Properties of the mixed adsorption layer: neutral detergent-tetramethylthiourea at interface electrode/solution

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The mixed adsorption layers of tetramethylthiourea and a neutral detergent formed at the electrode surface in 1 M $NaClO_4$ are described in this paper. The systems were characterized by the measurement of differential capacity, zero charge potential, and surface tension at the same potential. The data were analyzed to obtain the surface pressure and relative surface excess of tetramethylthiourea as a function of electrode charge and bulk concentration of the studied compounds. The values of the lateral interaction parameters, obtained in the presence and in the absence of decanoyl-N-methylglucamide ($C_{17}H_{35}NO_6$), change differently depending on the isotherm used, but ΔG° values were clearly smaller in the presence of $C_{17}H_{35}NO_6$. Electrostatic parameters of the inner layer were assigned. A compensation for the inhibition and accelerating effect was obtained for the bulk concentrations ratio $c_{TMTU}:c_{detergent} \approx 13.3$. For $c_{TMTU} > 0.01$ M the acceleration of Zn^{2+} electroreduction appeared.

Introduction

Study of the adsorption of organic molecules on electrodes constitutes a major sector of electrochemical surface research. The properties of electrode surfaces are substantially modified by adsorbed molecules, which strongly

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affect electrode reactions. In the study of the influence of organic additives as the corrosion inhibitors or so-called brighteners used to deposit glossy electroplated coating, it is important to know the adsorption behavior of these additives. In these studies the coadsorption of 2 organic substances is often used.[1,2]

Adsorption should always be considered a competitive process between the adsorbate and the solvent. When investigating the adsorption of 2 different organic substances a competiveness problem emerges not only with water but also between these substances. The work presented herein is part of a broader project concerning the formation of the mixed adsorption layers on the mercury/detergent, tetramethylthiourea (TMTU), ClO_4^-, H_2O interface. The choice of these organic substances was based on their different affinity to mercury. Our studies involved cationic, anionic, and neutral detergents with similar molecular masses. Our choice of TMTU was based on availability of TMTU's adsorption parameters in aqueous solutions in the literature.[3-5] Adsorption of TMTU in the presence of neutral detergent—decanoyl-N-methylglucamide ($C_{17}H_{35}NO_6$)—was described in this paper by means of the adsorption isotherm constants, electrostatic parameters of the inner layer, and kinetic parameters of Zn^{2+} ions electroreduction. The choice of a $NaClO_4$ solution resulted from the fact that ClO_4^- ions cause the strongest disruption in the water structure.[6]

Experimental

The experiments were performed in a 3-electrode system with a dropping mercury electrode as a working electrode, Ag/AgCl 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.

Polarographic and voltammetric curves, as well as differential capacity (C) of the double layer, were measured with Autolab (Eco Chemie, the Netherlands). The reproducibility of the average capacity measurements was $\pm 0.5\%$. The measurements were made at several frequencies in a range from 400 Hz to 2000 Hz, with an amplitude of 5 mV. The equilibrium capacities were obtained by extrapolation of the dependence of the measured capacity versus the square root of 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. The interfacial tension γ_z at E_z was measured by the maximum bubble pressure method according to Schiffrin as in our previous study.[4] The charge density and surface tension for the studied systems: 7.5×10^{-4} M $C_{17}H_{35}NO_6$ + increasing concentration of TMTU from 3×10^{-4} M to 0.05 M in 1 M $NaClO_4$ were derived by the back integration of differential capacity–potential dependences. The values of E_z and γ_z were the integration constants. The maximum concentration of TMTU was limited by its solubility. No corrections were made for the effects of the medium on the activity of the supporting electrolyte[7,8] or activity coefficient of the adsorbate.[9] The complex impedance data for Zn^{2+} ions reduction were collected at 36 frequencies ranging from 100 Hz 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 $C_{17}H_{35}NO_6$, TMTU, and $NaClO_4$ (Fluka) were used without 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.

Results and discussion

Analysis of experimental data

The parameters of the double layer for TMTU adsorption were obtained from the differential capacity versus potential data. Figure 1 presents differential capacity curves obtained experimentally in 1 M $NaClO_4$ (a), in 1 M $NaClO_4$ + 7.5 × 10^{-4} M $C_{17}H_{35}NO_6$ (b), and with the addition of chosen TMTU concentrations. The chosen detergent's concentration was lower than its critical point of micellation.
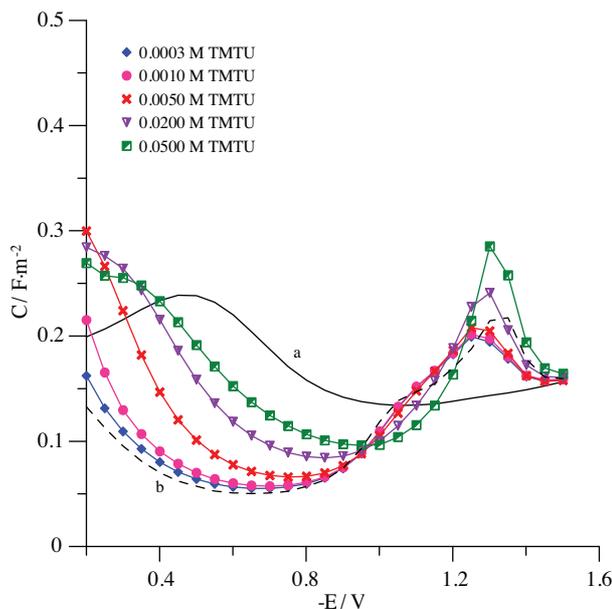

Figure 1. Differential capacity-potential curves extrapolated to zero frequency of: Hg/1 M $NaClO_4$ (a), Hg/1 M $NaClO_4$ + 7.5 × 10^{-4} M $C_{17}H_{35}NO_6$ (b), and Hg/1 M $NaClO_4$ + 7.5 × 10^{-4} M $C_{17}H_{35}NO_6$ + various TMTU concentrations as in figure legend.

By introducing $C_{17}H_{35}NO_6$ to the 1 M $NaClO_4$ solution a decrease in differential capacity was observed in a wide range of potentials from –0.1 V to –1.05 V. The introduction of increasing TMTU concentrations caused an increase in differential capacity. It is worth mentioning that even the highest TMTU concentration caused a clear decrease in differential capacity in relation to 1 M $NaClO_4$. The increasing TMTU concentrations caused a range of capacity decreases moving into more negative potentials; for TMTU concentration 5 × 10^{-2} M the range was from –0.4 V to –1.15 V. For the 1 M $NaClO_4$ + 7.5 × 10^{-4} M $C_{17}H_{35}NO_6$ solution there was a clear desorption peak at the potential of about –1.35 V on the differential capacity curve, which after the addition of TMTU shifted in the direction of less negative potentials, and its height at TMTU highest concentration rose. For the highest tested concentrations of TMTU there was a noticeable tendency for adsorption peak creation. A similar tendency occurred for pure TMTU in 1 M $NaClO_4$ but the desorption peaks' potentials were more negative. This might have been a sign of a narrowed potential range in which TMTU adsorption took place in $C_{17}H_{35}NO_6$ presence and with TMTU's adsorption domination.[4] As not all of the obtained $C-E$ curves converged at sufficiently negative potentials with the corresponding curve for the base solution, the capacity

against potential data was numerically integrated from the point of E_z. The integration constants, E_z and γ_z values, are collected in Table 1.

Table 1. The values of zero charge potentials, E_z vs. Ag/AgCl electrode and surface tension, γ_z, at E_z for the systems: 1 M NaClO$_4$ + 7.5 × 10^{-4} M C$_{17}$H$_{35}$NO$_6$ + TMTU.

c_{TMTU}/M	$-E_z$/V	γ_z/mN m^{-1}
0.0000	0.447	411.6
0.0003	0.405	410.8
0.0005	0.438	410.0
0.0010	0.449	408.4
0.0030	0.455	406.4
0.0050	0.472	404.5
0.0100	0.557	397.5
0.0200	0.625	395.9
0.0300	0.630	392.0
0.0400	0.635	390.4
0.0500	0.640	388.1

The introduction of 7.5 × 10^{-4} M C$_{17}$H$_{35}$NO$_6$ into 1 M NaClO$_4$ shifted the value of E_z from –0.468 V to –0.447 V. This was a sign of the detergent's dipole adsorption with its positive end, i.e. hydrocarbon chain directed towards the mercury surface. The lowest TMTU concentrations strengthened this tendency, which might have been related to a certain systematic order of the C$_{17}$H$_{35}$NO$_6$ molecules. For $c_{TMTU} \geq$ 0.01 M potential of zero charge shifted in the direction of more negative values. Such changes in E_z values indicate TMTU molecule adsorption with its negative pole that is with the sulfur atom placed on the mercury surface. The values of surface tension, γ_z at E_z presented in Table 1, decreased with the increase in TMTU concentration, but these changes were smaller than those in the absence of the detergent.[4]

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

$$\Gamma' = \frac{1}{RT} \left(\frac{\partial \Phi}{\partial lnc} \right)_\sigma, \tag{1}$$

where c is the bulk concentration of TMTU and Φ is the surface pressure:
$\Phi = \Delta\xi = \xi_o - \xi$ (ξ_o is the value of Parsons' auxiliary function for the base electrolyte: 1 M NaClO$_4$ + 7.5 × 10^{-4} M C$_{17}$H$_{35}$NO$_6$, and ξ is the same function for systems containing TMTU). Figure 2 shows the dependence $\Gamma'_{TMTU} = f(\sigma)$ for the studied TMTU concentrations. The Γ'_{TMTU} values increased with increasing electrode charge for the highest TMTU concentrations in the bulk and were higher than the appropriate Γ'_{TMTU} values in the detergent's absence. In the detergent's absence a significant increase in Γ' for small TMTU concentrations occurred[4] and they were higher than the appropriate Γ'_{TMTU} values in the detergent's presence. In low

TMTU concentrations the adsorption was more difficult due to the detergent's presence contrary to the highest concentrations of TMTU in the bulk.

The obtained effects point to a more difficult adsorption of TMTU in the presence of $C_{17}H_{35}NO_6$ certainly for smaller TMTU concentrations. It should be stated that the relative surface excess for maximal TMTU concentrations and positive electrode charges were higher than in the detergent's absence.[4]

Adsorption isotherms

TMTU adsorption in the presence of $C_{17}H_{35}NO_6$ was further analyzed using the Frumkin isotherm. The Frumkin isotherm constants were determined from the equation

$$\beta x = [\Theta/(1 - \Theta)]\exp(-2A\Theta), \tag{2}$$

where x is the molar 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 $1/\Gamma'$ versus $1/c_{TMTU}$ dependence at different electrode charges, to $1/c_{TMTU} = 0$. The value of Γ_s obtained in this way was 1.03 mol m^{-2}. The surface occupied by one TMTU molecule, S ($S \equiv 1/\Gamma_s$), was 0.161 nm^2 and was clearly smaller than the theoretical ones calculated for the vertical (0.47 nm^2) or horizontal (0.51 nm^2) orientation.[3] Such a small value could have been the result of strong deformation of the TMTU molecule in the presence of a big detergent's molecule. Figure 3 presents the linear test of the Frumkin isotherm for the electrode charges used.
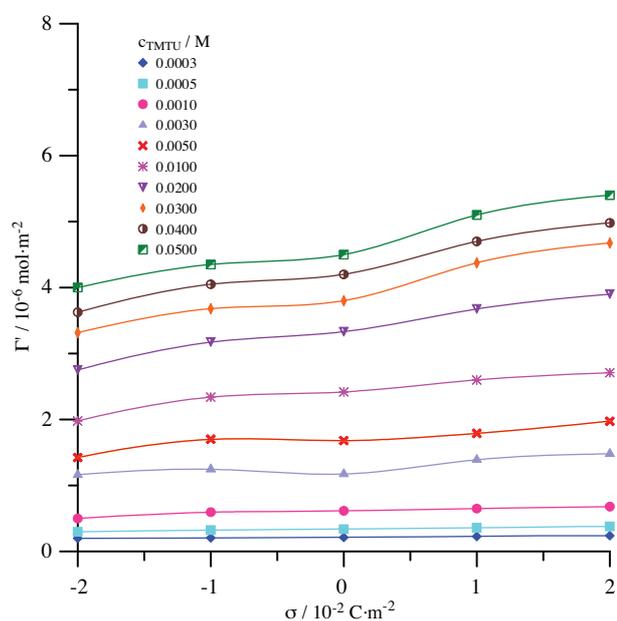

Figure 2. Relative surface excess of TMTU as a function of the electrode charge and TMTU concentration as in figure legend for 1 M NaClO$_4$ + 7.5 × 10^{-4} M C$_{17}$H$_{35}$NO$_6$.
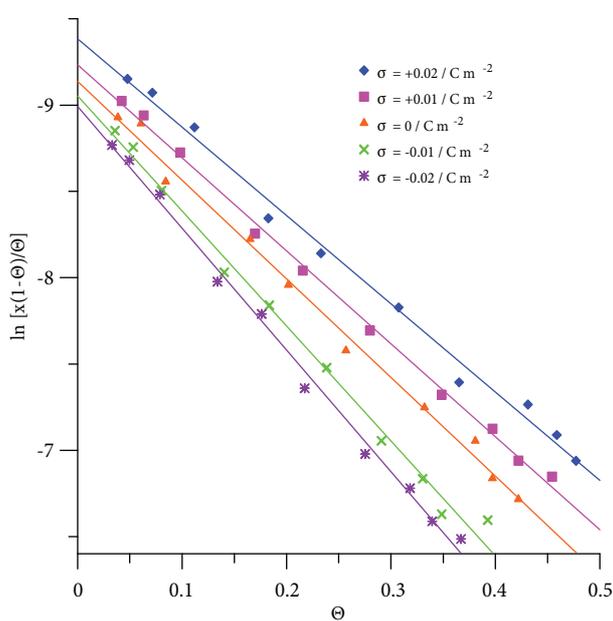
Figure 3. Linear test of the Frumkin isotherm for the system: 1 M NaClO$_4$ + 7.5 × 10^{-4} M C$_{17}$H$_{35}$NO$_6$ + TMTU.

The A_F parameter values were calculated from the line slopes on the linear test of the Frumkin isotherm and the corresponding values of ΔG_F^0 were determined by the extrapolation of the $\ln[(1-\Theta)x/\Theta]$ vs. Θ curve to the value of $\Theta = 0$. Table 2 presents the obtained constants of the Frumkin isotherm. The A_F interaction parameters point to repulsive interactions between the adsorbed TMTU molecules decreasing towards the positive electrode charge, whereas the values of free adsorption energy increased in a manner typical to specific adsorption, i.e. in the direction of positive charges. The obtained ΔG_V^0 values were significantly lower than those obtained in the detergent's absence, whereas the repulsive interaction was much stronger. Additionally in the detergent's absence the A_F parameter increased with the increase in the electrode charge.[4] The obtained values of total surface excess Γ based on Parsons' function ζ were clearly greater in comparison to Γ' values derived from Eq. (1). This suggests that the adsorbing TMTU molecules displaced water molecules from the electrode surface but not the detergent's molecules.

The TMTU adsorption in the presence of $C_{17}H_{35}NO_6$ was further analyzed based on constants obtained from the modified Flory-Huggins isotherm for the long-range particle-particle interaction:

$$\beta x = \left[\frac{\Theta}{n\left(1-\Theta\right)^n} \right] \exp\left(-2A\Theta\right), \tag{3}$$

where $n = 1.31$ is the number of water molecules replaced by one TMTU molecule. In the present paper the projected area for water[10] is 0.123 nm^2. As ClO_4^- ions caused the strongest disruption in the water structure, the surface of one water molecule was used in calculations instead of water clusters. Figure 4 shows the plots of $\ln[x(1-\Theta)^n/\Theta]$ versus Θ for the chosen values of σ.
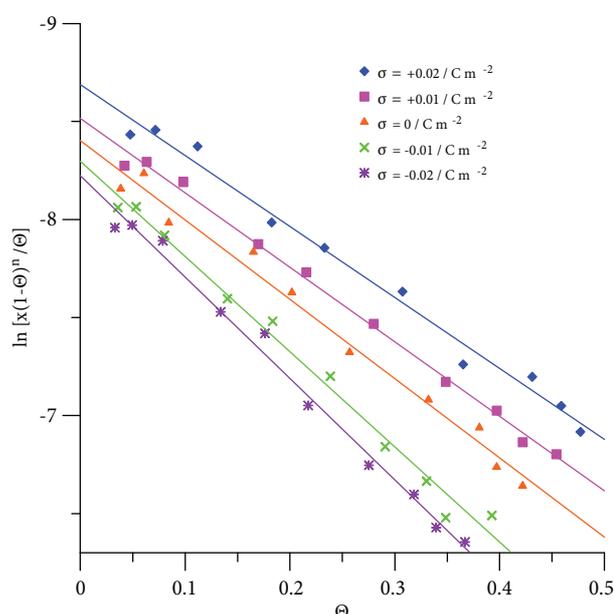

Figure 4. Linear test of the modified Flory-Huggins isotherm for the system: 1 M $NaClO_4$ + 7.5×10^{-4} M $C_{17}H_{35}NO_6$ + TMTU.

The obtained constants of the modified Flory-Huggins isotherm are collected in Table 2.

Table 2. The constants of Frumkin (F) and corrected Flory-Huggins isotherm (H) for system: 1 M NaClO$_4$ + 7.5 × 10^{-4} M C$_{17}$H$_{35}$NO$_6$ + TMTU; $\sigma/10^{-2}$ C m^{-2}, ΔG_0/kJ mol^{-1}.

σ	$-\Delta G_F^0$	$-A_F$	$-\Delta G_H^0$	$-A_H$	$-\Delta G_V^0$	B_V
-2	20.24	2.0	17.66	0.9	100.46	0.40
-1	20.56	1.7	18.06	0.8	100.69	0.34
0	20.56	1.6	18.11	0.6	100.80	0.34
$+1$	20.68	1.3	18.33	0.4	100.91	0.30
$+2$	20.81	1.1	18.48	0.3	101.08	0.28

The trend of changes in these values was similar to those presented for the Frumkin isotherm. Values of ΔG_H^0 obtained from the Flory-Huggins isotherm were smaller than those obtained from the Frumkin isotherm and smaller than those obtained in the detergent's absence.[4] The A_H parameter was higher than A_F and greater than the A_H determined in the detergent's absence. The obtained data from the above-mentioned isotherms were verified using the virial isotherm (Figure 5). The virial isotherm application did not need knowledge of the Γ_s value. The virial isotherm equation is:

$$\ln \beta c = \ln \Gamma + 2B\Gamma, \tag{4}$$

where B was the two-dimensional ($2D$) second virial coefficient.

The $2D$ second virial coefficient values were calculated from the slopes of lines on the linear test of the virial isotherm and the corresponding ΔG_V^0 values were obtained from the intercepts of these lines with the axis log (Γ'/c) using the standard state 1 M in the bulk solution and 1 mol cm^{-2} on the surface.
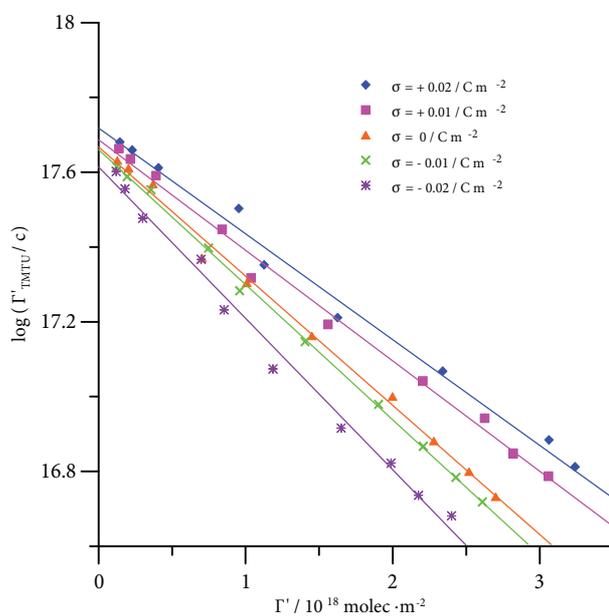

Figure 5. Linear test of the virial isotherm for the system: 1 M NaClO$_4$ + 7.5 × 10^{-4} M C$_{17}$H$_{35}$NO$_6$ + TMTU.

The obtained virial isotherm constants values are presented in Table 2. The ΔG_V^0 values were slightly lower than those obtained in the detergent's absence whereas the B parameter was twice lower. Summing up the adsorption parameters obtained from the 3 isotherms it is necessary to state that the smaller Γ'_{TMTU} values at lower TMTU concentrations compared with the Γ'_{TMTU} values in the detergents absence were linked with a smaller adsorption energy and stronger repulsive interaction between TMTU molecules, which were obtained solely from the Frumkin and corrected Flory-Huggins isotherms. The detergent's influence on higher Γ'_{TMTU} values at higher TMTU concentrations could only be explained by weaker repulsive interactions expressed by the virial parameter B.

The inner layer electrostatic parameters

The electrostatic parameters of the inner layer were calculated on the basis of the dependence of the potential drop across the inner layer Φ^{M-2} at constant electrode charge versus TMTU relative surface excess (Figure 6). According to Parson's electrostatic model, the potential Φ^{M-2} could be represented by a sum of 2 parts using the following equation:

$$\Phi^{M-2} = \frac{4\pi x_1}{\varepsilon_i}\sigma + \frac{4\pi\mu_{TMTU}}{\varepsilon_i}\Gamma', \tag{5}$$

where μ_{TMTU} is the dipole moment of an isolated TMTU molecule: $\mu_{TMTU} = 15.7 \times 10^{-30}$ C m, 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 the detergent and TMTU, while 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.
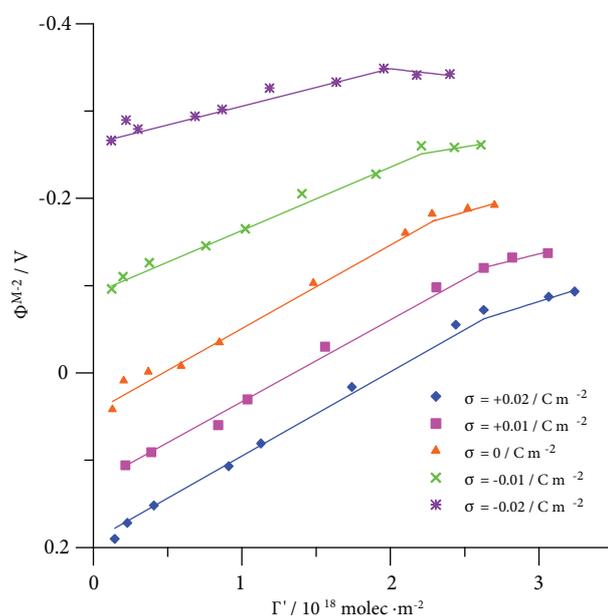

Figure 6. Potential drop across the inner layer Φ^{M-2} as a function of the surface concentrations of TMTU adsorbed at constant electrode charges for 1 M $NaClO_4$ + 7.5×10^{-4} M $C_{17}H_{35}NO_6$ + TMTU.

These dependencies were similar to dependencies Φ^{M-2} vs. Γ'_{TMTU} in the absence of the detergent,[4] and represent a model of the potential drop across the diffuse layer assuming that the inner layer only consisted of TMTU molecules. The lines in Figure 6 were analyzed in a similar way to those used previously by Jurkiewicz-Herbich and Jastrzbska.[11] The obtained values of ε_i, integral capacity κ^i, and x_1 are collected in Table 3. However, the obtained ε_i values were significantly higher than in the absence of the detergent.[4] Based on the following dependence of Φ^{M-2} vs. σ for $\Gamma' = $ const, the integral capacity values were determined. These values increased with the electrode charge. Large changes in κ^i values were present only in the studied systems. The values of κ^i in the absence of the detergent did not depend on the electrode charge.[4] The x_1 values for positive electrode charges appeared to be reasonable. The large x_1 value could confirm the detergent's molecules' perpendicular orientation to the electrode surface as well as a strong TMTU molecule deformation.

Table 3. Inner layer properties for the system: 1 M NaClO$_4$ + 7.5 $\times$ 10^{-4} M C$_{17}$H$_{35}$NO$_6$ + TMTU; $\sigma/10^{-2}$ C m^{-2}, $\kappa^i/10^{-2}$ F m^{-2}, x_1/nm.

		$\Gamma' = 0$		$\Gamma' = 1$	
σ	ε_i	κ^i	x_1	κ^i	x_1
−2	44.28	5.24	7.48	6.80	5.76
−1	23.62	6.62	3.16	7.87	2.65
0	18.64	9.09	1.81	10.20	1.62
1	18.64	13.33	1.24	13.89	1.19
2	18.64	30.30	0.54	21.74	0.76

Studies of TMTU adsorption at more negative potentials

To obtain information about the mixed adsorption layer of TMTU - C$_{17}$H$_{35}$NO$_6$ on the mercury surface at potentials distinct from E_z, kinetic studies of Zn^{2+} ions reduction as a piloting ion were carried out. The measurements allowed the following generalizations to be made:

- Zn^{2+} ions approximate diffusion coefficients (D_{ox}) in the examined solutions were calculated from limiting currents using the Ilković equation. The values of D_{ox} were generally lower than 6.6 $\times$ 10^{-6} cm^2 s^{-1} obtained for Zn^{2+} in 1 M NaClO$_4$ and reached the lowest value of 5.9 $\times$ 10^{-6} cm^2 s^{-1} in the presence of 7.5 $\times$ 10^{-4} M C$_{17}$H$_{35}$NO$_6$.

- Standard potentials, E_f^0 of Zn^{2+} ions reduction shifted in the presence of 7.5 $\times$ 10^{-4} M C$_{17}$H$_{35}$NO$_6$ from –0.962 V to –0.974 V but the addition of a maximum concentration of 5 $\times$ 10^{-2} M TMTU caused a shift of E_f^0 to –0.955 V. These changes in E_f^0 suggest an inhibiting action of C$_{17}$H$_{35}$NO$_6$ and an accelerating one of TMTU.

The above suggestions were confirmed by cyclic voltammetry and impedance spectrum measurements. Figure 7 presents the cyclic voltammetric curves for the studied systems.

The difference between potentials of anodic and cathodic peaks, ΔE, increased from 65 mV to 298 mV in the presence of 7.5 $\times$ 10^{-4} M C$_{17}$H$_{35}$NO$_6$. ΔE decreased to 38 mV, after the addition of maximal TMTU concentration. For the maximum TMTU concentration of 5 $\times$ 10^{-2} M a significant increase in the current of cathodic and anodic peak was observed. The obtained standard rate constant k_s^{app} values determined at E_f^0

decreased from 3.4×10^{-3} cm s^{-1} to 2.7×10^{-4} cm s^{-1} after adding only the detergent. In the presence of maximal tested TMTU concentration the k_s^{app} value equal to 5.3×10^{-2} cm s^{-1} was obtained. Figure 8 illustrates a k_s^{app} logarithmic dependence vs. TMTU concentration.
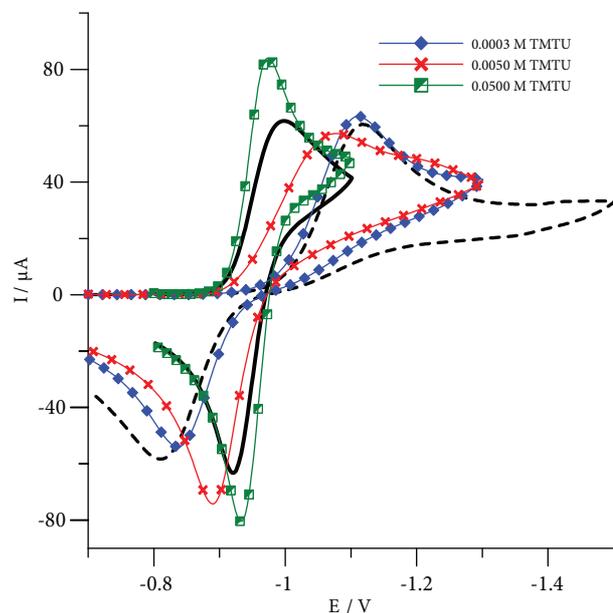

Figure 7. Cyclic voltammetric curves for Zn^{2+}/Zn(Hg) at the scan rate 0.1 V s^{-1} in 1 M NaClO$_4$ (solid line), in 1 M NaClO$_4$ + 7.5×10^{-4} M C$_{17}$H$_{35}$NO$_6$ (dashed line), and with addition of various TMTU concentrations as in figure legend.

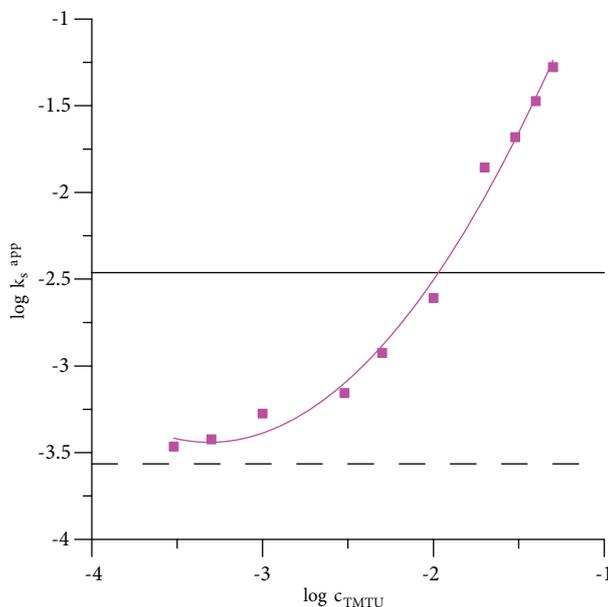**Figure 8.** Plots of log k_s^{app} for the 5×10^{-3} mol dm^{-3} Zn^{2+} in 1 M NaClO$_4$ (the dashed line), 1 M NaClO$_4$ + 5×10^{-3} M Zn^{2+} + 7.5×10^{-4} M C$_{17}$H$_{35}$NO$_6$ (the continuous line) and with the addition of TMTU (the continuous line with symbols).

The smallest tested TMTU concentrations caused an insignificant rise in k_s^{app}. This meant that TMTU surface concentration on the electrode was small at the above concentrations. A compensation for the inhibition and accelerating effect was obtained for the bulk concentrations ratio $c_{TMTU}:c_{detergent} \approx 13.3$. For $c_{TMTU} >$ 0.01 M acceleration of Zn^{2+} electroreduction appeared. It is worth mentioning that the largest studied TMTU concentration caused a stronger acceleration of Zn^{2+} ions reduction in the presence of C$_{17}$H$_{35}$NO$_6$ than in their absence.[12] The obtained results of kinetic measurements clearly pointed to occurrence of the mixed adsorption layers C$_{17}$H$_{35}$NO$_6$ – TMTU at the mercury surface electrode even at the potential of –1.0 V.

Conclusions

From the presented results it can be stated that:

1. The course of differential capacity curves, the changes in E_z, and the relative surface excess values pointed to the domination of TMTU molecules adsorbed at the electrode surface for the maximal tested TMTU concentration.

2. The obtained values of Γ' for small TMTU concentrations pointed to a much more difficult adsorption of TMTU in the presence of 7.5×10^{-4} M $C_{17}H_{35}NO_6$ whereas at the highest TMTU concentrations its adsorption was easier.

3. From a comparison of total surface excess, Γ, with the relative surface excess of TMTU, it can be concluded that the adsorbing TMTU molecules displaced water molecules from the electrode surface.

4. The values of A_F and A_H parameters pointed to stronger repulsive interactions between the adsorbed TMTU molecules in the presence of $C_{17}H_{35}NO_6$ compared to in the detergent's absence, whereas $\Delta G°$ values were clearly smaller in the presence of $C_{17}H_{35}NO_6$.

5. The permittivity, ε_i, of the inner layer was significantly higher in the presence of $C_{17}H_{35}NO_6$.

6. The kinetic measurements of Zn^{2+} electroreduction confirmed the formation of the mixed adsorption layers even at the potential range below –1.0 V in which it was impossible to calculate adsorption parameters by the thermodynamic method.

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