

**Description of the mixed polyethyleneglycoles  
– N,N'-dimethylthiourea adsorption layer on  
a mercury electrode and its effect  
on the electroreduction of Zn(II)**

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The properties of the mixed adsorption layers on a mercury electrode in the systems: 1 mol L<sup>-1</sup> NaClO<sub>4</sub> – polyethyleneglycoles of a mean molecular weight: 400 or 10000-N,N'-dimethylthiourea were investigated. The systems were characterized by the measurements of differential capacity, zero charge potential and surface tension at this potential. The data were analyzed to obtain the surface pressure and relative surface excess of N,N'-dimethylthiourea as a function of charge and bulk concentration of the studied compounds. The standard Gibbs energy of adsorption  $\Delta G^{\circ}$  and parameter B obtained from the virial isotherm were compared. In the range of more negative potentials, a mixed adsorption layer was found by investigating the kinetics of the reduction of Zn(II) ion as a pilot ion. Changes of the standard value of the constant rate  $k_s^{app}$  obtained by the cyclic voltammetric method in the range of four orders of size indicate great dynamics of the process. It was found that in the solutions containing PEG 400 or PEG 10000 in the concentration corresponding to the same number of mers the adsorption properties are a function of both molecular mass and molecule structure.

## 1. INTRODUCTION

The adsorption of organic sulfur compounds has been widely investigated. Many of these compounds act as corrosion inhibitors. Due to strong adsorption across the entire surface of metal they may at the same time inhibit anodic and cathodic processes. The inhibitor develops a mono- or polymolecular coating whose attributes depend on the energy of its bonding as well as its density. Also some of the surfactants belong to the group of efficient corrosion inhibitors. The use of a mixture of corrosion inhibitors often improves their efficiency

resulting in synergistic effects, however, an antagonistic effect is also possible [1].

Given the experimental data for adsorption of surface-active substances on different metals, it appears that the mechanism of creation of mixed adsorption layers on mercury will be a subject to similar rules. Obtaining insight into the laws governing the formation of mixed adsorption layers and their properties may constitute a further step on the way towards their more complete application.

In this paper, the selection of organic substances is based on their inhibiting and accelerating effects on Zn(II) ions electroreduction. The paper presents the results of studies on coadsorption of polyethyleneglycoles of the mean molecular weight: 400 (PEG 400) or 10000 (PEG 10000) as typical inhibitors of electrode processes [2] and N,N'-dimethylthiourea (DMTU) as the substance accelerating Zn(II) ions electroreduction [3]. Polyethyleneglycols are nonionic surfactants, readily soluble in water. This is a result of hydrogen bond formation between the ether atoms of oxygen PEG and water [4]. DMTU was chosen not only because of its accelerating activity on Zn(II) ions electroreduction but also of its characteristic adsorption properties on mercury due to the specific interaction of DMTU sulfur atom with the mercury surface.

The adsorption equilibrium within the area of the adsorption potential similar to the potential of the zero charge ( $E_z$ ) was examined using the classical thermodynamic methodology: the adsorption parameters of the double layer were determined using the virial isotherm. The influence of mixed adsorption layers on the Zn(II) ions reduction kinetics constitutes a new, original research methodology which enables a description of the properties of adsorption layers at the potentials which are distant from  $E_z$ , and by those taken close to the value of the corrosion potentials of non-precious metals.

## 2. EXPERIMENTAL

The study of adsorption relating to the formation of mixed adsorption layers was conducted in the following system: constant concentration PEG ( $10^{-4}$  mol L<sup>-1</sup> or  $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), and increasing concentration of DMTU from  $5 \cdot 10^{-4}$  mol L<sup>-1</sup> to 0.05 mol L<sup>-1</sup>. The maximum concentration of DMTU results from its solubility in the studied systems. Additionally, the systems containing  $2.5 \cdot 10^{-3}$  mol L<sup>-1</sup> PEG 400 were also used to show the effect of PEG 400 and PEG 10000 polymer structures on adsorption of DMTU and kinetics of Zn(II) ion reduction. The chosen concentration of PEG 400 corresponds to a number of mers  $-\text{CH}_2-\text{CH}_2-\text{O}-$  included in the solution  $10^{-4}$  mol L<sup>-1</sup> PEG 10000.

Polarographic measurements were carried out using the polarograph PA-4 (Laboratni Pstroje, Prague). Cyclic voltammetric experiments were carried employing Model 270 Electrochemical Analysis System (EG & G PARC), and

an IBM 486 PC computer equipped with a data translation interface. A static mercury drop electrode (SMDE) was used, produced either by PARC Model 303 (EG & G PARC) or by Laboratorni Pristroje, Prague.

The double layer capacity was measured at the frequency of 800 Hz using the 9121 FR Analyser and 9131 Electrochemical Interface with appropriate program (Atlas Sollich, Gdańsk, Poland). A controlled – growth mercury drop electrode (CGME) MTM Poland was also used. As the reference electrode, Ag/AgCl with saturated NaCl was used. The reference electrode was connected to the electrolytic cell via an intermediate filled with the solution to be investigated. The counter electrode was a platinum wire. A few measurements were also carried out at 200 – 2000 Hz in order to check the frequency dependence of the results. In the potential range studied capacity was found to be frequency independent. This was thought to suggest that the experimental capacities are, in fact, equilibrium values.

The potential of zero charge  $E_z$  was measured using the streaming mercury electrode [5,6]. Interfacial tension at  $E_z$  was measured by the maximum bubble pressure method after Schiffrin [7].

The approximate diffusion coefficients of Zn(II) in the examined solutions were calculated from limiting currents using the Ilković equation. The polarographic wave of Zn(II) in  $0.1 \text{ mol L}^{-1} \text{ KNO}_3$  with the value of the Zn(II) diffusion coefficient  $D = 6.9 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [8] was used as a standard. The value of diffusion coefficient of zinc in mercury which is required for further calculations was taken from the literature [9] as equal to  $1.67 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . The formal potentials  $E_f^o$  of the reduction of Zn(II) were obtained from cyclic voltammetry with the reproducibility  $\pm 0.002 \text{ V}$ . The apparent rate constants for the investigated systems were calculated from the cyclic voltammetry measurements by the method described by Nicholson and Shain [10] using the equations for irreversible processes or by Nicholson's method [11] for quasi – reversible processes.

The measurements were carried out in  $1 \text{ mol L}^{-1} \text{ NaClO}_4$  solution of pH 5 at  $298 \pm 1 \text{ K}$ . The solutions were prepared from freshly twice distilled water and analytical grade chemicals (Merck) and deoxygenated by high purity nitrogen. This gas was passed over the solution during the measurements. Mercury was purified and twice distilled.

### 3. RESULTS AND DISCUSSION

**Adsorption of DMTU.** The adsorption of DMTU on the mercury electrode from the examined mixtures was investigated on the basis of the measurements of differential capacity. Figures 1–3 present  $C - E$  curves chosen for the base solutions and those containing DMTU at various concentrations. The differential capacity curves obtained in  $1 \text{ mol L}^{-1} \text{ NaClO}_4$  with the addition of increas-

ing PEG amounts are characterized by a significant decrease of differential capacity towards the basic electrolyte typical of inhibitors. The potential range in which this decrease occurs is wide from 0.2 V to  $-1.5$  V for  $5 \cdot 10^{-4}$  mol L $^{-1}$  PEG 400 but for PEG 10000 this range is even wider.

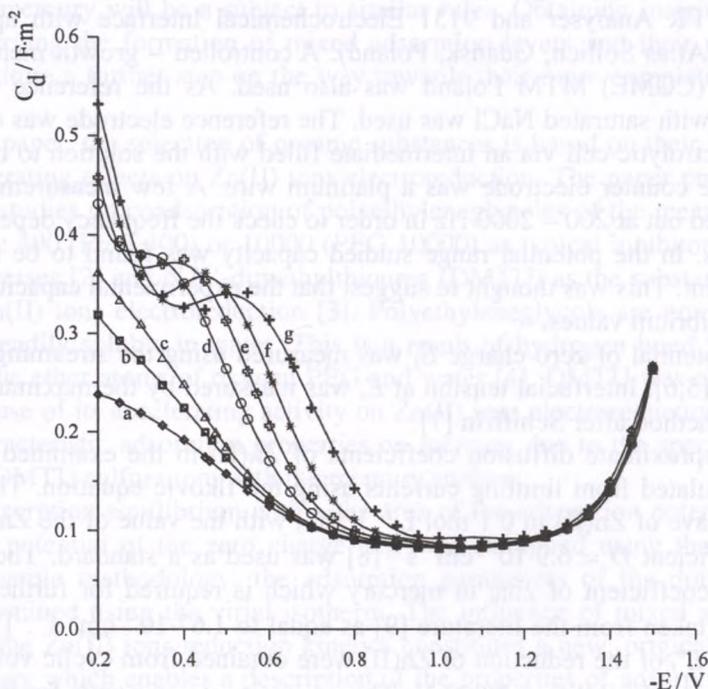


Figure 1. Differential capacity curves of Hg/ 1 mol L $^{-1}$  NaClO $_4$  +  $5 \cdot 10^{-4}$  mol L $^{-1}$  PEG 400 for different contents of DMTU: (a)  $c_{\text{DMTU}} = 0$  mol L $^{-1}$ , (b)  $5 \cdot 10^{-4}$  mol L $^{-1}$ , (c)  $1 \cdot 10^{-3}$  mol L $^{-1}$ , (d)  $5 \cdot 10^{-3}$  mol L $^{-1}$ , (e)  $1 \cdot 10^{-2}$  mol L $^{-1}$ , (f)  $2 \cdot 10^{-2}$  mol L $^{-1}$ , (g)  $5 \cdot 10^{-2}$  mol L $^{-1}$

The differential capacity decrease is also greater for PEG 10000 than for PEG 400 and the increase of PEG 10000 concentration has an insignificant effect on the differential capacity. Introduction of DMTU into the PEG solution always causes the increase of differential capacity. The area of potentials in which the increase takes place becomes wider with the increase of concentration of DMTU. At suitably higher concentrations of DMTU on the differential capacity curves there appears a characteristic "hump" typical of adsorption of large surface active anions or a polar neutral substance. It should be emphasized that this "hump" is larger and sharper for PEG 10000 than PEG 400. According to Parsons [12], the appearance of characteristic capacity hump may be a consequence of the change of the interactions (especially electrostatic interactions) in the adsorbed layer.

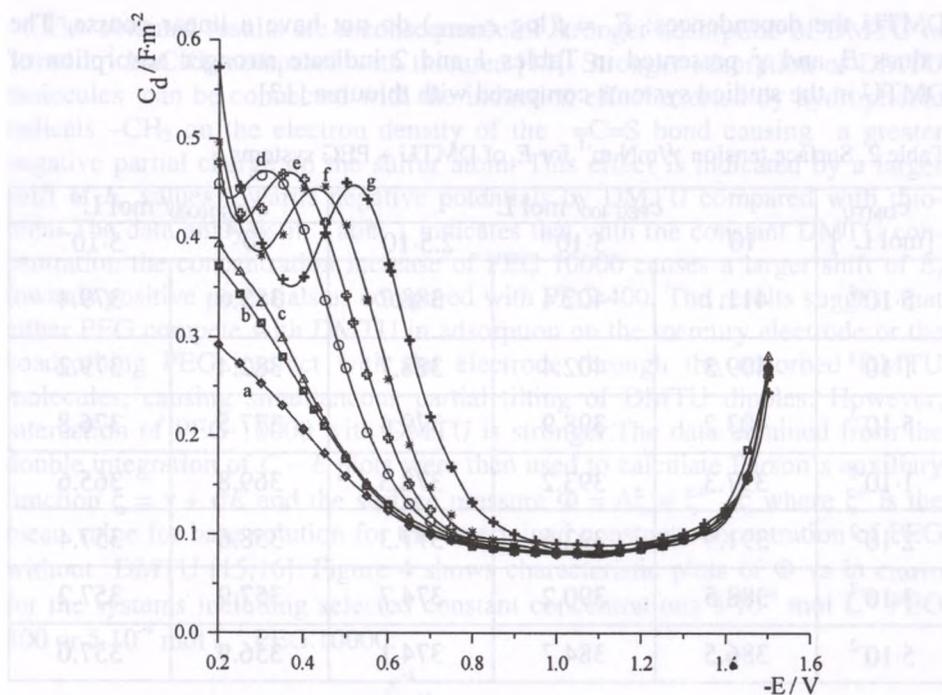


Figure 2. Differential capacity curves of Hg/ 1 mol L<sup>-1</sup> NaClO<sub>4</sub> + 2.5 · 10<sup>-3</sup> mol L<sup>-1</sup> PEG 400 for different contents of DMTU as indicated in Figure 1

Table 1. Potential of the zero charge  $-E_z/V$  vs Ag/AgCl electrode for DMTU + PEG systems

$C_{\text{DMTU}}$ [mol L <sup>-1</sup> ]	$C_{\text{PEG 400}}/\text{mol L}^{-1}$			$C_{\text{PEG 10000}}/\text{mol L}^{-1}$	
	10 <sup>-4</sup>	5 · 10 <sup>-4</sup>	2.5 · 10 <sup>-3</sup>	10 <sup>-4</sup>	5 · 10 <sup>-4</sup>
5 · 10 <sup>-4</sup>	0.488	0.436	0.395	0.442	0.371
1 · 10 <sup>-3</sup>	0.514	0.445	0.403	0.456	0.381
5 · 10 <sup>-3</sup>	0.574	0.504	0.453	0.479	0.425
1 · 10 <sup>-2</sup>	0.605	0.540	0.486	0.497	0.447
2 · 10 <sup>-2</sup>	0.633	0.578	0.521	0.527	0.464
3 · 10 <sup>-2</sup>	0.649	0.600	0.542	0.545	0.477
5 · 10 <sup>-2</sup>	0.684	0.628	0.575	0.578	0.494

Both adsorbable species: PEG and DMTU may interact with each other, leading to the formation of a more compact structure of the adsorbed layer. As all obtained curves  $C - E$  do not converge at sufficiently negative potentials with the corresponding curve for 1 mol L<sup>-1</sup> NaClO<sub>4</sub>, the capacity against potential data were numerically integrated from the point of  $E_z$ . The integration constants are presented in Tables 1 and 2. Apart from the system 10<sup>-4</sup> mol L<sup>-1</sup> PEG 400 +

DMTU the dependences:  $E_z = f(\log c_{\text{DMTU}})$  do not have a linear course. The values  $E_z$  and  $\gamma^*$  presented in Tables 1 and 2 indicate stronger adsorption of DMTU in the studied systems compared with thiourea [13].

Table 2. Surface tension  $\gamma^*/\text{mN}\cdot\text{m}^{-1}$  for  $E_z$  of DMTU + PEG systems

$c_{\text{DMTU}}$ [mol L <sup>-1</sup> ]	$c_{\text{PEG 400}}/\text{mol L}^{-1}$			$c_{\text{PEG 10000}}/\text{mol L}^{-1}$	
	10 <sup>-4</sup>	5·10 <sup>-4</sup>	2.5·10 <sup>-3</sup>	10 <sup>-4</sup>	5·10 <sup>-4</sup>
5·10 <sup>-4</sup>	411.1	402.4	388.7	383.6	379.4
1·10 <sup>-3</sup>	409.3	402.4	388.7	382.4	379.2
5·10 <sup>-3</sup>	403.2	398.9	379.4	377.5	376.8
1·10 <sup>-2</sup>	397.3	393.2	378.3	369.8	365.6
2·10 <sup>-2</sup>	391.9	392.6	377.3	358.6	357.4
3·10 <sup>-2</sup>	388.5	390.2	374.7	357.9	357.2
5·10 <sup>-2</sup>	386.5	384.7	374.1	356.9	357.0

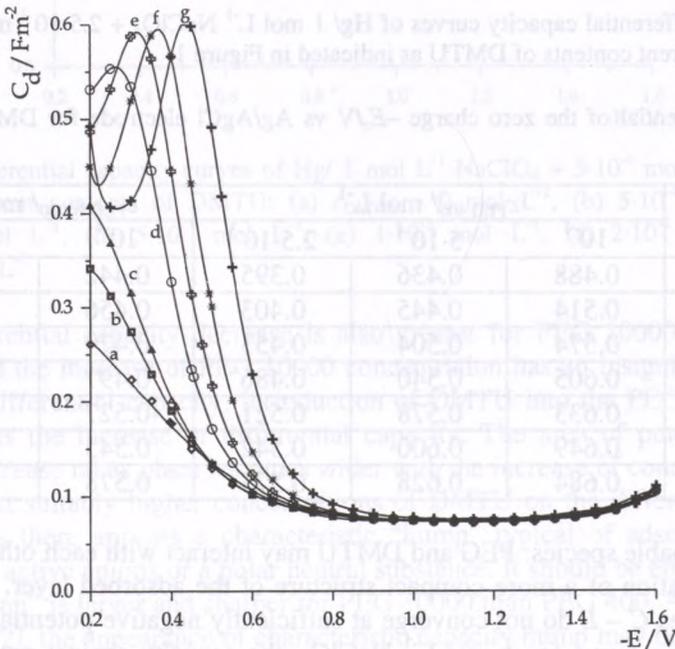


Figure 3. Differential capacity curves of Hg/1 mol L<sup>-1</sup> NaClO<sub>4</sub> + 5·10<sup>-4</sup> mol L<sup>-1</sup> PEG 10000 for different contents of DMTU as indicated in Figure 1

The obtained results are a consequence of stronger adsorption of DMTU in  $1 \text{ mol L}^{-1} \text{ NaClO}_4$  compared with thiourea [14]. Stronger adsorption of DMTU molecules can be connected with the induction effect exerted by hydrophobic radicals  $-\text{CH}_3$  on the electron density of the  $=\text{C}=\text{S}$  bond causing a greater negative partial charge on the sulfur atom. This effect is indicated by a larger shift of  $E_z$  values towards negative potentials by DMTU compared with thiourea. The data analysis in Table 1 indicates that with the constant DMTU concentration the concentration increase of PEG 10000 causes a larger shift of  $E_z$  towards positive potentials as compared with PEG 400. The results suggest that either PEG compete with DMTU in adsorption on the mercury electrode or the coadsorbing PEG interact with the electrode through the adsorbed DMTU molecules, causing simultaneous partial tilting of DMTU dipoles. However, interaction of PEG 10000 with DMTU is stronger. The data obtained from the double integration of  $C - E$  plots were then used to calculate Parson's auxiliary function  $\xi = \gamma + \sigma E$  and the surface pressure  $\Phi = \Delta\xi = \xi^o - \xi$  where  $\xi^o$  is the mean value for base solution for the determined constant concentration of PEG without DMTU [15,16]. Figure 4 shows characteristic plots of  $\Phi$  vs  $\ln c_{\text{DMTU}}$  for the systems including selected constant concentrations  $5 \cdot 10^{-4} \text{ mol L}^{-1}$  PEG 400 or  $5 \cdot 10^{-4} \text{ mol L}^{-1}$  PEG 10000.

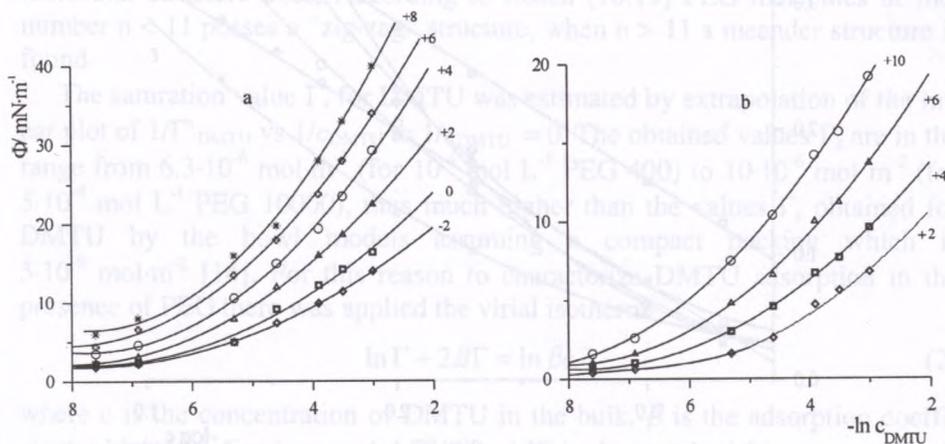


Figure 4. Surface pressure as a function of DMTU concentration in the bulk for solutions including: (a)  $5 \cdot 10^{-4} \text{ mol L}^{-1}$  PEG 400, (b)  $5 \cdot 10^{-4} \text{ mol L}^{-1}$  PEG 10000, the electrode charges ( $\sigma_M$  in  $10^{-2} \text{ C} \cdot \text{m}^{-2}$ ) indicated by each curve

The positive values  $\Phi$  were obtained for the studied systems most frequently in the range  $-2 \leq \sigma_M \leq +8 \mu\text{C} \cdot \text{cm}^{-2}$ , exceptionally for the solution containing  $5 \cdot 10^{-4} \text{ mol L}^{-1}$  PEG 10000 this range is  $+2 \leq \sigma_M \leq +8 \mu\text{C} \cdot \text{cm}^{-2}$ . The adsorption of DMTU has been estimated according to the Gibbs adsorption equation by the differentiation of  $\Phi$  vs  $\ln c$  curves. The relative surface excess of DMTU was

calculated from the following equation [17]:

$$\Gamma' = -\frac{1}{RT} \left( \frac{\partial \Phi}{\partial \ln c_{\text{DMTU}}} \right)_{\sigma, c_{\text{PEG}}} \quad (1)$$

where  $c_{\text{DMTU}}$  is the bulk concentration of DMTU. In writing equation (1), it is assumed that the mean activity coefficients of DMTU, PEG and  $\text{NaClO}_4$  do not change with the change in DMTU concentration. The estimated error in these calculations is approximately 10 times greater than that in the capacity data, that is from  $\pm 2\%$  to  $\pm 5\%$ .

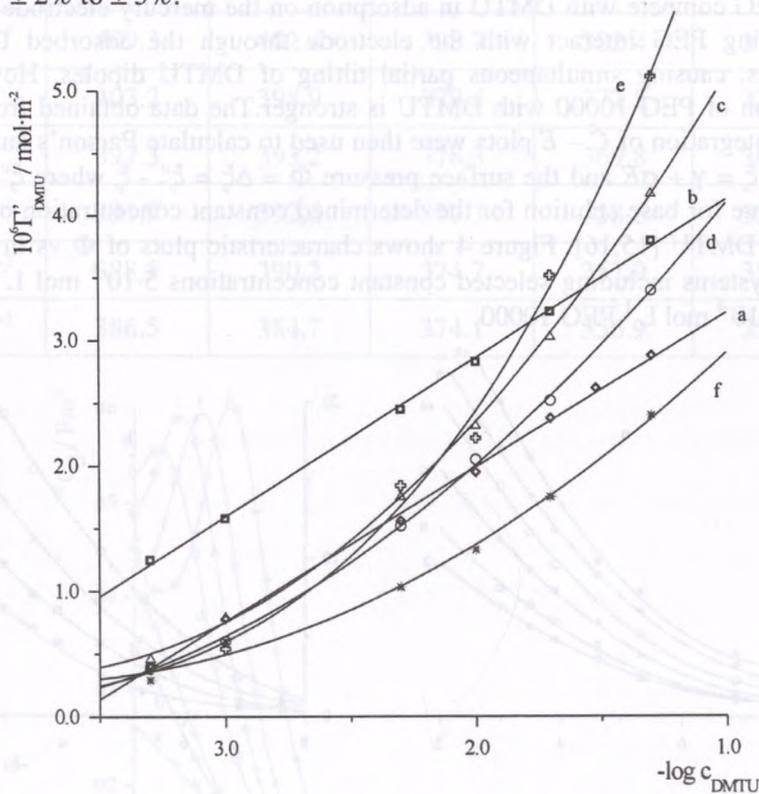


Figure 5. Relative surface excess of DMTU as a function of DMTU concentration at  $E_z$  for systems including: (a)  $0 \text{ mol L}^{-1}$  PEG, (b)  $10^{-4} \text{ mol L}^{-1}$  PEG 400, (c)  $5 \cdot 10^{-4} \text{ mol L}^{-1}$  PEG 400, (d)  $2.5 \cdot 10^{-4} \text{ mol L}^{-1}$  PEG 400, (e)  $10^{-4} \text{ mol L}^{-1}$  PEG 10000, (f)  $5 \cdot 10^{-4} \text{ mol L}^{-1}$  PEG 10000 for  $\sigma_M = +0.02 \text{ C} \cdot \text{cm}^{-2}$

The values  $\Gamma'_{\text{DMTU}}$  at  $E_z$  as a function of DMTU concentration in the bulk obtained for the investigated mixtures are shown in Figure 5. Exceptionally only for the solution containing  $5 \cdot 10^{-4} \text{ mol L}^{-1}$  PEG 10000 the dependence  $\Gamma'_{\text{DMTU}}$  vs  $\log c_{\text{DMTU}}$  refers to the electrode charge  $\sigma_M = +2 \mu\text{C} \cdot \text{cm}^{-2}$ . As fol-

lows from the dependences presented in Figure 5 only in the solution containing  $5 \cdot 10^{-4} \text{ mol L}^{-1}$  PEG 10000 (curve f) the surface concentration of DMTU is smaller than in the  $1 \text{ mol L}^{-1}$   $\text{NaClO}_4$  solution not containing an inhibitor (curve a). In turn, in the solution containing  $10^{-4} \text{ mol L}^{-1}$  PEG 400 the values  $\Gamma'_{\text{DMTU}}$  are greater by about  $0.8 \cdot 10^{-6} \text{ mol L}^{-1}$  than those obtained in the  $1 \text{ mol L}^{-1}$   $\text{NaClO}_4$  solution in the whole range of DMTU concentrations. The straight lines a and b showing these dependences have a parallel course. In the remaining systems (curves c, d, e) for the lowest concentrations of DMTU the values  $\Gamma'_{\text{DMTU}}$  are a bit lower than in  $1 \text{ mol L}^{-1}$   $\text{NaClO}_4$  but at the concentration  $0.05 \text{ mol L}^{-1}$  DMTU they exceed significantly the values  $\Gamma'_{\text{DMTU}}$  for the solution not containing an inhibitor.

The obtained results can be associated with the facilitated adsorption of DMTU molecules on mercury being a result of weaker hydration of the mercury surface in the presence of PEG adsorbed molecules. It is worth noting that the surface concentrations of DMTU in the presence of  $10^{-4} \text{ mol dm}^{-3}$  PEG 10000 are generally higher than in the presence of  $2.5 \cdot 10^{-3} \text{ mol L}^{-1}$  PEG 400. Therefore the same number of mers of  $-\text{CH}_2-\text{CH}_2-\text{O}$  in the above mentioned solutions does not decide about the adsorption properties of PEG under consideration but their molecular structure does. According to Rösch [18,19] PEG molecules of mer number  $n < 11$  possess a "zig-zag" structure, when  $n > 11$  a meander structure is found.

The saturation value  $\Gamma_s$  for DMTU was estimated by extrapolation of the linear plot of  $1/\Gamma'_{\text{DMTU}}$  vs  $1/c_{\text{DMTU}}$  to  $1/c_{\text{DMTU}} = 0$ . The obtained values  $\Gamma_s$  are in the range from  $6.3 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2}$  (for  $10^{-4} \text{ mol L}^{-1}$  PEG 400) to  $10 \cdot 10^{-6} \text{ mol m}^{-2}$  (for  $5 \cdot 10^{-4} \text{ mol L}^{-1}$  PEG 10000), thus much higher than the values  $\Gamma_s$  obtained for DMTU by the bowl models assuming a compact packing which is  $5 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2}$  [14]. For this reason to characterize DMTU adsorption in the presence of PEG there was applied the virial isotherm

$$\ln \Gamma + 2B\Gamma = \ln \beta c \quad (2)$$

where  $c$  is the concentration of DMTU in the bulk,  $\beta$  is the adsorption coefficient which is defined as  $\exp(-\Delta G^0/RT)$ ,  $\Delta G^0$  is the standard free energy of adsorption,  $B$  is the 2D second virial coefficient.

Figure 6 shows the linear test of the virial isotherm for  $5 \cdot 10^{-4} \text{ mol L}^{-1}$  PEG. Values of the  $B$  coefficient were calculated from the slopes of lines in Figure 6 and the corresponding  $\Delta G^0$  values were obtained from the intercepts of these lines (using the standard state of  $1 \text{ mol L}^{-1}$  in the bulk solution and  $1 \text{ molecule} \cdot \text{cm}^{-2}$  on the surface). The obtained values of the virial isotherm constants are presented in Table 3 and 4.

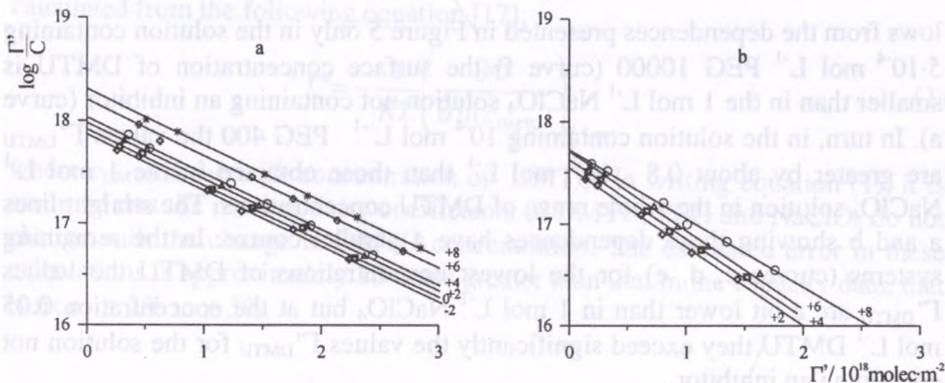


Figure 6. Linear test of the virial isotherm for (a)  $1 \text{ mol L}^{-1} \text{ NaClO}_4 + 5 \cdot 10^{-4} \text{ mol L}^{-1} \text{ PEG 400}$ , (b)  $1 \text{ mol L}^{-1} \text{ NaClO}_4 + 5 \cdot 10^{-4} \text{ mol L}^{-1} \text{ PEG 10000}$ , the electrode charges ( $\sigma_M$  in  $10^{-2} \text{ C} \cdot \text{m}^{-2}$ ) indicated by each line

Table 3. Comparison of the virial isotherm constants for  $1 \text{ mol L}^{-1} \text{ NaClO}_4 + \text{DMTU}$  systems in the absence and presence PEG 10000:  $\Delta G^\circ/\text{kJ mol}^{-1}$ ,  $B/\text{nm}^2 \text{ molecule}^{-1}$

$10^2 \sigma_M$ [C·m <sup>-2</sup> ]	1 mol L <sup>-1</sup> NaClO <sub>4</sub>		1 mol L <sup>-1</sup> NaClO <sub>4</sub> +10 <sup>-4</sup> mol L <sup>-1</sup> PEG 10000		1 mol L <sup>-1</sup> NaClO <sub>4</sub> +5·10 <sup>-4</sup> mol L <sup>-1</sup> PEG 10000	
	$-\Delta G^\circ$	$B$	$-\Delta G^\circ$	$B$	$-\Delta G^\circ$	$B$
-2	101.3	0.86	100.0	0.35	-	-
0	102.8	0.84	100.0	0.25	-	-
+2	105.2	0.75	100.0	0.20	100.0	0.75
+4	106.7	0.75	100.2	0.14	100.5	0.75
+6	-	-	-	-	100.8	0.75
+8	-	-	-	-	101.0	0.66

Table 4. Comparison of the virial isotherm constants for  $1 \text{ mol L}^{-1} \text{ NaClO}_4 + \text{PEG 400} + \text{DMTU}$  systems:  $\Delta G^\circ/\text{kJ mol}^{-1}$ ,  $B/\text{nm}^2 \text{ molecule}^{-1}$

$10^2 \sigma_M$ [C·m <sup>-2</sup> ]	10 <sup>-4</sup> mol L <sup>-1</sup> PEG 400		5·10 <sup>-4</sup> mol L <sup>-1</sup> PEG 400		2.5·10 <sup>-3</sup> mol L <sup>-1</sup> PEG 400	
	$-\Delta G^\circ$	$B$	$\Delta G^\circ$	$B$	$-\Delta G^\circ$	$B$
-2	107.2	0.96	101.8	0.56	-	-
0	107.6	0.96	102.2	0.56	101.4	0.60
+2	107.7	0.96	102.5	0.56	101.6	0.60
+4	108.2	0.96	102.8	0.56	101.9	0.60
+6	108.6	0.96	103.7	0.56	102.8	0.60
+8	109.2	0.84	104.1	0.56	103.9	0.48

As follows from the presented  $\Delta G^\circ$  values the free energy of DMTU adsorption is relatively the highest in the solution containing  $10^{-4} \text{ mol L}^{-1} \text{ PEG 400}$  and

exceeds the values  $\Delta G^o$  for DMTU obtained in the absence of the inhibitor. These results are in the agreement with the higher values of  $\Gamma'_{\text{DMTU}}$  (Figure 5) obtained in the solution containing  $10^{-4}$  mol l<sup>-1</sup> PEG 400 compared with the solution 1 mol l<sup>-1</sup> NaClO<sub>4</sub> and can confirm more favourable conditions for DMTU adsorption connected with weaker hydration of the electrode surface. In the other systems including the inhibitor the values  $\Delta G^o$  are generally lower than those obtained in the solution without the inhibitor which can be connected with the fact that in these systems weaker hydration of the electrode surface is accompanied by stronger adsorption of the molecules of the inhibitors used compared with adsorption of PEG 400 molecules in the system containing  $10^{-4}$  mol l<sup>-1</sup> PEG 400. Generally in the studied systems the increase of electrode charge  $\sigma_M$  is accompanied by the increase of  $\Delta G^o$  value due to the fact that the dipole molecule of DMTU adsorbs on mercury with the negative pole that is with the sulfur atom. Stability of  $\Delta G^o$  value or its slight changes occur in the systems containing a strong inhibitor in the form of PEG 10000. It follows from the comparison of the parameter B value that also its greatest values occur in the  $10^{-4}$  mol l<sup>-1</sup> PEG 400 solution. It can be stated that the change of PEG 400 concentration affects decisively adsorption of DMTU but the change of PEG 10000 concentration affects this process insignificantly. Comparison of the obtained values  $\Delta G^o$  and B for the systems containing  $2.5 \cdot 10^{-3}$  mol l<sup>-1</sup> PEG 400 and  $10^{-4}$  mol l<sup>-1</sup> PEG 10000 confirm the earlier statement that not only the size but also the structure of PEG molecule decide about adsorption of DMTU and the inhibitor.

**Kinetics of Zn(II) ion electroreduction.** The earlier presented results of investigations on DMTU adsorption in the presence of PEG concern some narrow ranges of electrode charges in which DMTU adsorption is strong. Studies on kinetics of reduction of Zn(II) ions as a pilot one allow to extend the area of electrode charge at which indirect description of adsorption mixed layer properties is possible. Figure 7 presents the cyclic voltammetric curves obtained in the presence of  $5 \cdot 10^{-4}$  mol l<sup>-1</sup> PEG 400 and DMTU. In all the systems including PEG 400 or PEG 10000 the increase of the concentration of DMTU in the solution causes the decrease in the difference of the cathodic and anodic peak potential:  $E_k - E_A$ . Thus for the solutions containing  $10^{-4}$  mol l<sup>-1</sup> PEG 400,  $5 \cdot 10^{-4}$  mol l<sup>-1</sup> PEG 400,  $2.5 \cdot 10^{-3}$  mol l<sup>-1</sup> PEG 400 and  $10^{-4}$  mol l<sup>-1</sup> PEG 10000 the values of  $E_k - E_A$  decrease: from 0.293 V to 0.040 V, from 0.363 V to 0.046 V, from 0.412 V to 0.055V and from 0.625 V to 0.421 V respectively (the scan rate was 0.020 Vs<sup>-1</sup>). In the 1 mol l<sup>-1</sup> NaClO<sub>4</sub> solution not containing organic substances the value  $E_k - E_A$  is 0.066 V. The obtained results indicate that the increase of PEG 400 concentration causes the increase of the inhibiting effect of Zn(II) ion on reduction. In case of PEG 10000 already at the concentration of  $10^{-4}$  mol l<sup>-1</sup> the maximum inhibition of the process occurs that is a fur-

ther increase of PEG 10000 concentration does not affect kinetics of the studied process.

Addition of DMTU into the solution containing PEG 400 eliminates its inhibiting activity and even there is observed an increase of the process reversibility compared with the basic electrolyte not containing organic substances. However, in the solution containing PEG 10000 addition of DMTU removes the inhibiting effect of PEG 10000 only partially. The presented results are confirmed by the obtained values  $E'_f$  necessary to determine constants  $k_s^{app}$  of Zn(II) ions reduction in the studied systems. Figure 8 presents a logarithmic dependence  $k_s^{app}$  of Zn(II) ions reduction on concentration of DMTU and PEG. Addition of DMTU into the solution containing a defined concentration of the inhibitor always causes acceleration of Zn(II) ion reduction. However, the size of this acceleration depends on PEG 400 concentration and practically does not depend on PEG 10000 concentration.

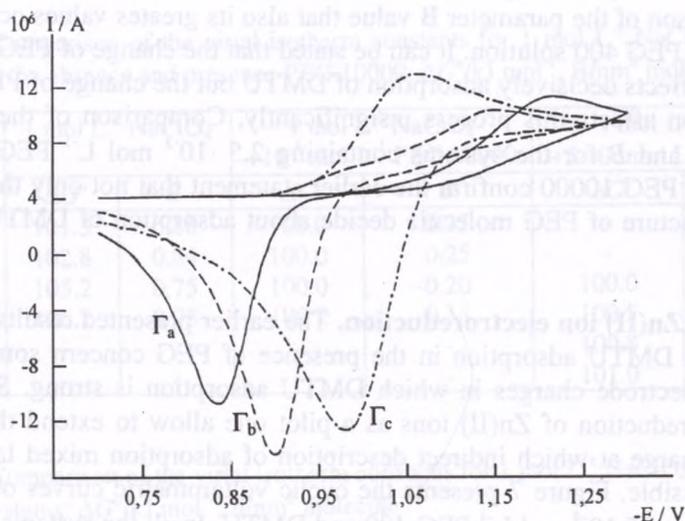


Figure 7. Cyclic voltammetric curves for Zn(II) / Zn (Hg) system at scan rate  $0.02 \text{ V s}^{-1}$  in  $1 \text{ mol L}^{-1} \text{ NaClO}_4 + 5 \cdot 10^{-4} \text{ mol L}^{-1} \text{ PEG 400}$  (a) and with addition of DMTU  $10^{-2} \text{ mol L}^{-1}$  (b),  $5 \cdot 10^{-2} \text{ mol L}^{-1}$  (c)

In the latter case the effect of inhibition suppression by DMTU is relatively the poorest. It follows from Figure 8 that only in the presence of  $10^{-4} \text{ mol L}^{-1}$  PEG 400 the dependence  $\log k_s^{app} = f(\log c_{\text{DMTU}})$  is presented by a straight line (curve b) almost parallel to be straight line presenting a suitable dependence in the  $1 \text{ mol L}^{-1} \text{ NaClO}_4$  solution not containing an inhibitor (curve a). For the other systems these dependences are not linear. In all solutions containing PEG 400 there occurs compensation of the inhibiting effect of Zn(II) ions reduction caused by DMTU molecules. The value  $k_s^{app} = 3.31 \cdot 10^{-3} \text{ cm s}^{-1}$  corresponding to

the neutral influence of adsorbate being in equilibrium with the mixture of these substances in the solution of Zn(II) ions reduction can be achieved for the systems containing  $10^{-4}$  mol L $^{-1}$ ,  $5 \cdot 10^{-4}$  mol L $^{-1}$ ,  $2.5 \cdot 10^{-3}$  mol L $^{-1}$  PEG 400 at the concentration ratio of DMTU: PEG 400 being: 250, 60 17 respectively. The decrease of this ratio can lead to the conclusion that with the increase of PEG 400 concentration, the access of DMTU molecules to the electrode surface increases, which can be explained by a more ordered structure of PEG 400 adsorbate layer. This fact can be confirmed also by an increase of dynamics of the accelerating process by DMTU in the presence of PEG compared with the 1 mol L $^{-1}$  NaClO $_4$  solution.

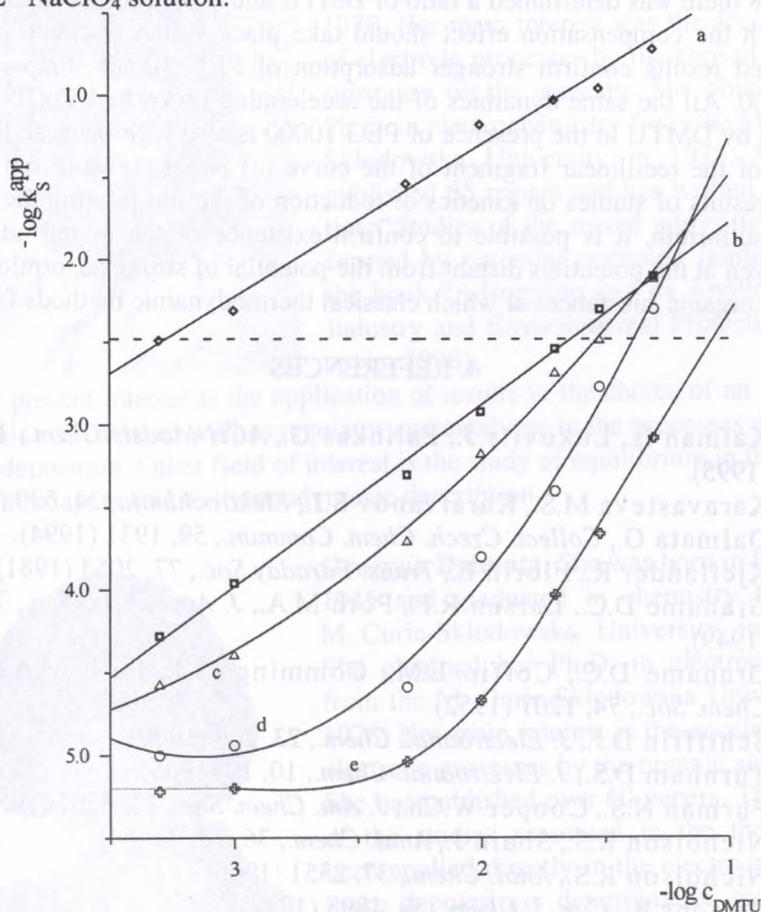


Figure 8. Dependence of standard rate constants of the Zn(II)/Zn(Hg) system on DMTU concentration in 1 mol L $^{-1}$  NaClO $_4$  for different contents of PEG: (a)  $c_{PEG} = 0$  mol L $^{-1}$ , (b)  $10^{-4}$  mol L $^{-1}$  PEG 400, (c)  $5 \cdot 10^{-4}$  mol L $^{-1}$  PEG 400, (d)  $2.5 \cdot 10^{-3}$  mol L $^{-1}$  PEG 400, (e)  $10^{-4}$  mol L $^{-1}$  PEG 10000. The dashed line denotes  $k_s^{app} = 3.31 \cdot 10^{-3}$  cm s $^{-1}$  for the Zn(II) reduction in 1 mol L $^{-1}$  NaClO $_4$ .

The inclination of the straight line (a) in Figure 8 presenting the dependence  $k_s^{app}$  on concentration of DMTU in 1 mol L<sup>-1</sup> NaClO<sub>4</sub> is 0.92 but that of the straight line (b) for the solution containing 10<sup>-4</sup> mol L<sup>-1</sup> PEG 400 is 1.09. The inclination of rectilinear fragments of the curves (c) and (d) for the solution containing 5·10<sup>-4</sup> mol L<sup>-1</sup> PEG 400 and 2.5·10<sup>-3</sup> mol L<sup>-1</sup> PEG 400 are 1.68 and 2.24 respectively.

In the solution containing PEG 10000 and a maximum amount of DMTU the compensation effect of inhibition and acceleration of Zn(II) ions reduction does not occur. From the extrapolation of a rectilinear fragment of the curve (e) in Figure 8 there was determined a ratio of DMTU and PEG 10000 concentrations at which the compensation effect should take place which is about 700. The presented results confirm stronger adsorption of PEG 10000 compared with PEG 400. All the same dynamics of the accelerating process of Zn(II) ions reduction by DMTU in the presence of PEG 10000 is also high because the inclination of the rectilinear fragment of the curve (e) is about 4.0. From the obtained results of studies on kinetics of reduction of the ion piloting the adsorption equilibrium, it is possible to confirm existence of the mixed adsorption layer even at the potentials distant from the potential of strong adsorption of the studied organic substances at which classical thermodynamic methods fail.

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## CURRICULA VITAE



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mixed adsorption layers on the mercury surface.

