Adsorption of Tetramethylthiourea in the Presence of Cationic Detergent at Interface Electrode / Aqueous Perchlorate Solutions

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Abstract. The mixed adsorption layers of tetramethylthiourea and a cationic detergent formed at electrode surface in $NaClO_4$ (1 mol dm^{-3}) are described. The systems were characterized by the measurement 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 tetramethylthoiurea as a function of electrode charge at bulk concentration of studied compounds. It was stated that the adsorbing tetramethylthoiurea molecule pushed out the water molecule instead of the detergent molecule from the electrode surface. The constants of the Frumkin and corrected Flory-Huggins isotherm point to a decreased TMTU adsorption energy in the cationic detergents presence and stronger repulsive interaction. Electrostatic parameters of the inner layer were assigned. In the range of more negative potentials, mixed adsorption layers were described by investigating the kinetics of the Zn^{2+} ions electroreduction as a piloting ion. (doi: 10.5562/cca1791)

Keywords: adsorption, cationic detergent, mixed adsorption layer, mercury electrode, tetramethylthiourea

INTRODUCTION

Adsorption processes play an important role in the phenomena occurring at interfaces including natural and technologically induced phase boundaries. These processes are conveniently studied by electrochemical methods. Spontaneous adsorption of sulphur-containing molecules from solutions onto metals to form close-packed and oriented monolayers provide a convenient method to assign desired chemical or physical properties to surfaces.[1,2] By using a mixture of adsorbates, it is therefore possible to introduce different chemical functionalities on a surface.[3–5] A large number of electrochemical studies dealing with adsorption of organic compounds are based on the differential capacitance of the double layer in relation to the bulk concentration and to the electrode potential measurements. The most intensive and extensive investigations were performed on the mercury electrode.[6–8] Electrode surfaces properties are substantially modified by adsorbed molecules which strongly affect the electrode reactions. It is important to know the adsorption behaviour of organic additive when studying its influence mechanisms on the process of metal electrocrystallization and electrochemical corrosion. The results presented in this paper concern tetramethylthiourea (TMTU) adsorption parameters, the electrostatic parameters of the inner layer as well as kinetic parameters of Zn^{2+} ions reduction in 7.5×10^{-4} mol dm^{-3} octyltrimethylammonium bromide ($C_{11}H_{26}NBr$) + TMTU + 1 mol dm^{-3} $NaClO_4$. The chosen detergents concentration was lower than its critical point of micellation. Adsorption mechanism of used organic substances was different, the cationic detergent underwent physical adsorption whereas TMTU chemical adsorption. Additionally, TMTU's adsorption parameters in aqueous solutions are presented in the literature.[9–11] The investigated compounds had an inverse effect on the kinetics of Zn^{2+} ions electroreduction. The studies on Zn^{2+} ions reduction kinetics as piloting ions allow on monitoring the used organic compounds adsorption equilibrium at potentials distant from maximum adsorption potential. This paper is only a part of complex studies on mixed adsorption layers: TMTU in the presence of different types of biological detergents. The later are used to separate nucleic acids and proteins from their cellular structures. The choice of $NaClO_4$ solution resulted from the fact that ClO_4^- ions caused the strongest disruption in the water structure.[12]

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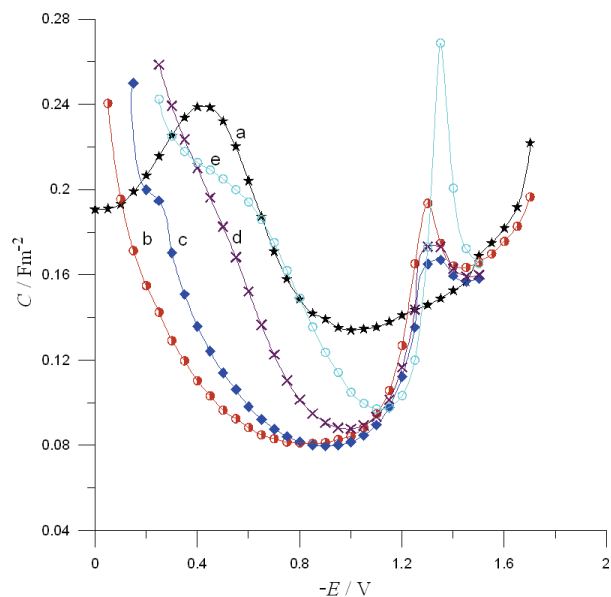
Figure 1. Differential capacity-potential curves extrapolated to zero frequency of: (a) Hg/1 mol dm^{-3} NaClO$_4$, (b) Hg/1 mol dm^{-3} NaClO$_4$ + 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$N$^+$, and Hg/1 mol dm^{-3} NaClO$_4$ + 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$N$^+$ + various TMTU concentrations: (c) 0.0003, (d) 0.005, and (e) 0.05 mol dm^{-3}.

EXPERIMENTAL

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 using the ac impedance technique was ±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 extrapolation of the dependence of the measured capacity versus square root of frequency. This procedure as-

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 mol dm^{-3} NaClO$_4$ + 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$N$^+$ + TMTU

$10^2 c_{TMTU}$ / mol dm^{-3}	$-E_z$ / V	γ_z / mN·m^{-1}
0.00	0.442	411.3
0.03	0.418	411.3
0.05	0.426	410.4
0.10	0.430	402.7
0.30	0.468	398.3
0.50	0.477	393.1
1.00	0.518	388.8
2.00	0.569	383.6
3.00	0.593	380.1
4.00	0.617	379.1
5.00	0.634	378.4

sumes that the double layer impedance is equivalent to a combination of a capacity-resistance series and that the rate of adsorption is diffusion-controlled. The experiments were performed in a three 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. The potential of zero charge, E_z, was measured using a streaming electrode.[13] The interfacial tension γ_z, at E_z was measured by the maximum bubble pressure method according to Schiffrin.[14] The charge density and surface tension for studied systems: 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$NBr + increasing concentration of TMTU from 3×10^{-4} to 0.05 mol dm^{-3} were obtained by the back integration of differential capacity – potential dependences. 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[15,16] and activity coefficient of the adsorbate[17] were made. The complex impedance data for Zn^{2+} ions reduction were collected at 36 frequencies ranging from 100 to 100000 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$_{11}$H$_{26}$NBr, 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

Experimental Data Analysis

Figure 1 presents diffential capacity curves obtained experimentally in 1 mol dm^{-3} NaClO$_4$, in 1 mol dm^{-3} NaClO$_4$ + 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$N$^+$, and with the addition of chosen TMTU concentration.

The studied cationic detergent decreased differential capacity in comparison to the one obtained in 1 mol dm^{-3} NaClO$_4$. At the potential about −1.3 V the desorption peak appeared. The addition of increasing amounts of TMTU caused an increase in differential capacity, but its value was always lower than the one obtained in 1 mol dm^{-3} NaClO$_4$. Addition of TMTU don't influence the detergent's desorption peak potential but changed the height of the peak. A similar relations were observed in other systems containing two different organic substances.[18,19] The change of differential capacity curves indicates that in the presence of 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$N$^+$ the range of TMTU adsorption potentials doesn't depend on its concentration. Such an effect was not observed in studied systems with TMTU as a com-

ponent of the mixed adsorption layers so far. 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 were numerically integrated from the point of E_z. The integration constants, E_z and γ_z, are collected in Table 1. The E_z values shifted towards negative potentials gradually with the increase of TMTU concentration which indicates a TMTU molecule adsorption with its negative pole, that is with the sulfur atom placed on the mercury electrode.

The values of E_z were similar for $c_{TMTU} \geq 0.01$ mol dm^{-3} in the detergents absence.[10] In the cationic detergents presence such E_z values changes are an experimental novelty and point to different adsorption-desorption equilibria. The γ_z values decreased in a comparable way to the changes in the detergents absence.[10] The data obtained by the integration of differential capacity curves were subsequently used to calculate Parsons' auxiliary function $\xi = \gamma + qE$, where q is the electrode charge and E is the electrode potential.[20,21] This function was used to calculate the summarized surface excess, Γ based on the dependence:

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial \xi}{\partial \ln c}\right)_q \quad (1)$$

where c is the bulk concentration of TMTU. The adsorption of ClO_4^- ions was demonstrated earlier[22] and the detergents adsorption was obvious. Therefore the adsorption of TMTU in the detergents presence was described using the relative surface excess, Γ' which, according to Gibbs adsorption isotherm, is given by:

$$\Gamma' = \frac{1}{RT}\left(\frac{\partial \Phi}{\partial \ln c}\right)_q \quad (2)$$

where Φ is the surface pressure: $\Phi = \Delta\xi = \xi_0 - \xi$ (ξ_0 is the value of Parsons' auxiliary function for the base electrolyte: 1 mol dm^{-3} NaClO$_4$ + 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$N$^+$, and ξ is the same function for systems containing TMTU). The obtained Γ values were greater for defined TMTU concentration than Γ' values. This indicates that the adsorption of TMTU molecule pushes out water instead of the detergents molecule from the electrode surface. The Γ' values obtained in the studied systems are presented in Figure 2.

The values of Γ' increased with increasing electrode charge more strongly as the TMTU concentration increased in the bulk. The dependencies $\Gamma' = f(q)$ for lower TMTU concentrations were similar both in the detergents presence and absence. This leads us to the conclusion that the cationic detergent did not hinder TMTU adsorption.
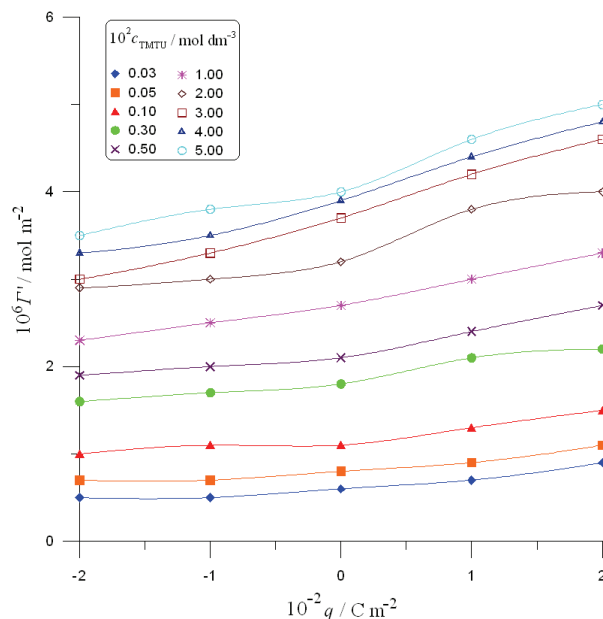
Figure 2. Relative surface excess of TMTU as a function of the electrode charge and TMTU concentration in the bulk.

Adsorption Isotherms

TMTU adsorption parameters in the presence of the cationic detergent were calculated based on Frumkin and corrected Flory-Huggins[23–26] isotherms. The Frumkin isotherm constants were determined from the equation:

$$\beta x = \frac{\Theta}{1-\Theta}\exp(-2A\Theta) \quad (3)$$

where x is the molar fraction of TMTU in the solution, β is the adsorption coefficient ($\beta = \exp(-\Delta G^o/RT)$), ΔG^o 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 surface occupied by one TMTU molecule S ($S \equiv 1/\Gamma_s$) was 0.137 nm^2 and was clearly smaller than in the detergents absence.[9] Such a small S value could have been the result of TMTU's dipole deformation in the presence of

Table 2. The constants of Frumkin (F) and corrected Flory-Huggins isotherm (H) for system: 1 mol dm^{-3} NaClO$_4$ + 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$N$^+$ + TMTU

$10^2 q$ / C m^{-2}	ΔG_F^0	$-A_F$	ΔG_H^0	$-A_H$
+2	24.47	3.60	23.83	3.50
+1	23.85	3.75	23.16	3.95
0	23.46	4.35	22.81	4.40
−1	23.28	4.65	22.64	4.85
−2	23.23	5.30	22.59	5.18
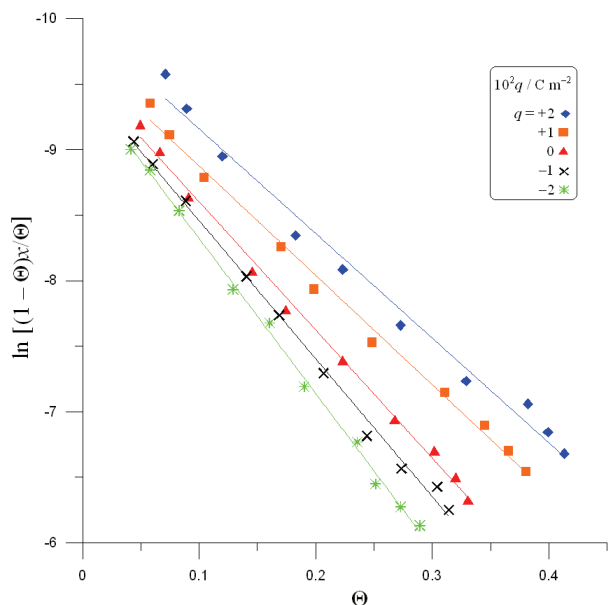
Figure 3. Linear test of the Frumkin isotherm for the system: 1 mol dm^{-3} NaClO$_4$ + 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$N$^+$ + TMTU

the detergents big molecule. Figure 3 presents the linear test of the Frumkin isotherm for used electrode charges.

The *A* parameter values were calculated from the line slopes on the linear test of the Frumkin isotherm and the corresponding values of ΔG^o were determined by the extrapolation of the ln[(1 – Θ)x/Θ] *vs*. Θ curve to the value of Θ = 0. The obtained results are presented in Table 2.

The obtained values of free adsorption energy increased in a manner typical for the adsorption *i.e.* in the
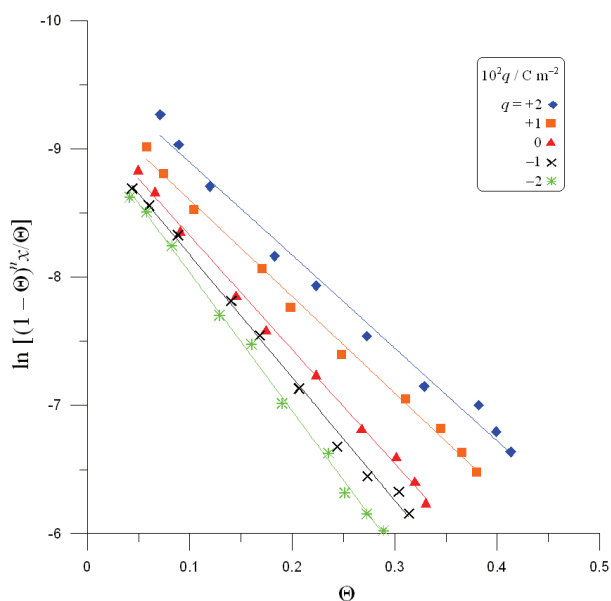
Figure 4. Linear test of the modified Flory-Huggins isotherm for the system: 1 mol dm^{-3} NaClO$_4$ + 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$N$^+$ + TMTU

direction of positive charges. The *A* interaction parameters pointed to repulsive interactions between the adsorbed TMTU molecules decreasing towards the positive electrode charge.

It should be stressed that the obtained ΔG^o values were clearly smaller than those obtained in the detergents absence. The repulsive interactions between the adsorbed TMTU molecules were considerably stronger than those obtained in detergents absence. The obtained Frumkin isotherm constants pointed to the fact that despite of lower ΔG^o values and stronger repulsive interactions in the presence of the studied detergent, TMTU's relative surface excess remained unchanged. This could have been the result of weaker hydration of the electrode surface.

TMTU adsorption in the presence of C$_{11}$H$_{26}$N$^+$ was further analyzed based on constants obtained from the modified Flory-Huggins isotherm[23–26] for the long-range particle-particle interaction:

$$\beta x = \frac{\Theta}{n(1-\Theta)^n} \exp(-2A\Theta) \qquad (4)$$

where n = 1.12 is the number of water molecules replaced by one TMTU molecule. In the present paper the projected area for water[25] is 0.123 nm^2. As ClO$_4^-$ ions caused the strongest disruption in water structure,[12] the surface of one water molecule was used in calculations instead of water clusters.

Figure 4 shows the linear test of the modified Flory-Huggins isotherm for the chosen values of q.

The obtained constants of this isotherm are presented in Table 2. The ΔG^o values were smaller than those obtained from the Frumkin isotherm however the *A* parameter values were similar. The obtained results from Flory-Huggins isotherm were the result of n value, which was close to one.

The Inner Layer Electrostatic Parameters

The electrostatic parameters of the inner layer were calculated from the dependence of the potential drop across the inner layer Θ^{M-2} at constant charge due to the relative surface excess of TMTU (Figure 5). According to Parson's electrostatic model,[21] the potential Θ^{M-2} can be described by the following dependence:

$$\Phi^{M-2} = \frac{4\pi x_1}{\varepsilon_i} q + \frac{4\pi \mu_{TMTU}}{\varepsilon_i} \Gamma' \qquad (5)$$

where μ_{TMTU} is the dipole moment of an isolated TMTU molecule: μ_{TMTU} = 15.7×10^{-30} C m[26], ε_i is the permittivity of the inner layer and x_1 is the inner layer thickness. The value of $\Theta^{M-2} = E - E_z - \Theta^{2-s}$, where: E and E_z are

respectively the measured potential and the potential of the zero charge in the absence of TMTU and Θ^{2-s} is the potential drop across the diffuse layer, which can be calculated using the Gouy-Chapman theory. The changes in the potential drop across the inner layer presented in Figure 5 are almost linear.

The linear course of the above dependences confirms the congruence of the obtained isotherms with respect to the electrode charge. The results presented in Figure 5 were analyzed in a way similar to that used previously by Jurkiewicz-Herbich[28] and the values of ε_i, integral capacity - K^i, and x_1 are presented in Table 3.

The obtained K^i value did not depend on the electrode charge just like in the detergents absence[10] but was considerably lower. Whereas the ε_i values were similar to those obtained in the detergents absence and raised with the increase of electrode charge.

In consequence the inner layer thickness, x_1 slightly increased with the increasing electrode charge. The large x_1 value was undoubtedly the result of the cationic detergent molecules length which rose with the increase of electrode charge. This effect was probably the outcome of the repulsive interaction between detergents positive end, and the electrode positively charged surface.

Studies of Adsorption at More Negative Potentials

The results presented earlier concerning TMTU adsorption in the presence of $C_{11}H_{26}N^+$ provided information about the mixed adsorption layers structure and covered these substances potential range of strong adsorption. The studies on kinetics of Zn^{2+} ion reduction as a piloting ion broaden this range. The necessary values to determine Zn^{2+} ions reduction in the studied systems changed as follows:

- Zn^{2+} ions approximate diffusion coefficients (D_{ox}) in the examined solutions were calculated from limiting currents using the Ilkovič equation. The values of D_{ox} slightly increased from 6.6×10^{-6} cm^2 s^{-1} to 6.8×10^{-6} cm^2 s^{-1}. The used organic substances decreased the solutions viscosity. The zinc diffusion coefficient value (D_{red}), which was required for further calculations was taken from the literature[29] as equal to 1.67×10^{-5} cm^2 s^{-1}.
- The difference between potentials of anodic and cathodic peaks on cyclic voltammetric curves, ΔE changed from 65 mV for Zn^{2+} in 1 mol dm^{-3} NaClO$_4$ to 512 mV for Zn^{2+} in the presence of 7.5×10^{-4} mol dm^{-3} $C_{11}H_{26}N^+$ to 38 mV after the addition of 5×10^{-2} mol dm^{-3} TMTU. The obtained results allowed a quality based assessment of reduction kinetics of Zn^{2+} ions in the studied systems: the used concentration of cationic detergent inhibited strongly the electrons transfer however the introduction of higher concentrations of TMTU compensated this inhibition and even accelerated the Zn^{2+} ions electroreduction process.
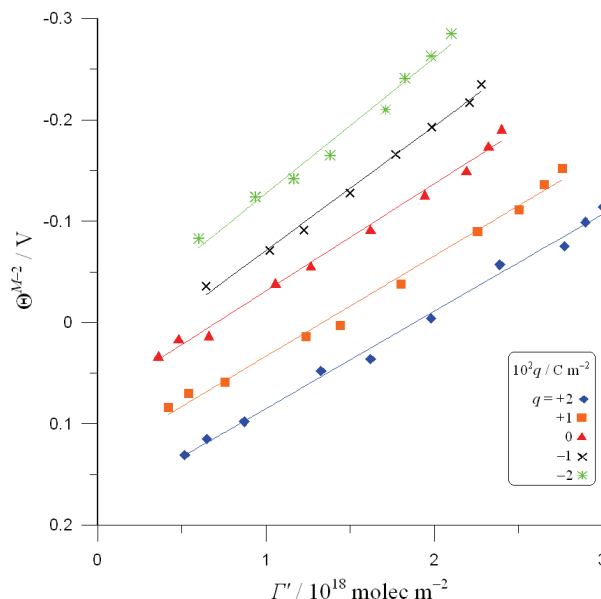

Figure 5. Potential drop across the inner layer Θ^{M-2} as a function of the surface concentrations of TMTU adsorbed at constant electrode charges for 1 mol dm^{-3} NaClO$_4$ + 7.5×10^{-4} mol dm^{-3} $C_{11}H_{26}N^+$ + TMTU.

- The addition of 7.5×10^{-4} mol dm^{-3} $C_{11}H_{26}N^+$ to the Zn^{2+} solution caused the shift of the formal potential, E_f^0, from -0.960 V to -1.01 V however the addition of increasing amounts of TMTU caused the E_f^0 final shift to -0.950 V. Figure 6 presents a logarithmic dependence, apparent standard rate constant, k_s^{app} of Zn^{2+} ions reduction on TMTU concentration. The determined k_s^{app} values are a quantitative confirmation of the mentioned above effects concerning ΔE and E_f^0 value changes. A compensation for the inhibiting and accelerating effect was obtained for the bulk concentrations ratio $c_{TMTU} : c_{detergent} = 250$. It is worth pointing out that even the smallest TMTU concentration of TMTU clearly decreased the cationic detergents inhibiting activity. Whereas the largest tested TMTU concentration to a much higher degree caused a Zn^{2+} ions electroreduction acceleration effect in the cationic detergents presence than in its absence.

Table 3. Inner layer properties for the system: 1 mol dm^{-3} NaClO$_4$ + 7.5×10^{-4} mol dm^{-3} $C_{11}H_{26}N^+$ + TMTU, 10^2 q / C m^{-2}

		$\Gamma' = 0$		$\Gamma' = 1$	
q	ε_i	$10^2 K^i$ / F m^{-2}	x_1 / nm	$10^2 K^i$ / F m^{-2}	x_1 / nm
-2	14.17	8.33	1.50	9.09	1.38
-1	14.17	8.33	1.50	9.09	1.38
0	16.55	8.33	1.76	9.09	1.61
1	17.71	8.33	1.88	9.09	1.72
2	18.64	8.33	1.98	9.09	1.81
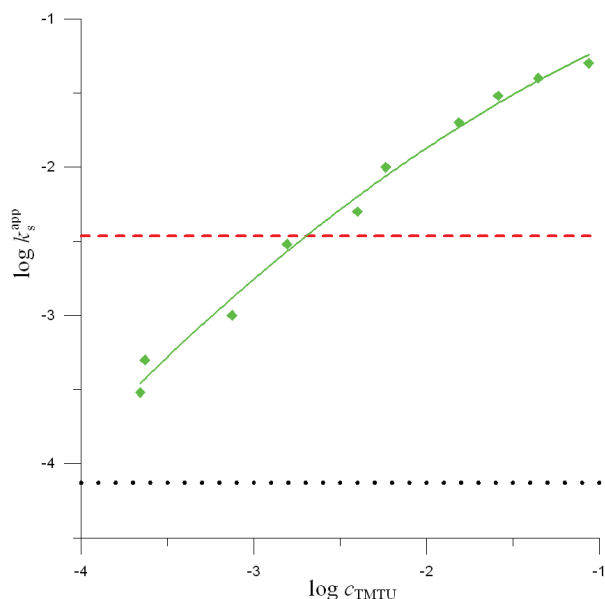
Figure 6. Plots of log $\sqrt{k_s^{app}}$ for the 5×10^{-3} mol dm^{-3} Zn^{2+} in 1 mol dm^{-3} NaClO$_4$ (the dashed line), 1 mol dm^{-3} NaClO$_4$ + 5×10^{-3} mol dm^{-3} Zn^{2+} + 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$N$^+$ (the dotted line) and with the addition of various TMTU concentrations (the continous line).

- The kinetic measurements confirmed the mixed adsorption layers presence on the mercury electrode surface even in the potential range of -1.0 V in which it was impossible to calculate adsorption parameters by means of the thermodynamic method.

CONCLUSIONS

Based on the TMTU adsorption measurements in the cationic detergents presence and Zn^{2+} reduction kinetics in the studied systems, the following statements referring to the mixed adsorption layer on the mercury electrode can be made:

1. By comparing the summarized surface excess, Γ, and the relative surface excess, Γ', it followed that the adsorbing itself TMTU molecule pushed out the water molecule instead of the detergents molecule from the electrode surface.
2. The presence of 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$N$^+$ at the electrode surface to a small degree influenced the surface TMTU concentration.
3. The small surface occupied by one TMTU molecule in the cationic detergents presence might have been a sign of a strong deformation of that molecule.
4. The constants of the Frumkin and corrected Flory-Huggins isotherm point to a decreased TMTU adsorption energy in the cationic detergents presence and stronger repulsive interaction.
5. The linear changes of Θ^{M-2} *vs.* Γ'_{TMTU} confirmed the

congruence of the obtained isotherms with respect to the electrode charge
6. The permittivity, ε_i of the inner layer was similar to the one obtained in the detergents absence.
7. Bigger accelerating effect on Zn^{2+} ion electroreduction caused by TMTU in the presence of 7.5×10^{-4} mol dm^{-3} C$_{11}$H$_{26}$N$^+$ than just in 1 mol dm^{-3} NaClO$_4$ was a confirmation of earlier observations[30,31] and might have been the result of a weaker electrode surface hydration during adsorption of the used organic substances.

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