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# Catalytic activity of thiourea and its selected derivatives on electroreduction of In(III) in chlorates(VII)

**Review Article**

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**Abstract:** It was found that thiourea, N-methylthiourea, N,N'-dimethylthiourea and N-allylthiourea accelerate the electroreduction process of In(III) ions in chlorates(VII). These substances are adsorbed on mercury from chlorates(VII). The relative surface excesses of thiourea and its derivatives increase with the increase of their concentrations and electrode charge. After adding thiourea, N-methylthiourea, N,N'-dimethylthiourea and N-allylthiourea to the solution an acceleration of the electroreduction process of In(III) ions occurs. This process depends on two factors: the adsorption of an accelerating substance on mercury and on the formation of complexes between a depolarizer and an accelerating substance on the electrode surface. The equilibrium of this complexing reaction determines the magnitude of the catalytic effect.

**Keywords:** *Electroreduction of In(III) ions • Thiourea • N-methylthiourea • N,N'-dimethylthiourea • N-allylthiourea*



## 1. Introduction

Indium is interesting because of its properties and applications in many branches of industry. It is a component of many alloys, which are employed in the construction of electrodes (used for the protection of steel structures in a water environment [1-4]), dental and jewellery alloys [5] for their hardness and corrosion resistance. Indium alloys have remarkable resistance to the activity of bases and good wetting properties which allows their application in soldering materials [4]. Indium oxides also have a wide spectrum of applications such as in liquid crystal displays, energy-saving windows, picture detectors, solar cells and alkaline batteries [6-9]. Indium oxide (III) is applied in the modification of electrodes used to study kinetics in bioelectric systems with: ferredoxin [10], cytochrome c [11] or mioglobin [12,13].

According to Molodov [14], Lawson [15] and Armstrong [16] in weakly acidic, neutral and basic solutions of non-complexing electrolytes, the In(III) ions exist in the form of hydroxycomplexes: $[In(OH)]^{2+}$ and $[In(OH)_2]^{+}$. In pH<3 solutions the simple In(III) ions dominate, which is confirmed by different values of hydrolysis constant of In(III) ions presented in literature [17,18-21]. Using the NMR method, Cannon, Fratiello and co-workers [22,23] proved that in acidic solutions of non-complexing electrolytes the In(III) ions exist in the form of $[In(H_2O)_6]^{3+}$. Such a statement was confirmed by Celeda and Maeda in their studies using dilatometry methods [24] and X-ray diffraction [25].

In acidic solutions of non-complexing electrolytes $[In(H_2O)_6]^{3+}$ ion is characterized by a very low rate of hydration water loss. In connection to this fact, the total electrode process also consists of chemical stages leading to the labilization of the hydration sphere of $[In(H_2O)_6]^{3+}$ [26,27]. According to Eyring and Owen [28]

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it is the stage of hydration water loss that decides about the rate of the electroreduction process of In (III), which also Zelič [29] confirmed in his studies. The electroreduction of In(III) ions is connected with the transfer of three electrons, which suggests that the mechanism of this process is complex and consists of several intermediate stages, leading to the product formation. Research conducted by Montemayor and Fatas [30] proved that In(III) ions do not undergo specific adsorption on a mercury electrode from the solutions of non-complexing electrolytes.

Nazmutdinov and co-workers [31] analysed in detail the different mechanisms of In(III) electroreduction, using the theory of charge transfer in polar environments as well as the quantum chemistry theories. According to Nazmutdinov [31] the mechanism of gradual electron transfer in the electroreduction process of In(III) ions is the most reliable. The following conclusions were a result of investigations conducted by Nazmutdinov and his co-workers:

- the contribution of inner layer in total reorganization energy is higher for In(III) aquacomplexes in comparison with its hydrolyzed form,
- the overlapping of electrode and substrate orbitals is stronger in the case of $[In(H_2O)_5OH]^{2+}$, which leads to higher values of electron transmission coefficient,
- the higher charge of the $[In(H_2O)_6]^{3+}$ complex compared to the $[In(H_2O)_5OH]^{2+}$ complex causes the fact that the work of maximal reagent approach is higher, which additionally favours the access of $[In(H_2O)_5OH]^{2+}$ on the electrode surface.

Therefore, one may state that aquahydroxycomplexes of In(III) strongly compete with aquacomplexes of In(III) and they are more active electrochemically. The electroreduction of In(III) ions in non-complexing solutions of electrolytes is an irreversible process. The electroreduction rate can be increased by adding organic substances fulfilling the conditions of the cap-pair rule to the supporting electrolyte [32].

In this paper, the catalytic activity of thiourea (TU), N-methylthiourea (MTU), N,N'-dimethylthiourea (DMTU) and N-allylthiourea (ATU) on the electroreduction process of In(III) ions in chlorates(VII) was compared. Thiourea and its allyl derivatives have free electron pairs at sulphur and nitrogen atoms, therefore they show similar tendency for formation of complex compounds. Moreover these substances are adsorbed on mercury electrode surfaces [33-35], fulfilling the conditions of the cap-pair rule. The choice of chlorates(VII) as the supporting electrolyte is connected to the fact that $ClO_4^-$ ions show weak complexing properties and is adsorbed on mercury to a lower degree, which allows for omission of their competitiveness in adsorption with organic substances. It is also worth mentioning that $ClO_4^-$ ions have a strong tendency to destroy the water structure [36].

This paper presents different electrochemical techniques such as: dc polarography, cyclic and SWV woltammetry and chronocoulometry.

## 2. Experimental procedure

The investigations were conducted in a three-electrode cell, containing a dropping mercury electrode (DME) (Laboratorni Pristroje Prague) or a static mercury drop electrode (SMDE) (model 303A, AG & G PARC) as working electrodes, saturated Ag/AgCl (NaCl) as a reference electrode and a platinum spiral or plate electrode as a counter electrode.

The reference electrode was connected to the cell via a electrolytic bridge ended with Luggin capillary. The measurements were carried at 298 ±0.1 K in thermostatic cells.

The solutions were prepared from freshly double-distilled water. Before measurements the solutions were deaerated using high-purity nitrogen. Earlier nitrogen was passed over the washers filled in turn by acidified solution of vanadyl sulfate and an adequate supporting electrolyte. As a supporting electrolyte the following 1 mol $dm^{-3}$ $NaClO_4$ pH=2 for In(III)-TU, In(III)-MTU, In(III)-DMTU and In(III)-ATU systems were used.

The concentration of In(III) ions in the solutions studied was always $1\times10^{-3}$ mol $dm^{-3}$.

The solution of $1\times10^{-3}$ mol $dm^{-3}$ In(III) in 1 mol $dm^{-3}$ $NaClO_4$ was prepared by dissolving the weighed amount of 99.999% $In(NO_3)_3\times5H_2O$ in a small quantity of 1 mol $dm^{-3}$ $HClO_4$, and then 1 mol $dm^{-3}$ $NaClO_4$ was added in order to make a 1 $dm^3$ solution. Such a procedure was necessary to avoid the hydrolysis of In(III). The pH of solutions studied was fixed by the addition of $HClO_4$ and NaOH, respectively.

The thiourea and its derivatives solutions were prepared directly before the measurements. The range of concentrations studied of thiourea and its derivatives were $10^{-4}$-$10^{-1}$ mol $dm^{-3}$.

During the measurements the following were applied: electrochemical analyzer Autolab PG STAT 10 (Eco Chemie), multifunctional polarograph PA-4 (Laboratorni Pristroje), electrochemical analyzer model 270 (EG & G PARC), pH-meter CPC-551 (Elmetron).

# 3. Results and discussion

## 3.1. Adsorption measurements

The differential capacity of the double layer ($C_d$) on the interface mercury/supporting electrolyte was measured by impedance method. The reproducibility of results obtained by differential capacity measurement was ±0.5%.

The measurements were carried out at frequencies of 200 Hz, 400 Hz, 600 Hz, 800 Hz 1200 Hz and amplitude 5 mV. In all of the systems studied the frequency dispersion was observed and therefore the differential capacity values obtained were extrapolated to zero frequency from linear dependence $C_d=f(\sqrt{\omega})$, where ($\omega$) is angular frequency, $\omega = 2\pi f$ [rad $s^{-1}$].

Fig. 1 presents the differential capacity curves of the double layer on the interface Hg/1 mol $dm^{-3}$ $NaClO_4$ and in the presence of $3\times10^{-3}$ mol $dm^{-3}$ TU, MTU, DMTU or ATU.

A capacitive hump appears on the differential capacity curve at ca -500 mV potential. According to Parsons and Payne [37] there are two reasons for this hump occurance: reorientation of water molecules and a change of $ClO_4^-$ anions adsorption along with the change of charge on the electrode surface.

The addition of TU and its derivatives to 1 mol $dm^{-3}$ $NaClO_4$ causes an increase of the differential capacity in a range of potentials from –200 to –1400 mV. At potentials higher than –1400 mV the differential capacity curves are joined with the differential capacity curve of the supporting electrolyte, in the presence of all studied concentrations of TU and its derivatives, which proves that TU and its derivatives are not adsorbed on mercury in this range of potentials [33-35].

The “hump”, characteristic of the same concentrations of TU and its derivatives, is shifted towards the more negative potentials in the following order TU<MTU<ATU<DMTU. The position change of the hump seems to be connected with the molecular weight of accelerating substance, which increases in the order TU<MTU<DMTU<ATU. The presence of a double bond in ATU molecule disturbs this order.

The zero charge potentials ($E_z$) were determined by the use of a streaming electrode [38,39], with the accuracy ± 0.1 mV. The surface tension at potential of zero charge ($\gamma_z$) was measured using the method of highest pressure inside the mercury drop presented by Schiffrin [40]. The surface tension values were determined with an accuracy of ± 0.2 nN $m^{-1}$.

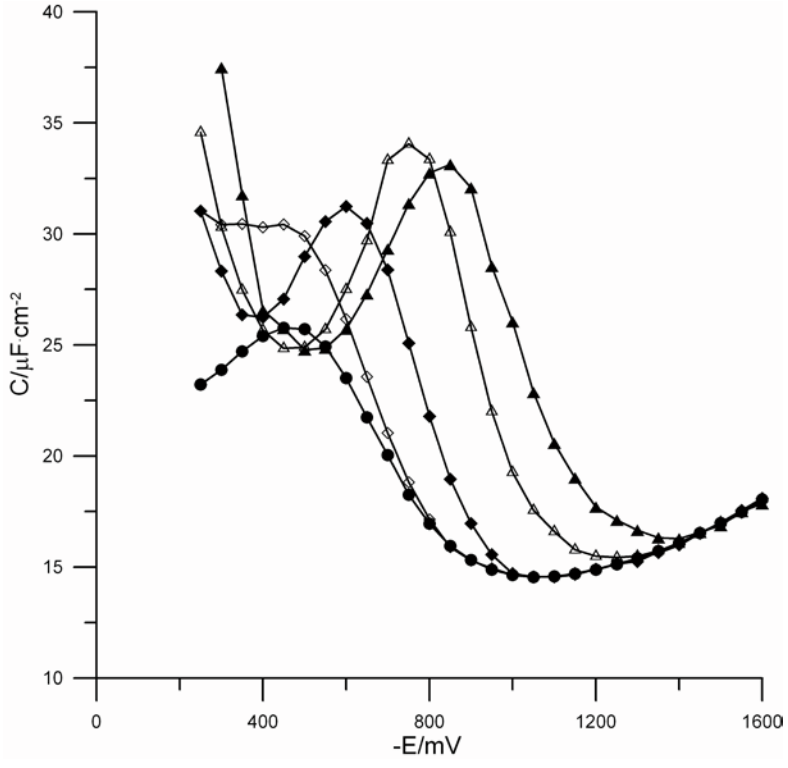


**Figure 1.** The differencial capacity curves of double layer interface Hg/1 mol $dm^{-3}$ $NaClO_4$ (•) and Hg/1 mol $dm^{-3}$ $NaClO_4$ in the presence of $3\times10^{-3}$ mol $dm^{-3}$ TU (◊) [33], MTU (♦), ATU (Δ) [35] and DMTU (▲) [34]

**Table 1.** Potential of zero charge $-E_z$ / mV *vs.* Ag / AgCl electrode and surface tension $\gamma_z$ /mN m$^{-1}$ for $E_z$ of $NaClO_4$ +TU [33], MTU, ATU [35] and DMTU [34] systems.

| $10^3$ c / mol dm$^{-3}$ | TU | | MTU | | DMTU | | ATU | |
|---|---|---|---|---|---|---|---|---|
| | $-E_z$/mV | $\gamma_z$/mN m$^{-1}$ | $-E_z$ / mV | $\gamma_z$ / mN m$^{-1}$ | $-E_z$ / mV | $\gamma_z$/mN m$^{-1}$ | $-E_z$/mV | $\gamma_z$/m Nm$^{-1}$ |
| 0.00 | 469.9 | 423.5 | 469.9 | 423.5 | 469.9 | 423.5 | 469.9 | 423.5 |
| 0.50 | 478.0 | 423.4 | 495.3 | 420.8 | 521.4 | 415.2 | 522.6 | 420.5 |
| 1.00 | 491.0 | 423.2 | 519.3 | 419.8 | 544.5 | 412.1 | 551.4 | 418.9 |
| 3.00 | 519.0 | 423.0 | 552.2 | 414.2 | 592.1 | 409.3 | 600.3 | 415.7 |
| 5.00 | 539.0 | 422.7 | 575.2 | 418.2 | 611.2 | 406.5 | 623.9 | 413.4 |
| 8.00 | 553.0 | 422.5 | 597.0 | 417.2 | 631.0 | 404.2 | 645.8 | 411.5 |
| 10.0 | 564.0 | 421.7 | 614.0 | 416.2 | 644.1 | 403.1 | 653.8 | 408.9 |

The zero charge potential $E_Z$ values and the surface tension values at zero charge potential $\gamma_z$ on the interface Hg/1 mol dm$^{-3}$ $NaClO_4$ and Hg/1 mol dm$^{-3}$ $NaClO_4$ in the presents of studied TU derivatives are presented in Table 1. As Table 1 indicates, together with the increase of TU and its derivatives concentration of zero charge potential $E_Z$ values are shifted towards the more negative potentials, which is characteristic of anion adsorption. The surface tension at zero charge potential values decrease together with the increase of TU and its derivatives concentration. The zero charge potential $E_Z$ for the same concentrations of TU and its derivatives decrease together with the increase in molecular weight of the accelerating substances studied. The capacity curves were numerically integrated twice from the point of $E_Z$.The integration constants are presented in Table 1. The values of charge ($\sigma_m$) and surface tension ($\gamma$) were used for the calculation of Parsons auxiliary function $\zeta$, $\zeta = \gamma \sigma_m E$ and interfacial pressure $\Phi = \Delta\zeta^{\circ} - \zeta$ [41,42], where index $^{\circ}$ refers to supporting electrolyte containing the accelerating substance.

In accordance to Gibbs's adsorbance isotherm the relative surface excesses ($\Gamma$) of thiourea and its derivatives was determined at constant charge with the support of equation:

$$\Gamma = \left(\frac{1}{RT}\right)\left(\frac{d\Phi}{d\ln c_a}\right)_{\sigma} \quad (1)$$

where: $c_a$ – adsorbate concentration, R – gas constant, T – temperature.

In the equation above an assumption was made that the average activity coefficients of particular organic substances in the solution do not change together with the increase of their concentration.

The relative surface excesses increases together with the increase of TU and its derivatives concentration [33-35]. The changes of relative surface excesses in the function of electrode charge for concentration $3\times10^{-3}$ mol dm$^{-3}$ of TU and its studied derivatives are presented in Fig. 2.

As Fig. 2 shows the $\Gamma$ values increase with the increase of electrode charge, what is characteristic for compounds containing a divalent sulphur atom in their structure [43]. The weaker adsorption at negative charges than in the range of positive charges points at a strong chemisorption of TU and its derivatives on mercury, which is a result of specific interactions between the mercury and the sulphur atom. The $\Gamma$ values increase in the series TU<MTU<ATU<DMTU.

To find out whether or not In(III) can be accumulated on the surface layer by interaction with the adsorbed thiourea or N-methylthiourea, N,N'-dimethylthiourea and N-allylthiourea molecules, chronoculometric measurements were carried out in $1\times10^{-3}$ mol dm$^{-3}$ of TU and its studied derivatives in 1 mol dm$^{-3}$ $NaClO_4$. The plot of the maximal charge of In(III) electroreduction at potential equal to – 700 mV *versus* the integration time was linear and crossed the origin of the coordinates after subtraction of the double layer charge, recorded for blank solution. This points out that under such conditions the cathode reduction of In(III) is limited by diffusion and that induced adsorption of In(III) cannot be detected within the limits of experimental error.

## 3.2. Kinetic measurements

The pH range, in which the reduction process of In(III) ions can be studied is limited by the hydrolysis of hydrated $[In(H_2O)_6]^{3+}$ ions [44].

$$[In(H_2O)_6]^{3+}(aq) + H_2O \longrightarrow [In(H_2O)_5OH]^{2+}(aq) + H_3O^{+}(aq) \quad (2)$$

Together with the increase of pH the reversibility of the electroreduction process of In(III) ions in chlorates(VII) increases, and this is connected to the presence of In aquahydroxycomplexes in the solution, which show higher electrochemical activity than aquacomplexes.

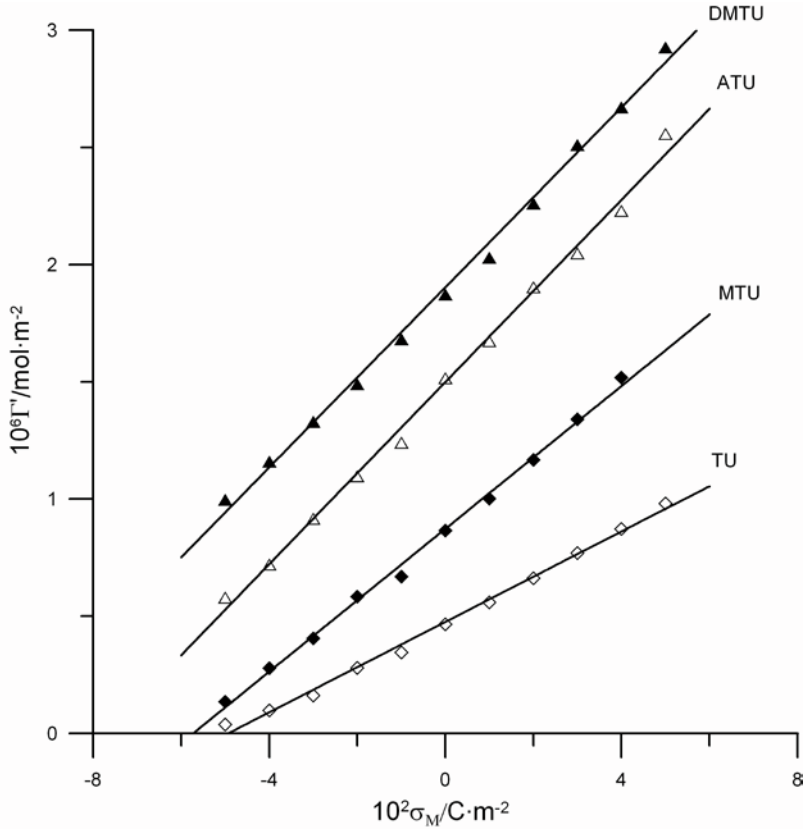


**Figure 2.** The relative surface excesses (Γ') of $3\times10^{-3}$ mol dm$^{-3}$ TU (◊) [33], MTU (♦), ATU (Δ) [35] and DMTU (▲) [34] as a function of the electrode charge

After the addition of TU [45], MTU, DMTU [46] or ATU to the solution the acceleration of the electroreduction process of In(III) ions occurs.

The DC wave of In(III) ions electroreduction in 1 mol dm$^{-3}$ $NaClO_4$ pH = 2 is well-defined (Fig. 3). The addition of TU and its derivatives to the solution does not cause the height change of the DC wave, but the slope of the wave increases, which points to an increase of reversibility of the electroreduction process of In(III) ions in 1 mol dm$^{-3}$ $NaClO_4$ pH = 2 in the presence of TU and its studied derivatives.

The limiting current of In(III) ions electroreduction in 1 mol dm$^{-3}$ $NaClO_4$ pH = 2 in the presence of TU and its derivatives does not depend on the height of the mercury reservoir, which points to a kinetic control of the process.

After adding TU or its studied derivatives to the In(III) ions solution in 1 mol dm$^{-3}$ $NaClO_4$, the SWV peaks of In(III) ions electroreduction increase with the increase of organic substances concentration (Fig. 4). It should be noticed that the highest increase of the currents values of the SWV peaks of In(III) ions electroreduction were obtained in the presence of MTU. The potentials of the SWV peaks did not undergo changes in the presence of accelerating substances, which points out that stable complexes In-organic substance are not formed in the solution.

Fig. 5 presents cyclic chronovoltammetric curves recorded in a $1\times10^{-3}$ mol dm$^{-3}$ In(III) in 1 mol dm$^{-3}$ $NaClO_4$ pH = 2 solution in the presence of different MTU concentrations. The cathode peaks, similar that found in the presence of TU [45], DMTU [46] or ATU, are considerably lower and worse-defined than the anodic peaks, which confirms that the electroreduction process of In(III) ions is controlled by the preceding reaction [47].

With the increase of TU concentration and its derivatives studied the distances between the cathode and anodic peaks decrease, which points to an increase of reversibility of the electroreduction process of In(III) ions in the presence of the studied organic substances.

Assessment of the influence of the polarization rate (ν) on the potential difference of cathode and anodic peaks $\Delta E_{ca}$ shows that after addition of TU or its derivatives to the $1\times10^{-3}$ mol dm$^{-3}$ In(III) in 1 mol dm$^{-3}$ $NaClO_4$ pH = 2 solution, results in slight changes in the potential difference of cathode and anodic peaks $\Delta E_{ca}$ of the polarization rate ν. These changes decrease with

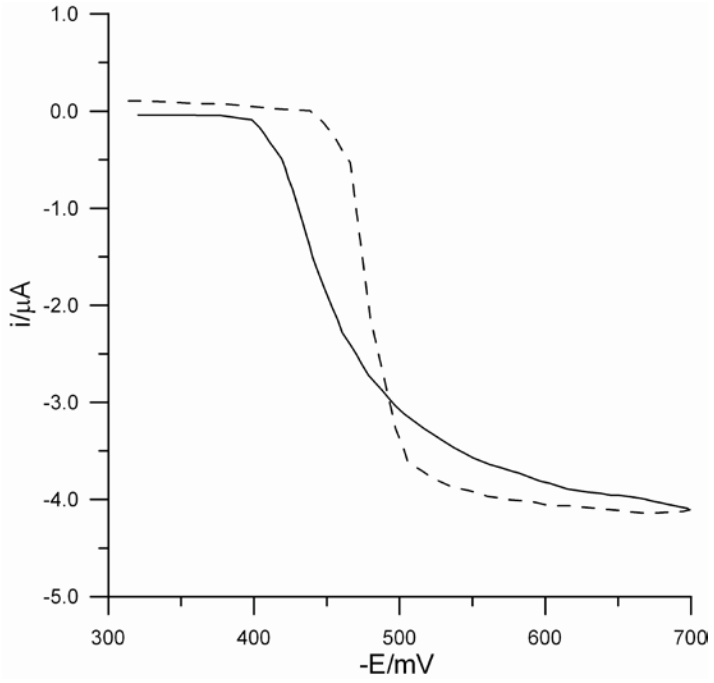


**Figure 3.** The DC polarograms of $1\times10^{-3}$ mol dm$^{-3}$ In(III) in 1 mol dm$^{-3}$ $NaClO_4$ pH 2 (solid line) and thesis in the presence of $1\times10^{-2}$ mol dm$^{-3}$ MTU (dotted line)

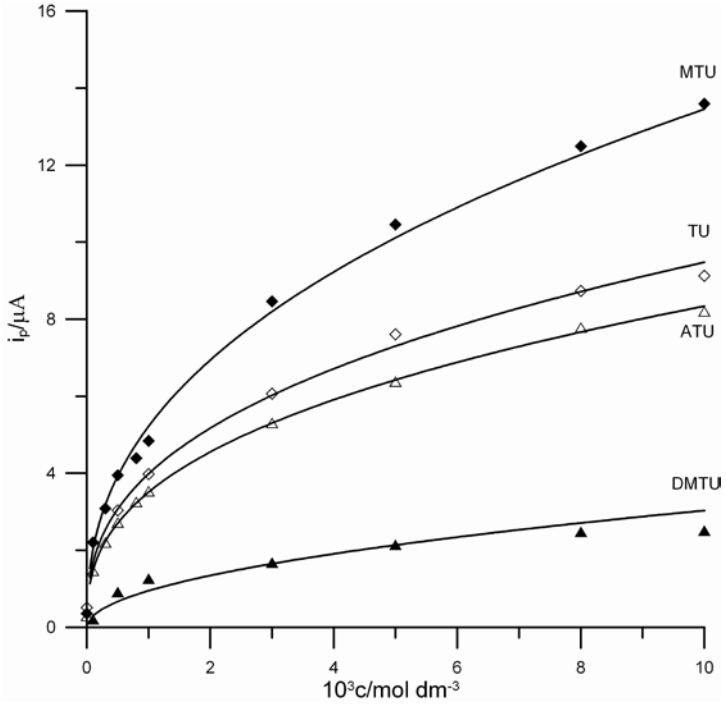


**Figure 4.** The dependence of $1\times10^{-3}$ mol dm$^{-3}$ In(III) in 1 mol dm$^{-3}$ $NaClO_4$ pH 2 SWV peak current on concentration of TU (◊) [45], MTU (♦), ATU (Δ) and DMTU [46] (▲) (mol dm$^{-3}$)

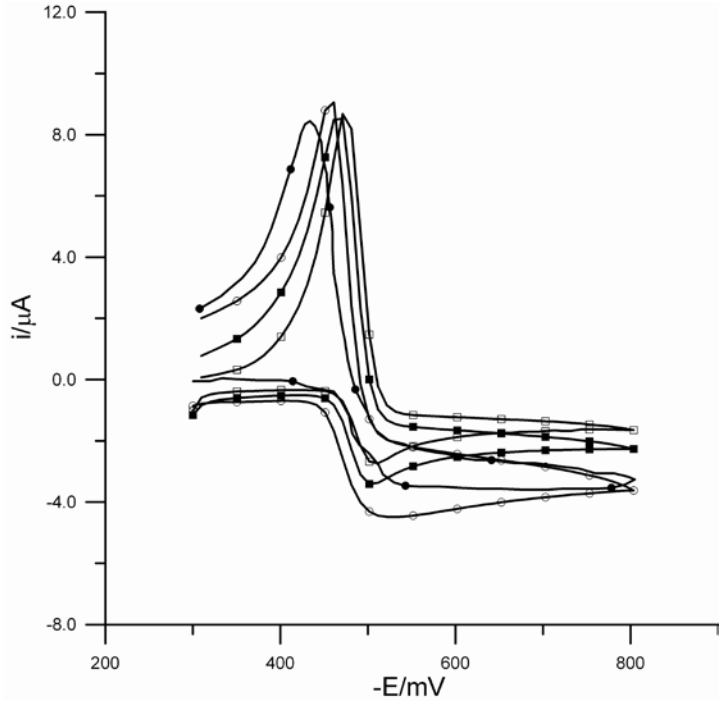


**Figure 5.** The cyclic voltammogram of $1\times10^{-3}$ mol dm$^{-3}$ In(III) in 1 mol dm$^{-3}$ $NaClO_4$ pH 2 in the presence of MTU. The concentration of MTU in mol dm$^{-3}$: 0 (•); $3\times10^{-4}$ (o); $5\times10^{-4}$ (■); $8\times10^{-4}$ (□)

increase in concentration of the organic substances studied. This leads to a theory that the chemical reaction stage is the one that controls the electroreduction rate of In(III) ions in the presence of the accelerating substances studied. This reaction is probably the result of complex In-X formation (where X = TU, MTU, DMTU or ATU) on the electrode surface, because the adsorption of TU and its derivatives on the electrode favourably shifts the equilibrium of the complexing reaction.

The kinetic parameters values for systems In(III)-TU and In-DMTU were taken from [45,46]; and for systems In(III)-MTU and In(III)-ATU from chronovoltammetric measurements. All calculations were based on the theoretical equations of Nicholson and Shain for the processes proceeding on plate electrodes [48,49], which can be applied with a slight error for globular electrodes, fulfilling the condition $r^2\nu \geq 10^{-4}$ cm$^2$ V s$^{-1}$ [50,51] ($r$ – electrode radius). The application of electrode of $r = 0.065$ cm and polarization rate $\nu = 0.050$ V s$^{-1}$ gives the value of $r^2\nu = 2.1\times10^{-4}$ cm$^2$ V s$^{-1}$. Therefore the required condition was fulfilled. This method can also be used in the processes preceded by a chemical reaction [49].

For the irreversible processes the standard rate constants $k_s$ values were determined from cathode peaks potential, whose dependence on the kinetic parameters is described by the following equation [49,52]:

$$E_{pk} = E_f^0 - \frac{RT}{\alpha n_\alpha F}[0.78 - \ln k_s + \ln\sqrt{D_{Ox}b}] \quad (3)$$

where:

$b = \frac{\alpha n_\alpha F v}{RT}$

$E_f^0$ - formal potential, $\alpha n_\alpha$ - cathode transfer coefficient

For the quasi-reversible processes the $k_s$ values were determined using the Nicholson [48] method based on the equation:

$$\Psi = (\frac{D_{ox}}{D_{red}})^{\alpha/2} \frac{k_s (RT)^{1/2}}{(\pi n F v D_{ox})^{1/2}} \quad (4)$$

The dependent $\Psi$ functions values from $n(E_{pa} - E_{pk})$ are presented in Table [48]

The diffusion coefficient ($D_{ox}$) of In(III) ions in the studied solutions was determined from Randles and Ševčik equation [53-54]:

$$i_c = 3.01 \times 10^5 \, n(\alpha n)1/2 \, A D_{ox}^{1/2} \, C_{ox} v^{1/2} \quad (5)$$

where:

c- depolarizer concentration in bulk solution, A – electrode surface.

The formal potentials ($E_f^0$) for electrode processes were determined using Randles [55] modified method from the equation:

$$E_f^0 = \frac{1}{2}[E_{a/4} + E_{c/4} + \frac{(E_{a/4} + E_{c/4}) - (E_{3a/4} + E_{3c/4})}{g - 1}] \quad (6)$$

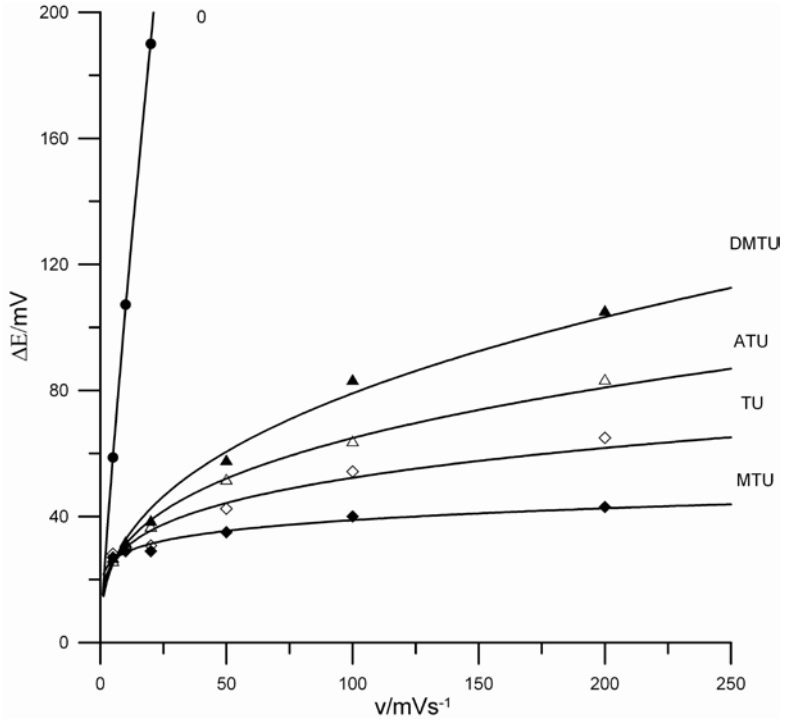


**Figure 6.** The influence of polarization rate on the difference between potentials of cathodic and anodic peaks for the In (III)/In(Hg) couple in 1 mol $dm^{-3}$ $NaClO_4$ pH 2 in the presence of $5\times10^{-3}$ mol $dm^{-3}$ TU (◊) [45], MTU (♦), ATU (Δ) and DMTU (▲) [46]

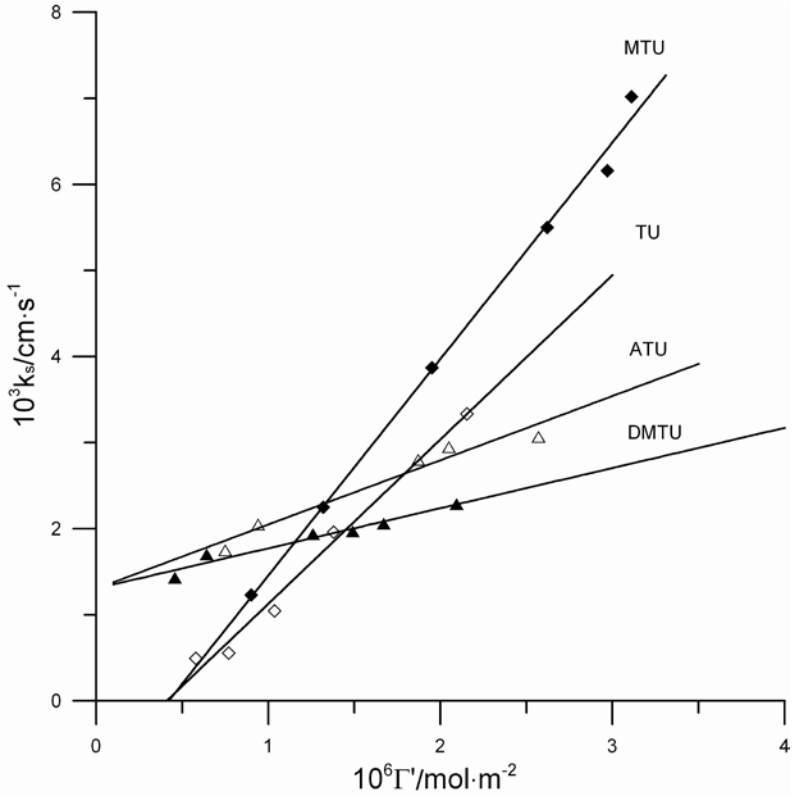


**Figure 7.** The dependence of standard rate constants $k_s$ of $1\times10^{-3}$ mol $dm^{-3}$ In(III) electroreduction in 1 mol $dm^{-3}$ $NaClO_4$ pH = 2 in the presence of: thiourea (◊) [45], N-methylthiourea (♦), N,N'-dimethylthiourea (▲) [46], N-allylthiourea (Δ) on adsorbate surface excess (Γ').

where $g = \frac{(E_{3a/4} - E_{3c/4})}{(E_{a/4} - E_{c/4})}$

$E_{a/4}$ or $E_{3a/4}$ - the potentials of accordingly one fourth or three fourth of the anodic peaks height.

$E_{c/4}$ or $E_{3c/4}$ - the potentials of accordingly one fourth or three fourth of the cathode peaks height.

The transfer coefficient ($\alpha n_\alpha$) of electroreduction reaction of In(III) ions in the studied systems was determined using equation [56,57]:

$$\alpha n_\alpha = \frac{0.048}{E_{pk/4} - E_{3pk/4}} \quad (7)$$

The transfer coefficient values depended on the polarization rate, therefore the extrapolation was conducted at such polarization rates, at which $\alpha n_\alpha$ receives constant values. The determination of kinetic parameters values error and diffusion coefficients $D_{ox}$ were estimated at ±5%.

Table 2 presents formal potentials $E_f^0$ values and cathode transfer coefficients $\alpha n_\alpha$ of In(III) ions electroreduction in 1 mol dm$^{-3}$ $NaClO_4$ pH = 2 in the presence of MTU and ATU. For systems In(III)-TU and In(III)-DMTU the data were taken from papers [45,46].

The addition of TU, DMTU or ATU to the solution as well as the increase of concentration of these substances did not influence the $E_f^0$ value. Whereas the addition of 5×10$^{-4}$ mol dm$^{-3}$ MTU to the solution caused a shift in the formal potential of 11 mV. With further increase of MTU concentration in the solution the changes of $E_f^0$ were minimal. Such changes point out that the stable complexes In-studied organic substance are not formed in the solution.

The determined values $\alpha n_\alpha$ point out that the electroreduction process of In(III) ions in 1 mol dm$^{-3}$ $NaClO_4$ is irreversible, while in the presence of the substances studied the reversibility of the process increases. The $\alpha n_\alpha$ values rise with the increase of TU, MTU, DMTU and ATU concentration from 0.3 to 1.1 which according to Petrii and co-workers [58] indicates an asymmetry of intramolecular reorganization change and the coefficient arbitrary asymmetry factor $\nu$ »1 for zero overvoltage $\eta$ = 0.

The diffusion coefficient $D_{ox}$ value of In(III) ions in 1 mol dm$^{-3}$ $NaClO_4$ pH = 2 was determined to be $D_{ox}$ = 1.56×10$^{-6}$ cm$^2$ s$^{-1}$ [59]. In the presence of the organic substances studied the $D_{ox}$ values changes are very low.

With the increase of TU, MTU, DMTU or ATU concentration in the supporting electrolyte, the $D_{ox}$ values of In(III) ions increase minimally. In the presence of 1×10$^{-2}$ mol dm$^{-3}$ of adsorbate $D_{ox}$ values are [in 10$^{-6}$ cm$^2$ s$^{-1}$ ] 1.61; 1.65, 1.79, 1.69, respectively for TU [45], MTU, DMTU [46] and ATU.

Fig. 7 presents standard rate constants $k_s$ dependencies of In(III) ions electroreduction in 1 mol dm$^{-3}$ $NaClO_4$ pH = 2 in the function of surface excesses of TU and its derivatives studied with $E_f^0$. Where the $\Gamma$ value with $E_f^0$ is from the curve $\Gamma = f(E)$.

The linear course of dependencies $k_s = f(\Gamma)$ can serve as proof for active complex formation on the electrode surface, which mediates the electron transfer in the electroreduction process of In(III) ions [60].

## 4. Conclusions

Thiourea, N-methylthiourea, N,N'-dimethylthiourea and N-allylthiourea are adsorbed on mercury from chlorates(VII). Together with the increase of TU and its derivatives studied concentration the differential capacity of the double layer increases and the capacity hump is shifted towards the negative potentials, which shows that electrode polarization influences the orientation of the adsorbate molecules. It was found that TU and its derivatives studied are adsorbed on mercury electrode by a sulphur atom directed to mercury. The presence of sulphur, strongly interacting with mercury, leads to the chemisorption of molecules on the electrode and

**Table 2.** Values of formal potentials $E_f^0$ /mV and cathodic transfer coefficients $\alpha n_\alpha$ of In(III) ions electroreduction in 1 mol dm$^{-3}$ $NaClO_4$ pH = 2 in the presence of TU [45], MTU, DMTU [46] and ATU.

| $10^3$ c/mol dm$^{-3}$ | TU | | MTU | | DMTU | | ATU | |
|---|---|---|---|---|---|---|---|---|
| | $-E_f^0$ /mV | $\alpha n_\alpha$ | $-E_f^0$ /mV | $\alpha n_\alpha$ | $-E_f^0$ /mV | $\alpha n_\alpha$ | $-E_f^0$ /mV | $\alpha n_\alpha$ |
| 0.00 | 469 | 0.30 | 469 | 0.30 | 469 | 0.30 | 469 | 0.30 |
| 0.50 | 468 | 0.51 | 480 | 0.45 | 468 | 0.33 | 468 | 0.45 |
| 1.00 | 469 | 0.69 | 480 | 0.54 | 467 | 0.36 | 467 | 0.42 |
| 5.00 | 469 | 0.90 | 483 | 0.69 | 468 | 0.36 | 468 | 0.45 |
| 10.00 | 470 | 1.11 | 483 | 0.96 | 469 | 0.42 | 469 | 0.48 |

stronger adsorption in the range of positive charges of the electrode in comparison with the range of negative charges. For the same concentrations of TU and its derivatives studied the relative surface excesses increase in the order TU<MTU<ATU<DMTU. The reduction of In(III) on mercury from the chlorates solution always proceeds in the range of labile adsorption potentials of TU and its derivatives.

The acceleration of the electroreduction process of In(III) ions occurs after the addition of TU, MTU, DMTU and ATU to the $1\times10^{-3}$ mol $dm^{-3}$ In(III) solution in 1 mol $dm^{-3}$ $NaClO_4$.

The reduction of In(III) complexes at the mercury electrode is a stepwise electron transfer (ET) process. From the results reported by Nazmutdinov and his co-workers [44], the acceptor orbital (AO) of $[In(H_2O)_6]^3$ is localized mainly on the central atom. It may be assumed that the formation of a "surface" complex changes the AO structure which increases the electrode – reactant orbital overlap and facilitates ET.

In the In(III) electroreduction complex mechanism the acceleration substance seems to be similar.

It was proved that the electroreduction process of In(III) ions in the presence of the organic substances studied is controlled by the kinetics of a chemical reaction preceding the electron transfer.

The absence of distinct changes in the formal potential values of the In(III) ions electroreduction in the presence of catalyzing substances proves that the stable complexes of In(III) ions with the studied substances are not formed in the solution. The acceleration of the electrode processes only by such organic substances, which have free electron pairs at sulphur or nitrogen atoms suggest a possibility of a complex formation under specific conditions, which exist on the surface of the electrode. Therefore the adsorption does not restrict the electrode surface, but it additionally strengthens its activity.

By comparing the influence of TU derivatives on the electroreduction process of In(III) ions in chlorates(VII) it can be assumed that the catalytic activity increases in the order DMTU<ATU<MTU for $\Gamma^*$ >2 mol $m^{-2}$, while adsorption decreases in the same order.

The lower activity of TU compared to MTU may be caused by lack of asymmetry in the MTU molecule, which not only influences the placement of molecules on the electrode surface but also its balance in reacting to active complex formation, which is observed only in higher surfaces excesses $\Gamma^*$ >2 mol $m^{-2}$ when a defined active In – acceleration substance complex is created.

It suggests that although the adsorption of catalyzing substance is a necessary condition for the acceleration of the electroreduction process of In(III) ions, it does not decide the magnitude of the catalytic effect. Probably the magnitude of the catalytic effect is connected to the equilibrium of reaction of active complexes formation before the transfer of consecutive electrons. A similar effect was observed by Dalmata [61] in his study on the catalytic activity of organic substances on the electroreduction process of Zn(II).

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