ON THE CATALYTIC EFFECT OF DIALKYL DERIVATIVES OF THIOUREA ON THE ELECTROCHEMICAL REDUCTION OF ZINC(II) IONS

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N,N'-Dimethyl-, N,N'-diethyl-, N,N'-diisopropyl- and N,N'-dibutylthiourea increase the rate of Zn(II) electroreduction in 1 M $NaClO_4$. Increasing size of alkyl radical for the successive derivatives causes increase of their adsorption on mercury which, in turn, causes the increase of Zn(II) electroreduction rate. Electroreduction rate is also influenced by the change of molecule orientation on the electrode.

Various factors governing electrode kinetics have been reviewed with respect to the electroreduction of inorganic cations in the presence of organic adsorbates[1,2].

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 an accelerating or a decelerating sense. Usually this type of effect shows up only in the value of the reduction or oxidation rate constant, which can be measured by several methods, assuming control by charge and mass transfer.

From the literature it is known that thiourea influences several electrode processes, catalyzes reduction of In^{3+} (ref.[3]), H_3O^+ (ref.[4]), Zn^{2+} (refs[2,5,7]), Bi^{3+} (ref.[2]), Cd^{2+} (ref.[6]).

The adsorption of thiourea at the mercury/electrolyte solution interface has been ascribed to the strong localization of the molecular dipole within the inner layer[8], leaving the bond between the mercury and the sulfur atom intact even at rather negative potential differences across the interface.

Thiourea derivatives also show catalytic activity. Methylthiourea, ethylthiourea, dimethylthiourea and phenylthiourea accelarate electroreduction of H_3O^+. At constant bulk concentration the catalytic effect increases with the molecular weight of the derivatives. It seems, however, that the observed variations mostly reflect differences in adsorbability[4].

Adsorption effects of dimethylthiourea and tetramethylthiourea on electrode kinetics of Zn(II) were studied by Ikeda et al.[7]. The standard rate constant for Zn(II) is controlled by the inner-layer permittivity. Its effect has been explained in terms of the solvent

reorganization energy. Unstable Zn(II)–adsorbate complexes, mediating the electron exchange, are localized inside the adsorption layer according to Ikeda.

It was stated[9] that with increasing size of alkyl radical for the successive dialkyl derivatives of thiourea there was increase of (i) surface excess at unchanged bulk concentration, (ii) negative standard free energy of adsorption ΔG^0, (iii) concentration changes of zero charge potential.

Differences in adsorption properties of successive dialkyl derivatives of thiourea are mainly caused by interaction of aliphatic chains due to changes of their hydrophobicity and polarizability and should be reflected in their influence on electroreduction.

The aim of the paper was to investigate the influence of thiourea dialkyl derivatives on kinetics of Zn(II) reduction at the hanging mercury electrode in 1 M NaClO$_4$ solution.

The influences of *N,N′*-dimethylthiourea (DMTU), *N,N′*-diethylthiourea (DETU) in concentrations ranging from 0.5 to 50 mmol l^{-1} and *N,N′*-diisopropylthiourea (DIPTU), *N,N′*-dibutylthiourea (DBTU) in concentration range from 0.1 to 1 mmol l^{-1} (limited with their solubility) were studied.

EXPERIMENTAL

Technique of Measurement

The measurements were performed using a three electrode cell, containing the hanging or dropping mercury electrode (SMDE Laboratorni pristroje, Prague) as the working electrode, a cylindrical platinum plate (area of ca 2 cm^2) as the counter electrode and the Ag/AgCl reference electrode. The latter was connected to the cell via a salt bridge filled with cell solution. Surface of a mercury drop was 0.01827 cm^2. The potentials were referred to the sodium chloride saturated calomel electrode (SSCE). The temperature of the cell was maintained at 25 ± 0.1 °C.

The solutions were prepared from freshly twice-distilled water and analytical grade chemicals (Merck). All solutions were deoxygenated by high-purity nitrogen, previously purified using a vanadium(II) perchlorate solution and equilibrated with the background electrolyte solution.

DC polarograms were obtained using a polarograph PA4 (Laboratorni pristroje, Prague). The differential capacity of the double layer was calculated from the data obtained at the frequency of 800 Hz using an impedancemeter EIM-2 (manufactured by the Lodz University) with on line computer control. The reproducibility of the average capacity measurements was ± 1% over the wide range of potentials.

For the whole polarization range the capacity dispersion was tested at five different frequencies between 275 – 1 990 Hz. In the potential range studied, no dispersion of the capacitance was observed.

Cell impedances and cyclic chronovoltammetric curves were taken using Model 388 and 270 Electrochemical Impedance and Analysis System AG&G PARC. The complex cell impedance was obtained at 18 frequencies between 100 – 20 000 Hz within faradaic region at the formal potential. The accuracy of measurements of Z' and Z'' was about 2%.

Elaboration of Experimental Data

Surface excess Γ at constant charge was obtained using Eq. (1)

$$\Gamma = -(1/RT) \, (\delta\xi/\delta\ln c_{org})_\sigma \; , \qquad (1)$$

where c_{org} is the concentration of dialkyl derivatives of thiourea and ξ is the Parsons function $\xi = \gamma + \sigma E$ as in ref.[19].

The diffusion coefficients of Zn(II) in the examined solutions were calculated using the Ilkovic equation for a diffusion-controlled limiting current. The polarographic wave of Zn(II) in 0.1 M KNO$_3$ with the value of the Zn(II) diffusion coefficient $D_{ox} = 6.9 \cdot 10^{-6}$ cm^2 s^{-1} (ref.[10]) being used as a standard. The diffusion coefficient D_{ox} of Zn(II) ions in 1 M NaClO$_4$ was found to be $6.9 \cdot 10^{-6}$ cm^2 s^{-1} at 25 °C. The reproducibility of the results obtained was ±5%.

The diffusion coefficient $D_R = 16.7 \cdot 10^{-6}$ cm^2 s^{-1} for Zn in the mercury was taken from the literature[11].

The formal potentials E_f^0 of the reduction of Zn(II) ions were determined from cyclic voltammetry curves[12] at a polarization rate of 0.005 – 0.02 V s^{-1} with the reproducibility of ±0.002V.

The ohmic resistance of the electrolyte solution was obtained as the real impedance component at a frequency of 10 kHz and at a potential outside the faradaic region.

The activation polarization resistances R_A were determined for E_f^0 and calculated from the dependence $Z' = f(\omega Z'')$ or $Z'' = f(Z')$ (refs[13–15]), where Z' is the real and Z'' the imaginary parts of the cell impedance.

The reaction standard rate constants k_s were calculated according to the expression[14]

$$k_s = \frac{RT}{n^2 F^2 c R_A} \; , \qquad (2)$$

where c is the concentration of depolarizer.

RESULTS AND DISCUSSION

Methodology of the experiment was checked determining the kinetic parameters of Zn(II) electroreduction in 1 M NaClO$_4$. The obtained values $k_s = 3 \cdot 10^{-3}$ cm s^{-1}, $E_f^0 = -0.990$ V (SSCE) as well as the diffusion coefficient of Zn(II) ions in 1 M NaClO$_4$ $D_{ox} = 6.9 \cdot 10^{-6}$ cm^2 s^{-1} are in good agreement with literature data[16,17].

Four series of solutions with different dialkyl derivatives of thiourea have been investigated. Each of them contained $\approx 10^{-3}$ M Zn^{2+} in 1 M NaClO$_4$ and following concentrations of thiourea derivatives: $0.5 – 50 \cdot 10^{-3}$ M DMTU, $0.5 – 50 \cdot 10^{-3}$ M DETU, $0.1 – 1 \cdot 10^{-3}$ M DIPTU and $0.1 – 1 \cdot 10^{-3}$ M DBTU.

The dialkyl derivatives of thiourea (in the range of studied concentrations) do not affect the change of diffusion coefficient of Zn(II) ions.

Tables I – IV present the estimated formal potential E_f^0, standard rate constants k_s, and surface excesses Γ at the formal potentials. The value shown for each parameter is an average calculated from four measurements. It follows from tables that the changes

TABLE I
Values of formal potentials, standard rate constants of the (Hg)Zn $(1 \cdot 10^{-3}$ M$)$/Zn(II) $(1 \cdot 10^{-3}$ M$)$ system and surface excesses at the potential E_f^0 in solutions of 1 M NaClO$_4$ at various concentrations of DMTU (c)

Parameter	$c \cdot 10^3$, mol l^{-1}						
	0.5	1.0	5.0	10.0	20.0	30.0	50.0
$-E_f^0$, V	0.990	0.992	0.991	0.990	0.989	0.989	0.990
$k_s \cdot 10^3$, cm s^{-1}	3.2	4.9	29.0	66.3	94.3	117.5	155.0
$\Gamma \cdot 10^{11}$, mol l^{-1} cm^{-2}	0.8	1.3	2.5	4.2	5.9	7.1	9.2

TABLE II
Values of formal potentials, standard rate constants of the (Hg)Zn $(1 \cdot 10^{-3}$ M$)$/Zn(II) $(1 \cdot 10^{-3}$ M$)$ system and surface excesses at the potential E_f^0 in solutions of 1 M NaClO$_4$ at various concentrations of DETU (c)

Parameter	$c \cdot 10^3$, mol l^{-1}							
	0.5	1.0	5.0	10.0	15.0	20.0	30.0	50.0
$-E_f^0$, V	0.988	0.987	0.988	0.988	0.987	0.988	0.988	0.989
$k_s \cdot 10^3$, cm s^{-1}	9.5	26.0	55.3	73.7	53.2	30.1	29.7	31.2
$\Gamma \cdot 10^{11}$, mol l^{-1} cm^{-2}	1.8	2.5	5.7	8.5	10.2	11.7	13.4	15.8

TABLE III
Values of formal potentials, standard rate constants of the (Hg)Zn $(1 \cdot 10^{-3}$ M$)$/Zn(II) $(1 \cdot 10^{-3}$ M$)$ system and surface excesses at the potential E_f^0 in solution of 1 M NaClO$_4$ at various concentrations of DIPTU (c)

Parameter	$c \cdot 10^3$, mol l^{-1}				
	0.10	0.25	0.50	0.75	1.00
$-E_f^0$, V	0.988	0.989	0.989	0.988	0.990
$k_s \cdot 10^3$, cm s^{-1}	5.9	7.7	9.8	14.3	23.7
$\Gamma \cdot 10^{11}$, mol l^{-1} cm^{-2}	0.9	1.1	1.4	2.3	4.2

of formal potentials with the change of concentration and kind of the studied thiourea derivatives are minimal. It was concluded therefore, that complex formation between Zn(II) and dialkyl derivatives of the thiourea in the solution does not occur to a significant extent. Dialkyl derivatives of thiourea increase the rate of Zn(II) electroreduction in 1 M NaClO$_4$ and at the same time this activity increases with increasing size of alkyl radical.

Analyzing the data in Tables I – IV it is possible to divide studied dialkyl derivatives of thiourea into 2 groups: DMTU and DIPTU as well as DETU and DBTU because of analogous catalytic activity.

The standard rate constant of Zn(II) electroreduction increases with rising concentration of DMTU or DIPTU in the solution. A linear relationship between the standard rate constant of the electrochemical reduction of Zn(II) ions and the surface excess of DMTU or DIPTU (Fig. 1) could be interpreted as so called "bridging model"[18] where

TABLE IV

Values of formal potentials, standard rate constants of the (Hg)Zn (1 . 10^{-3} M)/Zn(II) (1 . 10^{-3} M) system and surface excesses at the potential E_f^0 in solutions of 1 M NaClO$_4$ at various concentrations of DBTU (c)

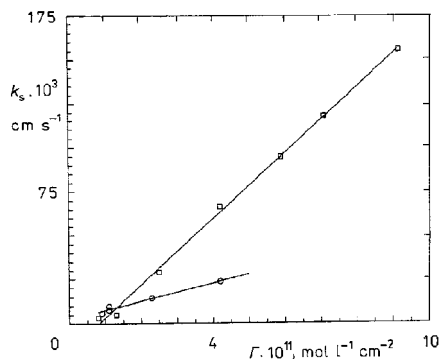| Parameter	c . 10^3, mol l^{-1}				
	0.10	0.25	0.50	0.75	1.00
$-E_f^0$, V	0.988	0.990	0.989	0.988	0.989
k_s . 10^3, cm s^{-1}	63.0	40.2	14.6	7.6	6.9
Γ . 10^{11}, mol l^{-1} cm^{-2}	6.1	8.7	10.7	13.3	15.1

FIG. 1

Dependence of k_s on Γ for (Hg)Zn (1 . 10^{-3} M)/Zn(II) (1 . 10^{-3} M) system at potential E_f^0 for DMTU (▢) and DIPTU (◯)

the adsorbed species are assumed to facilitate the transfer of electrons across the inner layer.

The accelerating activity of all examined thiourea dialkyl derivatives increases with the increase of alkyl chain length but only for the concentration below $0.5 \cdot 10^{-3}$ mol l^{-1}. With the increase of DETU or DBTU concentration the standard rate constant of electroreduction of Zn(II) reaches maximum and then decreases asymptotically to the values exceeding significantly k_s of Zn(II) electroreduction in 1 M NaClO$_4$ (Tables II, IV).

It was shown in the earlier papers[5,7,20] that the acceleration of the electrode process was caused by the adsorption of organic substances on the electrode surface (in the region of depolarizer reduction potentials) forming unstable complexes.

The differences in catalytic activities of the examined thiourea dialkyl derivatives should result mainly from their adsorption properties as the complex creating group is the same.

Figures 2 – 5 present curves of differential capacity vs potential $C–E$ for varying concentrations of dialkyl derivatives of thiourea.

In the region of Zn(II) reduction potentials the differential capacity increases with rising concentration of DMTU, DIPTU as well as DETU up to 10^{-2} mol l^{-1} and DBTU up to 10^{-4} mol l^{-1}.

At higher concentrations of DETU and DBTU the $C–E$ curves show some lowering indicating formation of an oriented coherent monomolecular film on the electrode surface. This suggests that with the change of electrode potential the change of interaction
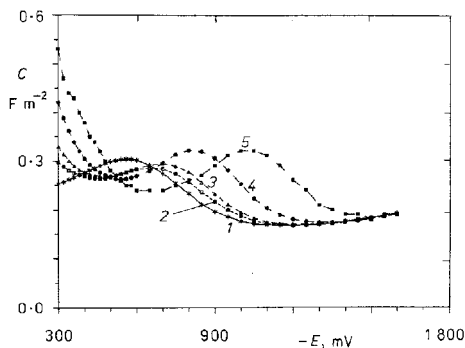

FIG. 2

Differential capacity–potential curves of the mercury electrode in 1 M NaClO$_4$ for different contents of DMTU (in mmol l^{-1}): *1* 0, *2* 0.5, *3* 1, *4* 5, *5* 50
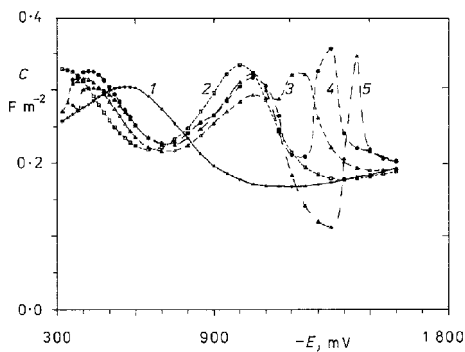
FIG. 3

Differential capacity–potential curves of the mercury electrode in 1 M NaClO$_4$ for different contents of DETU (in mmol l^{-1}): *1* 0, *2* 5, *3* 15, *4* 30, *5* 50

between mercury and thiourea dialkyl derivatives takes place, but molecules are always oriented with sulfur towards mercury surface. At less negative potentials the orientation of molecules is parallel to the electrode surface and thickness of adsorption layer decreases with the increase of bulk concentration. In the range of more negative potentials, the thickness of the adsorption layer increases with rising bulk concentration. It may be caused by a rather perpendicular orientation of molecules to the mercury surface. Such a change of molecule arrangement involves greater screening of nitrogen atoms which form with Zn(II) ions active complexes mediating the electron exchange.

The increase of surface excesses for the same concentrations of successive dialkyl derivatives of thiourea is undoubtedly connected with the increase of their hydrophobicity. A different tendency is observed for DIPTU which results from the presence of branched chains in the molecule.

The value of limiting current for the Zn(II) reduction process does not depend on concentration of the studied derivatives. In the presence of DETU at concentrations higher than $15 \cdot 10^{-3}$ mol l^{-1} polarographic maxima localized in the range of potentials $1.00 - 1.10$ V were observed. The maximum was observed only for DETU. Rapid changes of capacity occur on the curves of differential capacity in this range. Such behaviour can be explained by disturbances of depolarizer due to rapid changes of adsorption equilibrium.

It follows from the studies that with increasing size of alkyl radical for the successive derivatives, their adsorption on mercury and catalytic activity to Zn(II) electroreduction increase.
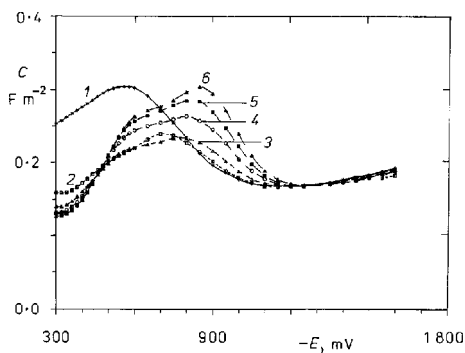

Fig. 4

Differential capacity–potential curves of the mercury electrode in 1 M NaClO$_4$ for different contents of DIPTU (in mmol l^{-1}): *1* 0, *2* 0.1, *3* 0.25, *4* 0.5, *5* 0.75, *6* 1
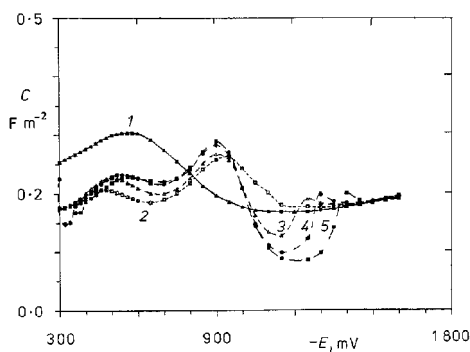
Fig. 5

Differential capacity–potential curves of the mercury electrode in 1 M NaClO$_4$ for different contents of DBTU (in mmol l^{-1}): *1* 0, *2* 0.1, *3* 0.25, *4* 0.5, *5* 0.75

Reorientation of DETU and DBTU molecules on the mercury surface, which takes place in the range of Zn(II) reduction potentials, decreases catalytic activity of these derivatives.

It is worth noting that alcohols derived from alkyl radicals of the studied derivatives are known inhibitors of electrode processes. However, when they perform a role of substituents in thiourea, they lose inhibiting character. In the case of successive alcohols, inhibiting activity increases with the increase of adsorption on mercury. Adsorption of corresponding thiourea derivatives also increases but it causes an inverse effect i.e. the increase of electroreduction rate. Also the influence of changes of electron density within the molecule on the C=S bond causes "bridge" activation.

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