

The Adsorption of Tetramethylthiourea at the Interface Electrode – NaClO₄ in the Presence of Sodium 1-decanesulfonate

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Abstract

Mixed adsorption layers properties made by two organic substances in which 1-decanesulfonic acid sodium salt undergoes physical adsorption and tetramethylthiourea (TMTU) chemical adsorption in 1M NaClO₄ on the mercury electrode are described. Based on differential capacity data – potential curves obtained at mercury electrode the double layers TMTU adsorption parameters were calculated whereas the adsorption constants were derived from pressure data as a function of electrode charge density and TMTU's bulk concentration. The interaction parameters point to weak repulsive interaction between the adsorbed TMTU molecules. The free adsorption energy was clearly smaller than in the detergent's absence. The potential drop rectilinear segments across the inner layer dependence on the relative surface excess were analyzed in order to calculate the electrostatic parameters of the inner layer. Zn²⁺ ions reduction in kinetic studies provided information concerning adsorption equilibrium at potentials distant from adsorption maximum.

Keywords: Adsorption isotherm, sodium 1-decanesulfonate, electrostatic parameters, electroreduction of Zn²⁺ ions, tetramethylthiourea.

1. Introduction

Molecular interaction at the metal – electrolyte interface is one of the most interesting problems in modern electrochemistry both from experimental and theoretical points of view. Co-adsorption of two organic substances on an electrode is one of these problems. Selection of these substances was based on different assumptions.^{1–6} In this paper, organic substances selection was based on their different adsorption mechanism on the mercury electrode: 1-decanesulfonic acid anion C₁₀H₂₁SO₃[–] undergoes physical adsorption and tetramethylthiourea (TMTU) chemical adsorption.⁷ 1-decanesulfonic acid sodium salt is a biological detergent used to separate nucleic acids and proteins from their cellular structures. Our choice of TMTU was based on the symmetric structure of the TMTU molecule due to presence of four methyl groups. Such structure allows a little changes only in orientation of adsorbed molecule on the electrode surface.⁸ Additionally, TMTU's adsorption parameters in aqueous solutions are presented in the literature.^{8–10} In experimental studies on adsorption

from solutions, the double layer capacitance was usually chosen as the primary experimental quantity. A comprehensive analysis of the experimental data concerning adsorption of surface-active compounds on different solid metals seems to support the view that mixed adsorption on mercury electrode should proceed analogously. Mercury surface homogeneity and purity provide excellent reproducibility of adsorption phenomena. A 1M NaClO₄ solution at pH 3 was used in these studies to protect the hydrolysis of Zn²⁺ ions. Our choice of NaClO₄ as a supporting electrolyte comes from the fact that ClO₄[–] ions cause the strongest disruption in water structure,¹¹ show low tendency to form complexes, and the double layer data needed are available from the literature.^{12–15} The results presented in this paper concern TMTU's adsorption parameters in the presence of 1-decanesulfonic acid sodium salt, the electrostatic parameters of the inner layer as well as Zn²⁺ ions reduction in 7.5 · 10^{–4} M C₁₀H₂₁SO₃[–] + TMTU + 1M NaClO₄ kinetic parameters. The chosen detergent concentration is lower than its critical micellar point.

2. Experimental

The experiments were performed in a three electrode system with a dropping mercury electrode as a working electrode, Ag/AgCl with saturated sodium chloride as a reference electrode, and a platinum spiral as a counter electrode. A controlled growth mercury drop electrode (CGMDE) manufactured by MTM, Poland was used. The differential capacity of the double layer (C) was measured using the ac impedance technique with Autolab frequency response analyzer (Eco Chemie, Netherlands). The reproducibility of the average capacity measurements was $\pm 0.5\%$. The measurements were carried out at several frequencies in the range from 400 Hz to 2000 Hz, with an amplitude of 5 mV. The equilibrium capacities were obtained by the extrapolation of the measured capacity versus square root of the frequency to zero frequency. This procedure assumed that the double layer impedance was equivalent to a combination of a capacity-resistance series and that the rate of adsorption was diffusion-controlled.

The potential of zero charge, E_z , was measured using a streaming electrode.¹⁶ The interfacial tension γ_z at E_z was measured by the maximum – bubble pressure method according to Schiffrin.¹⁷ The charge density and surface tension for studied systems: $7.5 \cdot 10^{-4}$ M $C_{10}H_{21}SO_3^-$ + increasing concentration of TMTU from $3 \cdot 10^{-4}$ M to 0.05 M were derived by the back integration of differential capacity – potential dependencies. The maximum concentration of TMTU was limited by its solubility. No corrections to the effects of the medium on the activity of the supporting electrolyte^{18,19} and adsorbate activity coefficient²⁰ were made. Polarographic measurements and voltammetric experiments were performed employing the Autolab frequency response analyzer (Eco Chemie, Netherlands). The impedance measurements were carried out with 9121FR analyzer and 9131 Electrochemical Interface (Atlas-Sollich, Gdańsk, Poland). The complex impedance data were collected at 36 frequencies ranging from 100 to 100 000 Hz within the Faradaic potential region with 10 mV intervals. The ohmic resistance of the electrolyte solution was obtained at a potential outside the Faradaic region. Analytical grade $C_{10}H_{21}SO_3Na$, TMTU, and $NaClO_4$ (Fluka) were used without any further purification. Water and mercury were double distilled before use. The solutions were deaerated by passing high purity nitrogen over the solutions during the measurements, which were carried out at 298 ± 0.1 K.

3. Results and Discussion

3.1. Analysis of Experimental Data

Figure 1 presents differential capacity curves obtained experimentally in 1M $NaClO_4$ (a), 1M $NaClO_4$ + $7.5 \cdot 10^{-4}$ M $C_{10}H_{21}SO_3^-$ (b), and with the addition of a chosen TMTU concentration. By introducing TMTU to the solu-

tion containing $7.5 \cdot 10^{-4}$ M detergent an increase of differential capacity was caused in a wide range of potentials, as well as a distinct TMTU desorption peak formation.

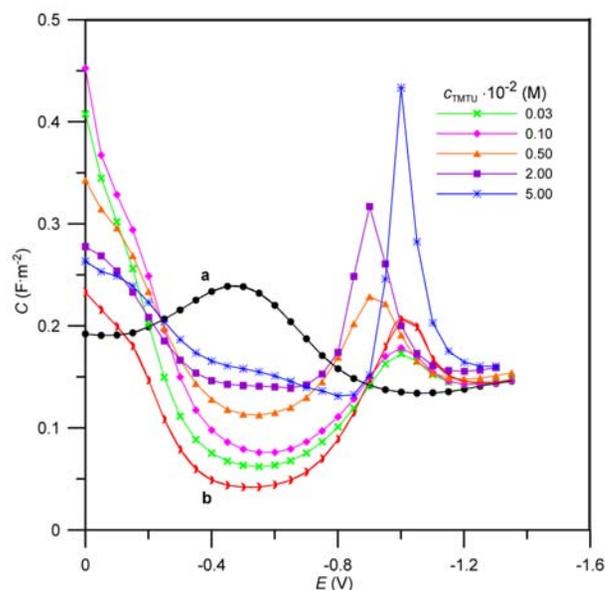


Fig. 1. Differential capacity-potential curves of: Hg / 1M $NaClO_4$ (a), Hg / 1M $NaClO_4$ + $7.5 \cdot 10^{-4}$ M $C_{10}H_{21}SO_3^-$ (b) and Hg / 1M $NaClO_4$ + $7.5 \cdot 10^{-4}$ M $C_{10}H_{21}SO_3^-$ + various TMTU concentrations as in figure legend.

It is worth mentioning that even the highest TMTU concentration causes a clear differential capacity decrease in relation to 1M $NaClO_4$. Differential capacity curves for the mixture of TMTU and 1-decanesulfonic acid are similar to those of pure TMTU⁹ but desorption peaks potentials are less negative. This may be a sign of a narrowed potential range in which TMTU adsorption takes place in $C_{10}H_{21}SO_3^-$ presence.

The addition of TMTU to the solution containing the detergent shifts the potential of zero charge, E_z towards negative potentials (Table 1) in a manner similar to 1M $NaClO_4$ solution without the detergent.⁹ Such changes

Table 1. The values of the potential of zero charge, E_z vs Ag/AgCl electrode and surface tension γ_z at E_z for the system: 1 M $NaClO_4$ + $7.5 \cdot 10^{-4}$ M $C_{10}H_{21}SO_3^-$ + TMTU.

$c_{TMTU} \cdot 10^{-2} (M)$	$-E_z (V)$	$\gamma_z (mN m^{-1})$
0.00	0.455	411.6
0.03	0.469	411.3
0.05	0.493	409.6
0.10	0.515	409.6
0.30	0.600	400.1
0.50	0.617	396.6
1.00	0.636	389.7
2.00	0.646	385.3
3.00	0.652	382.7
4.00	0.655	380.1
5.00	0.667	378.0

of E_z value indicate a TMTU molecule adsorption with its negative pole that is with the sulphur atom placed on the mercury surface. The values of surface tension, γ_z at E_z presented in Table 1, decrease distinctly with the increase of TMTU concentration.

As not all of the obtained curves $C-E$ converge at sufficiently negative potentials with the corresponding curve for the base solution, the capacity versus the potential data were numerically integrated from the point of E_z to get electrode charge values. Changes in electrode charges from -2 to $+2 \mu\text{C cm}^{-2}$ are referred to following potential changes: in 1M NaClO_4 from -0.561 V to -0.371 V, in the presence of 1-decanesulfonic acid at $7.5 \cdot 10^{-4}$ M from -0.805 V to -0.201 V, and with addition of $5 \cdot 10^{-2}$ M TMTU from -0.795 V to -0.548 V. For pure $5 \cdot 10^{-2}$ M TMTU in 1M NaClO_4 such changes are as follows; from -0.762 V to -0.567 V. Presented changes of electrode potentials indicate that 1-decanesulfonic acid has stronger influence on electrode potential than TMTU.

The data obtained from differential capacity curves integration was subsequently used to calculate Parsons' auxiliary function $\xi = \gamma + \sigma_M E$, where σ_M is the electrode charge and E is the electrode potential.²¹ TMTU adsorption was described using the relative surface excess Γ' which according to Gibbs adsorption isotherm is given by:

$$\Gamma' = \frac{1}{RT} \left(\frac{\partial \Phi}{\partial \ln c} \right)_{\sigma_M} \quad (1)$$

where c is the bulk concentration of TMTU and Φ is the surface pressure: $\Phi = \Delta\xi = \xi_0 - \xi$ (ξ_0 is the value of Parsons' auxiliary function for the base electrolyte with the detergent

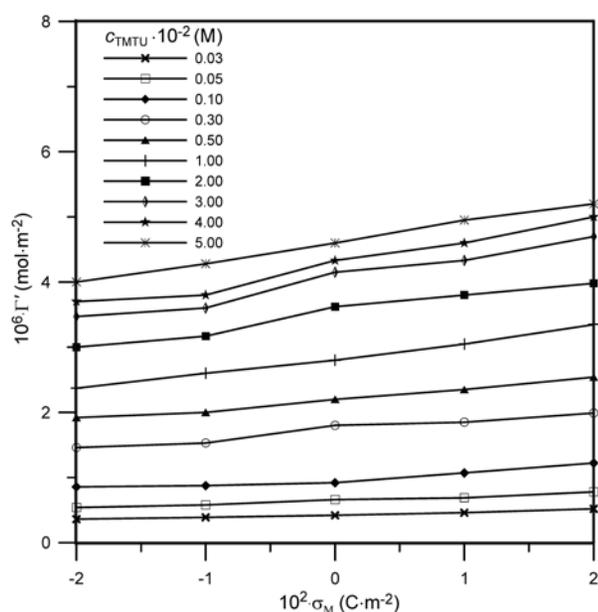


Fig. 2. Relative surface excess of TMTU in the presence of $7.5 \cdot 10^{-4}$ M $\text{C}_{10}\text{H}_{21}\text{SO}_3^-$ as a function of TMTU bulk concentration and electrode charge.

but without TMTU and ξ is the same function for the solution containing TMTU).²² Figure 2 shows the dependence $\Gamma'_{\text{TMTU}} = f(\sigma_M)$ for studied TMTU concentrations.

The values of Γ' increase in the direction of increasing electrode charges, especially for the greater TMTU concentrations. It should be stated that the relative surface excesses for maximal TMTU concentrations were slightly higher than in the detergent's absence.⁹ Whereas at lower TMTU concentrations the dependence was opposite which show that the detergent's influence on TMTU adsorption is strongly dependent on TMTU concentration.

3. 2. Adsorption Isotherms

TMTU adsorption parameters in the studied system were calculated based on of Frumkin and corrected Flory-Huggins isotherms.^{23–26} The Frumkin isotherm constants were determined from the equation:

$$\beta x = [\Theta/(1-\Theta)] \exp(-2A\Theta) \quad (2)$$

where x is the mole fraction of TMTU in the solution, β is the adsorption coefficient: $\beta = \exp(-\Delta G^\circ/RT)$, ΔG° is the standard Gibbs energy of adsorption, A is the interaction parameter and Θ is the coverage ($\Theta = \Gamma/\Gamma_s$). The surface excess at saturation Γ_s was estimated by extrapolating the $1/\Gamma'$ vs. $1/c_{\text{TMTU}}$ curves at different electrode charges to $1/c_{\text{TMTU}} = 0$. The Γ_s value obtained in this way was $1.09 \cdot 10^{-5}$ mol m^{-2} . The surface occupied by one TMTU molecule S ($S \equiv 1/\Gamma_s$) was 0.152 nm² and was clearly smaller than in the detergent's absence which is 0.42 nm² for $\sigma_M < 0$ and 0.35 nm² for $\sigma_M \geq 0$.⁹ The experimental S values are also smaller than the theoretical ones calculated for the vertical (0.47 nm²) or horizontal (0.51 nm²) orientation.⁸ Such small S value could be a result of TMTU molecule deformation in the presence of a big detergent's molecule.

The A parameter values were calculated from the slopes of the lines on the linear test of the Frumkin isotherm, and the corresponding ΔG°_F values were determined by the extrapolation of the lines of $\ln[(1-\Theta)/\Theta]$ versus Θ to the value $\Theta=0$. The obtained values of the free adsorption energy increase in a manner typical to specific adsorption i.e. in the direction to positive charges (Table 2).

The A interaction parameters point to weak repulsive interactions between the adsorbed TMTU molecules de-

Table 2. The constants of Frumkin (F), corrected Flory-Huggins (H) and virial (V) isotherms for the system $1\text{M NaClO}_4 + 7.5 \cdot 10^{-4}$ M $\text{C}_{10}\text{H}_{21}\text{SO}_3^- + \text{TMTU}$: $10^2 \sigma_M$ (C m^{-2}), ΔG° (kJ mol^{-1}).

σ_M	$-\Delta G^\circ_F$	$-A_F$	$-\Delta G^\circ_H$	$-A_H$	$-\Delta G^\circ_V$	B_V
-2	20.4	2.60	22.1	3.20	102.5	0.54
-1	20.6	2.45	22.2	2.95	102.7	0.52
0	20.8	2.00	22.4	2.55	102.9	0.46
+1	21.1	1.80	22.7	2.35	103.2	0.44
+2	21.5	1.80	23.1	2.30	103.5	0.42

creasing towards the positive electrode charges (Table 2).

The obtained greater values of total surface excess Γ in comparison to Γ' for TMTU indicate that the adsorbing TMTU molecules displace water molecules but not the detergent's molecules.

The TMTU adsorption in the presence of $C_{10}H_{21}SO_3^-$ was further analyzed based on constants obtained from the modified Flory-Huggins^{23–26} isotherm for the long-range particle-particle interaction:

$$\beta x = [\Theta/n(1-\Theta)^n] \exp(-2A\Theta) \quad (3)$$

where: $n = 1.24$ is the number of water molecules replaced by one TMTU molecule.

In the presented case the projected area for water²⁵ is 0.123 nm^2 . As ClO_4^- ions cause the strongest disruption in water structure,¹¹ the surface of one water molecule was used in calculations instead of water clusters. Figure 3 shows the modified Flory-Huggins isotherm linear test. This isotherm obtained constants presented in Table 2 are greater than those obtained from the Frumkin isotherm.

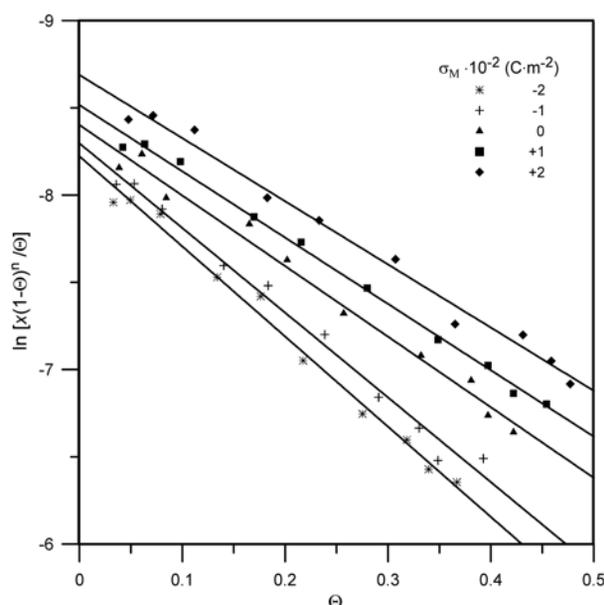


Fig. 3. Linear test of the corrected Flory-Huggins isotherm for the system $1M NaClO_4 + 7.5 \cdot 10^{-4} M C_{10}H_{21}SO_3^- + TMTU$.

The obtained data from above mentioned isotherms were verified using the virial isotherm. The virial isotherm application does not need the knowledge of the value of Γ_s . The virial isotherm equation is:

$$\ln \beta c = \ln \Gamma + 2B\Gamma \quad (4)$$

where B is two-dimensional (2D) second virial coefficient.

The 2D second virial coefficient values were calcu-

lated from the slopes of lines on the linear test of the virial isotherm and the corresponding ΔG_v° values were obtained from the intercepts of these lines with the axis $\log(\Gamma'/c)$ using the standard state 1 mol L^{-1} in the bulk solution and 1 mol cm^{-2} on the surface. The obtained virial isotherm constants values are presented in Table 2. The trend of changes of these values is similar to the described above isotherms. The free energy of adsorption increase and the decrease of repulsive interaction between adsorbed TMTU molecules with increase of electrode charge explain the greater values of the relative surface excess for positive electrode charges.

3.3. The Inner Layer Electrostatic Parameters.

The dependence of the potential drop across the inner layer Φ^{M-2} at constant charge due to TMTU relative surface excess (Figure 4) allows the calculation of the electrostatic parameters of the inner layer. According to Parsons' electrostatic model²², the potential Φ^{M-2} can be

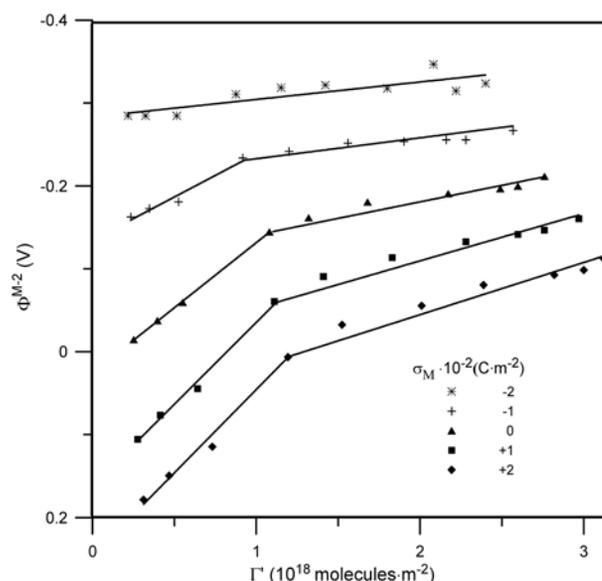


Fig. 4. Potential drop across the inner layer Φ^{M-2} as a function of TMTU surface concentrations adsorbed at constant electrode charges for $1M NaClO_4 + 7.5 \cdot 10^{-4} M C_{10}H_{21}SO_3^- + TMTU$.

described by the following dependence:

$$\Phi^{M-2} = \frac{4\pi x_1}{\epsilon_i} \sigma_M + \frac{4\pi \mu_{TMTU}}{\epsilon_i} \Gamma' \quad (5)$$

where μ_{TMTU} is the dipole moment of an isolated TMTU molecule: $\mu_{TMTU} = 15.7 \cdot 10^{-30} \text{ C m}$,²⁷ ϵ_i is the permittivity of the inner layer and x_1 is the inner layer thickness. The value of $\Phi^{M-2} = E - E_z - \Phi^{2-s}$, where: E is the measured potential in the presence of TMTU and E_z is the potential

of the zero charge in the absence of TMTU, and Φ^{2-s} is the potential drop across the diffuse layer, which can be calculated using the Gouy-Chapman theory.²⁸

The changes in the potential drop across the inner layer in Figure 4 are nonlinear for $\sigma_M \geq -1 \mu\text{C cm}^{-2}$. This nonlinearity may be caused by a change in TMTU's molecule orientation and the contribution of a covalent bond between TMTU sulphur and the mercury electrode.⁸ The rectilinear segments in Figure 4 obtained for smaller values of Γ' were analyzed in a similar way to those used previously by Jurkiewicz-Herbich and Jastrzębska.²⁹

The obtained ε_i , K^i – the integral capacity and x_i values are presented in Table 3. The inner layer permittivity, ε_i , decreases towards the electrode positive charges. For $\sigma_M > 0$ the ε_i values are similar to those in the detergent's absence. Based on the following dependence of Φ^{M-2} vs σ_M for $\Gamma' = \text{const}$, integral capacity K^i values were determined.

Table 3. Electrostatic parameters of the inner layer for the system 1 M NaClO₄ + 7.5 · 10⁻⁴ M C₁₀H₂₁SO₃⁻ + TMTU : 10² σ_M (C m⁻²), 10² Kⁱ (F m⁻²), x_i(nm).

σ _M	Γ' = 0			Γ' = 1	
	ε _i	K ⁱ	x _i	K ⁱ	x _i
-2	36.90	5.85	5.58	9.26	3.53
-1	20.84	6.58	2.80	9.80	1.88
0	12.47	7.30	1.51	10.20	1.08
+1	10.18	8.85	1.02	11.24	0.80
+2	9.84	10.99	0.79	12.05	0.72

The K^i values are distinctly smaller than in the detergent's absence⁹ and slightly smaller than in the tertbutanol presence.³⁰ But in the above systems the K^i values were independent on electrode charge. The x_i for positive charges appears to be reasonable. Large x_i values can confirm the detergents molecules perpendicular orientation to the electrode surface as well as a strong TMTU molecule deformation.

3. 4. Zn²⁺ Ion Reduction Kinetics

The results presented earlier concerning TMTU adsorption in the presence of anionic detergent provide information about the structure of a mixed adsorption layer but they also cover a range of strong adsorption potentials of these substances. The studies on kinetics of Zn²⁺ ion reduction as a piloting ion broaden this range. The approximate diffusion coefficients of Zn²⁺ ions (D_{ox}) in the examined solutions were calculated using the Ilkovič equation for diffusion controlled limiting current. The addition of 7.5 · 10⁻⁴ M C₁₀H₂₁SO₃⁻ into solution containing 5 · 10⁻³ M Zn²⁺ in 1M NaClO₄ changed the D_{ox} value from 6.6 · 10⁻⁶ cm² s⁻¹ to 6.2 · 10⁻⁶ cm² s⁻¹. In the presence of growing TMTU concentrations the D_{ox} increased to maximum value of 6.9 · 10⁻⁶ cm² s⁻¹ whereas in the absence of

the detergent the D_{ox} value increased to $D_{ox} 7.3 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. D_{ox} values changes are the result of limiting current changes, which depend on the solution viscosity, the zinc aqua complex composition and on studied organic substances adsorption. The reversible half wave potentials, $E'_{1/2}$ and the formal standard potentials, E_f^0 of Zn²⁺ ions reduction are shifted in the presence of the studied organic substances only 4 mV towards positive potentials. Therefore it was concluded that the Zn²⁺ – TMTU complexes formed in the solution are very unstable.³¹ Both organic substances used in these studies accelerate Zn²⁺ ions electroreduction. Cyclic voltammetry and impedance spectrum measurements confirm this (Fig. 5).

The potential difference $\Delta E = E_{pa} - E_{pc}$ (where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively) decrease in the presence of the detergent from 65 to 52 mV. Along with greater TMTU concentrations a further decrease of ΔE to 38 mV appeared. The obtained

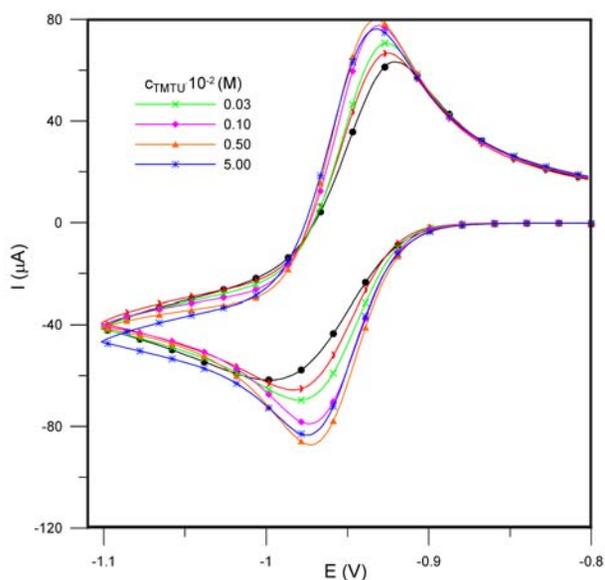


Fig. 5. Cyclic voltammetric curves for Zn²⁺/Zn(Hg) at the scan rate 0.1 V s⁻¹ in 1M NaClO₄ (black line), in 1M NaClO₄ with 7.5 · 10⁻⁴ M C₁₀H₂₁SO₃⁻ (red line) and with addition of various TMTU concentrations as in figure legend.

standard rate constant k_s^{app} values determined at E_f^0 increase from 3.4 · 10⁻³ cm s⁻¹ to 6.2 · 10⁻³ cm s⁻¹ after the detergents addition only. In the presence of maximal TMTU concentration 0.05M the k_s^{app} value equal 0.16 cm s⁻¹ was obtained. It should be highlighted that in the detergents absence the k_s^{app} values increase only to 0.01M TMTU concentration, the k_s^{app} values did not change with TMTU's concentration further rise.³² In the detergent's absence the maximal k_s^{app} value equal 7.3 · 10⁻² cm s⁻¹ was obtained. Whereas in the presence of 7.5 · 10⁻⁴ M C₁₀H₂₁SO₃⁻ a monotonically k_s^{app} value increase takes place. Figure 6 illustrates a k_s^{app} logarithmic dependence on TMTU concentration.

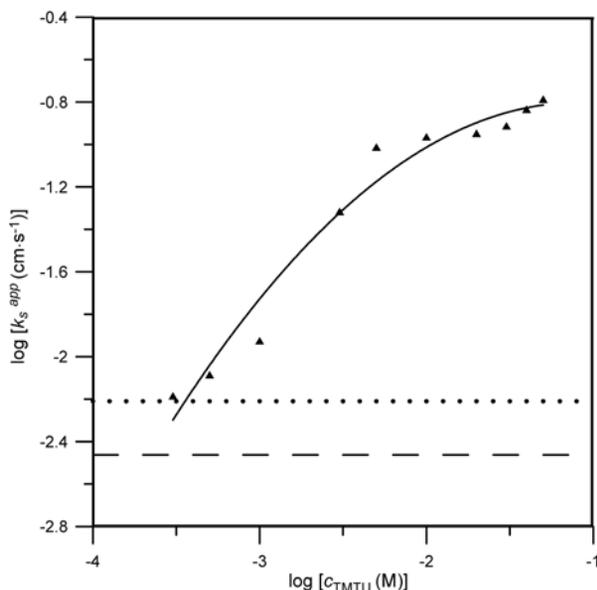


Fig. 6. Plots of the k_s^{app} for the $5 \cdot 10^{-3}$ M Zn^{2+} in 1M $NaClO_4$ (the dashed line), 1M $NaClO_4 + 5 \cdot 10^{-3}$ M $Zn^{2+} + 7.5 \cdot 10^{-4}$ M $C_{10}H_{21}SO_3^-$ (the dotted line) and with the addition of TMTU (the continuous line).

By comparing maximal standard rate constants values in the absence and in the presence of anionic detergent conclusions about the additive influence of $C_{10}H_{21}SO_3^-$ and TMTU on the Zn^{2+} electroreduction kinetics can be drawn. The causes of this effect may lay in the unstable adsorption–desorption balance of both these organic substances in the boundaries of developed desorption peak potentials which are the same as the Zn^{2+} ions electroreduction potentials. Another reason for this effect is a weaker electrode surface hydration during the used organic substances adsorption, which was observed earlier for other mixed adsorption layers.^{33,34} Zn^{2+} electroreduction kinetic results confirm the existence of mixed adsorption layers for potentials more distant to the maximal adsorption potential.

4. Conclusions

The presented results led us to the following conclusions to be made:

- the changes of E_z and γ_z with the increase of TMTU concentration are similar in the presence as well in the absence of the detergent.⁹
- Γ_{TMTU}^* relative surface excesses for a higher TMTU concentrations were greater in the presence of the detergent than in their absence.
- The determined constants of adsorption isotherms: the interaction parameter, A , and the free adsorption energy, ΔG° , are generally lower than the ones obtained in the detergent's absence.

- Weaker repulsive interaction in the detergent's presence may be a sign of a compensational influence on the repulsive interaction between adsorbed anionic detergent and TMTU dipole positive poles.
- Relatively high inner layer thickness values result from a strong TMTU molecule deformation and perpendicular orientation of adsorbed detergent molecules.
- The results Zn^{2+} electroreduction kinetic studies confirm the existence of a mixed adsorption layer at potentials distant from maximum adsorption. $C_{10}H_{21}SO_3^-$ has a positive influence on TMTU's accelerating action and on Zn^{2+} ions quasireversible electroreduction.

5. References

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Povzetek

Raziskovali smo lastnosti adsorpcijskih dvoplasti na živosrebri elektrodu, sestavljenih iz natrijeve soli 1-dekansulfonske kisline in tetrametilthiouree (TMTU) v 1 M raztopini NaClO₄. Za 1-dekansulfonske kisline lahko privzamemo, da poteka fizikalna adsorpcija, medtem ko je za TMTU bolj verjetna kemisorpcija. S pomočjo eksperimentalnih podatkov za odvisnost kapacitivnosti od potenciala za dvoplast na živosrebri elektrodu smo izračunali adsorpcijske parametre za TMTU, konstante adsorpcije pa smo določili s pomočjo podatkov za tlak v odvisnosti od elektrodne gostote naboja in koncentracije TMTU. Dobljeni parametri kažejo na šibke odbojne interakcije med adsorbiranimi molekulami TMTU. Prosta energija adsorpcije je znatno nižja kot v raztopini brez prisotne natrijeve soli 1-dekansulfonske kisline.