

THE INFLUENCE OF *N,N'*-DIALKYLTHIOUREAS ON THE TWO-STEP ELECTROREDUCTION OF Zn(II) IONS

Grazyna DALMATA

Faculty of Chemistry, M. Curie-Sklodowska University, 20031 Lublin, Poland;
e-mail: jszar@hermes.umcs.lublin.pl

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A two-step reduction of Zn(II) ions at the dropping mercury electrode in 1 M NaClO₄/0.001 M HClO₄ in the presence of *N,N'*-dialkylthioureas was examined in wide potential and frequency ranges, using the impedance method. The rate constant of the first electron transfer increases with increasing concentration of *N,N'*-dialkylthioureas, whereas that of the second electron transfer depends largely on the double layer effects, particularly, on the orientation of molecules on the electrode surface.

Key words: Catalytic activity; Two-step electroreduction of Zn(II) ions; *N,N'*-Dimethylthiourea; *N,N'*-Diethylthiourea; *N,N'*-Diisopropylthiourea; *N,N'*-Dibutylthiourea; Electrochemistry; Polarography; Dropping mercury electrode.

The electroreduction of Zn(II) ions at mercury electrode is accelerated in the presence of adsorbed nonelectroactive species¹⁻⁸. The importance of this effect can be deduced from the compilation of standard rate constants made by Tamamushi and Tanaka^{9,10} for many electrode reactions and compositions of supporting electrolytes. Various models have been published¹¹⁻¹⁹ describing specific interactions in the inner double layer between the adsorbed species and the reactant in an electrode reaction. However, interpretation of the experimental results in terms of such a model cannot be done only by correlation of double layer data with the standard rate constant. The reason is the increasing evidence²⁰⁻²⁶ that the electroreduction of Zn(II) ions proceeds *via* elementary reaction steps, either single electron transfer or chemical conversions. Each of these steps may be influenced individually by the double layer structure.

It was found earlier⁶ that dialkylthioureas increase the standard rate constant of Zn(II) electroreduction in 1 M NaClO₄. Increasing the size of the alkyl groups causes an increase in their adsorption on mercury which, in turn, causes an increase in the Zn(II) electroreduction rate.

This paper presents the study of the effect of *N,N'*-dialkylthioureas on kinetic parameters of the individual steps rather than on the overall kinetic parameters, with the aim of better understanding the reaction mechanism and the nature of the catalytic effect.

EXPERIMENTAL

The experiments were performed in a three-electrode cell with a dropping mercury electrode constructed according to Randles²⁷ as a working electrode, an external saturated NaCl calomel electrode (SSCE) as a reference electrode and the platinum spiral as a counter 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 Merck analytical grade chemicals. The solution of $1 \cdot 10^{-3}$ M Zn(II) was prepared by dissolving zinc oxide in a small excess of perchloric acid. In order to avoid hydrolysis of Zn(II) the excess was chosen to make the final solution 0.001 M H⁺. The catalytic activity of *N,N'*-dimethylthiourea (DMTU), *N,N'*-diethylthiourea (DETU), *N,N'*-diisopropylthiourea (DIPTU) and *N,N'*-dibutylthiourea (DBTU) were studied in the concentration ranges 0.0005–0.01, 0.0005–0.02, 0.0001–0.001 and 0.0001–0.00075 mol l⁻¹ (limited by their solubilities). Only freshly prepared solutions of the dialkylthioureas were used.

The solutions were deaerated using nitrogen which had been passed through a vanadous sulfate solution and presaturated with the investigated solvent. The gas was passed over the solution during the measurements. All measurements were carried out at 298 ± 1 K.

DC polarograms were obtained using a polarograph PA-4 (Laboratorni pristroje, Prague, Czech Republic). The impedance measurements were carried out with a 9121 FR Analyser and 9131 Electrochemical Interface (Atlas–Sollich Gdansk, Poland). Chronocoulometric experiments were performed using a static mercury drop electrode (Laboratorni pristroje, Prague, Czech Republic) employing a Model 270 Electrochemical Analysis System (AG & G PARC Princeton (NJ), U.S.A.).

RESULTS AND DISCUSSION

Double Layer Analysis

Curves of the differential capacitance as a function of potential for several concentrations of the studied *N,N'*-dialkylthioureas were presented in earlier papers^{6,28}. Calculations of the double layer parameters for the adsorption are based on the data collected from these curves. Details are described elsewhere²⁹.

Figures 1 and 2 present the surface excess of dialkylthioureas plotted *versus* the potential in the reaction plane ϕ^r .

To calculate the potential in the reaction plane, it was assumed that the reaction takes place at the outer Helmholtz plane (oHp), where the potential can be calculated by subtracting the diffuse layer potential ϕ_{2-s}

$$\phi^r = \phi^{oHp} = E - \phi_{2-s} \quad (I)$$

The latter is

$$\phi_{2-s} = \frac{2RT}{F} \sin h^{-1} \left(\frac{\sigma^M + \sigma^I}{11.73} \right) \quad (2)$$

for 1 M NaClO₄ at 298 K, where σ^M is the electrode charge density and σ^1 the charge due to specifically adsorbed ClO₄⁻ (taken from the study of Parsons and Payne³⁰).

Earlier it was argued³¹ that the hydrated Zn(II) ion is larger than the Na(I) ion, and therefore the plane of the closest approach for Zn(II) is more remote from the electrode than the oHp. Andreu *et al.*²⁵ proved that the reaction plane is 0.28 nm farther from the electrode, which corresponds to the diameter of an H₂O molecule, d_{H_2O} . The potential at the reaction site was calculated²⁶ from

$$\phi^r = \phi^{oHp} + 0.28 = E + \frac{4RT}{F} \tan h^{-1} \left[\tan h / \frac{F\phi_{2-s}}{4RT} / \exp(-kd_{H_2O}) \right] \quad (3)$$

with $k = 3.29 \cdot 10^7 \text{ cm}^{-1}$ for 1 M NaClO₄ at 298 K.

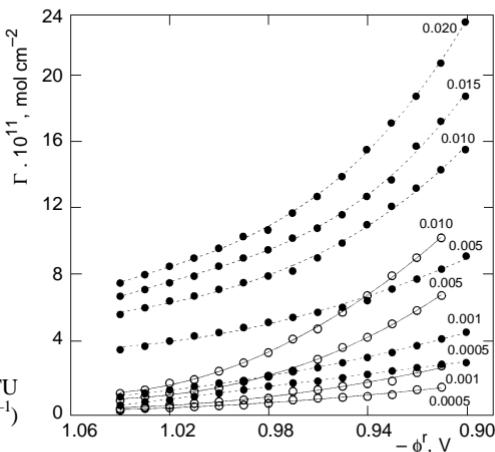


FIG. 1

Surface excess Γ of DMTU (solid line) and DETU (dotted line) vs ϕ^r at various concentrations (mol l⁻¹) indicated for each curve

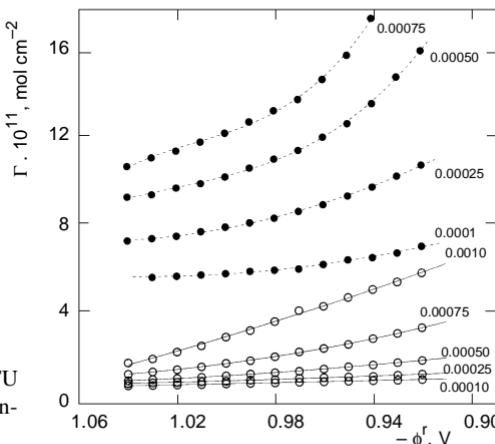


FIG. 2

Surface excess of DIPTU (solid line) and DBTU (dotted line) vs ϕ^r at various concentrations (mol l⁻¹) indicated for each curve

Polarographic Measurements

From the limiting current in the DC polarograms, the diffusion coefficient D_0 of Zn(II) ions was derived. Details are described elsewhere⁶. The diffusion coefficient of Zn(II) ions in 1 M NaClO₄/0.001 M HClO₄ was found to be $6.6 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and independent of the solution composition for the concentration range of the dialkylthioureas considered. The diffusion coefficient $D_R = 1.67 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for Zn in mercury was selected from literature³².

Chronocoulometric Detection of Zn(II) Coadsorption

To find out whether or not Zn(II) can be accumulated in the surface layer by the interaction with the adsorbed dialkylthioureas molecules, chronocoulometric measurements of the maximal charge Q_d of Zn(II) electroreduction as a function of the integration time (t_p) were carried out in 0.005 M DMTU and DETU or 0.0005 M DIPTU and DBTU in 1 M NaClO₄/0.001 M HClO₄.

The charge Q_d of Zn(II) electroreduction was measured at potential of -1.00 V (refs^{34,35}). The plot of Q_d vs $t_p^{1/2}$ was linear and intersected the origin of coordinates after subtraction of the double layer charge, recorded for blank solutions. This indicates that under such conditions, the cathodic reduction of Zn(II) is limited by diffusion and the induced adsorption of Zn(II), if any, is within the limits of experimental error.

The Rate of Electroreduction

The complex impedance data were collected at 21 frequencies in the range 200–50 000 Hz within the Faradaic potential region in 10 mV intervals. The frequency analysis was performed in a usual way^{33,36}. The reversible half-wave potential $E_{1/2}^r$ was taken from ref.⁶. An optimum value of $E_{1/2}^r = -0.985 \text{ V}$ was formed from the DC potential dependence of charge-transfer resistance³³. It is interesting to point out that $E_{1/2}^r$ was found to be independent on the concentration of dialkylthioureas. These results indicate the absence of Zn-dialkylthiourea complexes in the solution.

The values of apparent rate constants k_f were obtained from the charge-transfer resistance²⁵. The details are described elsewhere²⁹. The true rate constants k_f^t can be obtained from Eq. (4) (ref.²⁶):

$$k_f(\phi^r) = k_f^t(\phi^r) \exp \left[-(E - \phi^r) \frac{nF}{RT} \right]. \quad (4)$$

The values of the true rate constants of electroreduction of Zn(II) ions plotted as $\ln k_f^t$ obtained at various dialkylthioureas concentrations as a function of the potential ϕ^r are presented in Figs 3–6. From curves in Figs 3–6 it follows:

- the dependences $k_f^t = f(\phi^r)$ are not rectilinear and the slope of the curves changes with the potential and the concentrations of dialkylthioureas;
- the accelerating effect due to the studied dialkylthioureas is larger at the most negative potentials and seems to be absent or even turned into inhibition in the most positive potential region;
- the values k_f^t increase with increasing in DMTU and DIPTU concentrations (Figs 3, 5);
- the true rate constants (Fig. 4) increase with the rising concentration of DETU from 0.0005 to 0.01 mol l⁻¹. For higher DETU concentrations, the regularity is observed only at more negative potentials, while at positive potentials DETU catalytic activity decreases;
- the true rate constants for Zn(II) ion electroreduction increase with increasing DBTU concentration (Fig. 6) only for $\phi^r < -0.99$ V. At more positive potentials, the catalytic activity of DBTU on concentration is inverted.

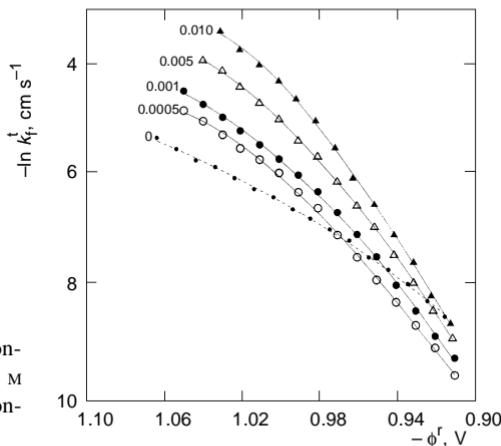


FIG. 3

The natural logarithms of the corrected rate constants vs ϕ^r for the Zn(II)/Zn(Hg) system in 1 M NaClO₄/0.001 M HClO₄ at various DMTU concentrations (mol l⁻¹) indicated for each curve

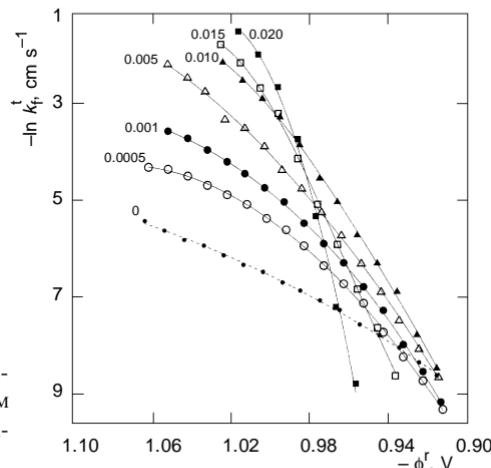


FIG. 4

The natural logarithms of the corrected rate constants vs ϕ^r for the Zn(II)/Zn(Hg) system in 1 M NaClO₄/0.001 M HClO₄ at various DETU concentrations (mol l⁻¹) indicated for each curve

As shown earlier⁶, the drop of DETU or DBTU catalytic activity with rising concentration is caused by the reorientation of DETU or DBTU molecules on the mercury surface in the range of Zn(II) reduction potentials.

Analysis in Terms of the EE Mechanism

Assuming that the charge transfer proceeds *via* two consecutive one-electron transfer steps^{25,26}, the first electron transfer is rate determining $k_f^t = k_i^t$ at the most negative potentials. At more positive potentials, the overall rate is determined by both steps simultaneously

$$\frac{1}{k_f^t} = \frac{1}{k_i^t} + \frac{K_1}{k_2^t} . \quad (5)$$

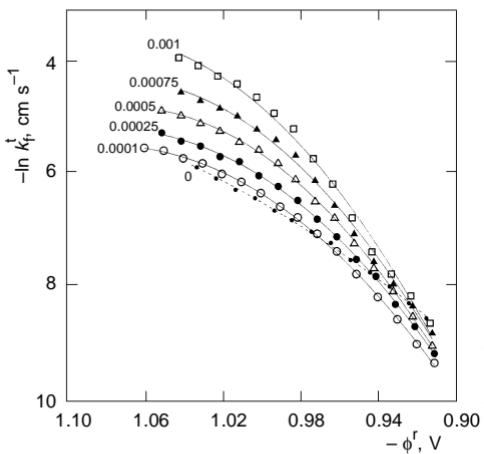


FIG. 5

The natural logarithms of the corrected rate constants vs ϕ^r for the Zn(II)/Zn(Hg) system in 1 M NaClO₄/0.001 M HClO₄ at various DIPTU concentrations (mol l⁻¹) indicated for each curve

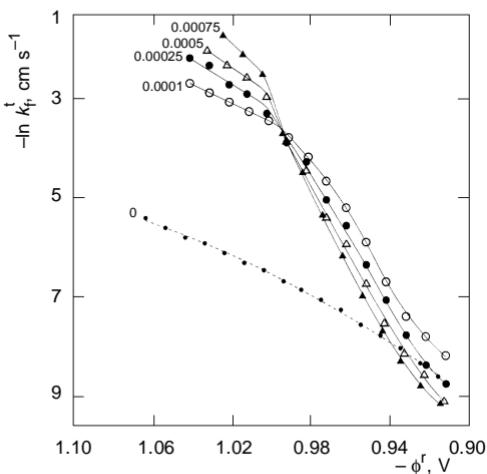


FIG. 6

The natural logarithms of the corrected rate constants vs ϕ^r for the Zn(II)/Zn(Hg) system in 1 M NaClO₄/0.001 M HClO₄ at various DBTU concentrations (mol l⁻¹) indicated for each curve

The individual standard rate constants of the electroreduction of Zn(II) in 1 M $\text{NaClO}_4/0.001\text{ M HClO}_4$ corrected for the double layer are $k_{s1}^t = 0.97 \cdot 10^{-3} \text{ cm s}^{-1}$ and $k_{s2}^t = 5 \cdot 10^{-2} \text{ cm s}^{-1}$. These values are in agreement with the literature data^{25,26}. Table I presents the values of individual rate constants of Zn(II) electroreduction extrapolated to the formal potential $E_f^0 = -0.991\text{ V}$ for various concentrations of studied dialkylthioureas.

The presence of dialkylthioureas on the electrode surface gives rise of the rate of the first electron transfer with the concentration of studied dialkylthioureas. The rate constants of the second electron transfer decrease at the lowest studied concentrations of DMTU, DETU or DIPTU and then increase with rising concentrations to values exceeding corresponding rate constants of the first electron transfer. However, in presence of 0.0001 M DBTU, k_{s2}^t increases rapidly and then decreases with further rising of DBTU concentration.

In the presence of 0.015 to 0.020 M DETU, the rate constant of the second electron transfer also decreases. Such changes in individual standard rate constants with increasing dialkylthioureas concentrations indicate that the reorientation of the accelerating substance molecules on the mercury surface affects only the second electron transfer rate.

TABLE I

Corrected individual rate constants of the Zn(II) ion electroreduction extrapolated to the E_f^0 , and surface excesses at the E_f^0 in 1 M $\text{NaClO}_4/0.001\text{ M HClO}_4$ solutions for various concentrations of dialkylthioureas

$C \cdot 10^3$ mol l ⁻¹	$\Gamma \cdot 10^{11}$ mol cm ⁻²	$k_{s1}^t \cdot 10^3$ cm s ⁻¹	$k_{s2}^t \cdot 10^2$ cm s ⁻¹	$C \cdot 10^3$ mol l ⁻¹	$\Gamma \cdot 10^{11}$ mol cm ⁻²	$k_{s1}^t \cdot 10^3$ cm s ⁻¹	$k_{s2}^t \cdot 10^2$ cm s ⁻¹
0	—	0.97	5.0				
DMTU				DIPTU			
0.5	0.8	1.42	2.53	0.10	0.9	1.36	2.66
1.0	1.3	1.87	4.06	0.25	1.1	1.80	3.34
5.0	2.5	3.55	6.30	0.50	1.4	2.85	3.70
10.0	4.2	6.50	11.32	0.75	2.3	4.09	5.41
DETU				DBTU			
				1.00	4.2	6.74	8.15
0.5	1.8	4.80	3.23				
1.0	2.5	6.34	6.79	0.10	6.1	19.06	22.17
5.0	5.7	11.11	12.67	0.25	8.7	21.28	10.45
10.0	8.5	21.49	26.70	0.50	10.7	22.82	7.28
15.0	10.2	30.19	9.01	0.75	13.3	27.87	6.38
20.0	11.7	37.63	3.28				

Correlation of k_f^t with Specific Adsorption

The catalytic activity of dialkylthioureas can be better described on a k_f^t or $\ln k_f^t$ (at given Γ) vs ϕ^r plot such as those in Figs 7–10. These plots were constructed using functions $\Gamma = f(\phi^r)$ and $\ln k_f^t = f(\phi^r)$.

They show a definitely a more regular behaviour as compared to the plots at constant concentrations in Figs 3–6. The relations $k_f^t = f(\Gamma)$ at a given ϕ^r presented in Figs 11–14 are quite interesting. They are straight lines which have a point of intersection on the horizontal axis at the “value” Γ of DMTU $-0.5 \cdot 10^{-11}$ mol cm $^{-2}$ (Fig. 11) and Γ of DIPTU $-0.75 \cdot 10^{-11}$ mol cm $^{-2}$ (Fig. 13). It seems that k_f^t values of the Zn(II) ion electroreduction in the presence of DMTU and of DIPTU vary according to Eq. (6)

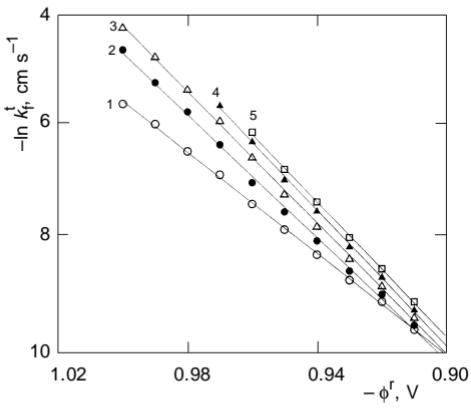


FIG. 7

The potential dependence of the natural logarithm of the corrected rate constants of the Zn(II) reduction at the fixed surface excess of DMTU (10^{-11} mol cm $^{-2}$) indicated for each curve

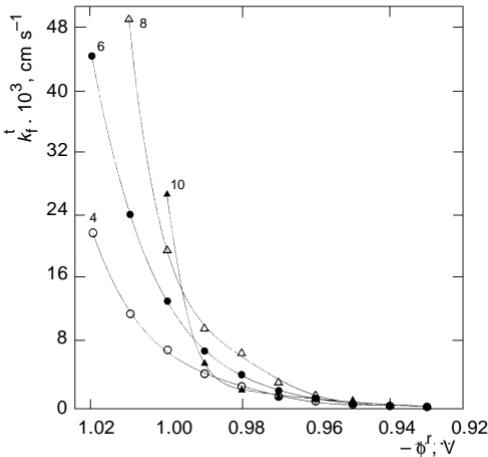


FIG. 8

The potential dependence of the corrected rate constants of the Zn(II) reduction at the fixed surface excess of DETU (10^{-11} mol cm $^{-2}$) indicated for each curve

$$k_f^t(\phi^r)/k_f^{0,t}(\phi^r) = 1 + A \Gamma , \quad (6)$$

where $k_f^{0,t}(\phi^r)$ denotes the true rate constant determined at a certain potential in the absence of DMTU or DIPTU. The values of A $1.8 \cdot 10^{11}$ for DMTU and $1.3 \cdot 10^{11}$ for DIPTU are comparative measures of catalytic activities of these compounds. The relation (6) was obtained earlier in a paper by Souto *et al.*³⁷ which concerns the catalytic effect of thiourea on the electroreduction of Cd(II) ions, and also in the papers dealing with the Zn(II) ion electroreduction acceleration^{29,38}.

The relation $k_f^t = f(\Gamma)$ seems to be of particular interest in the presence of DETU (Fig. 12). At $-0.99 \text{ V} < \phi^r < -0.96 \text{ V}$ and $\Gamma \leq 8 \cdot 10^{-11} \text{ mol cm}^{-2}$, a linear increase in k_f^t with increasing Γ of DETU is observed. The straight lines have a point of intersection on the

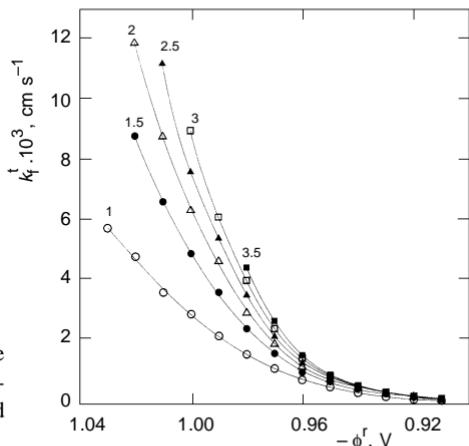


FIG. 9
The potential dependence of the corrected rate constants of the Zn(II) reduction at the fixed surface excess of DIPTU ($10^{-11} \text{ mol cm}^{-2}$) indicated for each curve

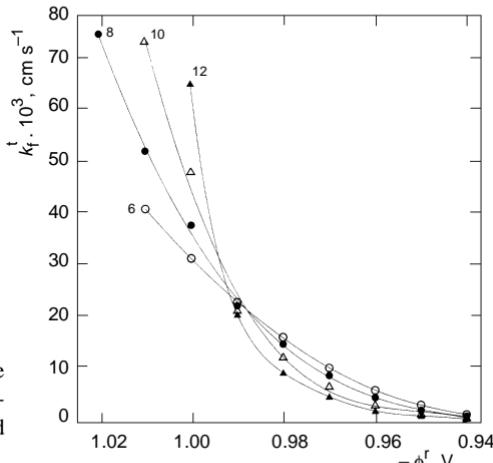


FIG. 10
The potential dependence of the corrected rate constants of the Zn(II) reduction at the fixed surface excess of DBTU ($10^{-11} \text{ mol cm}^{-2}$) indicated for each curve

horizontal axis at the Γ value of $\text{DETU } 1.5 \cdot 10^{-11} \text{ mol cm}^{-2}$, however, at $\Gamma > 8 \cdot 10^{-11} \text{ mol cm}^{-2}$, k_f^t values of Zn(II) electroreduction decrease with increasing DETU surface excess. The relations are also straight lines intersecting the horizontal axis at the Γ value of $\text{DETU } 12 \cdot 10^{-11} \text{ mol cm}^{-2}$. Such a course of the $k_f^t = f(\Gamma)$ relation indicates that the reorientation of DETU molecules on the mercury surface takes place at $\Gamma \geq 8 \cdot 10^{-11} \text{ mol cm}^{-2}$. This relation is different for DBTU. With increasing DBTU surface excess (Fig. 14), the k_f^t decrease for $\phi^r \geq -0.99 \text{ V}$, but at more negative potentials the corrected rate constants of the electroreduction of Zn(II) ions increase rapidly.

As relations $k_f^t = f(\Gamma)$ at a given ϕ^r are always straight lines, the "bridging model" (ref.¹¹) can be accepted for Zn(II) electroreduction acceleration by all studied dialkylthioureas. The results may suggest that the bridging enhances the rate of all steps of the Zn(II) ion reduction mechanism.

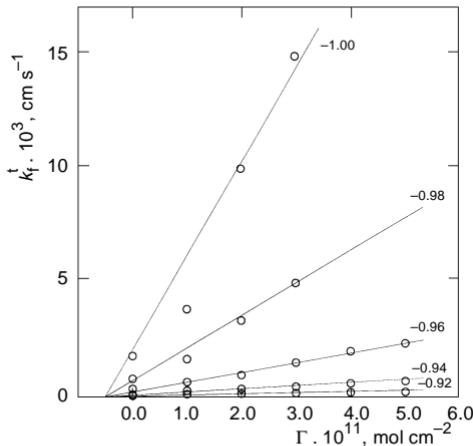


FIG. 11
Corrected rate constant of the Zn(II) reduction vs the surface excess of DMTU at constant ϕ^r (V) indicated for each curve

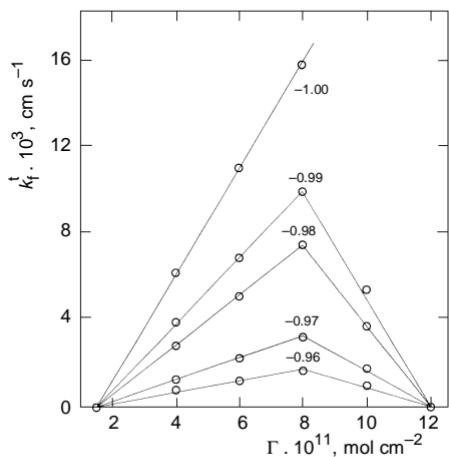


FIG. 12
Corrected rate constant of the Zn(II) reduction vs the surface excess of DETU at constant ϕ^r (V) indicated for each curve

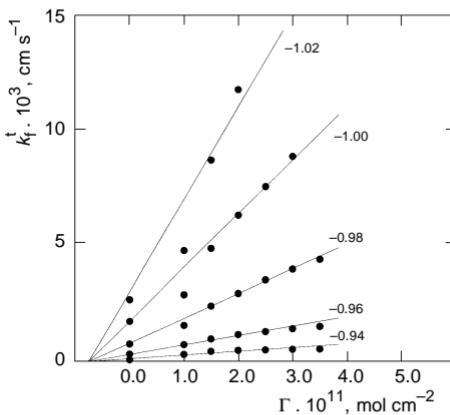


FIG. 13

Corrected rate constant of the Zn(II) reduction *vs* the surface excess of DIPTU at constant ϕ^r (V) indicated for each curve

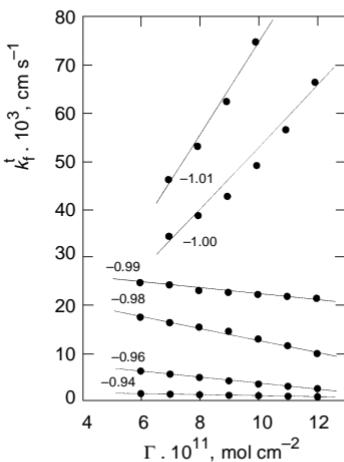


FIG. 14

Corrected rate constant of the Zn(II) reduction *vs* the surface excess of DBTU at constant ϕ^r (V) indicated for each curve

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