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The Accelerating Influence of Thiourea on the Electroreduction of Zn(II) at a Mercury Electrode in Water/Methanol Mixtures

B. Marczewska

Faculty of Chemistry, Maria Curie-Skłodowska University, PL-20031 Lublin, Poland

Summary. The influence of thiourea on the Zn(II)/Zn(Hg) electrode process was studied in water/methanol mixtures under addition of $NaClO_4$. Diffusion coefficients, formal potentials, and charge transfer rate constants have been determined. It is postulated that the composition of the active complex formed on the electrode plays the dominant role in the acceleration of the electrode processes.

Keywords. Electroreduction of Zn(II); Mixed solvent; Thiourea; Acceleration; Adsorption; Active Zn-complex.

Der beschleunigende Einfluß von Thioharnstoff auf die Elektroreduktion von Zn(II) an einer Quecksilberelektrode in Wasser-Methanol-Gemischen

Zusammenfassung. Der Einfluß von Thioharnstoff auf den Elektrodenprozeß Zn(II)/Zn(Hg) wurde in Wasser-Methanol-Mischungen unter Zusatz von $NaClO_4$ untersucht. Diffusionskoeffizienten, Potentiale und Geschwindigkeitskonstanten der Ladungsübertragung wurden bestimmt. Es wird angenommen, daß bei der Beschleunigung der Elektrodenprozesse die Zusammensetzung des an der Elektrode gebildeten aktiven Komplexes eine entscheidende Rolle spielt.

Introduction

An acceleration of electroreduction at a mercury electrode by organic substances takes place when the accelerating substance is adsorbed on the electrode and forms a weak complex with the depolarizer [1]. Investigations in mixed aqueous-organic solutions in which zinc is solvated by the organic solvent have led to the conclusion that the structure of the active complex reduced on the mercury electrode plays the dominant role in the process of aceleration of zinc electroreduction [2, 3]. Acceptance of the hypothesis of *Taraszewska et al.* [4] that Zn(II) ions are preferentially hydrated in $H_2O/MeOH$ mixtures up to MeOH ratios of 95% v/v leads to the conclusion that the accelerating effect of thiourea on zinc electroreduction in water and in methanol solutions with the same degree of electrode coverage by thiourea should be the same. However, studies on such a system have not yet been reported.

Results and Discussion

Adsorption of thiourea

The adsorption of thiourea (*TU*; concentrations from 0.03 to 0.3 $\text{mol}\cdot\text{dm}^{-3}$) at the mercury electrode at MeOH concentrations of 36, 65, and 91% v/v in presence of 1 $\text{mol}\cdot\text{dm}^{-3}$ $NaClO_4$ was investigated on the basis of differential capacity measurements. At potentials more cathodic than −0.4 V, the capacity was found to be frequency independent. In all cases examined, a *TU* addition to the investigated solutions caused an increase in the differential capacity of the double layer at the zinc reduction potential.

The differential capacity curves were integrated twice. The values of γ^0 and E^0 for the investigated solution were taken as the constants for the integration of C–E curves. The data obtained for the interfacial tension γ were recalculated as ξ values according to *Parsons*' relation [9]

$$\xi = \gamma + \sigma_M \cdot E \tag{1}$$

and, further, as the surface pressure

$$\Phi = \Delta\xi = \xi^0 - \xi \tag{2}$$

at the selected constant charge densities (σ: surface charge density; ξ^0: value of ξ without addition of *TU*).

The adsorption of *TU* was estimated according to the *Gibbs* adsorption equation by differentiation of Φ *vs.* $\ln c$ curves. The estimated error in the graphical differentiation technique was the same as in Ref. [10].

The relative surface excess of the investigated substances was calculated from Eq. (3) [11].

$$\Gamma' = -\frac{1}{\mathrm{RT}}\left(\frac{\partial\Phi}{\partial(\ln c)}\right)_{c\mathrm{NaClO_4},c\mathrm{MeOH},c\mathrm{aq},\sigma\mathrm{M}} \tag{3}$$

Figure 1 shows the values of relative surface excess Γ' obtained for *TU* concentrations of 0.05 and 0.25 $\text{mol}\cdot\text{dm}^{-3}$ in 36, 65, and 91% v/v MeOH as a function of potential E. The values of the relative surface excess for 0.05 $\text{mol}\cdot\text{dm}^{-3}$ *TU* do not differ much for the different MeOH concentrations. The values obtained for the same amounts of methanl in the presence of 0.25 $\text{mol}\cdot\text{dm}^{-3}$ *TU* are higher; yet the differences between them are still relatively small.

The calculated values of θ (surface coverage degree) of the electrode by *TU* at the zinc reduction potential for *TU* concentrations of 0.05 $\text{mol}\cdot\text{dm}^{-3}$ in 36, 65, and 91% v/v MeOH are 0.04, 0.03, and 0.03, respectively, whereas for *TU* concentrations of 0.25 $\text{mol}\cdot\text{dm}^{-3}$ they amount to 0.09, 0.06, and 0.07. The saturation value of Γ_s from Ref. [10] was employed in the calculations. These values are 4.4×10^{-6} $\text{mol}\cdot\text{m}^{-2}$, 4.4×10^{-6} $\text{mol}\cdot\text{m}^{-2}$, and 4.7×10^{-6} $\text{mol}\cdot\text{m}^{-2}$ for the different MeOH concentrations, respectively.

Diffusion coefficient

The approximate diffusion coefficients of Zn(II) in the examined solutions were calculated from limiting currents using the *Ilkovič* equation. The polarographic

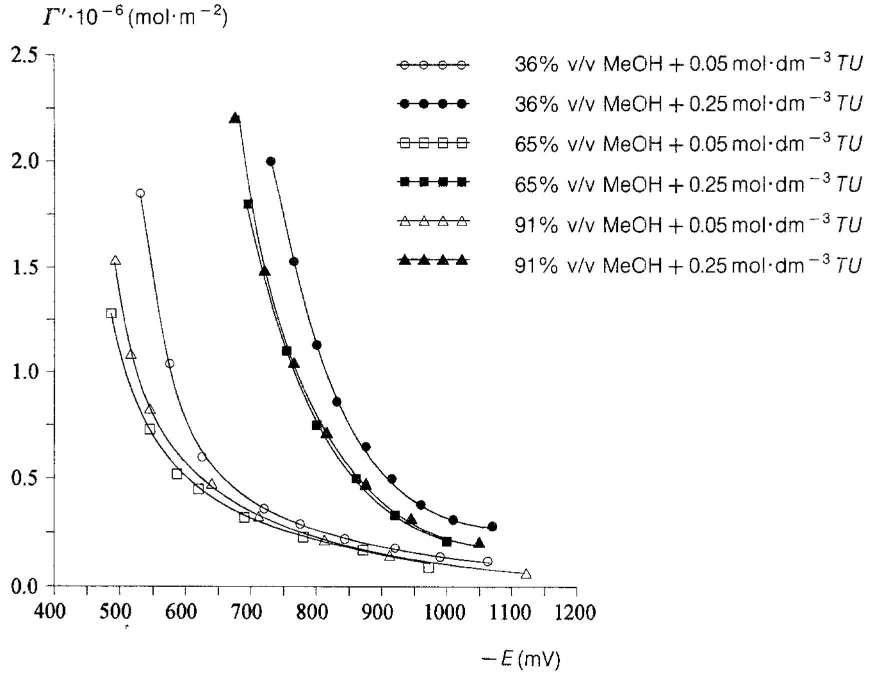

Fig. 1. Dependence of the relative surface excess of *TU* on the potential in the presence of 0.05 and $0.25\,\mathrm{mol\cdot dm^{-3}}$ of *TU* in 36, 65, and 91% v/v MeOH (*vs.* SSCE)

wave of Zn(II) in $0.1\,M\,\mathrm{KNO_3}$ with a Zn(II) diffusion coefficient value of $D = 6.9 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ [12] was used as a standard. The reproducibility of the results obtained was ±10%. The values of the diffusion coefficients of zinc in mercury which were required for further calculations were taken from the literature ($1.67 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$, [13]).

The influence of the MeOH content in the mixture on the diffusion coefficients of Zn(II) in the absence and presence of *TU* is shown in Table 1. The presence of *TU* did not cause a change in the values of the diffusion coefficients of Zn(II).

*Formal potential of the Zn(II)/Zn(Hg) system**

The formal potentials E_f of the reduction of Zn(II) were calculated on the basis of $E^\mathrm{r}_{1/2}$ values determined by cyclic voltammetry. The procedure is described in Ref. [14]. The formal potentials for irreversible processes were calculated using the modification of *Randles*' method for cyclic voltammetry [14, 15]. They were determined with an accuracy of ±3 mV. These potentials as a function of MeOH and *TU* concentration are given in Table 1.

Kinetic parameters of the Zn(II)/Zn(Hg) system

The standard rate constants k_s for the investigated systems were calculated from impedance measurements. The equivalent circuit, proposed by *Randles* [16], illus-

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* "Formal potential" at amalgam electrode in analogy to a Zn(II)/metal electrode

Table 1. Kinetic parameters of the Zn(II)/Zn(Hg) system in H_2O/MeOH (1 mol·dm^{-3} $NaClO_4$) in the absence and presence of *TU*

c_{MeOH} (% v/v)	c_{TU} (mol·dm^{-3})	$10^6 \cdot D_{ox}$ (cm^2 s^{-1})	$-E_f$(V) (*vs.* F_c)	$10^3 \cdot k_s$ (cm·s^{-1})		α
0	0.00	6.6	1.064		3.3^2	0.29
0	0.05	6.6	1.064		65.5^2	0.48
0	0.25	6.6	1.066		109.0^2	0.48
36	0.00	4.3	1.137	1.9^1	2.2^2	0.30
36	0.05	4.3	1.140	14.6^1	14.4^2	0.42
36	0.25	4.3	1.140	37.6^1	37.6^2	0.52
65	0.00	3.8	1.150		0.5^2	0.27
65	0.05	3.8	1.142	9.6^1	9.3^2	0.38
65	0.25	3.8	1.154	18.5^1	19.7^2	0.48
91	0.00	4.2	1.166	0.6^1	0.6^2	0.29
91	0.05	4.2	1.203	7.8^1	5.5^2	0.42
91	0.25	4.2	1.215	15.2^1	17.6^2	0.58

[1] Cyclic voltammetry; [2] impedance measurements

trates the process occuring at the electrode, where the faradaic impedance is a sum of the activation polarization resistance R_A of the electrode reaction and the *Warburg* impedance. Knowing the value of R_A at equilibrium potential, one may calculate the reaction rate constants k_s according to Eq. (4) [17] where c is the concentration of the depolarizer in solution.

$$k_s = \frac{RT}{n^2F^2cR_A} \tag{4}$$

The activation polarization resistances R_A were determined for E_f and calculated from $Z' = f(wZ'')$ and $Z'' = f(Z')$ [17, 18], where Z' is the real and Z'' the imaginary part of the cell impedance.

The ohmic resistance of electrode, solution, and mercury capillary was obtained as the real impedance component at a frequency of 10 kHz and at a potential outside the faradaic region. Figure 2 presents the impedance diagrams for the electroreduction of Zn(II) in 36% v/v MeOH in the absence and presence of *TU*.

The kinetic parameters of the investigated system were also calculated from cyclic voltammetry measurements by the method described by *Nicholson* and *Shain* [19] using the equations for an irreversible process where E_p^c and $E_{p/2}^c$ are the potentials of the cathodic and half-cathodic peaks, respectively, αn_α is the observed cathodic transfer coefficient. V is the potential scan rate, and the other symbols have their usual meanings.

$$E_p^c = E_f - \frac{RT}{\alpha n_\alpha F}\left(\ln\left(D_{ox}\frac{\alpha n_\alpha FV}{RT}\right)^{1/2} - \ln k_s + 0.78\right) \tag{5}$$

$$E_{p/2}^c - E_p^c = \frac{0.048}{\alpha n_\alpha} \tag{6}$$

Parameters αn_α are calculated from Eq. (6).

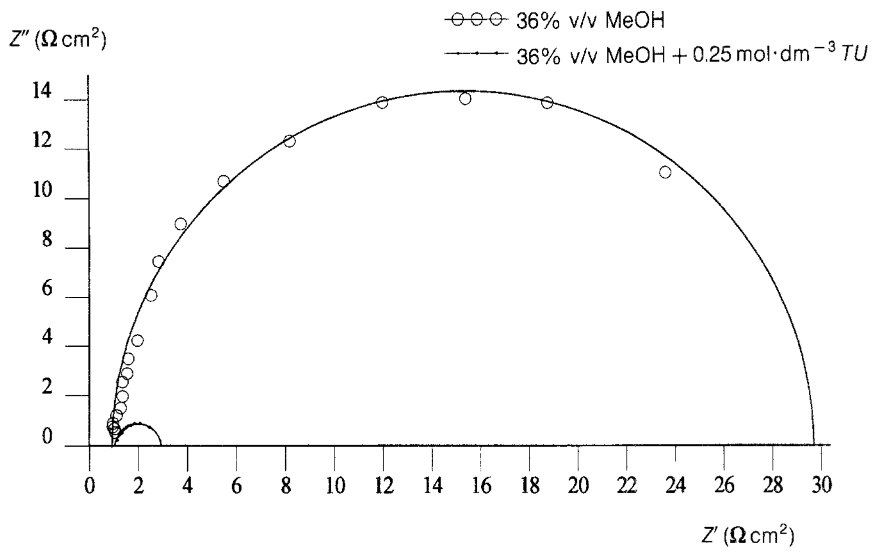

Fig. 2. Impedance diagrams measured at E_f for the electroreduction of Zn(II) in 36% v/v MeOH in the absence and presence of 0.25 mol·dm^{-3} *TU*

For the quasi-reversible processes, the standard rate constants were calculated by *Nicholson*'s method from Ref. [20]. This method uses the parameter Ψ which is a tabulated function of the separation between the cathodic and anodic peaks of the cyclic voltammogram and which is related to the standard rate constant by Eq. (7).

$$\Psi = \left(\frac{D_{\mathrm{ox}}}{D_{\mathrm{red}}}\right)^{\alpha/2} \frac{k_s(\mathrm{R}T)^{1/2}}{(\pi nFVD_{\mathrm{ox}})^{1/2}} \tag{7}$$

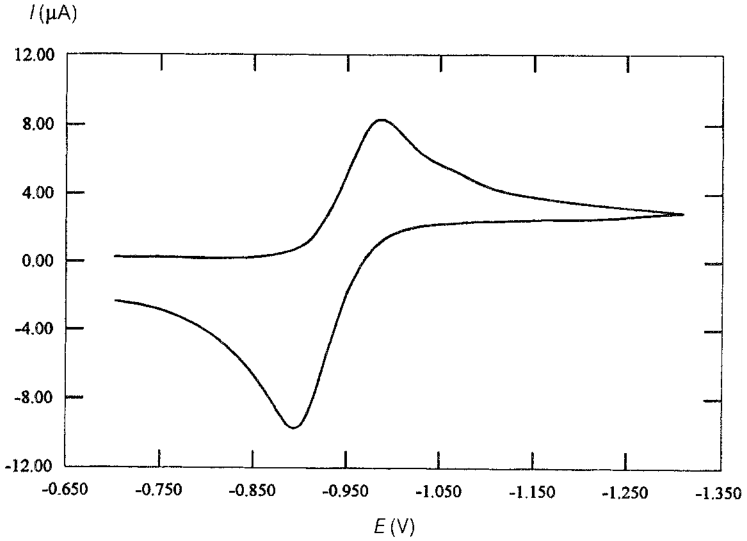

Fig. 3. Cyclic voltammetric curves for the Zn(II)/Zn(Hg) system at a scan rate of 0.1 V·s^{-1} in 36% v/v MeOH (potential *vs.* Ag/AgCl electrode)

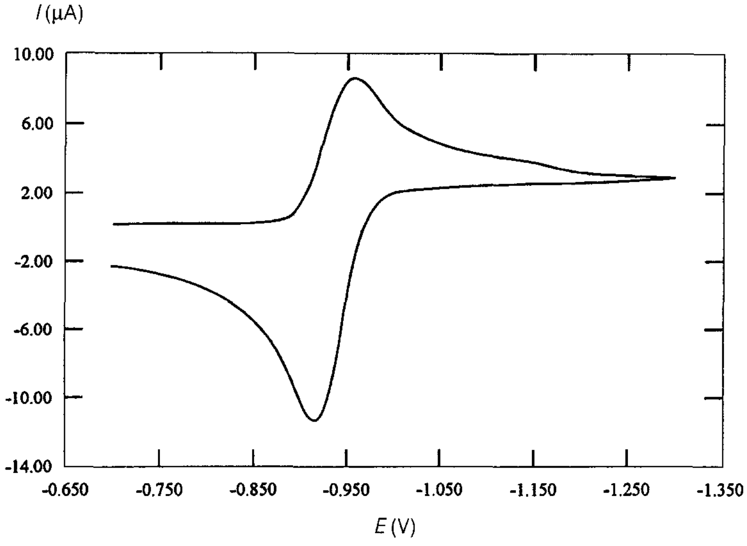

Fig. 4. Cyclic voltammetric curves for the Zn(II)/Zn(Hg) system at a scan rate of 0.1 V·s^{-1} in 36% v/v MeOH containing 0.05 mol·dm^{-3} TU (potential *vs.* Ag/AgCl electrode)

Figures 3 and 4 give examples of the cyclic voltammetric curves for the Zn(II)/Zn(Hg) system in 36% v/v MeOH in the presence of 0.05 mol·dm^{-3} TU.

The cathodic transfer coefficient α for a quasi-reversible process was determined using cyclic voltammetry measurements on the basis of the dependence of the formal values αn_α on $1/V$. The obtained value αn_α for $1/V = 0$ has been accepted as the best one for the determination of the cathodic transfer coefficient.

The results of the kinetic calculations for the Zn(II)/Zn(Hg) system in the investigated solutions are compiled in Table 1. The apparent standard rate constants k_s of the zinc electroreduction process for MeOH mixtures are in good agreement with the values given in Ref. [4]. In the presence of TU, they were higher than in the pure methanolic solutions.

In agreement with the expectations, the acceleration of the zinc electroreduction process by thiourea was observed in all systems examined as indicated by the values of the standard rate constants of the Zn(II) electroreduction process which increased with increasing TU concentration (Table 1). However, with the same degree of electrode converge with thiourea in aqueous and methanol solutions, these constants did not differ significantly (Table 2). This suggests that the structure of the active complex in both solutions is the same.

On the other hand, the difference between the values of formal potentials of the Zn(II)/Zn(Hg) system in water and H_2O/MeOH mixtures in the presence of TU is not higher than 20 mV if the values of formal potentials are calculated according to the *bis*-biphenylchromium(I)/*bis*-biphenyl-chromium(0) reference system [21]. This observation constitutes an independent confirmation of the suggestion that it is the same form of the zinc active complex that undergoes reduction in both water and methanol solutions. It should be added that if the F_c reference system is employed, then the differences between formal potentials in water and methanol solutions are

Table 2. Standard rate constants of the electrode reduction of the Zn(II)/Zn(Hg) system in H_2O and H_2O/MeOH mixtures at the same values of *TU* surface coverge of the Hg electrode

θ	$k_{sH_2O} \cdot 10^3$ (cm·s^{-1})	c_{MeOH} (% v/v)	$k_{sMeOH} \cdot 10^3$ (cm·s^{-1})
0.04	14.6	36	14.4, 14.6
0.09	34.5	36	37.6, 36.9
0.03	8.5	65	9.3, 9.6
0.06	21.0	65	19.7, 18.5
0.03	8.5	91	5.5, 7.8
0.07	23.0	91	17.6, 15.2

much higher. Still, the chromium system is recommended as a more satisfactory reference system [21, 22].

The values of the cathodic transfer coefficient α in the presence of *TU* do not differ significantly in water and methanol solutions. This, in turn, implies a similar mechanism of the electroreduction process in both solutions.

Summing up, the obtained results confirm the suggestion that in acceleration of the zinc electroreduction process by thiourea, the decisive role is played by the active complex being reduced on the mercury electrode. Along with an increase in *TU* adsorption, there is a greater probability of formation of the active complex which is reflected in an increased rate constant of the Zn(II) electroreduction process within a given concentration of the organic solvent.

Experimental

Apparatus and measurements

Measurements were carried out with a polarograph PA-4 (Laboratorni Pristroje Prague) and with a Model 270 Electrochemical Analysis System and a Model 388 Electrochemical Impedance System (EG&G PAR) employing a static mercury drop electrode (SMDE) with a surface area of 0.01827 cm^2 manufactured by Laboratorni Pristroje Prague. As the reference electrode, Ag/AgCl with saturated NaCl was used. The reference electrode was connected to the electrolytic cell *via* an intermediate vessel filled with the solution to be investigated. The counter electrode was a platinum wire.

The kinetic parameters for the reduction of Zn(II) were determined using cyclic voltammetry (sweep rates from 0.005 to 20 Vs^{-1} precision: ±7%) and by impedance measurements (precision: ±5%). The complex cell impedance was obtained at 20 frequencies in the range from 100 to 25000 Hz at formal potential. Additionally, the voltammetric curves of the ferrocene-ferricinium system (F_c) were recorded. All potentials in Table 1 refer to this internal reference system.

The double-layer capacity was measured using the AC impedance technique at a frequency of 800 Hz with an impedance meter EJM-2 (Łódź University). The capacitance was measured with a precision of ±0.2%. For these measurements, a dropping Hg electrode constructed according to *Randles* was used [5]. The balance of the bridge was achieved after 6 s of drop growth. The drop time was 8 s and the flow rate 0.762 mg·s^{-1} at a mercury column height of 50 cm. For measurements of differential capacitance, a saturated NaCl aqueous calomel electrode (SSCE) was used as the reference electrode.

For the whole polarization range, capacity dispersion was tested at five different frequencies between 400 and 2000 Hz. In the potential range studied no dispersion of the capacitance was observed.

The potential of zero charge (E^0) was measured using the streaming mercury electrode [6, 7]. Interfacial tension at E^0 was measured by the maximum bubble pressure method according to *Schiffrin* [8].

Reagents

Chemicals of analytical grade from Merck were used. Water and mercury were distilled twice. $Zn(NO_3)_2 \cdot 6H_2O$ was used without further purification. The Zn(II) concentration in the solutions was always $10^{-3}\,mol \cdot dm^{-3}$. The concentration of $NaClO_4$ in the investigated mixtures was $1\,mol \cdot dm^{-3}$. The specific conductivity of methanol determined to be $8 \times 10^{-5}\,S \cdot m^{-1}$. The MeOH concentration was 36, 65, and 91% v/v. Measurements were carried out at 298 ± 0.1 K. Solutions were deaerated using nitrogen which had been presaturated with the investigated solution. The same gas was passed over the solution during the measurements.

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