

The Influence of Thiourea on the Two-Step Electroreduction of Zn(II) Ions

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Summary. The two-step reduction of Zn(II) ions at a dropping mercury electrode in 1 M NaClO₄/0.001 M HClO₄ in the presence of thiourea was examined in wide potential and frequency ranges using the impedance method. The catalytic activity of thiourea concerns both electron transfer steps. It was found that the acceleration of the electroreduction process depends on the surface concentration of thiourea.

Keywords. Catalytic activity; Electroreduction; Zn(II); Thiourea.

Der Einfluß von Thioharnstoff auf die zweistufige Elektroreduktion von Zn(II)-Ionen

Zusammenfassung. Die zweistufige Reduktion von Zn(II)-Ionen an einer Quecksilbertropfelektrode in 1 M NaClO₄/0.001 M HClO₄ in Gegenwart von Thioharnstoff wurde in einem breiten Potential- und Frequenzbereich mittels der Impedanzmethode untersucht. Die katalytische Aktivität von Thioharnstoff betrifft beide Elektronenübertragungsschritte. Es wurde beobachtet, daß die Beschleunigung der Elektroreduktion von der Oberflächenkonzentration des Thioharnstoffs abhängt.

Introduction

The mechanism of electrode process acceleration at a mercury electrode has not been sufficiently explained yet. It is known that two simultaneous phenomena play an important role: the adsorption of an organic substance on the electrode surface and the formation of an active complex between the depolarizer ions and the organic substance adsorbed on the mercury electrode [1]. A typical example of this behaviour is the electroreduction of Zn(II) ions at a mercury electrode in the presence of thiourea (*TU*).

From the literature it is known that *TU* also catalyzes the reduction of In³⁺ [2], H₃O⁺ [3], Bi³⁺ [4], and Cd²⁺ [5]. The catalytic activity of *TU* [4, 6, 7] is probably caused by the presence of sulfur and nitrogen atoms with electron pairs capable of forming coordinate bonds.

The electroreduction of Zn(II) ions from NaClO₄ solutions at a mercury electrode is supposed to involve two consecutive one-electron transfer steps in the overall reaction [8]. Since the kinetics of the electron transfer steps are potential

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dependent, the nature of the rate controlling step can change with potential. Furthermore, the reaction involves charged reactants in the double layer; therefore, double layer effects are expected to be important in these processes.

This paper presents the study of the effect of TU on kinetic parameters of the individual steps with the aim of gaining better insight in the reaction mechanism and the nature of the catalytic effect.

Results and Discussion

Double layer analysis

The calculations of the double layer parameters for the adsorption are based on data from differential capacity-potential curves obtained experimentally for several concentrations of TU (Fig. 1).

In the potential range of $Zn(II)$ reduction (*c.a.* -0.951 V) a capacitive, hump occurs which is characteristic for strongly adsorbing anions or polar substances. The height of this hump increases with increasing TU concentration up to 0.055 M and then decreases with further increasing TU concentration and simultaneously shifts towards more negative potentials. The occurrence of this hump results mainly from changes in the electrostatic interactions between adsorbed molecules [9].

As can be seen from the differential capacity curves in Fig. 1 there is an increase in differential capacity in relation to the basic electrolyte (curve a) in the range of the $Zn(II)$ ion reduction potentials, thus satisfying one of the electrode process acceleration conditions according to the cap-pair rule [1].

The surface excess Γ at constant charge σ was determined using Eq. (1) where c is the concentration of TU , ξ the *Parsons* function [10] ($\xi = \gamma + \sigma E$), γ surface

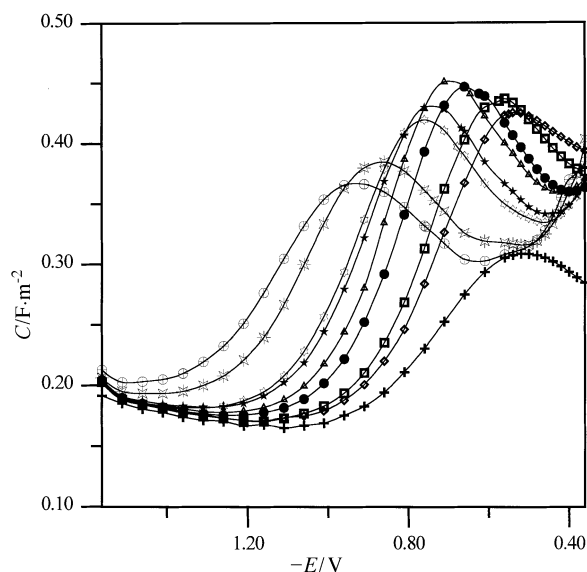


Fig. 1. Differential capacitance of a mercury electrode in contact with 1 M $NaClO_4$ containing different concentrations of TU ; $+$: 0 M, \diamond : 0.0055 M, \square : 0.011 M, \bullet : 0.033 M, Δ : 0.055 M, \star : 0.088 M, $\hat{\star}$: 0.11 M, \ast : 0.33 M, \oplus : 0.55 M

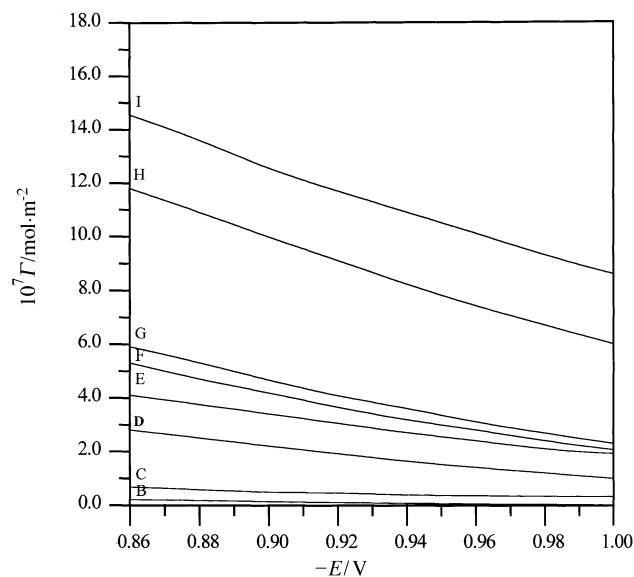


Fig. 2. Surface excess Γ of TU vs. E at various concentrations of TU as indicated in Fig. 1

tension, the σ electrode charge, and E the electrode potential. In Eq. (1) it is assumed that the mean activity coefficients of TU and NaClO_4 do not change with changing TU concentration.

$$\Gamma = - \left(\frac{1}{RT} \right) \left(\frac{d\xi}{d \ln c} \right)_{\sigma} \quad (1)$$

Figure 2 presents the surface excess of TU plotted vs. electrode potential. In the range of Zn(II) ion reduction potentials, the values of TU surface excesses decrease with increasing negative electrode. At higher concentrations of TU an evident dependence of the surface excess on the electrode potential is observed. These effects are typical for the adsorption of many organic substances in this potential range.

Polarographic measurements

The approximate diffusion coefficients of Zn(II) in the examined solution were calculated using the *Ilkovic* equation for a diffusion-controlled limiting current. The polarographic wave of Zn(II) in $0.1 M \text{KNO}_3$ with a value of $D_{\text{ox}} = 6.9 \cdot 10^{-6} \text{cm}^2 \cdot \text{s}^{-1}$ for the Zn(II) diffusion coefficient [11] was used as a standard. The diffusion coefficient of Zn(II) ions in $1 M \text{NaClO}_4$ was found to be $6.6 \cdot 10^{-6} \text{cm}^2 \cdot \text{s}^{-1}$ at 298 K. The value of the diffusion coefficient of zinc in mercury, which was required for further calculations, was taken from the literature as $1.67 \cdot 10^{-5} \text{cm}^2 \cdot \text{s}^{-1}$ [12]. The reproducibility of the results obtained was $\pm 5\%$.

The reversible potential of the half-wave ($E_{1/2}^r$) was determined by means of the cyclic voltammetry method using Eq. (2) [E_{pc} ; cathode peak potential, E_{pa} ; anode peak potential).

$$E_{1/2}^r = \frac{E_{\text{pc}} + E_{\text{pa}}}{2} \quad (2)$$

The presence of TU in the supporting electrolyte influences the values D_{ox} and $E_{1/2}^{\text{r}}$ insignificantly. D_{ox} decreases from $6.6 \cdot 10^{-6} \text{cm}^2 \cdot \text{s}^{-1}$ to $6.3 \cdot 10^{-6} \text{cm}^2 \cdot \text{s}^{-1}$ with increasing TU concentration, $E_{1/2}^{\text{r}}$ from -0.956 to -0.951 V. The insignificant changes of $E_{1/2}^{\text{r}}$ indicates the absence of stable complexes of Zn(II) with TU .

Impedance measurements

The complex impedance data were collected at 36 frequencies in the range from 25 to 100000 Hz within the faradaic potential region in 10 mV intervals. The frequency analysis was performed in the usual way [14, 15]. The values of the apparent rate constant k_f were obtained from the charge-transfer resistance [8]. The details have been described elsewhere [16, 17]. Figure 3 presents the dependence of k_f on $f(\Gamma)$. In the obtained range of surface excesses, two areas of reverse changes of k_f can be distinguished. The first area from $1 \cdot 10^{-7} \text{mol} \cdot \text{m}^{-2}$ to $3 \cdot 10^{-7} \text{mol} \cdot \text{m}^{-2}$ correspond TU concentrations in the bulk from 0.0055 to 0.055 M and is characterized by a linear increase of k_f , indicate the formation of an active complex between Zn(II) ions and adsorbed TU molecules on the electrode surface. At concentrations above 0.055 M an insignificant decrease of k_f is observed. However, in solutions containing TU the values of k_f are always higher compared with those obtained in 1 M NaClO_4 . The characteristic maximum in Fig. 3 corresponds to concentrations of TU in the bulk at which a decrease of the capacitive hump due to the change of intermolecular interactions of the adsorbed TU is observed in the differential capacity curves. The character of the dependence of k_f on $f(\Gamma)$ is undoubtedly connected with the change of the structure of the adsorption layer on the electrode surface.

It seems that the catalytic influence of TU can be better described using $\ln k_f$ (at a given Γ) vs. E plots (Fig. 4). This plot was constructed from using the curves in

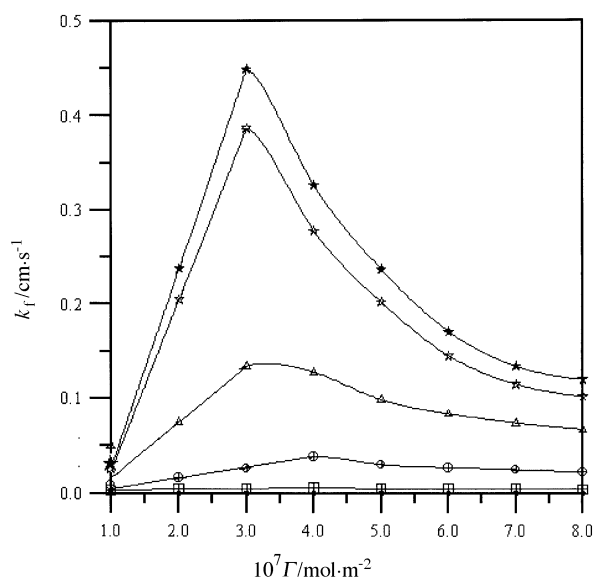


Fig. 3. Rate constant of the Zn(II) reduction in 1 M $\text{NaClO}_4/0.001$ M HClO_4 vs. surface excess of TU at constant E ; \square : $E = 0.90$ V, \oplus : $E = 0.92$ V, Δ : $E = 0.94$ V, \star : $E = 0.96$ V, \blackstar : $E = 0.98$ V

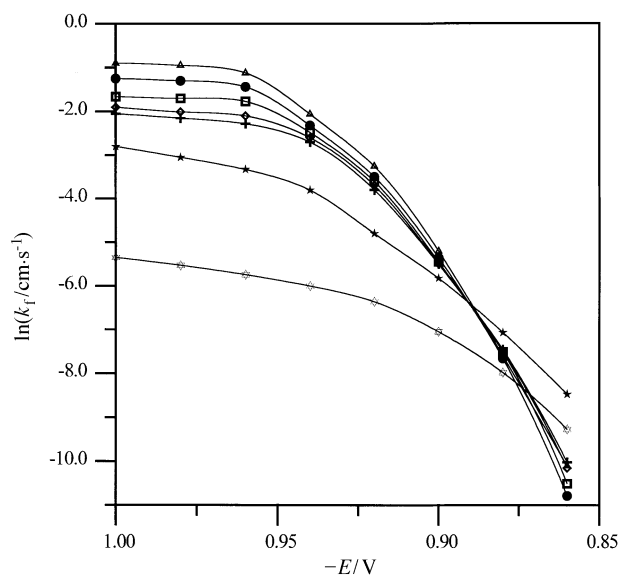


Fig. 4. Potential dependence of the natural logarithm of the rate constant of the Zn(II) reduction in 1 M NaClO₄/0.001 M HClO₄ at different surface excesses of TU; \circ : $\Gamma = 0 \text{ mol} \cdot \text{m}^{-2}$, \star : $\Gamma = 1 \cdot 10^{-7} \text{ mol} \cdot \text{m}^{-2}$, $+$: $\Gamma = 2 \cdot 10^{-7} \text{ mol} \cdot \text{m}^{-2}$, \diamond : $\Gamma = 3 \cdot 10^{-7} \text{ mol} \cdot \text{m}^{-2}$, \square : $\Gamma = 4 \cdot 10^{-7} \text{ mol} \cdot \text{m}^{-2}$, \bullet : $\Gamma = 5 \cdot 10^{-7} \text{ mol} \cdot \text{m}^{-2}$, Δ : $\Gamma = 6 \cdot 10^{-7} \text{ mol} \cdot \text{m}^{-2}$

Fig. 2 and the potential dependence of $\ln k_f$ at various concentrations of TU. The accelerating effect due to TU is larger at more negative potentials and seems to be absent or even turned into an inhibition at potentials above -0.890 V . The obtained dependence of $\ln k_f$ vs. $f(E)$ indicates the step character of Zn(II) electroreduction in the presence of TU. According to Hurd [18], for the two-electron reduction the process proceeds *via* two energetic barriers which correspond to the transfer of single electrons.

Analysis in terms of EE mechanism

Assuming that the charge transfer proceeds *via* two consecutive one-electron transfer steps as has been clearly demonstrated in the case of the pure perchlorate supporting electrolyte [8], at the most negative potentials the first electron transfer is rate determining: $k_f = k_{\text{lim}} = k_1$. At more positive potentials, the overall rate is determined by both steps simultaneously (K_1 ; equilibrium constant of the first electron transfer process).

$$\frac{1}{k_f} = \frac{1}{k_1} + \frac{K_1}{k_2} \quad (3)$$

The values of the individual standard rate constants of the electroreduction of Zn(II) in 1 M NaClO₄ are $k_{s1} = 3.5 \cdot 10^{-3} \text{ cm} \cdot \text{s}^{-1}$ and $k_{s2} = 7.1 \cdot 10^{-2} \text{ cm} \cdot \text{s}^{-1}$. These values are in agreement with literature data [8]. The values k_s , k_{s1} , and k_{s2} refer to the formal potentials E_f^0 determined from $E_{1/2}^r$.

Figure 5 presents the dependencies of k_{s1} on $f(\Gamma)$ and k_{s2} on $f(\Gamma)$. The change of the values k_{s1} and k_{s2} is similar to the change of the value k_f in Fig. 3. The presence

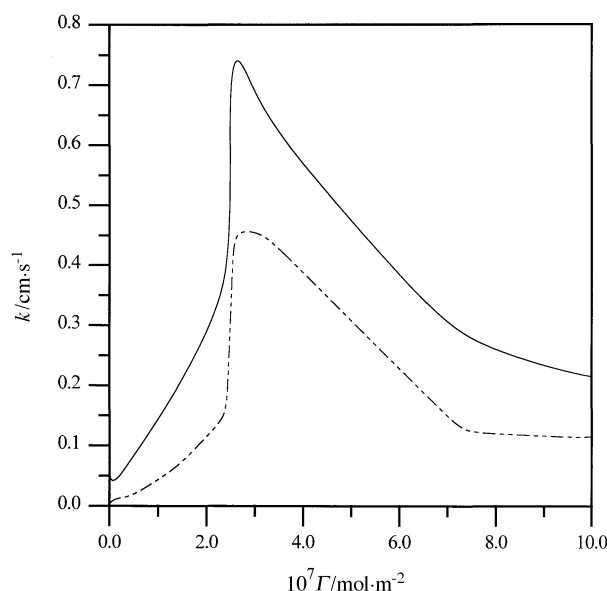


Fig. 5. Individual standard rate constants for the Zn(II) reduction in 1 M NaClO₄/0.001 M HClO₄ plotted against the surface excess of TU; k_{s1} : dotted line, k_{s2} : -solid line

of TU on the electrode surface causes a rise of the rate of the first electron transfer with increasing TU concentration. The rate constants of the second electron transfer decrease at the lowest studied concentrations of TU and then increase with rising concentration. For all concentrations of TU, the first electron transfer is accelerated to a higher extent than the second one. It seems noteworthy that k_{s1} and k_{s2} attain stable values at suitably high surface excesses.

As follows from a comparison of k_{s1} and k_{s2} obtained for Zn(II) reduction in 1 M NaClO₄, TU accelerates both the first and the second electron transfer; at optimal values of surface excesses there, a tenfold increase of the value k_{s2} and a hundredfold increase of the value k_{s1} is obtained. The course of the dependencies of k_{s1} and k_{s2} on $f(\Gamma)$ indicates that the mechanisms of the first and second electron transfer are similar.

Comparison of Figs. 1 and 2 indicates that the increase of TU concentration from 0 to 0.055 M caused an increase of the capacity hump as well as an increase of k_{s1} and k_{s2} . For higher concentrations of TU a decrease of these quantities is observed. The results indicate a direct dependence of the electroreduction rate of Zn(II) ions on the adsorption layer properties at the electrode.

Experimental

All experiments were performed at 298 ± 1 K. Polarographic measurements were carried out using a polarograph PA-4 (Laboratorni Pstroje, Prague, Czechoslovakia) or a Polarographic Analyzer model 384B EG and GPARC. The impedance measurements were effected a 9121 FR Analyzer and a 9131 Electrochemical Interface of Atlas-Sollich (Gdańsk).

The measurements were performed using a three electrode cell containing a HMDE made by MTM Poland, Ag/AgCl, and a platinum spiral as an auxiliary electrode. The reference electrode was equipped with a Luggin capillary probe. The capillary was filled with the cell solution.

Solutions were prepared from freshly double-distilled water and analytical grade chemicals (Merck). Zinc perchlorate was prepared by dissolving ZnO in a small excess of perchloric acid. In order to avoid hydrolysis of Zn(II), the excess of perchloric acid was chosen to make the final solution 0.001 M in H⁺. Optimal accuracy was obtained by a Zn(II) concentration of about 0.003 M. Adsorption and catalytic activity of TU were examined in the concentration range from 0.0055 to 0.55 M.

Solutions were deaerated using nitrogen which was passed through a vanadous sulfate solution and presaturated with the investigated solution. This gas was also passed over the solution during the measurements.

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