ADSORPTION OF THIOUREA AND ITS METHYL DERIVATIVES FROM CHLORATE(VII) WITH VARIED WATER ACTIVITY

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The comparison of thiourea, methylthiourea, dimethylthiourea and tetramethylthiourea adsorption at mercury|sodium chlorate(VII) interface was done. For the sake of due to the specific interactions between sulfur and mercury all the compounds examined are pointed with their negative end towards mercury, even at the negative values of an electrode charge. However the change of an electrode charge is connected with the change of an adsorbate reorientation. It was found that with the increase of the methyl group amount in a molecule of thiourea methyl derivatives: (i) the range of adsorption potentials is expanded, (ii) the values of zero charge potentials and surface tension decrease, (iii) the surface excesses increase. Whereas the considerable changes of adsorption energy values were not fund. The lack of symmetry results in a molecule, while the methylthiourea interaction constants are much more higher than the interaction constants of the other compounds examined. The changes of adsorption parameters as a function of the supporting electrolyte concentration are analogous for all the adsorbates examined. They point to the competitive adsorption of thiourea methyl derivatives and ClO_4^-.
Keywords: Adsorption; Mercury; Sulfur; Thiourea; Methylthiourea; Dimethylthiourea.

Adsorption of thiourea (TU) and its derivatives on mercury is a result of specific interactions between adsorbate sulfur and mercury, what causes that even at positively charged electrode, the partial electron transfer between sulfur atom and mercury[1,2] occurs. Adsorption of TU and its derivatives at the mercury|aqueous solution interface was also examined in the presence of electrolytes with the specifically adsorbed anions, which is connected with the occurrence of competitive adsorption[3–7].

In the last years, the papers concerning the thiourea and its derivatives adsorption, taking into consideration the hydrogen bond among water molecules as well as the degree of electrode surface hydration, were published[8,9]. The good objects of such studies are the methyl derivatives of TU

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for the sake of the appearance of mercury–CH_3 hydrophobic group interactions.

In the present paper, the adsorption of TU and its methyl derivatives at mercury|aqueous solution of $NaClO_4$ interface as a function of supporting electrolyte concentration was compared. Among the thiourea, methyl derivatives methylthiourea (MTU) and dimethylthiourea (DMTU) were chosen to be examined[9]. The lack of symmetry in a MTU molecule should influence the change in the structural adsorbate arrangement at the interface comparing with the symmetrical molecules of TU and DMTU.

EXPERIMENTAL

Chemicals

The solutions were prepared using the analytical-grade reagents $NaClO_4$, thiourea, *N*-methylthiourea and *N*,*N*′-dimethylthiourea (Fluka). Water and mercury were double-distilled. The concentrations of TU, MTU and DMTU were from 5×10^{-4} to 1×10^{-2} mol l^{-1}. The maximum concentration was limited by the solubility of these compounds in the supporting electrolyte.

The solutions were deaerated using high-purity nitrogen which was passed over the washer with an examined solution.

Adsorption of MTU and DMTU was examined in 0.1, 1 and 5 M $NaClO_4$. The water activity in these solutions is equal to 0.995, 0.966 and 0.776, respectively[10,11].

Electrochemical measurements were carried at 298 ± 1 K in a three-electrode cell containing a controlled-growth mercury drop electrode (CGMDE) made by MTM Poland, Ag|AgCl| saturated NaCl as a reference electrode and a platinum spiral as a counter electrode. The reference electrode was connected to the electrolytic cell via an intermediate vessel filled with the solution to be investigated.

The differential capacity of the double layer (C_d) was measured at frequencies 200–1200 Hz and amplitude 5 mV using the AC impedance technique with the Autolab frequency response analyser (Eco Chemie). The reproducibility of the differential capacity measurements was equal to ±0.5%.

The potential of zero charge (E_z) was measured for each solution by the method of streaming mercury electrode[13]. The interfacial tension γ_z between mercury and the electrolyte solutions at (E_z) was measured with a conventional maximum bubble-pressure capillary electrometer described earlier[14].

Calculation Procedure

In all the systems studied the frequency dispersion of differential capacity values obtained was found. Therefore the C_d values were extrapolated to zero frequency from the notation $C_d = f(\omega^{1/2})$, where $\omega = 2\pi f$. This procedure assumes that the impedance of the double layer is equivalent to a series capacity-resistance combination, and the rate of adsorption is diffusion-controlled[15]. From the integration of differential capacity curves extrapolated to zero frequency, the values of charge density on electrode surface σ_M and the values of surface tension γ_z were obtained. The determined values of E_z and γ_z were used as the integration constants. No corrections for the effects of the medium on the activity of the supporting electrolyte[16,17] and the activity coefficient of the adsorbate were made[18]. The values E_z and γ_z obtained from the integration were applied to calculate the Parsons' auxiliary function ξ (ref.[19]), $\xi = \gamma + \sigma_M E$, where σ_M is the electrode charge and E is the electrode potential. To calculate the surface pressure Φ

$$\Phi = \Delta\xi = \xi_0 - \xi \tag{1}$$

where ξ_0 is the value of Parsons' auxiliary function for the supporting electrolyte and ξ is the value for the solution containing adsorbate.

The relative surface excess Γ' of adsorbate was determined which according to the Gibbs adsorption isotherm is given by

$$\Gamma' = \left(\frac{1}{RT}\right)\left(\frac{\mathrm{d}\Phi}{\mathrm{d}\ln c}\right)_{\sigma_M} \tag{2}$$

where c is the bulk concentration of adsorbate.

RESULTS AND DISCUSSION

Analysis and Experimental Data

The addition of TU, MTU or DMTU to chlorate(VII) solution causes the increase of differential capacity in all the potential range studied. Figure 1 presents the differential capacity curves at the mercury|5 M $NaClO_4$ + TU interface. With the increase of TU concentration, the differential capacity increases and the hump occurring on the curves is shifted towards the negative potentials. Such changes on the differential capacity curves occur as well with the increase of the supporting electrolyte concentration (Fig. 2). From Figs 1 and 2 results that the hump position and height on curves $C_d = f(E)$ are dependent not only on the adsorbate concentration but also on the supporting electrolyte concentration, what points at the considerable participation of water molecules in the adsorption-desorption processes.

Moreover, it was found that at the same values of water activity and adsorbate concentration, the hump shift on the curves $C_d = f(E)$ increases with the increase of the amount of methyl groups in an adsorbate molecule, what is presented in Fig. 3.

Figure 3 shows as well the differential capacity curve in the presence of tetramethyltiourea (TMTU) from the paper presented by Gugała and co-workers[8], what testifies this regularity. It should also be noticed that with the increase of the amount of methyl groups in a molecule, the range of adsorption potentials of examined adsorbates expands.

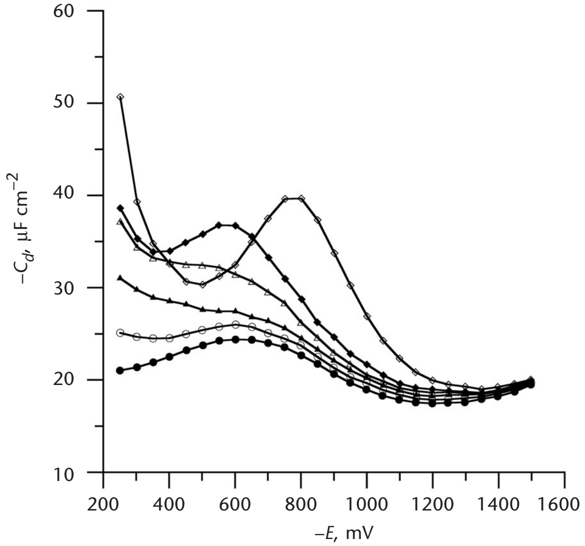

FIG. 1
Differential capacity–potential curves of the mercury electrode in 5 M $NaClO_4$ with various concentrations of thiourea (in mol l^{-1}): 0 (●), 5×10^{-4} (○), 1×10^{-3} (▲), 5×10^{-3} (△), 1×10^{-2} (◆) and 1×10^{-1} (◇)

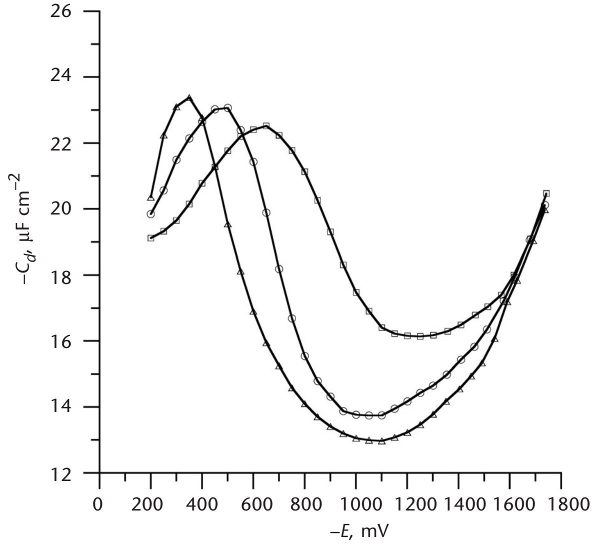

FIG. 2
Differential capacity–potential curves of the mercury electrode in various concentration of $NaClO_4$ (in mol l^{-1}): 0.1 (△), 1 (○) and 5 (□)

The values of zero charge potentials E_z and surface tension γ_z at zero charge potential as a function of TU, MTU, DMTU and TMTU concentrations in 1 M $NaClO_4$ are presented in Table I.

TABLE I
Potential of zero charge E_z vs Ag|AgCl electrode and surface tension γ_z for E_z of 1 M $NaClO_4$ + adsorbate systems for the equal adsorbate concentrations. The values were taken from the literature: TU [20], DMTU [9] and TMTU [8]

Adsorbate	0.5×10^{-3} mol l^{-1}		1×10^{-3} mol l^{-1}		5×10^{-3} mol l^{-1}	
	$-E_z$ mV	γ_z mN m^{-1}	$-E_z$ mV	γ_z mN m^{-1}	$-E_z$ mV	γ_z mN m^{-1}
TU	478.0	423.4	491.0	423.2	539	422.7
MTU	495.0	420.8	519.3	419.8	575.2	418.2
DMTU	521.0	415.0	544.0	412	611.0	406.0
TMTU	542.0	415.0	579.1	413.1	642.7	405.1

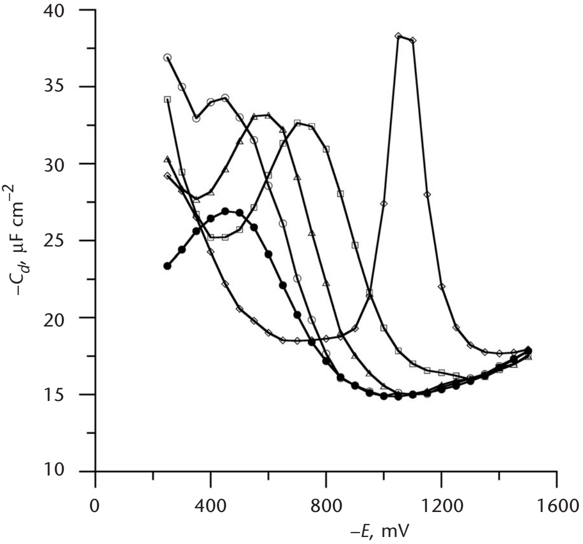

FIG. 3
Differential capacity–potential curves of the mercury electrode in 1 M $NaClO_4$ (●), and with 5×10^{-3} M TU (○), MTU (△), DMTU (□) and TMTU[8] (◇)

As the concentration of TU and its methyl derivatives increases, the values of zero charge potentials are shifted towards the negative potentials[9,20]. For the equal concentrations of examined adsorbates, the shift of E_z value increases with the increase of the amount of methyl groups in an adsorbate molecule, whereas γ_z values decrease. It points at the adsorption increase of the methyl derivatives of thiourea in a series TU < MTU < DMTU < TMTU.

Figure 4 presents the changes of E_z and γ_z values as a function of MTU concentration in 0.1, 1 and 5 M $NaClO_4$. Such dependences run analogously for the rest of thiourea methyl derivatives examined. Therefore it could be said that the increase of the supporting electrolyte concentration causes the similar changes in E_z and γ_z values as the increase of the concentration of TU methyl derivatives[8,9]. This fact confirms the meaningful role of water activity in the adsorption-desorption processes.

The relative surface excesses of thiourea and its methyl derivatives were determined at the constant electrode charge. The congruence of adsorption isotherms versus charge is confirmed by the linear dependences of the potential decrease in the inner layer versus surface excess of each thiourea derivative[8,9,20]. As it was found in the previous papers, the values of TU [20], DMTU [9] and TMTU [8] surface excesses increase with the increase of the thio-

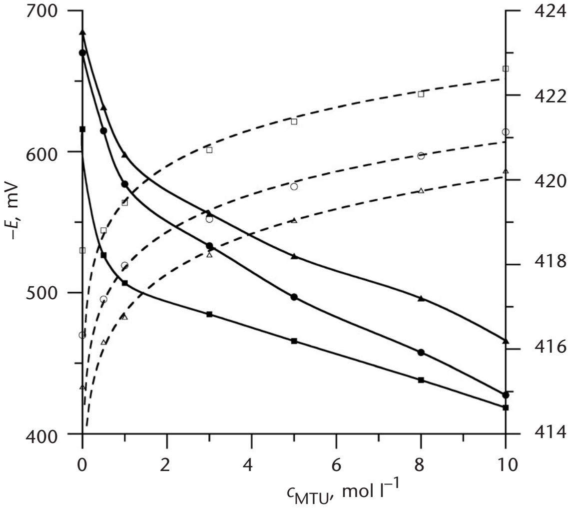

FIG. 4

Potential of zero charge E_z (– – –) vs Ag|AgCl electrode as a function of MTU concentration for 0.1 M $NaClO_4$ + MTU (△), 1 M $NaClO_4$ + MTU (○) and 5 M $NaClO_4$ + MTU (□) systems, and surface tension γ_z (——) at E_z for 0.1 M $NaClO_4$ + MTU (▲), 1 M $NaClO_4$ + MTU (●) and 5 M $NaClO_4$ + MTU (■) systems urea methyl derivative concentrations, electrode charge and water activity. The same dependences were obtained for MTU as well (Fig. 5).

Figure 6 presents the adsorption isotherms of the thiourea derivatives examined in 1 M $NaClO_4$ for the electrode charges $\sigma_M = -2 \times 10^{-2}$ C m^{-2} and $\sigma_M = +2 \times 10^{-2}$ C m^{-2}. With the increase of the amount of methyl groups in an adsorbate molecule, the surface excesses increase in all the range of the electrode charges examined.

For the description of thiourea and its methyl derivatives adsorption, the Frumkin and virial isotherms were applied. For all the systems examined, the linear dependences $\ln x(1 - \Theta)/\Theta = f(\Theta)$ (Frumkin isotherm) and $\log (\Gamma'/c) = f(\Gamma')$ (virial isotherm) were obtained, what substantiated such a choice[8,9,20]. The determined values of adsorption energy ΔG^0 and interaction constants A point that with the increase of electrode charge, the values of ΔG^0 increase.

Figure 7 shows the dependence of ΔG^0 of MTU versus the electrode charge. In 0.1, 1 and 5 M chlorate(VII) it is a linear dependence, which indicates the preferential participation of stable MTU dipoles that influence the value of ΔG^0 (ref.[2]).

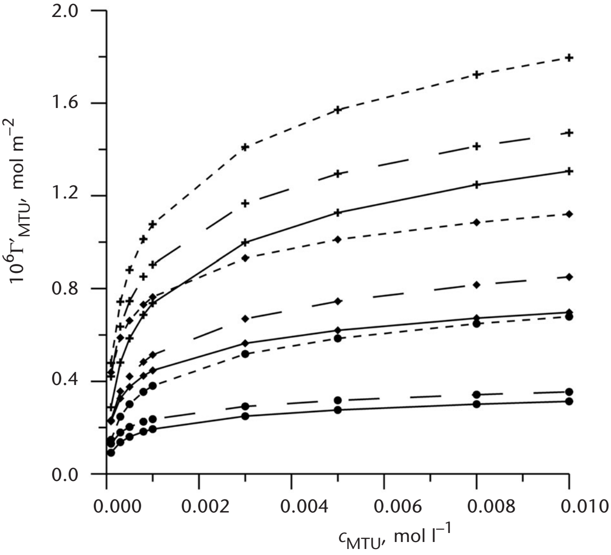

FIG. 5

Relative surface excess of MTU as a function of MTU concentration in the bulk for 0.1 (- - -), 1 (– – –) and 5 M $NaClO_4$ (——) at the electrode charges σ_M (in 10^{-2} C m^{-2}) –3 (●), 0 (◆) and +3 (+)

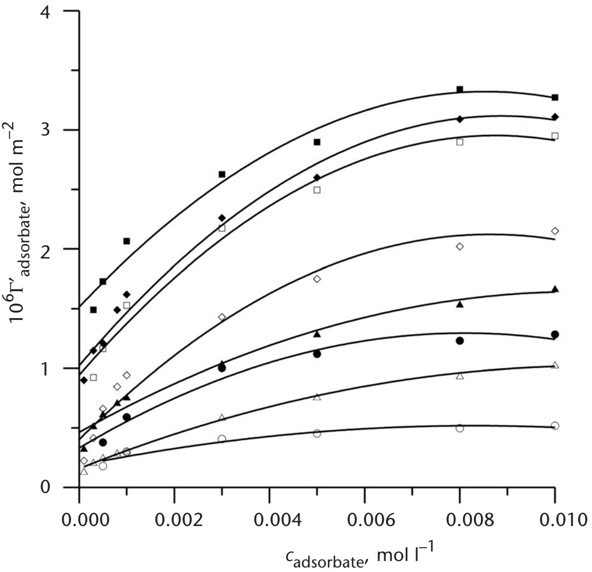

FIG. 6

Relative surface excess of TU (○), MTU (△), DMTU (□) and TMTU (◇) as a function of adsorbate concentration in the bulk for 1 M $NaClO_4$ at the electrode charges σ_M (in 10^{-2} C m^{-2}) –2 (empty symbols) and +2 (full symbols)

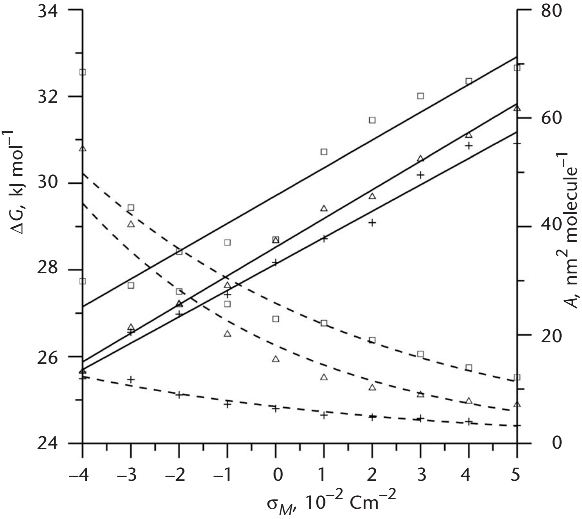

FIG. 7

Adsorption energy ΔG (——) and the values of interactions constant A (– – –) of MTU as a function of the electrode charge for 0.1 (+), 1 (△) and 5 M (□) $NaClO_4$

The values of *A* decrease with the increase of charge what is a result of ClO_4^- anions penetration among the positively charged amine groups of MTU at $\sigma_M > 0$ [21,22] and consequently, the screening of repulsive interactions between adsorbed MTU molecules leading to an increase of MTU adsorption. The similar effect occurs for TU [20] and DMTU [9]. With the increase of the supporting electrolyte concentration, the values of free adsorption energy as well as the values of interaction constants among MTU and DMTU molecules increase[9].

The obtained values of the virial isotherms constants as a function of the chlorate(VII) concentration and the electrode charge confirm analogous changes obtained for the Frumkin isotherm.

In the presence of TMTU [8] the different dependences were obtained, what according to the authors is the result of the lack of linearity $\Gamma' = f(\sigma_M)$ for TMTU concentrations higher than 3×10^{-3} mol l^{-1}.

Table II shows the virial isotherm constants for the systems of 0.1, 1 and 5 M $NaClO_4$ containing TU [20], MTU, DMTU [9] and TMTU [8]. It seems that the increase of the amount of methyl groups in molecules of the thiourea derivatives examined influences in a slight degree the values of ΔG^0, whereas the *B* values present the distinct tendency to decrease. It should be also no-

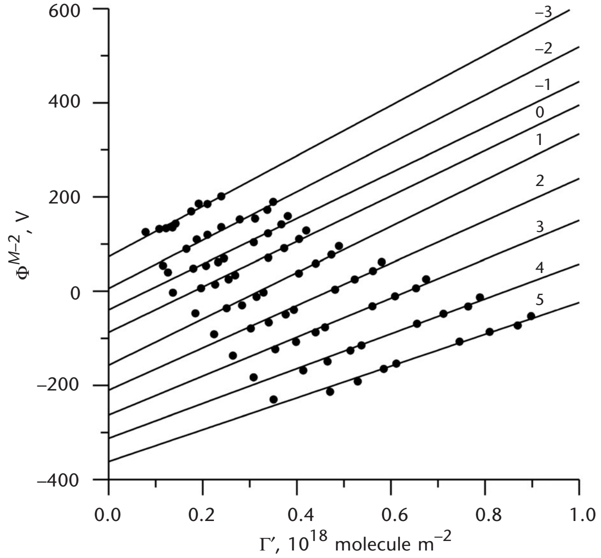

FIG. 8
Potential drop across the inner layer Φ^{M-2} as a function of the quantity of MTU adsorbed at constant electrode charges (σ_M in 10^{-2} C m^{-2}) for 5 M $NaClO_4$

ticed that in the presence of MTU, the interaction constants *B* are much higher than those ones existing in the presence of the rest of the thiourea derivatives examined. This fact is undoubtedly connected with the lack of symmetry in a MTU molecule.

The determination of the changes in the potential drop across the inner layer Φ^{M-2} at constant charge, caused by the adsorption of the thiourea methyl derivatives, was studied. These changes are the result of the participation of free charges and oriented dipoles. Experimental separation of these effects is in principle impossible[23].

In all examined systems the dependences $\Phi^{M-2} = f(\Gamma'_{ads})$ are linear, which confirms the congruence of the adsorption isotherms at the constant charge. The dependence of Φ^{M-2} on the surface excess Γ′ at a constant charge density as a function of the quantity of MTU for 5 M $NaClO_4$ is presented in Fig. 8. Such a shape of the dependence $\Phi^{M-2} = f(\Gamma'_{ads})$ for all the thiourea derivatives examined in 0.1, 1 and 5 M $NaClO_4$ was obtained. The

TABLE II
Comparison of the virial isotherm constants for systems 0.1, 1 and 5 M $NaClO_4$ containing TU [20], MTU, DMTU [9] and TMTU [8]

Adsorbate	σ_M 10^{-2} C m^{-2}	ΔG, kJ mol^{-1}			B, nm^2 $molecule^{-1}$		
		0.1 M $NaClO_4$	1 M $NaClO_4$	5 M $NaClO_4$	0.1 M $NaClO_4$	1 M $NaClO_4$	5 M $NaClO_4$
TU	–3	–	98.5	–	–	1.25	–
	0	–	99.0	–	–	1.15	–
	+3	–	102.0	–	–	0.62	–
MTU	–3	104.5	104.6	107.2	4.2	10.9	11.6
	0	106.2	106.6	107.6	2.2	3.9	5.3
	+3	108.3	108.3	110.9	1.7	2.3	3.9
DMTU	–3	102.6	104.1	105.2	0.9	1.0	1.5
	0	104.2	105.4	107.0	0.8	0.9	1.1
	+3	106.4	107.8	108.7	0.7	0.8	1.0
TMTU	–3	112.7	106.0	–	1.9	0.8	–
	0	115.0	108.5	–	2.0	1.0	–
	+3	121.9	111.8	–	1.3	1.1	–

slope $\Phi^{M-2} = f(\Gamma'_{\mathrm{ads}})$ decreases with the increase of the electrode charge, which allows to suppose that the adsorbed molecules change their reorientation with the change of the electrode charge. However the thiourea and its methyl derivatives are always oriented with its negative end towards the mercury even at the most negative values of σ_M, in spite of a very strong adsorption on mercury caused by the highly specific interaction between sulfur and mercury.

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