

ADSORPTION OF TETRAMETHYLTHIOUREA IN CONCENTRATED NaClO_4 SOLUTIONS

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Tetramethylthiourea electrosorption behaviour on the mercury electrode in 2, 3 and 4 mol l^{-1} NaClO_4 was determined by means of double-layer differential capacity measurements. The relative surface excess Γ' of the adsorbate calculated from the surface pressures depended on the NaClO_4 concentration. A clear influence of NaClO_4 concentration appeared in the changes of interaction parameter A obtained from the Flory-Huggins isotherm and in the permittivity parameter of the inner layer.

Keywords: Differential capacity; Adsorption isotherm; Electrostatic parameters; Tetramethylthiourea; Mercury electrode.

The adsorption of an organic substance on the electrode is always associated with a competition among of this substance, water and ions of the supporting electrolyte. Hydrogen bonds between interfacial water molecules¹⁻³ play an important role in the adsorption process. The role of water molecules in studies on the adsorption of organic substances is very often neglected. Our previous research⁴⁻⁶ revealed an increasing adsorption of tetramethylthiourea (TMTU) and *tert*-butyl alcohol with increasing NaClO_4 concentration in the range 0.1–1.0 mol l^{-1} . It is therefore worth answering whether a similar dependence takes place in more concentrated solutions of NaClO_4 .

This paper is part of a broader project concerning the influence of water activity on the mercury/TMTU, ClO_4^- , H_2O interface structure. On the basis of the literature relating to thiourea and its alkyl derivatives⁷ it is suggested that one of the interfacial properties susceptible to a large change with adsorbates is the inner-layer permittivity. The choice of TMTU was based on

the expectation that the vertical orientation of thiourea molecules due to metal–sulfur interactions⁸ may affect the possibility of metal–hydrophobic group interactions⁹. The choice of NaClO_4 solution resulted from the fact that ClO_4^- ions cause the strongest disruption in the water structure¹⁰. In our studies on adsorption from solutions, the double-layer capacitance was usually chosen as the primary experimental quantity. Such a measurement is far more accurate when made on liquid rather than on solid metal surfaces, which is why mercury has played a dominant role as an electrode material in our studies. This is due to highly reproducible, readily renewable and smooth surface of mercury drops. The adsorption of TMTU from 2, 3 and 4 mol l⁻¹ NaClO_4 on mercury electrode is described here by means of the adsorption isotherm constants derived from the surface pressure data as a function of electrode charge density and bulk concentration. This paper presents a small fraction of our complex studies involving the influence of TMTU adsorption on the kinetics of electroreduction of metal cations. NaClO_4 solutions at pH 3 were used in these studies to protect metal cations from hydrolysis.

EXPERIMENTAL

Reagents

Analytical grade TMTU and NaClO_4 (Fluka) were used without further purification. Water and mercury were double-distilled before use. TMTU solutions of concentrations from 3×10^{-4} to 5×10^{-2} mol l⁻¹ were prepared. The maximum concentration of TMTU was limited by its solubility. The solutions were deaerated by passing high purity nitrogen over the solutions during the measurements at 298 ± 0.1 K.

Apparatus

The experiments were performed in a three electrode system with a dropping mercury electrode as a working electrode, $\text{Ag}|\text{AgCl}$ 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 differential capacity, C , of the double layer was measured with Autolab frequency response analyzer (Eco Chemie, The Netherlands) using the ac impedance technique. The reproducibility of the average capacity measurements was $\pm 0.5\%$. The measurements were carried out at several frequencies in the range from 400 to 2 000 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 to zero frequency. Figure 1 presents an example of dependencies of the measured capacity at -0.4 V in 3 mol l⁻¹ NaClO_4 and at the desorption peak potential of -0.8 V versus the square root frequency.

The potential of zero charge, E_z , was measured using a streaming electrode¹¹. The interfacial tension, γ_z , at E_z was measured by the maximum bubble pressure method according to

Schiffrin¹². The charge density and surface tension in the presence of TMTU were obtained by the back integration of differential capacity–potential dependences¹³. No corrections for the effects of the medium on the activity of the supporting electrolyte^{14,15} and activity coefficient of the adsorbate¹⁶ were made.

RESULTS AND DISCUSSION

Analysis of Experimental Data

The parameters of the double layer for the TMTU adsorption were obtained from the differential capacity versus potential data for ten concentrations of TMTU in the supporting electrolytes consisting of 2, 3 and 4 mol l⁻¹ NaClO₄. Figure 2 presents the chosen differential capacity–potential curves in 3 mol l⁻¹ NaClO₄ extrapolated to zero frequency. This procedure assumes that the impedance of the double layer is equivalent to combination of a capacity–resistance series and that the rate of adsorption is diffusion-controlled. The capacity values (Fig. 2) in the vicinity of E_z for the solutions containing TMTU are lower than those for the base solution. Such an effect was not observed in solutions containing thiourea^{17,18} but it appeared in solutions containing alkyl derivatives of thiourea^{4,19}. With increasing TMTU and NaClO₄ concentrations this potential region of lowered capacity narrows down. Desorption peaks appear on the differential capac-

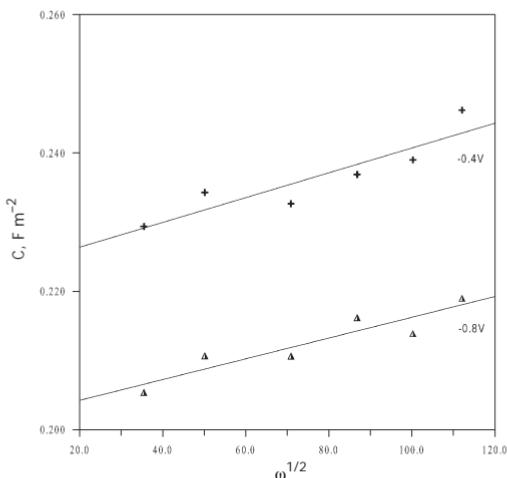


FIG. 1
Dependence of the capacity measured at potentials -0.4 and -0.8 V in 3 mol l^{-1} NaClO₄ versus square root of the frequency

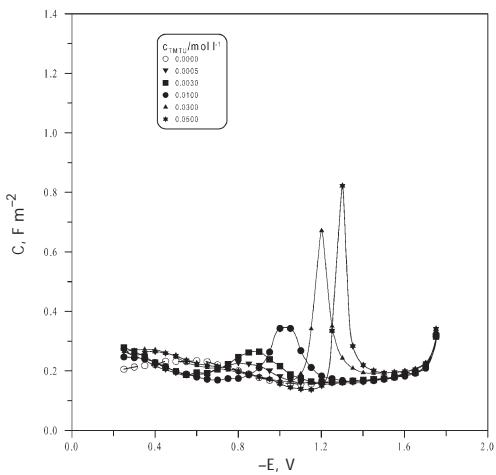


FIG. 2

Differential capacity-potential curves on the mercury electrode in contact with 3 mol l^{-1} NaClO_4 containing different concentrations of TMTU

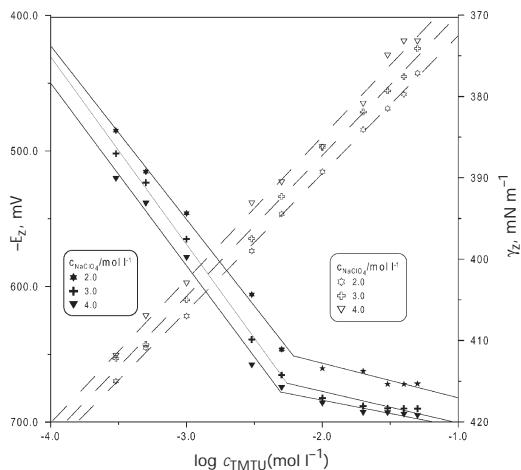


FIG. 3

Potentials of zero charge E_z (solid line) and interfacial tensions at the zero charge γ_z (dashed line) as a function of NaClO_4 concentration and as a function of the logarithm of TMTU concentration

ity curves, with peak potentials moving toward more negative values as the TMTU and NaClO_4 concentrations rise. However, the desorption peaks height is smaller than in $1 \text{ mol l}^{-1} \text{ NaClO}_4$ (ref.⁴).

As not all of the obtained C - E curves converge at sufficiently negative potentials with the corresponding curve for the base solution, the capacity versus potential data were numerically integrated from the point of E_z . The integration constants, E_z and γ_z values, are presented in Fig. 3. The E_z vs $\log c$ dependence has a linear course with different slopes in two sections, depending on the TMTU concentration: for the lower TMTU concentrations that slope is approximately 135 mV whereas for the higher concentrations of TMTU it drops to 28 mV. Maximum changes of ΔE_z are smaller than in $1 \text{ mol l}^{-1} \text{ NaClO}_4$ and slightly drop with increasing NaClO_4 concentration⁴. The straight line slopes obtained for γ_z values do not, on the other hand, depend on TMTU concentration. TMTU causes a considerably higher decrease of γ_z compared to the appropriate decrease of γ_z in $1 \text{ mol l}^{-1} \text{ NaClO}_4$ (ref.⁴). It is also worth mentioning that the section slopes presented in Fig. 3 do not depend on NaClO_4 concentration. The shift of E_z towards the negative values with increasing TMTU concentration confirms the adsorption of TMTU molecules with the sulfur atoms at the mercury electrode. Whereas the shift of E_z towards negative potentials with increasing NaClO_4 concentration as well as the decrease in γ_z prove that the adsorption of ClO_4^- ions takes place. The data obtained by the integration of differential capacity curves were subsequently used to calculate Parsons' auxiliary function $\xi = \gamma + \sigma E$, where σ is the electrode charge and E is the electrode potential²⁰. As the adsorption of ClO_4^- ions was demonstrated earlier²¹, adsorption of TMTU was described using the relative surface excess Γ' which, according to Gibbs adsorption isotherm, is given by:

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

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 and ξ is the same function for the solution containing TMTU). The values of Γ' obtained in $3 \text{ mol l}^{-1} \text{ NaClO}_4$ depending on surface charge and TMTU concentration are presented in Fig. 4. Slightly lower Γ' values were obtained in $2 \text{ mol l}^{-1} \text{ NaClO}_4$ whereas in 3 and $4 \text{ mol l}^{-1} \text{ NaClO}_4$ these values were comparable. For higher concentrations of TMTU a small dependence of Γ' on the surface charge should be highlighted. A stronger de-

pendence of Γ' on the TMTU bulk concentration is observed for $\sigma < 0$ than for $\sigma > 0$ in all tested systems. In higher TMTU concentrations the Γ' values are comparable to those obtained in 1 mol l⁻¹ NaClO₄, however, in lower TMTU concentrations the relative surface excess is considerably higher in concentrated NaClO₄ solutions.⁴

Adsorption Isotherms

The adsorption of TMTU was further analyzed on the basis of constants obtained from the modified Flory-Huggins²²⁻²⁵ isotherm for long-range particle-particle interactions

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

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 energy of adsorption, A is the interaction parameter, Θ is the coverage and n is the number of ClO₄⁻ ions replaced by one adsorbate molecule. The surface excess at saturation Γ_s was estimated by extrapolating the $1/\Gamma'$ vs $1/c$ dependence at different charge, to $1/c = 0$. The values of Γ_s were used to calculate the surface

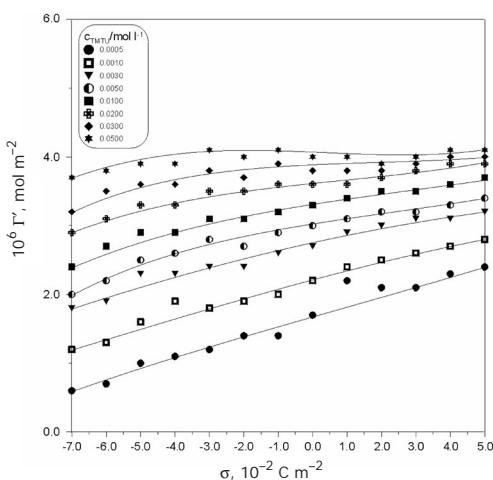


FIG. 4

Relative surface excess of TMTU as a function of the electrode charge and TMTU concentration in the bulk for 3 mol l⁻¹ NaClO₄

occupied by one TMTU molecule S ($S \equiv 1/\Gamma_s$). Values of S decrease from 0.43 to 0.33 nm 2 with increasing NaClO $_4$ concentration. The experimental values of S are smaller than the theoretical ones calculated for the vertical (0.47 nm 2) or horizontal (0.51 nm 2) orientation⁹. The smaller values of S could be a result of TMTU dipole deformation in the electric field. The S values decrease with increasing concentration of NaClO $_4$, this indicates an influence of ClO $_4^-$ ions present on the electrode surface. The S values obtained from NaClO $_4$ solutions at $0.1 \leq c \leq 1.0$ mol l $^{-1}$ concentration level clearly depend on electrode charge and at $\sigma < 0$ decrease from 0.62 to 0.42 nm 2 , whereas at $\sigma \geq 0$ decrease from 0.41 to 0.35 nm 2 with increasing NaClO $_4$ concentration⁴. In this case the values of n were calculated as a ratio of S for TMTU to S for the projected area of ClO $_4^-$ (0.31 nm 2). The obtained values of n were 1.40, 1.26 and 1.05 in 2, 3 and 4 mol l $^{-1}$ NaClO $_4$, respectively. Figure 5 shows the linear test of the modified Flory-Huggins isotherm for the chosen values of σ in 3 mol l $^{-1}$ NaClO $_4$. The A parameter values were calculated from the line slopes shown in Fig. 5 and the corresponding values of ΔG° were determined by the extrapolation of the $\ln [x(1 - \Theta)^n/\Theta]$ vs Θ curve to the value of $\Theta = 0$. The obtained results are presented in Fig. 6. The ΔG° values slightly depend on NaClO $_4$ concentration rising with increasing electrode charge. The obtained ΔG° values are distinctly

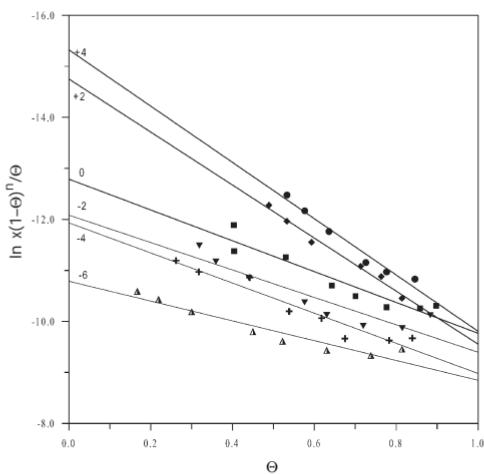


Fig. 5
Linear test of the Flory-Huggins isotherm for the system TMTU-3 mol l $^{-1}$ NaClO $_4$. The electrode charges (σ in 10^{-2} C m $^{-2}$) indicated by each line

higher than those obtained for 1 mol l⁻¹ NaClO₄ (ref.⁴). In 2 mol l⁻¹ NaClO₄ the ΔG° values increase linearly with increasing electrode charge (and are the highest). Whereas in 3 and 4 M NaClO₄ the ΔG° values are similar and increase jumpwise near $\sigma = 0$. It is worth mentioning that for $\sigma \leq -4 \mu\text{C cm}^{-2}$ the ΔG° values practically do not depend on the base electrolyte concentration.

The determined values of parameter A indicate a clear dependence of interaction between adsorbed TMTU molecules on the electrode charge: for $\sigma < 0$ there is a very weak repulsive interaction, for $\sigma = 0$ repulsive interactions increase in jumps. For $\sigma > 0$ the repulsive interaction remains at a constant level although the strongest repulsive interaction appears in 4 M NaClO₄ solution. The presence of ClO₄⁻ ions on the electrode surface, especially at $\sigma > 0$, has an undoubtedly significant influence on the intermolecular interaction of adsorbed TMTU. The A parameter values for σ near zero changed jumpwise, at $\sigma < 0$ repulsive interaction was stronger than at $\sigma > 0$ in NaClO₄ solution at $c \leq 1.0$ M concentration levels⁴.

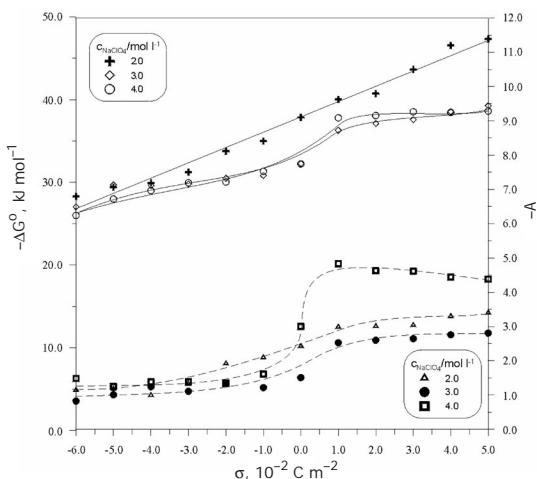


FIG. 6

Variation of the Gibbs energy of adsorption ΔG° (solid line) and of the interaction parameter A (dashed line) due to charge density

Electrostatic Parameters of the Inner Layer

The change in the potential drop across the inner layer Φ^{M-2} at constant charge due to the relative surface excess of TMTU provides multiple infor-

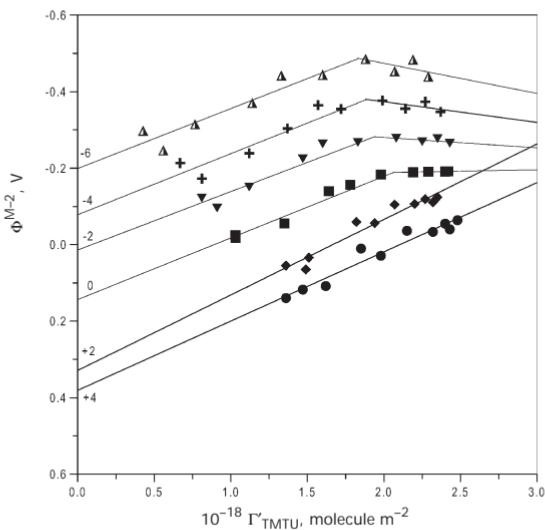


FIG. 7

Potential drop across the inner layer as a function of the amount of TMTU adsorbed at constant electrode charges (σ in 10^{-2} C m^{-2}) for $3 \text{ mol l}^{-1} \text{ NaClO}_4$

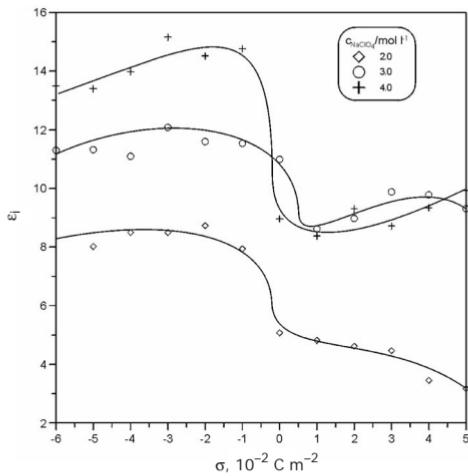


FIG. 8

Permittivity of the inner layer as a function of electrode charge and NaClO_4 concentration

TABLE I

Inner-layer properties for TMTU adsorbed at the mercury/aqueous NaClO_4 interface: $10^2 \sigma (\text{C m}^{-2})$, x_1 (nm), $10^{-18} \Gamma'$ (molecule m^{-2}), $10^2 K^i (\text{F m}^{-2})$

σ	2 mol l^{-1} NaClO_4				3 mol l^{-1} NaClO_4				4 mol l^{-1} NaClO_4			
	$\Gamma' = 0$		$\Gamma' = 1$		$\Gamma' = 0$		$\Gamma' = 1$		$\Gamma' = 0$		$\Gamma' = 1$	
	K^i	x_1	K^i	x_1	K^i	x_1	K^i	x_1	K^i	x_1	K^i	x_1
-6	8.66	-	11.9	-	16.94	0.59	17.85	0.56	15.15	0.64	16.12	0.60
-5	0.82		0.60		0.59		0.56		0.77		0.77	
-4	0.87		0.63		0.58		0.55		0.82		0.77	
-3	0.87		0.63		0.63		0.60		0.89		0.83	
-2	0.89		0.65		0.61		0.58		0.85		0.80	
-1	0.81		0.59		0.61		0.57		0.86		0.81	
0	0.52		0.38		0.57		0.55		0.52		0.49	
1	0.49		0.36		0.45		0.43		0.49		0.46	
2	0.47		0.34		0.47		0.45		0.54		0.51	
3	0.46		0.33		0.52		0.49		0.51		0.48	
4	0.35		0.26		0.51		0.49		0.55		0.51	
5	0.32		0.24		0.49		0.46		0.58		0.55	

mation about the double-layer structure. According to Parsons' electrostatic model⁸, the potential Φ^{M-2} can be described by the dependence:

$$\Phi^{M-2} = \frac{4\pi x_1}{\epsilon_i} \sigma \frac{4\pi \mu_{\text{TMTU}}}{\epsilon_i} \Gamma' \quad (3)$$

where μ_{TMTU} is the dipole moment of an isolated TMTU molecule ($\mu_{\text{TMTU}} = 15.7 \times 10^{-30}$ C m)²⁶, ϵ_i is the permittivity of the inner layer and x_1 is the inner-layer thickness. The value of $\Phi^{M-2} = E - E_z - \Phi^{2-s}$, where E and E_z are the measured potential and the potential of the zero charge in the absence of TMTU for a given concentration of NaClO_4 , respectively, and Φ^{2-s} is the potential drop across the diffuse layer, which can be calculated using the Gouy-Chapman theory²⁷. The dependence of Φ^{M-2} on the Γ' at a constant charge density for $3 \text{ mol l}^{-1} \text{ NaClO}_4$ is presented in Fig. 7. Figure 7 shows that the changes in the potential drop across the inner layer for $\sigma \leq 0$ are nonlinear. The nonlinearity in Fig. 7 may be due to a change in the TMTU molecule orientation and the contribution of a covalent bond between sulfur of TMTU and the mercury electrode⁹. The rectilinear segments in Fig. 7 obtained for smaller values of Γ' were analyzed in a way similar to those used previously by Jurkiewicz-Herbich and Jastrzębska²⁸. The obtained values of ϵ_i are presented in Fig. 8. It can be seen from Fig. 8 that for $\sigma < 0$ the values of ϵ_i increase with increasing NaClO_4 concentration. For $\sigma > 0$ the values of ϵ_i are smaller than for $\sigma < 0$, they are similar in 3 and $4 \text{ mol l}^{-1} \text{ NaClO}_4$ and significantly lower in $2 \text{ mol l}^{-1} \text{ NaClO}_4$. For the range of charges $-1 < \sigma < 0$, a rapid drop of the ϵ_i value appears (the strongest in $4 \text{ mol l}^{-1} \text{ NaClO}_4$). It should be pointed out that in this electrode charge range a significant rise in repulsive interactions between TMTU molecules occurs, increasing with the rise of NaClO_4 concentration (Fig. 6). In the studied systems the magnitude of ϵ_i appears to be reasonable. On the basis of the following dependence of Φ^{M-2} vs σ for $\Gamma' = \text{const}$, values of the integral capacity K^i were determined.

The K^i and x_1 values presented in Table I show that the values of K^i do not depend on the electrode charge, but depend in a slight degree on the concentration of NaClO_4 , whereas in $2 \text{ mol l}^{-1} \text{ NaClO}_4$ the values of K^i are clearly lower. Generally, the x_1 values decrease with increasing electrode charge. This may be the result of TMTU molecule deformation. The presented results point out that the supporting electrolyte concentration is a factor influencing the TMTU adsorption process on the mercury electrode.

CONCLUSIONS

The presented results led to the following conclusions:

1. An increase in NaClO_4 concentration causes:
 - narrowing potential range in which the differential capacity decreases,
 - a shift of desorption peak potentials towards more negative potential values.
2. A smaller Γ' dependence on the TMTU concentration in the bulk for $\sigma > 0$ is associated with higher repulsive interactions between the already adsorbed TMTU molecules.
3. For $\sigma < 0$ the repulsive interactions are very weak and practically independent of NaClO_4 concentration. In contrast, for $\sigma > 0$ the repulsive interactions rise, most significantly in 4 mol l⁻¹ NaClO_4 .
4. The changes of NaClO_4 concentration show the strongest influence on the obtained permittivity of the inner layer ε_i , which increases with increasing NaClO_4 concentration. Near $\sigma = 0$, a rapid drop of the ε_i values is observed (the strongest in 4 mol l⁻¹ NaClO_4). In this range of electrode charges, an increase in repulsive interactions between TMTU molecules appears (the strongest in 4 mol l⁻¹ NaClO_4).

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