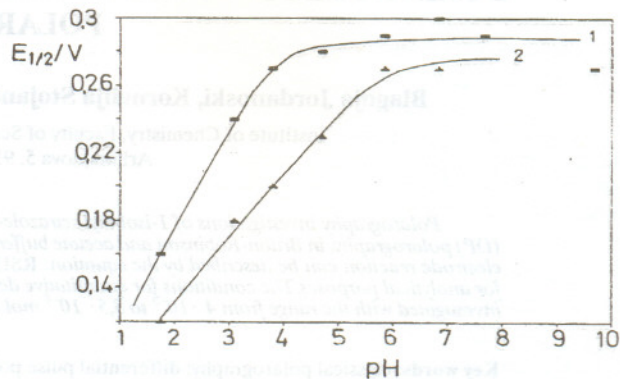
Fig. 2 – Half-wave potential of *RSH* vs. pH in Briton-Robinson (1) and acetate buffers (2) , c (*RSH*) = $1 \cdot 10^{-4}$ mol · dm^{-3}

Fig. 1 – a) Polarograms of $1 \cdot 10^{-4}$ mol·dm^{-3} *RSH* in acetate buffers curves: 1 (pH - 1.5); 2 (pH -2.0); 3 (pH - 3.0); 4 (pH - 4.0); 5 (pH - 6.0); 6 (pH - 7.0)
   b) Polarograms of $1 \cdot 10^{-4}$ mol·dm^{-3} *RSH* in Briton-Robinson buffers curves: 1 (pH -1.76); 2 (pH -3.10); 3 (pH - 3.80); 4 (pH - 4.72); 5 (pH - 5.82); 6 (pH - 6.84; 7.60)

With detailed examinaton of the polarographic waves, it can be seen that the changes of pH values have an influence on the change of the waves through both axes of the E–I coordinate system. In other words, the magnitudes of the cathodic and anodic current change, as well as their percentage participation in the total diffusion current (Table I.).

T a b l e I.

Dependence of cathodic (i_c) and anodic (i_a) current of pH in acetate buffers c(RSH) = $1 \cdot 10^{-4}$ mol · dm^{-3}

pH	2,0	4,0	6,0	7,0
i_c/nA	60.3	49.0	37.0	33.9
i_a/nA	232.0	276.0	264.1	279.2
i_d/nA	292.0	316.9	301.8	313,1
i_c/%	20.6	15.4	12.5	10.8
i_a/%	79.4	84.6	87.5	89.2

This effect of altering the ratio between anodic and cathodic current is much more striking with the alteration of the *RSH* concentration in the solutions of constant pH (Fig.3.). The curves in Fig. 3. show that an increase in the concentrations of *RSH* causes an increase in anodic percentage participation in the total current, while the cathodic participation decreases. The decrease of concentration causes the opposite result.

Polarographic reversibility of the electrode process was also investigated. The slope of the straight line
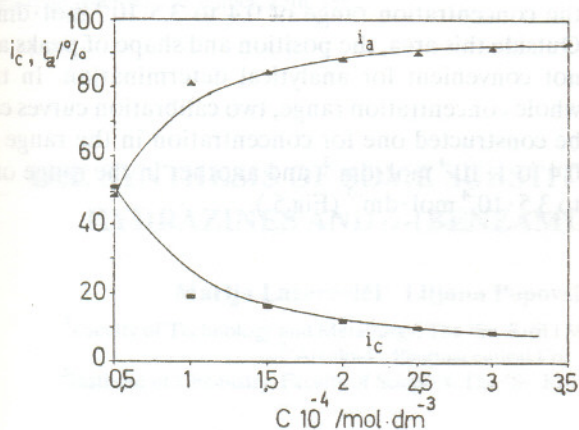
Fig. 3 – Dependence of cathodic (i_c) and anodic (i_a) current of concentration of *RSH* in acetate buffer at pH – 1, 5

of dependence of $E - \log(i_c - i/i - i_a)$ is approximately 70 mV, which is in good agreement with the theoretical value of 59 mV, characteristic for electrode reactions which involve one electron per molecule.

Previous investigations on some thioles have shown that they can be electrochemicaly oxidized, giving anodic diffusion waves [2−7]. The reversible process on mercury electrode results in formation of mercaptide [6]:

$$RSH + Hg \leftrightarrows RSHg + H^+ + e^- \quad (1)$$
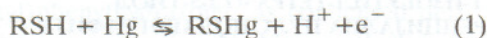
which is generally unstable and decomposes in solution forming mercury and $(RS)_2Hg$:

$$2RSHg \leftrightarrows (RS)_2Hg + Hg. \quad (2)$$
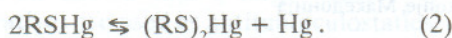
If $(RS)_2Hg$ is introduced into solution, only cathodic wave on polarograms can be seen, as a result of the reduction of *RSHg*. Apparently, the equilibrium (2) is very mobile.

In our case, the cause for obtaining an anodic wave is the electrode process described by equation (1). The appearance of the cathodic wave is probably a result of a rapid transformation of *RSHg* to $(RS)_2Hg$ and its concentration on the surface of the mercury drop. This allows a shifting of the equilibrium (2) to the left side. Thus, the *RSHg* being the compound which is reduced.

Similar dependence of half-wave potential ($E_{1/2}$) on pH is found in the case of glutathione and cysteine. The constant magnitude of $E_{1/2}$ at a higher pH is connected with the ability of the *SH* group to dissociate.

The electrode activity of *RSH*, as well as its approximate polarographic reversibility behavior, present the possibility of the application of DP polaro-

graphy for analytical purposes. DP polarography is a more convenient method for analytical determination, as it is a more precise and sensitive method than classical (DC) polarography [8, 9].

The study of DP peaks at different pH values shows that well defined peaks are obtained in acidic media. DPP peaks determined in acetate buffers with pH 1.5 and the concentration of *RSH* $2 \cdot 10^{-4}$ mol·dm^{-3} are shown on Fig.4.

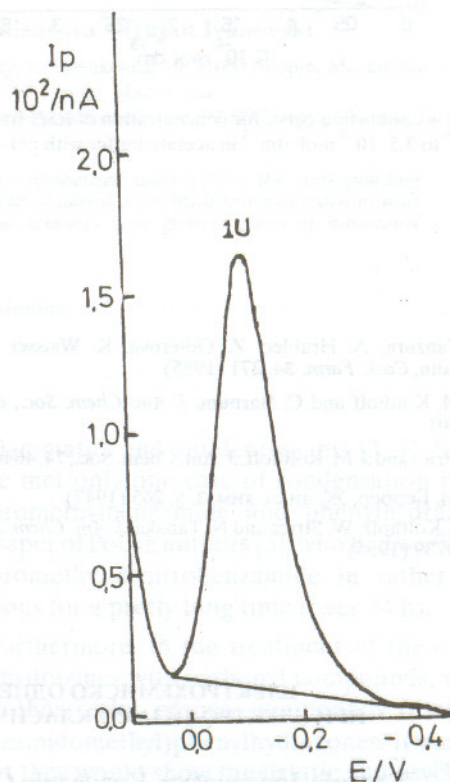Fig. 4 – DPP peak in acetate buffer at pH – 1,5; c(*RSH*) = $2 \cdot 10^{-4}$ mol·dm^{-3}

The investigation of DPP peaks is more convenient in acetate buffers. Data for the position (expressed as peak potential Ep/V) and for the height (expressed as current at the top of the peak Ip/nA) of peaks, correlated with the concentration of RSH component, are shown in Table II.

Table II.

Dependence of Ep and Ip of concentration of RSH in acetate buffer with pH – 1,5

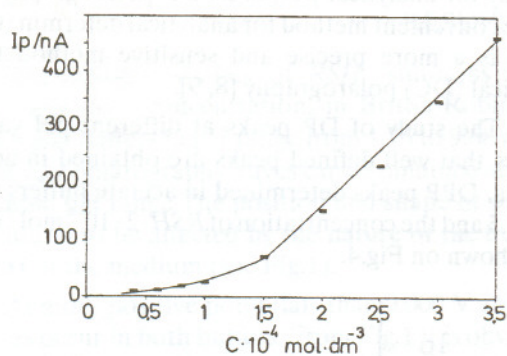| $\dfrac{c \cdot 10^{-4}}{\text{mol}\cdot\text{dm}^{-3}}$	0.4	0.6	0.8	1.0	1.5	2.0	2.5	3.0	3.5
−Ep/V	0.20	0.20	0.18	0.20	0.10	0.10	0.10	0.10	0.05
Ip/nA	7.58	11.8	17.7	24.5	70.8	153	232	350	462

Fig. 5 – Calibration curve for concentration of *RSH* from $4 \cdot 10^{-5}$ to $3,5 \cdot 10^{-4}$ mol·dm^{-3} in acetate buffer with pH –1,5

DPP peaks can be used for analytical purposes in the concentration range of 0.4 to 3.5 10^{-4} mol·dm^{-3}. Outside this area, the position and shape of peaks are not convenient for analytical determination. In the whole concentration range, two calibration curves can be constructed one for concentration in the range of 0.4 to $1 \cdot 10^{-4}$ mol·dm^{-3}, and another in the range of 1 to $3.5 \cdot 10^{-4}$ mol·dm^{-3} (Fig.5.).

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Р е з и м е

ЕЛЕКТРОХЕМИСКО ОДНЕСУВАЊЕ НА 1-ИЗОБУТИЛ-ТЕТРАЗОЛ-5-ТИОЛ ПРИ ЕЛЕКТРОЛИЗА СО КЛАСИЧНА И ДИФЕРЕНЦИЈАЛНА ПУЛС ПОЛАРОГРАФИЈА

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Клучни зборови: класична поларографија; диференцијална пулс поларографија;
1-изобутил-тетразол-5-тиол

Поларографските испитувања беа спроведени со класична (DC) и диференцијална пулс (DP) поларографија, во Британ-Робинсонови и ацетатни пуфери, со вредности на pH од 1,76 до 9,68. DC поларографијата покажа дека електродната реакција може да се опише со равенката:

$$RSH + Hg \leftrightarrows RSHg + H^+ + e^-$$

DP поларографијата беше искористена за аналитички цели. Најдени се услови за квантитативно определување во концентрациски ранг на испитуваната компонента од $4 \cdot 10^{-5}$ до $3,5 \cdot 10^{-4}$ mol·dm^{-3}.