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Note

Acceleration of Zn(II) Electroreduction by Thiourea and Dialkylderivatives of Thiourea at the Hg Electrode in Water + Ethanol Mixtures

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The influence of thiourea (TU) and dialkylderivatives of thiourea: *N,N'*-dimethyl-(DMTU), *N,N'*-diethyl-(DETU) and *N,N'*-dibuthyl-thiourea-(DBTU) on the electroreduction of Zn (II) was studied in water + ethanol 98% vol. + $NaClO_4$ mixtures. The results obtained are discussed taking into account TU, DMTU, DETU, DBTU adsorption on the electrode surface as well as the possibility of formation of an active complex by a metal ion with TU and dialkylderivatives. The results suggest that the complex structure plays the dominant role of the electrode process acceleration.

INTRTODUCTION

The cap-pair principle determines the essential conditions under which reduction processes may be accelerated by some definite organic compounds in aqueous solutions.[1] It was found that both the formation of unstable complexes and labile binding of the adsorbate by the electrode surface jointly determine the occurrence of the effect. Yet, it has not been determined which of the processes is dominant.

Hopes for the solution of this problem rose when it was confirmed that the cap-pair rule also holds for aqueous-organic solutions. It is believed that introduction of nonaqueous and aquous-organic solutions into experiments creates a possibility of verifying the theories formulated for aqueous solutions.

So far studies have dealtt with the acceleration of the process of Zn(II) electroreduction by TU in water + dimethylsulfoxide[2] and water + ethanol solutions at concentrations ranging from 0 to 90% vol.[3]

The experiments presented below concern the effect of TU, DMTU, DETU and DBTU on Zn(II) electroreduction in an ethanol solution. The system was previously examined in an aqueous solution.[4]

The ethanol concentration of 98% vol. has been chosen taking into account the results reported in study,[5] *i.e.* the same rate constants of the electroreduction on zinc ions at this ethanol concentration and in water, total solvation of zinc ions by ethanol in this solution[6] and good solubility of TU and its derivatives.

EXPERIMENTAL

Apparatus and measurements

The experimental methods, apparatus, electrodes and data analysis used for the electroreduction studies were the same as those reported in my previous works.[3,7]

Reagents

Chemicals of analytical grade from Merck were used. Water and mercury were distilled twice. $Zn(NO_3)_2$ 6 H_2O was used without further purification. The Zn(II) concentration in solutions was always $4 \cdot 10^{-4}$ M. The concentration of $NaClO_4$ in the investigated mixtures was 0.7 M. The specific conductivity of ethanol was $1.36 \cdot 10^{-6}$ Q^{-1} cm^{-1}. The EtOH concentration in the solution was 98% vol. Measurements were carried out at 298 ± 0.1 K.

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

RESULTS

The adsorption of TU-derivatives (concentration from 0.004 to 0.1 M) on mercury from 98% vol. EtOH mixtures containing 0.7 M $NaClO_4$ was investigated on the basis of the measurements of differential capacity.[7] At potentials more cathodic than –0.4 V, the capacity was found to be frequency independent. Figures 1–4 show the values of relative surface excess (Γ') obtained for different concentrations of TU and thiourea derivatives as a function of charge (σ_M). The electroreduction process in the presence of TU and DMTU took place within a range of charges from –6 to –8, and for DETU and DBTU from –4 to $-6 \cdot 10^{-2}$ cm^{-2}. The higher the concentration of the surfactant, the more negative the charge at which the electroreduction process occurs.

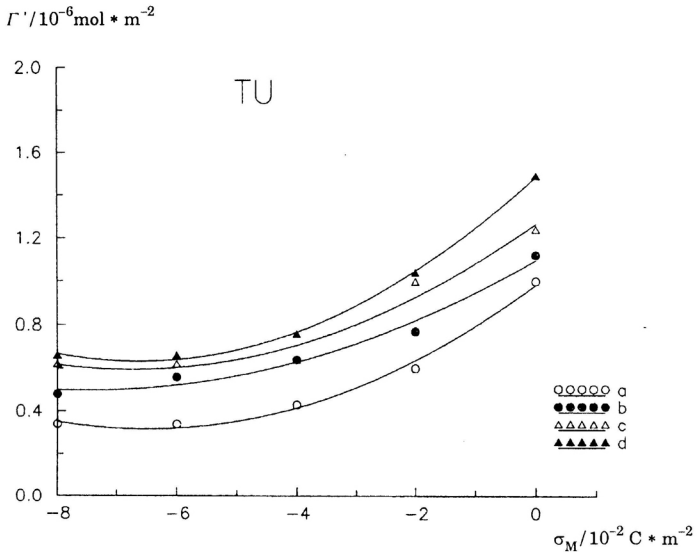

Figure 1. Relative surface excess of TU as a function of surface charge at TU concentrations: a – 0.02; b – 0.04; c – 0.08; d – 0.1 M.

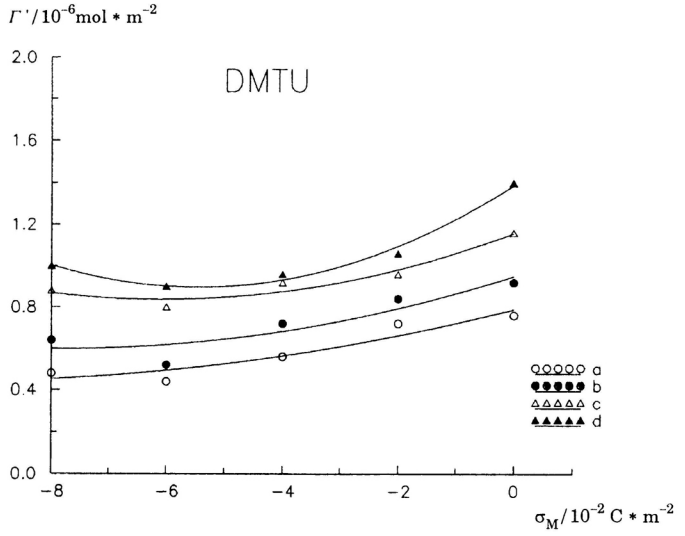

Figure 2. Relative surface excess of DMTU as a function of surface charge at DMTU concentrations: a – 0.02; b – 0.04; c – 0.08; d – 0.1 M.

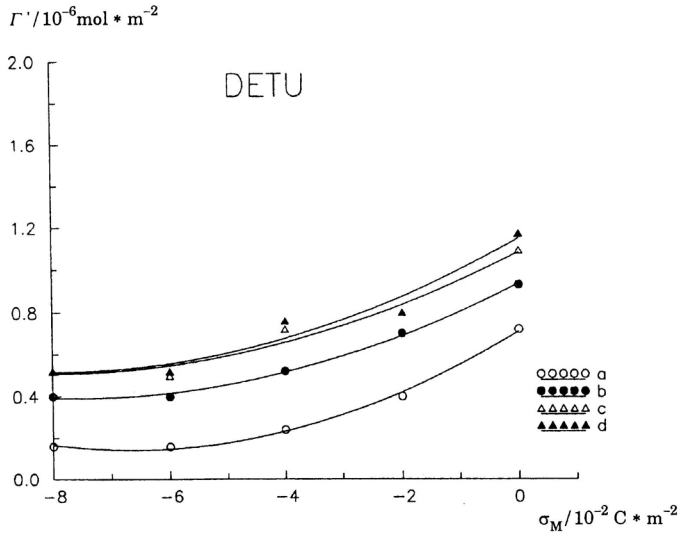

Figure 3. Relative surface excess of DETU as a fubnction of surface charge at DETU concentrations: a – 0.02; b – 0.04; c – 0.08; d – 0.1 M.

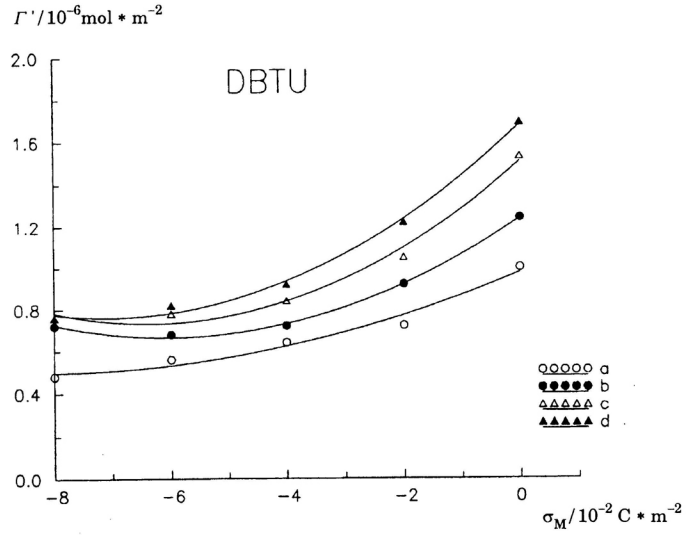

Figure 4. Relative surface excess of DBTU as a function of surface charge at DBTU concentrstions: a – 0.02; b – 0.04; c – 0.08; d – 0.1 M.

TABLE I

Kinetic parameters of the Zn(II) /Zn (Hg) system in 0.7 M $NaClO_4$ + EtOH mixtures in the absence and presence of 0.04 M TU or its derivatives

Composition	$D_{ox}10^6/cm^2s^{-1}$	$-E_f^0$ / V *vs.* F_c	k_s^{app} $10^3/cm\ s^{-1}$	α^{app}
98% vol. EtOH	5.6	1.127	1.4	0.31
98% vol. EtOH + TU	5.6	1.130	5.6	0.56
98% vol. EtOH + DMTU	5.4	1.127	5.9	0.57
98% vol. EtOH + DETU	5.5	1.135	7.1	0.56
98% vol. EtOH + DBTU	5.4	1.143	8.3	0.58

The formal potential E_f° (Table I) was determined using the cyclic voltammetry technique.[3] The E_f° values in the presence of TU and its derivatives underwent only very slight changes.

The approximate diffusion coefficients of Zn(II) were calculated from limiting currents using the Ilković equation.[3] No effect of TU and its derivatives was observed on the value of zinc diffusion coefficients (Table I).

Kinetic parameters of the Zn(II) /Zn (Hg) system for mixtures under investigation were calculated from cyclic voltammetry measurements by Nicholson's method. The procedure of measurements is described in Ref. 3. The standard rate constants k_s of the zinc electroreduction process in the presence of TU and its derivatives were higher than in the ethanol solution (Table I). The acceleration is small and practically the same in the presence of TU and DMTU whereas it is higher in the case of DETU and DBTU.

DISCUSSION

In an attempt to explain which of the two factors, adsorption or complex formation, plays the dominant role in the process of acceleration of zinc electroreduction, a comparison was made of aqueous and ethanol solutions. In the former, zinc occurs in the form of the aquo-complex while it is completely solvated by ethanol in the latter.

In the presence of TU and its derivatives, similarly to the aquous solution, the E_f° value undergoes no change and the diffusion coefficient is the same. This could suggest that, in the bulk, no formation of stable complexes occurs. Higher values of the standard rate constants of the zinc electroreduction process in the presence of TU and its derivatives indicate that these substances accelerate the zinc electroreduction process.

The necessary condition of electrode processes acceleration is the adsorption of the accelerating substance with a small surface coverage degree of the electrode.[8] The condition was fulfilled by the examined system because,

in the region of zinc reduction, a slight increase occurred in the value of the differential capacity of the double layer, as compared with the basic electrolyte.[7,9] In the potential range studied, the capacity was found to be frequency independent. This suggests that the adsorption investigations are performed under equilibrium conditions.

The phenomenon of acceleration of cadmium electroreduction process occurs at low TU concentrations (0.05 M TU).[10,11] At higher TU concentrations, the process of cadmium electroreduction is inhibited.[2] Similarly, in the presence of DETU and DBTU and a surface coverage degree above 0.25, there is a gradual decrease in the rate of the electrode process of zinc in aqueous solution in comparison to its maximum value obtained.[4] The same effect was also observed in the case of ethanol solutions for surface coverage degrees above 0.12, 0.16, 0.16 and 0.33 for TU, DMTU, DETU and DBTU, respectively. For this reason, the investigations involved a surfactant concentration of 0.04 M, at which the surface coverage degress are 0.1, 0.12, 0.16 and 0.26 for TU, DMTU, DETU and DBTU, respectively.

Comparison of the zinc reduction process acceleration in aqueous[4] and ethanol solutions shows that, for the same surface coverage degree of the electrode by TU, which in both solutions equals 0.10, the relative acceleration was 20 and 4 times, respectively; for the surface coverage degree of the electrode by DMTU equal to 0.12 it was 30 and 4 times; for the surface coverage degree of the electrode by DETU equal to 0.16 it was 17 and 5 times and for the surface coverage degree of the electrode by DBTU equal to 0.26 it was 19 and 6 times.

It seems to me that the more stable complex Zn-EtOH-X requires a higher activation energy than Zn-H_2O-X (where X denotes the molecules of TU, DMTU, DETU or DBTU).

The cathodic transfer coefficient α (about 0.5) in the presence of TU or its derivatives is similar to that in pure aqueous solutions in the presence of TU.[3] This suggests that the mechanism of the electrode process in H_2O + EtOH solutions is similar to that in pure aqueous solutions.

The experiments carried out seem to indicate that the main role in the acceleration of the zinc electroreduction process may be played by the structure of the active complex being reduced at the electrode surface.

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SAŽETAK

Ubrzavanje elektroredukcije iona Zn(II) na živinoj elektrodi u smjesi vode i etanola pomoću tioruee i njenih dialkil-derivata

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Istraženi su utjecaji tiouree, *N,N'*-dimetiltiouree, *N,N'*-dietiltiouree i *N'*-dibutiltiouree na brzinu elektroredukcije iona Zn(II) na živinoj elektrodi u otopini $NaClO_4$ u smjesi vode i 98% vol. etanola. Tiourea i njeni dialkil-derivati adsorbiraju se na površinu živine elektrode i kompleksiraju ione cinka. Rezultati mjerenja ukazuju da se brzina elektroredukcije cinka povećava zbog stvaranja nestabilnih kompleksa na površini elektrode.