# Influence of the Mixed Adsorption Layer 1-Butanol/Thiourea on the Two-step Electroreduction of Zinc(II) Ions

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Influence of a constant 1-butanol (BuOH) concentration and various thiourea (TU) concentrations in the bulk on the two consecutive one-electron transfer steps in the electroreduction of $Zn^{2+}$ ions at Hg electrode is described. It was found that in the range of $Zn^{2+}$ ions reduction potentials BuOH has the predominant effect on formation of the adsorption mixed layer. The values determined for the total surface excesses of BuOH and TU in the function of $\phi^r$ potential are linear and, except for the highest TU concentrations, insignificantly depend on the potential. As it follows from the dependence $k^t_f = f(\phi^r)$, in the presence of 0.11 mol dm$^{-3}$ BuOH even the smallest amounts of TU accelerate $Zn^{2+}$ ion reduction compared with 1 mol dm$^{-3}$ NaClO$_4$ solution. However, in a solution containing 0.33 mol dm$^{-3}$ or 0.55 mol dm$^{-3}$ BuOH this effect takes places only for $c_{TU} \geq 0.033$ mol dm$^{-3}$. The course of the $k^t_{s1} = f(\Gamma)$ and $k^t_{s2} = f(\Gamma)$ dependence indicates that one kind of active complex is formed on the electrode surface in the 0.11 mol dm$^{-3}$ BuOH solution but in solutions of a larger amount of BuOH two kinds of active complexes are formed, differing in the extent of hydration. The obtained results indicate that the stage of the first electron transfer is less susceptible to inhibition by BuOH than the stage of the second electron transfer.

*Key words:* electroreduction of $Zn^{2+}$, mixed adsorption, thiourea, 1-butanol.

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## INTRODUCTION

Electroreduction of $Zn^{2+}$ ions on the mercury electrode is a typical example of a reaction controlled both by diffusion and charge transfer. In the literature, several papers discuss[1–6] the possibility of a mechanism with two single electron transfers.

The best technique for the study of multi-step electrode reactions is impedance measurement because it allows kinetic data to be obtained at controlled potentials in a wide potential range.

It is known that the adsorption at the electrode/electrolyte solution interface plays an important role in the study of electrode kinetics. The presence of adsorbed nonelectroactive species can have a drastic influence on the rate of an electrode reaction, either in the accelerating or inhibiting sense. Thiourea is an example of an organic substance that accelerates several electrode processes in an aqueous solution.[7–12] The mechanism of electrode process acceleration on the mercury electrode has not been sufficiently explained yet.

Still, it is known that two phenomena, taking place simultaneously, play an important role here, namely, adsorption of an organic substance on the electrode and formation of an active complex between the depolarizer ions and the organic substance reduced on the mercury electrode.[10] The decisive role in the acceleration of electrode processes is probably played by the structure of this active complex.

The effect of the mixed adsorption layer formed by two organic substances on a mercury electrode upon the kinetics of $Zn^{2+}$ ion electroreduction has been published earlier. It was found that, in solutions containing a suitable inhibitor and a substance accelerating $Zn^{2+}$ ion electroreduction, *e.g.* tween 80/thiourea,[13] polyethyleneglycols/thiourea,[14,15] 1-butanol/ thiourea,[16] changing the relative concentration of these substances causes inhibition, acceleration or compensation of these effects.

The paper is a continuation of the studies described in Ref. 16, especially taking into consideration the influence of the mixed adsorption layer on the stages of $Zn^{2+}$ electroreduction process.

Electroreduction of $Zn^{2+}$ ions from $NaClO_4$ solutions at a mercury electrode in the presence of thiourea (TU) and 1-butanol (BuOH) is claimed to involve two consecutive one-electron transfer steps in the overall reaction. Since the kinetics of the electron transfer steps will be potential dependent, the nature of the rate controlling step can change with potential. Furthermore, as the reaction involves charged reactants in the double layer, double layer effects are expected to be important in these processes.

## EXPERIMENTAL

Solutions were prepared from freshly double-distilled water and Fluka analytical grade chemicals.

The zinc perchlorate was prepared by dissolving ZnO in a small excess of perchloric acid. In order to avoid hydrolysis of $Zn^{2+}$, this excess of perchloric acid was chosen to make the final solution 0.001 mol $dm^{-3}$ with respect to $H^+$.

Optimal accuracy was achieved by maintaining the $Zn^{2+}$ concentration around 0.005 mol $dm^{-3}$. Studies of the adsorption and catalytic activity were carried out in the BuOH concentration range from 0.11 mol $dm^{-3}$ to 0.55 mol $dm^{-3}$ and TU from 0.0055 mol $dm^{-3}$ to 0.55 mol $dm^{-3}$.

Water and mercury were triply distilled. Solutions were deaerated using nitrogen passed through a vanadous sulfate solution. All measurements were carried out at 298±1 K.

The experiments were performed in a three-electrode cell with a dropping mercury electrode made by MTM Poland as a working electrode, Ag/AgCl as a reference electrode and a platinum spiral as an auxiliary electrode. The reference electrode was fitted with a Luggin capillary probe. The capillary was filled with the cell solution.

The double layer capacity was measured using the ac impedance technique at a frequency of 800 Hz. A few measurements were also carried out at 50–1500 Hz in order to check the frequency dependence of the results. No dispersion of the capacitance was observed in the potential range studied. The potential of zero charge ($E_z$) was measured for each solution using the streaming mercury electrode.

Polarographic measurements were carried out using a polarograph PA-4 (Laboratorni Pristroje, Prague, Czech Republic) or a polarographic analyzer model 384 B (EG&G PARC).

Impedances were carried out with a 9121 FR Analyzer and 9131 Electrochemical Interface of Atlas-Sollich (Gdañsk).

## RESULTS AND DISCUSSION

### *Double Layer Analysis*

The differential capacity curves obtained in 1 mol $dm^{-3}$ $NaClO_4$ with the addition of increasing BuOH amounts are characterized by a significant decrease of differential capacity towards the basic electrolyte, typical of inhibitors. Introduction of TU into the BuOH solution causes an increase of the differential capacity connected with the appearance of the characteristic »hump« typical of TU adsorption.[17] The differential capacity curves obtained for the lowest concentration of BuOH (0.11 mol $dm^{-3}$) are shown in Figure 1, whereas Figure 2 presents the case of the highest concentration of BuOH (0.55 mol $dm^{-3}$). With the increase of TU concentration, »the hump« shifts towards negative potentials and the potential of its maximum is close to the
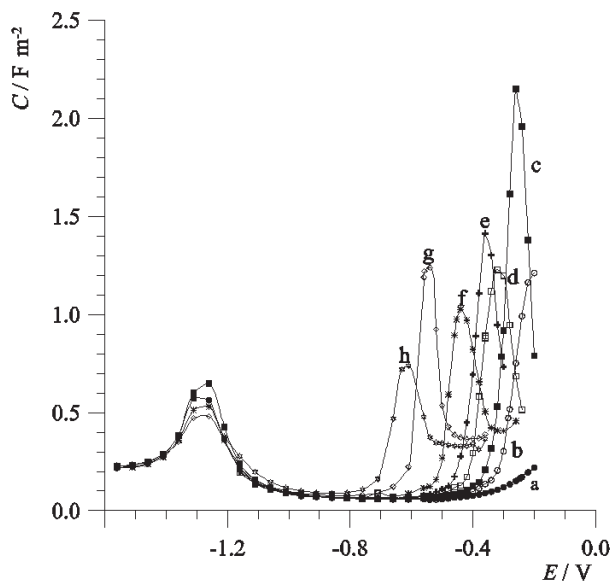
Figure 1. Differential capacity curves of Hg/1 mol dm$^{-3}$ NaClO$_4$ + 0.55 mol dm$^{-3}$ BuOH for different contents of TU: (a) $c_{TU}$ = 0 mol dm$^{-3}$, (b) 0.0055 mol dm$^{-3}$, (c) 0.011 mol dm$^{-3}$, (d) 0.033 mol dm$^{-3}$, (e) 0.055 mol dm$^{-3}$, (f) 0.11 mol dm$^{-3}$, (g) 0.33 mol dm$^{-3}$, (h) 0.55 mol dm$^{-3}$.

zero charge potential. However, with the increase of BuOH concentration at a given TU concentration, »the hump« shifts towards positive potentials and becomes higher and sharper, which may be associated with the decrease of repulsive interaction between the adsorbed TU molecules.[18] According to Parsons,[18] the appearance of a characteristic capacity hump in the case of adsorption of large surface active anions or a polar neutral substance may
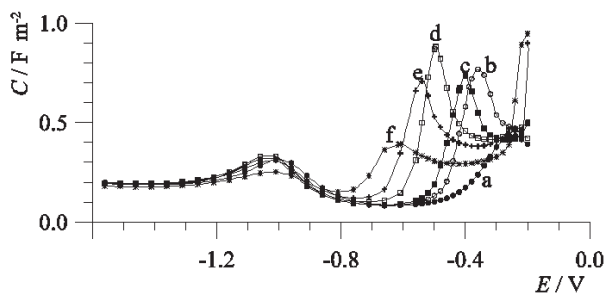


Figure 2. Differential capacity curves of Hg/1 mol dm$^{-3}$ NaClO$_4$ + 0.11 mol dm$^{-3}$ BuOH for different contents of TU as indicated in Figure 1.

be a consequence of the change of interactions (especially electrostatic inter-
actions) in the adsorbed layer. Both adsorbable species BuOH and TU may
interact with each other, leading to the formation of a more compact struc-
ture of the adsorbed layer. In turn, the increase of BuOH concentration
causes a shift of the BuOH desorption peak towards negative potentials but
the change of TU concentration does not influence the potential of this peak
at BuOH and only slightly its height. As it follows from the presented regu-
larities, the effect of TU is predominant in the mixed adsorption layer for-
mation at a less negative potential than –0.8 V but BuOH predominance oc-
curs at a more negative potential than –0.8 V. Similar observations are
found in literature.[19] The obtained values of zero charge potential $E_z$ in the
function of $c_{TU}$ and $c_{BuOH}$ confirm the above changes of the TU capacity
»hump« potential. Introducing the same amount of BuOH into the solution
containing relatively low TU concentrations causes a shift of the values of
$E_z$ towards positive potentials by approximately the same value. This may
indicate displacement of water molecules but not of BuOH molecules from
the electrode surface by TU. At higher TU concentrations, introduction of
BuOH causes ever smaller changes of $E_z$, which can also be a result of
BuOH molecules displacement by TU.

The capacity against potential data were numerically integrated from
the $E_z$ point. The obtained values of electrode charge density $q^m$ were used
to calculate the potentials of the outer Helmholtz plane (OHP) $\phi_2$ pertaining
to the potentials of the electroreduction of $Zn^{2+}$ ions. The values of $\phi_2$ were
derived in the usual manner assuming validity of the Gouy-Chapman-Stern
theory.[20]

$$\phi_2 = 0.0514 \sinh^{-1} \left[ \frac{q^m + q^i}{11.73 c^{1/2}} \right] \tag{1}$$

where $q^i$ is the charge due to specifically adsorbed $ClO_4^-$ ions (taken from
the study by Parsons)[21] and $c$ is the bulk concentration of $NaClO_4$.

Table I lists the $q^m$ and $\phi_2$ values for various TU and BuOH concentra-
tions.

To calculate the potential in the reaction plane $\phi^r$, it was assumed that
the reaction takes place at the OHP, where the potential can be calculated
by substracting the diffuse layer potential:

$$\phi^r = \phi^{OHP} = E - \phi_2 \tag{2}$$

Aramata and Delahay[22] proved that the hydrated $Zn^{2+}$ ion is larger than
the $Na^+$ ion, and therefore the plane of closest approach for $Zn^{2+}$ is more re-
mote from the electrode than the OHP, resulting in an overestimation of the

TABLE I

Charge densities $q^m$ and potentials of the outer Helmholtz plane $\phi_2$ as a function of TU and BuOH concentration at potentials within the faradaic region of the $Zn^{2+}$ ion reduction

| $c_{TU}$/mol dm$^{-3}$ | $E = -0.900$ V | | $E = -0.920$ V | | $E = -0.940$ V | | $E = -0.960$ V | | $E = -0.980$ V | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $-q^m/\mu C\,cm^{-2}$ | $-\phi_2/V$ | $-q^m/\mu C\,cm^{-2}$ | $-\phi_2/V$ | $-q^m/\mu C\,cm^{-2}$ | $-\phi_2/V$ | $-q^m/\mu C\,cm^{-2}$ | $-\phi_2/V$ | $-q^m/\mu C\,cm^{-2}$ | $-\phi_2/V$ |
| **0.11 mol dm$^{-3}$ BuOH + TU** | | | | | | | | | | |
| 0 | 7.5 | 0.041 | 7.9 | 0.042 | 8.5 | 0.043 | 9.0 | 0.043 | 9.6 | 0.044 |
| 0.0055 | 8.2 | 0.042 | 8.7 | 0.043 | 9.0 | 0.043 | 9.5 | 0.044 | 10.1 | 0.045 |
| 0.011 | 7.7 | 0.042 | 8.2 | 0.042 | 8.5 | 0.043 | 9.0 | 0.043 | 9.5 | 0.044 |
| 0.033 | 8.8 | 0.043 | 9.3 | 0.044 | 9.6 | 0.044 | 10.1 | 0.045 | 10.7 | 0.046 |
| 0.055 | 8.5 | 0.043 | 9.0 | 0.043 | 9.5 | 0.044 | 9.9 | 0.044 | 10.6 | 0.045 |
| 0.11 | 6.5 | 0.040 | 6.9 | 0.041 | 7.3 | 0.041 | 7.7 | 0.042 | 8.1 | 0.042 |
| **0.33 mol dm$^{-3}$ BuOH + TU** | | | | | | | | | | |
| 0 | – | – | – | – | 5.3 | 0.039 | 5.5 | 0.039 | 5.8 | 0.039 |
| 0.0055 | 5.7 | 0.039 | 5.9 | 0.040 | 6.0 | 0.040 | 6.2 | 0.040 | 6.4 | 0.040 |
| 0.011 | 5.6 | 0.039 | 5.8 | 0.039 | 6.0 | 0.040 | 6.2 | 0.040 | 6.4 | 0.040 |
| 0.033 | 6.5 | 0.040 | 6.7 | 0.040 | 6.9 | 0.041 | 7.1 | 0.041 | 7.3 | 0.041 |
| 0.055 | 8.0 | 0.042 | 8.2 | 0.042 | 8.4 | 0.042 | 8.7 | 0.043 | 8.9 | 0.043 |
| 0.11 | 7.1 | 0.041 | 7.3 | 0.041 | 7.4 | 0.041 | 7.6 | 0.041 | 7.9 | 0.042 |
| 0.33 | 5.9 | 0.040 | 6.2 | 0.040 | 6.4 | 0.040 | 6.7 | 0.040 | 7.0 | 0.041 |
| **0.55 mol dm$^{-3}$ BuOH + TU** | | | | | | | | | | |
| 0 | 4.8 | 0.038 | 5.0 | 0.039 | 5.1 | 0.039 | 5.3 | 0.039 | 5.4 | 0.039 |
| 0.0055 | 5.4 | 0.039 | 5.5 | 0.039 | 5.7 | 0.039 | 5.8 | 0.039 | 6.0 | 0.040 |
| 0.011 | 6.3 | 0.040 | 6.4 | 0.040 | 6.6 | 0.040 | 6.7 | 0.040 | 6.9 | 0.041 |
| 0.033 | 6.7 | 0.040 | 6.8 | 0.041 | 6.9 | 0.041 | 7.1 | 0.041 | 7.3 | 0.041 |
| 0.055 | 6.3 | 0.040 | 6.5 | 0.040 | 6.7 | 0.040 | 6.8 | 0.041 | 7.0 | 0.041 |
| 0.11 | 6.9 | 0.041 | 7.0 | 0.041 | 7.2 | 0.041 | 7.4 | 0.041 | 7.6 | 0.041 |
| 0.33 | 6.6 | 0.040 | 6.8 | 0.041 | 7.0 | 0.041 | 7.2 | 0.041 | 7.3 | 0.041 |
| 0.55 | 4.9 | 0.039 | 5.1 | 0.039 | 5.3 | 0.039 | 5.5 | 0.039 | 5.8 | 0.039 |

Frumkin effect. Andreu *et al.*[5] proved that the reaction plane is 0.28 nm further from the electrode, which corresponds to the diameter of one $H_2O$ molecule $d_{H_2O}$. The potential at the reaction location can be determined[6] from:

$$\phi^r = \phi^{OHP+0.28nm} = E + \frac{4RT}{F} \tanh^{-1}\left(\tanh\left[\frac{F\phi_2}{4RT}\right]\exp[-\kappa d_{H_2O}]\right) \qquad (3)$$

where $\kappa = 3.29 \times 10^7$ cm$^{-1}$ for 1 mol dm$^{-3}$ NaClO$_4$ at 298K.

The total surface excess $\Gamma$ for BuOH + TU at a constant BuOH concentration and constant charge $\sigma$ was determined using equation (4):

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial\xi}{\partial\ln c_{TU}}\right)_{c_{BuOH},\sigma} \qquad (4)$$

where $\xi$ is the Parsons function:[23] $\xi = \gamma + \sigma E$. The rectlinear dependence of the electrode potential on $\Gamma$ at constant charge confirms congruence of the obtained isotherms. In writing equation (4), it is assumed that the mean activity coefficients of TU, BuOH and NaClO$_4$ do not change with the change in TU concentration.

Figures 3 and 4 present the surface excess of TU and BuOH plotted for a constant BuOH concentration (0.11 mol dm$^{-3}$ and 0.55 mol dm$^{-3}$) *versus* the potential in the reaction plane $\phi^r$. In all applied systems, the presented
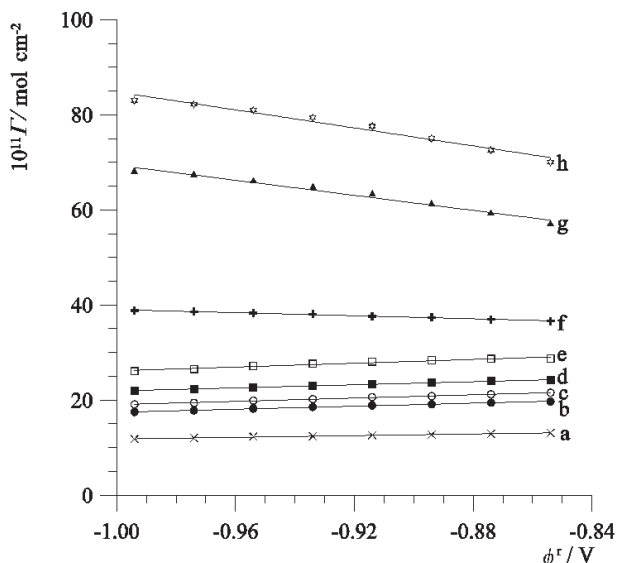


Figure 3. Surface excess $\Gamma$ of TU and BuOH *vs.* $\phi^r$ at varied concentrations of TU, as indicated in Figure 1 in the presence of 0.55 mol dm$^{-3}$ BuOH.
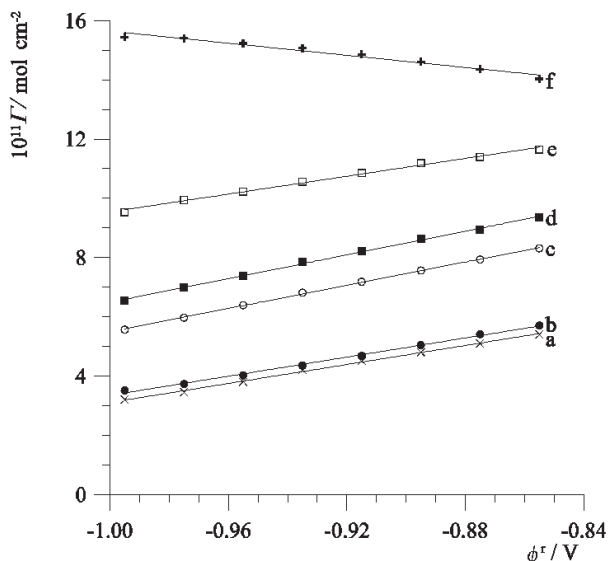
Figure 4. Surface excess $\Gamma$ of TU and BuOH *vs.* $\phi^r$ at varied concentration of TU as indicated in Figure 1 in the presence of 0.11 mol dm$^{-3}$ BuOH.

dependences are linear and depend insignificantly on the potential, except for the highest TU concentrations in the presence of 0.33 mol dm$^{-3}$ BuOH and 0.55 mol dm$^{-3}$ BuOH. It should be stressed that the obtained values $\Gamma$ depend to a smaller extent on the TU concentration in the bulk and very distinctly, almost in direct proportion, on the BuOH concentration in the solution. This confirms the above observation that BuOH molecules play a dominant role in the mixed adsorption layer formation in the range of $Zn^{2+}$ reduction potentials.

## *Polarographic Measurements*

Electroreduction of $Zn^{2+}$ ions at a mercury electrode in the 1 mol dm$^{-3}$ NaClO$_4$ solution as a supporting electrolyte with addition of TU and BuOH results in a single well-defined dc polarographic wave. Approximate diffusion coefficients of $Zn^{2+}$ ions in the examined solutions were calculated using the Ilkovic equation for the diffusion controlled limiting current.

The polarographic wave of $Zn^{2+}$ in 0.1 mol dm$^{-3}$ KNO$_3$ with the $Zn^{2+}$ diffusion coefficient $D_{ox} = 6.9 \times 10^{-6}$ cm$^2$ s$^{-1}$ at 298 K given in the literature[24] was used as a standard. The reproducibility of the results obtained was $\pm 5\%$. The observed changes of $D_{ox}$ with the increase of BuOH and TU concentrations are insignificant, like in the system containing only TU.[17]

The reversible potential of the half-wave ($E_{1/2}^r$) was determined by the cyclic voltammetry method using Eq. (5).[25]

$$E_{1/2}^r = (E_{pc} + E_{pa})/2 \qquad (5)$$

where $E_{pc}$ and $E_{pa}$ are the cathode or anode peak potentials, respectively. The increase of TU concentration causes, shift of $E_{1/2}^r$ value towards positive potentials in all solutions containing BuOH. The greatest shift of $E_{1/2}^r$ takes place in the presence of 0.55 mol dm$^{-3}$ BuOH and equals 23 mV.

The observed total effect of both compounds on the $E_{1/2}^r$ value suggests that the Zn$^{2+}$-TU complexes formed in the solution are very unstable.[12]

### The Rate of Electroreduction

The complex impedance data were collected at 36 frequencies in the range from 25 to 10000 Hz within the faradaic potential region at 10 mV intervals. The values of the apparent rate constant $k_f$ were obtained from the charge-transfer resistance.[5] Details are described elsewhere.[26–28]

The $k_f$ values obtained in the solutions of constant BuOH concentration and various TU concentrations in the function of the mean dc potential indicate an increase of the catalytic TU activity with the increase of its concentration and the decrease of BuOH concentration. The analysis of the dependence $k_f = f(E)$ allows us to distinguish two areas of potentials: at less negative potentials the increase of $k_f$ is much faster but at more negative potentials it proceeds more slowly.

The true rate constant $k_f^t$ can be obtained from Eq. (6).[6]

$$k_f(\phi^r) = k_f^t(\phi^r)\exp[-(E - \phi^r)nF/RT] \qquad (6)$$

The values of the true rate constants of electroreduction of Zn$^{2+}$ ions plotted as ln $k_f^t$, obtained at various TU concentrations as a function of potential $\phi^r$, are presented in Figures 5 and 6. It follows from the presented dependences that:

– the dependences ln $k_f^t = f(\phi^r)$ are not rectilinear and the slope of the curves changes with the potential and the concentrations of TU
– the accelerating effect due to the studied TU concentrations in the presence of constant BuOH amounts (0.11 mol dm$^{-3}$, 0.33 mol dm$^{-3}$, 0.55 mol dm$^{-3}$) is stronger at the most negative potentials
– the $k_f^t$ values increase with increasing the TU concentrations and achieve the highest values at the lowest BuOH concentration $c_{BuOH}$ = 0.11 mol dm$^{-3}$.

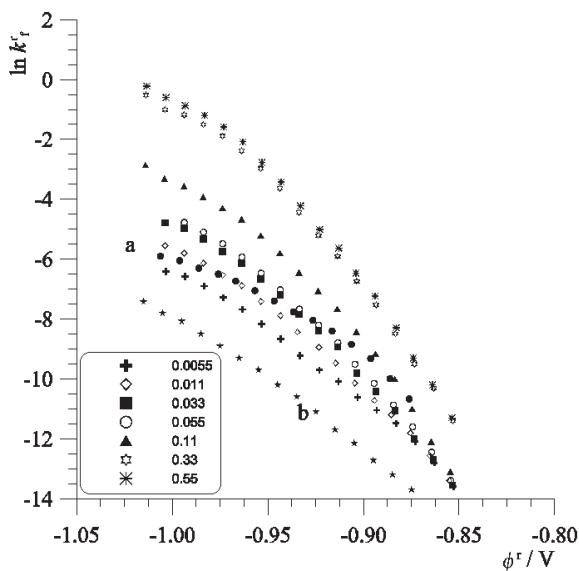Figure 5. Natural logarithms of corrected rate constants *vs.* $\phi^r$ for $Zn^{2+}/Zn(Hg)$ systems in 1 mol $dm^{-3}$ $NaClO_4$ (a), with addition of 0.55 mol $dm^{-3}$ BuOH (b) and 0.55 mol $dm^{-3}$ BuOH with various TU concentrations (in mol $dm^{-3}$).
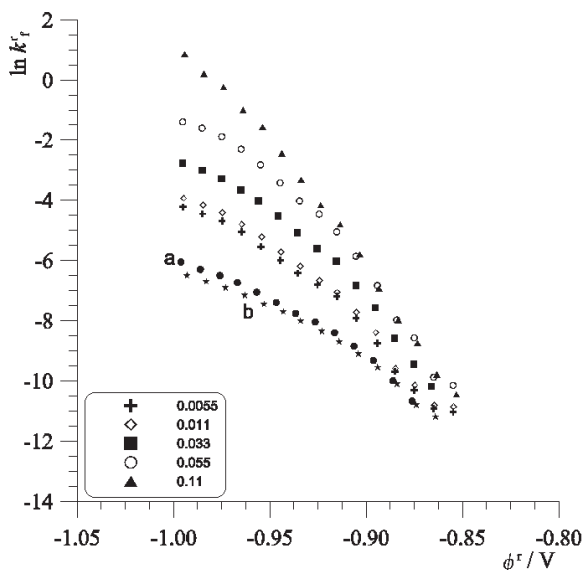


Figure 6. Natural logarithms of corrected rate constants *vs.* $\phi^r$ for $Zn^{2+}/Zn(Hg)$ systems in 1 mol $dm^{-3}$ $NaClO_4$ (a), with addition of 0.11 mol $dm^{-3}$ BuOH (b) and 0.11 mol $dm^{-3}$ BuOH with various TU concentrations (in mol $dm^{-3}$).

It follows from the foregoing that dependences $k_f = f(E)$ and $k^t_f = f(\phi^r)$ are similar. It is worth noting that in the solution containing 0.11 mol dm$^{-3}$ BuOH introduction of even the smallest amounts of TU causes an increase of the $k^t_f$ value of the Zn$^{2+}$ ion reduction compared with $k^t_f$ obtained in 1 mol dm$^{-3}$ NaClO$_4$, but in the solutions containing 0.33 mol dm$^{-3}$ and 0.55 mol dm$^{-3}$ BuOH this effect is observed only for $c_{TU} \geq 0.033$ mol dm$^{-3}$.

The course of the obtained dependences $\ln k^t_f = f(\phi^r)$ for electroreduction of Zn$^{2+}$ ions in the presence of various TU concentrations at definite BuOH concentration indicates a stage character of this process. The first stage is connected with the transfer of the first electron and the rate of this stage is characterized by constant $k^t_{s1}$, the second stage is described by constant $k^t_{s2}$ and is connected with the exchange of the second electron.[5,21,27] The values of $k^t_{s1}$ and $k^t_{s2}$ for the Zn$^{2+}$ reduction in 1 mol dm$^{-3}$ NaClO$_4$ are $k^t_{s1} = 1.3 \times 10^{-3}$ cm s$^{-1}$ and $k^t_{s2} = 4.8 \times 10^{-2}$ cm s$^{-1}$, respectively, which is in agreement with literature.[5]

Diagrams 7 and 8 presenting the dependence $k^t_{s1} = f(\Gamma)$ and $k^t_{s2} = f(\Gamma)$ for various BuOH concentrations lead to the following conclusions:

– In the solution containing TU and 0.11 mol dm$^{-3}$ BuOH, the rectilinear dependence $k^t_{s1} = f(\Gamma)$ and $k^t_{s2} = f(\Gamma)$ is observed, which indicates formation of an active complex mediating in the transfer of individual electrons.

– In the solution containing higher BuOH concentrations, two areas of linearity of the dependences $k^t_{s1} = f(\Gamma)$ and $k^t_{s2} = f(\Gamma)$ of different slopes can be distinguished, which may indicate formation of two complexes, but of different composition, depending on the surface TU concentration. In area I at lower surface TU concentrations, an active complex of Zn$^{2+}$ is probably formed on the electrode that contains more water in the hydration layer. In area II at higher surface TU concentrations a much faster increase of $k^t_{s1}$ and $k^t_{s2}$ values is observed which, according to the results presented in literature,[5] can result from partial dehydration of the active complex. This statement is justified by formation of condensed TU layers[29–31] in the presence of maximum TU concentrations used in the paper.

It follows from the comparison of the $k^t_{s1}$ and $k^t_{s2}$ values obtained for Zn$^{2+}$ reduction in 1 mol dm$^{-3}$ NaClO$_4$ with those obtained in solutions containing BuOH and TU that the stage of the first electron transfer is less sensitive to inhibition by BuOH than the stage of the second electron transfer, which is confirmed by the location of $k^t_{s1}$ and $k^t_{s2}$ (Figures 7 and 8) in relation to the broken line illustrating suitable $k^t_{s1}$ and $k^t_{s2}$ values for Zn$^{2+}$ reduction in 1 mol dm$^{-3}$ NaClO$_4$.

It is worth noting that in all studied systems $k^t_{s1}$ is always smaller than $k^t_{s2}$, like for Zn$^{2+}$ reduction in 1 mol dm$^{-3}$ NaClO$_4$. Therefore, the fundamental mechanism of successive electron transfer does not change. As it follows
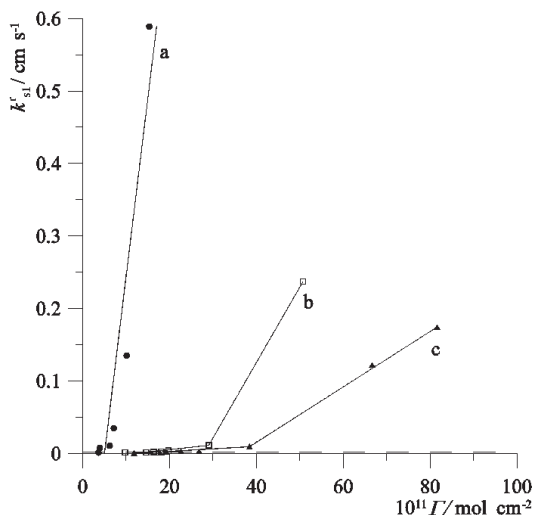
Figure 7. Values of $k^t_{s1}$ *vs.* $\Gamma$ of TU and BuOH for solutions containing 0.11 mol dm$^{-3}$ BuOH (a), 0.33 mol dm$^{-3}$ BuOH (b), 0.55 mol dm$^{-3}$ BuOH (c). The dashed line denotes $k^t_{s1} = 1.3 \times 10^{-3}$ cm s$^{-1}$ for Zn$^{2+}$ in 1 mol dm$^{-3}$ NaClO$_4$.



Figure 8. Values of $k^t_{s2}$ *vs.* $\Gamma$ of TU and BuOH for solutions containing 0.11 mol dm$^{-3}$ BuOH (a), 0.33 mol dm$^{-3}$ BuOH (b), 0.55 mol dm$^{-3}$ BuOH (c). The dashed line denotes $k^t_{s2} = 4.8 \times 10^{-2}$ cm s$^{-1}$ for Zn$^{2+}$ in 1 mol dm$^{-3}$ NaClO$_4$.
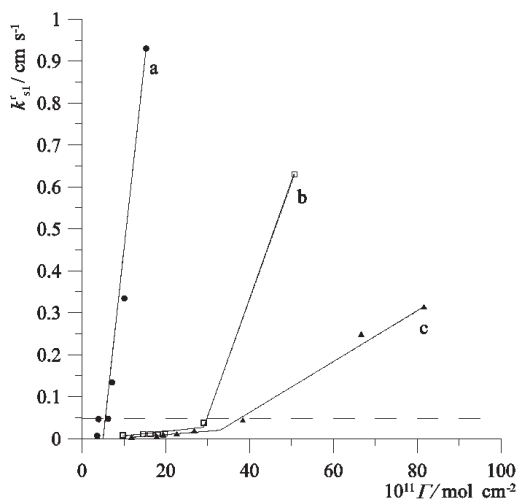
from the analysis of the increase of $k^t_{s1}$ and $k^t_{s2}$ values in the individual systems under investigations, the largest increase of $k^t_{s1}$ and $k^t_{s2}$ takes place in the presence of 0.55 mol dm$^{-3}$ BuOH. This is the evidence for the great

TABLE IIA

The apparent rate constant of $Zn^{2+}$ electroreduction at variable potentials and TU concentrations in the presence 0.11 mol $dm^{-3}$ BuOH

| $c_{TU}$ / mol $dm^{-3}$ | 0 | 0.0055 | 0.011 | 0.033 | 0.055 | 0.11 |
|---|---|---|---|---|---|---|
| $-E$/V | $10^3 \times k_f$ / cm $s^{-1}$ | | | | | |
| 0.84 | 0.01 | 0.004 | 0.008 | 0.002 | 0.01 | 0.017 |
| 0.85 | 0.02 | 0.02 | 0.2 | 0.04 | 0.06 | 0.07 |
| 0.86 | 0.05 | 0.05 | 0.07 | 0.14 | 0.31 | 0.37 |
| 0.87 | 0.11 | 0.16 | 0.25 | 0.53 | 1.07 | 1.44 |
| 0.88 | 0.20 | 0.36 | 0.66 | 1.57 | 3.26 | 4.09 |
| 0.89 | 0.34 | 0.68 | 1.29 | 3.28 | 8.41 | 10.05 |
| 0.90 | 0.52 | 1.09 | 2.18 | 6.46 | 16.82 | 22.37 |
| 0.91 | 0.75 | 1.60 | 3.35 | 11.15 | 31.05 | 49.79 |
| 0.92 | 1.04 | 2.21 | 5.09 | 18.60 | 55.20 | 103.0 |
| 0.93 | 1.35 | 3.05 | 7.10 | 29.0 | 94.70 | 217.0 |
| 0.94 | 1.68 | 3.79 | 8.67 | 38.60 | 142.0 | 361.0 |
| 0.95 | 1.93 | 4.36 | 9.56 | 43.70 | 169.0 | 474.0 |
| 0.96 | 2.31 | 4.77 | 10.6 | 48.80 | 188.0 | 593.0 |
| 0.97 | 2.67 | 5.6 | 12.0 | 56.10 | 206.0 | 754.0 |
| 0.98 | 3.58 | 7.13 | 14.2 | 65.90 | 237.0 | 771.0 |

TABLE IIB

The apparent rate constant of $Zn^{2+}$ electroreduction at variable potentials and TU concentrations in the presence 0.55 mol $dm^{-3}$ BuOH

| $c_{TU}$ / mol $dm^{-3}$ | 0 | 0.0055 | 0.011 | 0.033 | 0.055 | 0.11 | 0.33 | 0.55 |
|---|---|---|---|---|---|---|---|---|
| $-E$/V | $10^3 \times k_f$ / cm $s^{-1}$ | | | | | | | |
| 0.84 | 0.0017 | 0.017 | 0.0088 | 0.0086 | 0.0097 | 0.015 | 0.0083 | 0.011 |
| 0.85 | 0.0025 | 0.14 | 0.013 | 0.013 | 0.017 | 0.030 | 0.055 | 0.068 |
| 0.86 | 0.0042 | 0.35 | 0.021 | 0.024 | 0.030 | 0.081 | 0.26 | 0.34 |
| 0.87 | 0.0055 | 0.69 | 0.037 | 0.047 | 0.056 | 0.14 | 0.71 | 0.86 |
| 0.88 | 0.0074 | 1.14 | 0.063 | 0.085 | 0.11 | 0.30 | 1.54 | 1.98 |
| 0.89 | 0.0097 | 1.74 | 0.11 | 0.15 | 0.19 | 0.61 | 3.29 | 4.15 |
| 0.90 | 0.013 | 2.45 | 0.19 | 0.33 | 0.33 | 1.17 | 6.73 | 8.46 |
| 0.91 | 0.016 | 3.18 | 0.32 | 0.57 | 0.54 | 2.16 | 13.72 | 14.69 |
| 0.92 | 0.022 | 3.88 | 0.52 | 0.94 | 0.91 | 3.77 | 28.20 | 28.70 |
| 0.93 | 0.031 | 5.29 | 0.82 | 1.68 | 1.43 | 6.74 | 59.20 | 62.90 |
| 0.94 | 0.047 | 6.54 | 1.15 | 2.49 | 2.10 | 10.60 | 116.0 | 108.0 |
| 0.95 | 0.08 | 7.99 | 1.61 | 3.46 | 2.87 | 15.0 | 177.0 | 200.0 |
| 0.96 | 0.11 | 9.38 | 2.01 | 4.52 | 3.70 | 19.40 | 230.0 | 267.0 |
| 0.97 | 0.19 | 11.3 | 2.74 | 6.22 | 4.91 | 25.90 | 307.0 | 350.0 |
| 0.98 | 0.30 | 14.1 | 3.81 | 8.89 | 6.75 | 36.90 | 423.0 | 477.0 |

dynamics of acceleration of successive stages of $Zn^{2+}$ electroreduction in the presence of large amounts of the inhibitor (BuOH). It is undoubtedly connected with the poor hydration of the electrode surface due to TU and BuOH adsorption and smaller hydration of the active Zn-TU complex.

## LIST OF SYMBOLS

$C$ / F m$^{-2}$ — differential capacity
$E_z$ / V — zero charge potential
$q^m$ / $\mu$C cm$^{-2}$ — electrode charge density
$\phi^r$ / V — potential in the reaction plane
$D_{ox}$ / cm$^2$ s$^{-1}$ — diffusion coefficient
$E_{1/2}^r$ / V — reversible potential of the half wave
$k_f$ / cm s$^{-1}$ — apparent rate constant
$k_f^t$ / cm s$^{-1}$ — true rate constant
$k_{s1}^t$ / cm s$^{-1}$ — rate constants of the transition of the first electron
$k_{s2}^t$ / cm s$^{-1}$ — rate constants of the transition of the second electron
$\Gamma$ / mol cm$^{-2}$ — surface excess

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## SAŽETAK

### Utjecaj miješanog adsorpcijskog sloja 1-butanol/tiourea na dvostupnu elektroredukciju iona $Zn^{2+}$

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Opisan je utjecaj 1-butanola (BuOH), stalne koncentracije, i tiouree (TU), varirajuće koncentracije, na dva uzastopna jednoelektronska prijelaza pri elektrodepoziciji iona $Zn^{2+}$ na Hg-elektrodi. Ustanovljeno je da BuOH ima dominantnu ulogu pri nastajanju miješanog adsorpcijskog sloja u području redukcijskih potencijala iona $Zn^{2+}$. Nađeno je da je ukupni površinski višak BuOH i TU linearna funkcija potencijala $\phi^r$, izuzevši područje visokih koncentracija TU, gdje je ovisnost o potencijalu neznatna. Ovisnost $k^t_f = f(\phi^r)$, u prisutnosti 0,11 mol dm$^{-3}$ BuOH, pokazuje da TU ubrzava redukciju iona $Zn^{2+}$ i pri najnižim koncentracijama TU, u odnosu na 1 mol dm$^{-3}$ $NaClO_4$. Međutim, pri višim koncentracijama BuOH od 0,33 mol dm$^{-3}$ i 0,55 mol dm$^{-3}$ taj se efekt pojavljuje tek pri $c_{TU} \geq 0,33$ mol dm$^{-3}$. Ovisnost $k^t_{s1} = f(\Gamma)$ i $k^t_{s2} = f(\Gamma)$ upućuje na nastajanje jedne vrste kompleksa koji nastaje na površini elektrode u 0,11 mol dm$^{-3}$ BuOH. U otopinama s višim koncentracijama BuOH nastaju dvije vrste aktivnog kompleksa, koje se razlikuju u stupnju hidratacije. Rezultati pokazuju da je prijelaz prvog elektrona manje podložan inhibiciji s BuOH, nego prijelaz drugog elektrona.