

Electrochemical study of thiosemicarbazide

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In this paper results of an electrochemical study of thiosemicarbazide are presented. Electrochemical oxidation in aqueous solutions proceeds in two steps. In the first, four electrons are exchanged and in the second eight. In addition to the electron oxidation thiosemicarbazide chemical oxidation by electrolytically generated hypobromite has also been investigated. The most reliable coulometric titration results have been obtained when determining thiosemicarbazide in the 75—150 μg range of the species.

В работе представлены результаты электрохимического изучения тиосемикарбазида. Электрохимическое окисление в водных растворах протекает в две стадии. В первой происходит обмен четырьмя электронами, а во второй восемью. Кроме электронного окисления тиосемикарбазида также изучалось и его химическое окисление электролитически генерированным гипобромитом. Наиболее надежные результаты кулонометрического титрования были получены при определении тиосемикарбазида в образцах с содержанием 75—150 мкг.

Thiosemicarbazide ($\text{NH}_2\text{—NH—CS—NH}_2$) is used as an additive in the photographic and textile industries, in galvanic baths and in the manufacture of plastics. Because of their potent antivirus effect [1] thiosemicarbazide and its derivatives are being widely used in pharmacy. They are also an important component in certain agrochemicals.

Such a wide practical use of thiosemicarbazide is the reason for trying to find out a correct, exact and simple method for its analytical determination.

The present paper is a contribution to the electrochemical study of the properties of thiosemicarbazide by voltammetry at a stationary carbon electrode and also describes optimum conditions for determining microquantities of thiosemicarbazide by coulometric bromometric titration. Neither the voltammetric oxidation of thiosemicarbazide nor its determination by coulometric titration has so far been described in literature.

Experimental

All the employed chemicals were anal. grade commercially obtained materials. Thiosemicarbazide (Lachema, Brno) was purified from ethanol by multiple recrystallization. The degree of purity was determined by its melting point (181 °C) and verified by elemental analysis. The $[\text{Cu}(\text{tsc})_2]\text{SO}_4$ complex (tsc — thiosemicarbazide ligand) was prepared as described in [2, 3].

The following solutions were used for voltammetric and chronoamperometric measurements:

a) Britton—Robinson buffer solutions,

b) HCl (0.1 mol dm^{-3} and 0.01 mol dm^{-3}), KCl (0.2 mol dm^{-3}), H_2SO_4 (0.05 mol dm^{-3}).

Base electrolytes used in coulometric titration were:

c) 12 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 100 g KBr per 1 dm^3 of aqueous solution; pH was adjusted to 8.6 by a diluted HCl solution,

d) 100 g KHCO_3 , 30 g Na_2CO_3 , 100 g KBr per 1 dm^3 of aqueous solution, pH = 9.5.

Cyclic voltammetry as well as chronoamperometry were performed with the help of polarographs OH-102 and OH-105 (Radelkis, Budapest), each with three-electrode arrangement in a Kalousek polarographic cell.

The working electrode was a paraffin impregnated carbon disc electrode, 6 mm in diameter, of the SU type (Elektrokarbon, Topoľčany). The electrode paraffin coating was daily renewed. Before every curve recording the lower working surface of the electrode was carefully cleaned with a fine-grained abrasive paper and polished on filter paper.

The reference electrode consisted of a mercurousulfate electrode filled with an Na_2SO_4 solution (0.5 mol dm^{-3}) which was also present in the salt bridge terminated by a graphite connection. The reference electrode was placed in close proximity to the working electrode.

The auxiliary electrode was a large-surface paraffin impregnated carbon electrode.

In chronoamperometry, to the working electrode there was applied a constant potential, shifted by 100 mV towards the peak potential on the voltammetric $I-E$ curve, the shift being positive in oxidation and negative in reduction processes.

Alkaline hypobromite coulometric titration was done with a universal OH-404 coulometric analyzer (Radelkis, Budapest) in amperostatic mode. The working electrode used was an OH-935 platinum electrode (Radelkis, Budapest) of a surface area of 5.0 cm^2 . The auxiliary SU-type carbon electrode (Elektrokarbon, Topoľčany) of cylindrical shape, $d = 6 \text{ mm}$, was separated from the analyzed solution by a thick glass frit and immersed into base electrolyte.

Biamperometric indication was provided by a pair of platinum wire electrodes of the OH-938 type (Radelkis, Budapest), each 0.06 cm^2 in surface area, and of 150 mV potential difference.

Both the working and the indicating electrode were cleaned daily by being dipped into diluted HNO_3 (volume ratio = 1 : 2). The indicating electrodes were short-circuited for the night and kept immersed in base electrolyte.

Titration was done in an OH-930 coulometric titrating vessel (Radelkis, Budapest). 110 cm^3 of base electrolyte was poured into the vessel and 1 cm^3 of the sample transferred using a pipette. Another 1 cm^3 of the sample was added after titration was over. In this way it was possible to do 10 to 11 titrations without having to change the solution. The

first-titration result, influenced by oxidizable impurities in the base electrolyte, was not taken into consideration.

The pH measurement was made with an OP-205 pH-meter (Radelkis, Budapest) and with the help of a galvanic cell constituted of a glass and saturated calomel electrode. All measurements in this work are referred to the mercurousulfate electrode potential, which was +0.393 V vs. saturated calomel electrode.

Results and discussion

Thiosemicarbazide voltammetric behaviour

Fundamental voltammetric characteristics have been determined from voltammetric $I-E$ curves (Fig. 1). These have unambiguously shown that thiosemicarbazide is oxidized in two steps. Potential shift of thiosemicarbazide oxidation peaks has likewise been investigated, as well as pH dependence of changes in maximum currents (Table 1). In evaluating the oxidation potential shift, half-peak values, $E_{p/2}$, were taken into account which, from the potential measurement determination standpoint, provides greater accuracy than the determination of E_p .

Dependence of $E_{p/2}$ on pH is linear. With pH increasing, the half-peak position is shifted towards more negative values (the slope value being -0.053 V/pH unit). The position of the second half-peak has also changed being shifted as pH increased towards more negative values (slope value being -0.026 V/pH unit). From the great difference in E_p and $E_{p/2}$ values (Table 1) it follows that the electrode process is slow and therefore electrode oxidation must be irreversible.

pH Dependence of the second-step oxidation maximum current linearly increases at lower pH values (Fig. 2). This may be due to the fact that thiosemicarbazide oxidation to sulfate as final product proceeds through intermediates with the sulfur oxidation state value lower than six. The higher is the pH (more OH^- ions are at

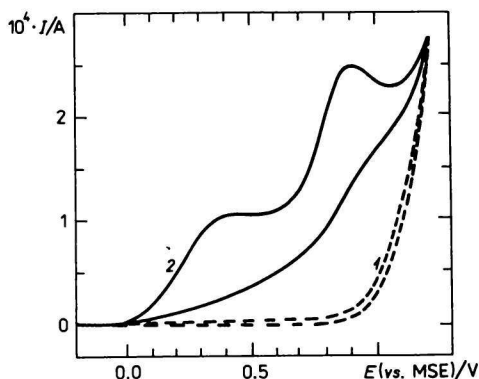


Fig. 1. Cyclic voltammetric $I-E$ curve of thiosemicarbazide ($c = 1 \times 10^{-3}$ mol dm^{-3}), pH = 7.48 (2). Base electrolyte $I-E$ curve (1). Scan-rate $v = 0.033$ V s^{-1} .

Table 1

Thiosemicarbazide oxidation voltammetric characteristics at various pH values of buffer solutions
 Thiosemicarbazide concentration $c = 1 \times 10^{-3} \text{ mol dm}^{-3}$, scan-rate $v = 0.033 \text{ V s}^{-1}$
 All potentials are referred to the mercurousulfate electrode*

pH	Oxidation peak 1			Oxidation peak 2		
	$E_{p/2}$	$10^4 \cdot I_p$	$E_p - E_{p/2}$	$E_{p/2}$	$10^4 \cdot I_p$	$E_p - E_{p/2}$
	V	A	mV	V	A	mV
2.40	0.43	0.98	95	**	1.10	**
3.85	0.36	0.95	120	**	1.27	**
5.05	0.29	0.93	145	0.765	1.40	125
6.35	0.24	0.94	155	0.75	1.47	140
7.50	0.15	1.01	170	0.73	1.69	155
8.25	0.13	0.93	185	0.705	1.70	170
10.05	0.00	0.95	205	0.65	1.69	180

* Reference electrode potential was +0.393 V vs. SCE.

** Undefined peak.

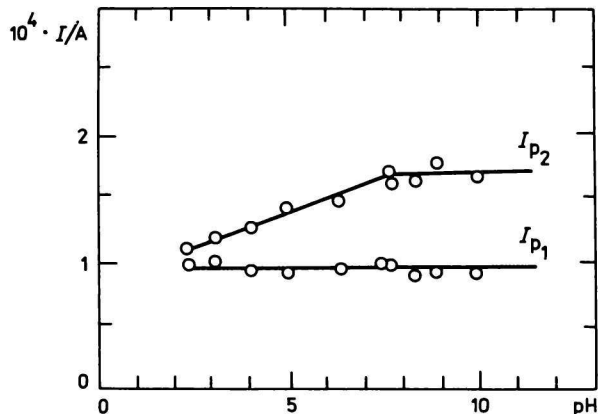


Fig. 2. Dependence of I_{p1} and I_{p2} maximum currents (for first and second oxidation step, resp.) on pH.
 Thiosemicarbazide concentration: $1 \times 10^{-3} \text{ mol dm}^{-3}$; scan-rate $v = 0.033 \text{ V s}^{-1}$.

the disposal for the oxidation), the more easily it is directly oxidized to SO_4^{2-} (see below). At lower pH values only partial thiosemicarbazide oxidation can take place under voltammetric conditions. At pH values higher than 8, the maximum current value undergoes no change, oxidation to sulfate proceeding in full.

Dependence $I_{p1} = f(\text{pH})$, shown in Fig. 2 (virtually no change in the first oxidation peak height) may be accounted for by the fact that there is an identical oxidation product formed at all pH values.

Dependence of anodic I_{p1} and I_{p2} maximum voltammetric currents on the thiosemicarbazide concentration was studied in the solution at $\text{pH} = 7.48$ (ionic strength adjusted to a value of 0.1 mol dm^{-3} using LiClO_4) within a concentration range of $(2-12) \times 10^{-4} \text{ mol dm}^{-3}$. The established linear dependence passing through the origin of the coordinate system, is proof of a simple electrode process taking place. With the concentration of thiosemicarbazide no change took place in E_p and $E_{p/2}$ values.

Chronoamperometric measurements

In analyzing voltammetric $I-E$ curves it is necessary to take into consideration the fact that the maximum current depends not only on the number of exchanged electrons but also on the reversibility of the electrode process and the corresponding rate constant. This is why voltammetry is not quite suitable for determining the number of exchanged electrons.

We have, therefore, employed chronoamperometric measurements instead, to determine the number of exchanged electrons in thiosemicarbazide oxidation and to clarify the mechanism of the latter at the same time. Measurement conditions in Britton—Robinson buffer solutions and in HCl ($c = 0.1 \text{ mol dm}^{-3}$) were chosen on the basis of voltammetric $I-E$ curves.

$It^{1/2}/c$ value was shown to be linearly dependent on $t^{1/2}$ (Fig. 3), which was in accordance with the theory valid for the diffusion towards an unshielded electrode with spherical diffusion contribution. Separate points of these dependences had been obtained by averaging values from eight measurements corrected to a blank experiment. By extrapolating values $It^{1/2}/c$ for time $t = 0$ it was possible to get the values of "chronoamperometric constants" satisfying the Cottrell equation. Ratio of "chronoamperometric constants" $It^{1/2}/c$ ($t = 0$) measured at the potentials of the second and the first oxidation step, numerically equal to 3:1, yielded the ratio of the number of electrons exchanged both in the first and the second oxidation step to that exchanged in the first. For the determination of the number of exchanged electrons in either of the thiosemicarbazide oxidation steps at a carbon electrode, chronoamperometric measurements with complex $[\text{Cu}(\text{tsc})_2]\text{SO}_4$ were performed. Copper(II) complex is reduced in two steps with an equal number of exchanged electrons, hence it follows that reduction $\text{Cu}(\text{II}) \rightarrow \text{Cu}(\text{I})$ proceeds in the first step and $\text{Cu}(\text{I}) \rightarrow \text{Cu}(0)$ in the second. In comparing the determined chronoamperometric constants (extrapolated to $t = 0$) for $\text{Cu}(\text{II})$ complex one-electron reduction and for the same complex anodic oxidation performed at the potential of the free ligand second oxidation step, a ratio 1:24 was established, which indicates that there is

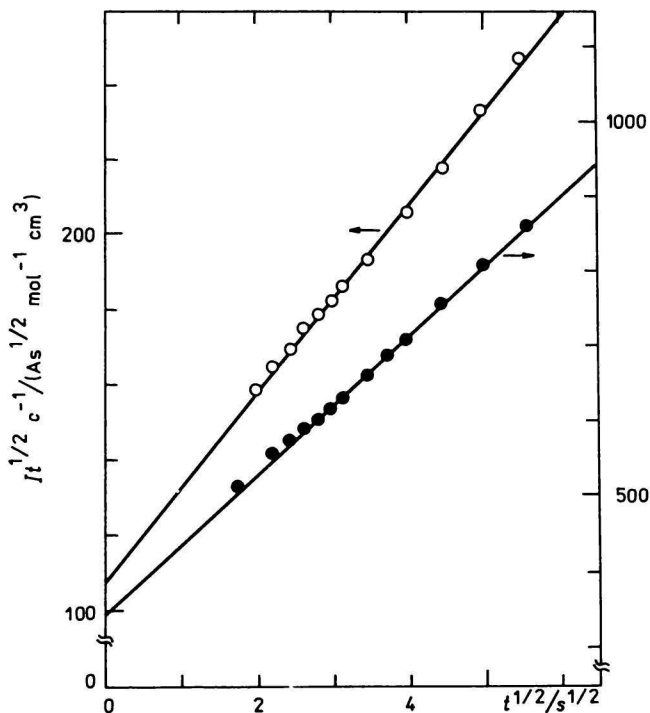


Fig. 3. Term value dependence: $It^{1/2}/c$ on $t^{1/2}$ in thiosemicarbazide solution ($c = 2 \times 10^{-4}$ mol dm $^{-3}$, pH = 7.48).

○ $E = +0.4$ V vs. MSE (ordinate left axis).

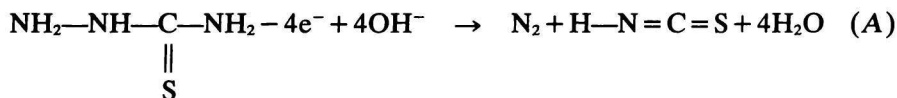
● $E = +0.85$ V vs. MSE (ordinate right axis).

here a loss of 12 electrons per ligand molecule in the complex oxidation, thus giving rise to the formation of sulfate as final product as claimed by the authors [4].

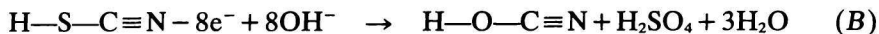
On thorough analysis of all the mentioned results the following mechanism of thiosemicarbazide oxidation may be assumed:

In the total oxidation of one molecule 12 electrons are exchanged. Thiosemicarbazide is oxidized in two oxidation steps and the ratio of the number of exchanged electrons in the first step to that in the second is 1:2, so that 4 electrons are exchanged in the first stage of oxidation. From the chronoamperometric measurements given above and on the basis of voltammetric experiments at a stationary carbon electrode the following thiosemicarbazide oxidation mechanism may be assumed

First oxidation step



Second oxidation step

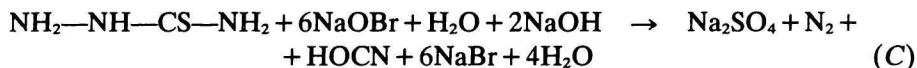


That sulfate is the final oxidation product can also be proved by the results obtained by coulometric titration (see below). After SO_4^{2-} ions had been formed in oxidation titration, an addition of Ba^{2+} salt produced the characteristic BaSO_4 precipitate in the titrated solution.

Thiosemicarbazide coulometric titration

Conditions found for a quantitative course of reaction between thiosemicarbazide and hypobromite as an oxidation agent gave rise to coulometric bromometric titration.

Data in [4] on volumetric titration determination have led to the assumption that this reaction proceeds in accordance with the following equation



According to this equation the number of exchanged electrons in thiosemicarbazide oxidation is 12. In our chronoamperometric measurements in solutions of pH values between 7.5 and 9.5 this number was found to be 11.8—12.2, which suggests that both electrode oxidation and thiosemicarbazide coulometric determination through hypobromite should yield identical products. In order to establish conditions for thiosemicarbazide coulometric titration determination it was necessary to find out the right composition of base electrolyte and the optimum values of pH, generating current, indicating current, and applied voltage.

The choice of base electrolyte used in determining the concentration by biamperometric indication depended on the proper value of pH needed for hypobromite formation through the disproportionation of bromine, primarily generated on the working electrode. Tetraborate buffer solution ($c = 3.15 \times 10^{-2} \text{ mol dm}^{-3}$) of pH = 8.6 proved to be the most suitable base electrolyte. The titrating agent was generated from a 0.8 M-KBr solution.

In the coulometric titration of a thiosemicarbazide standard solution of known concentration, the assumption that the number of exchanged electrons in thiosemicarbazide total oxidation is 12 has been proved correct. Results obtained from the thiosemicarbazide coulometric titration are summarized in Table 2. From the relative difference between the given and the found amounts of thiosemicarbazide it may be possible to judge the degree of accuracy of results at the different thiosemicarbazide concentration levels. The dependence of reliability interval relative width τ on concentration is illustrated in Fig. 4. The most precise results

Table 2

Results of thiosemicarbazide coulometric titration*

Given	Found		I_{gen}	I_{ind}
$m/\mu\text{g}$	$m/\mu\text{g}$		mA cm^{-2}	$\mu\text{A cm}^{-2}$
7.59	7.64	10	0.4	2.0
22.78	23.0	10	0.4	2.0
37.98	37.8	10	0.75	2.0
75.95	75.5	10	0.75	2.0
151.90	152	7	1.0	2.0
227.80	229	8	1.0	2.0
397.80	390	7	1.0	2.0

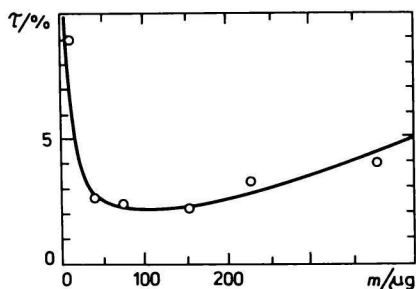
* n_m — number of measurements. I_{gen} — generating current density; I_{ind} — indicating current density.

Fig. 4. Dependence of relative width of reliability interval on the determined amount of thiosemicarbazide in its hypobromite coulometric titration.

have been obtained in the 75–150 μg thiosemicarbazide range in the 110–120 cm^3 of analyzed solution. These results have also proved to be the most accurate.

References

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