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The effect of tetramethylthiourea on the Zn^{2+} ions electroreduction in the presence of different detergents

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The effect of the mixed adsorption layers: tetramethylthiourea and chosen detergent on the Zn^{2+} ions electroreduction is described. The detergents concentration was $7.5 \cdot 10^{-4}$ M, which was lower of its critical micellation point. Three detergents: cationic, neutral and anionic were chosen for this study. First two detergents inhibited the Zn^{2+} ions reduction at mercury electrode, the last detergent accelerated this process. Tetramethylthiourea eliminated the inhibiting effect of the detergent and accelerated the studied process stronger than in the detergents absence. Standard rate constants of Zn^{2+} ions electroreduction were determined by cyclic voltammetry and impedance measurements

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. Coadsorption 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: detergents undergo physical adsorption and tetramethylthiourea (TMTU) chemical adsorption. Coadsorption of two or more substances results in the formation of mixed adsorption layers. The studies on mixed adsorption layers are of significant practical importance as far as the search for efficient corrosion

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inhibitors is concerned. Organic inhibitors of corrosion belong to the same group of compounds as inhibitors of metal etching in acids, or inhibitors of crystal growth. Both are called brighteners, and are used to appropriately regulate deposition of lustrous electroplated coatings. The use of a mixture of these substances often improves their efficiency resulting in synergistic effect, however an antagonistic effect is also possible [7]. This article is a part of broader project concerning the influence of the mixed adsorption layers on the Zn^{2+} electroreduction process [8-10]. From the literature it is known that TMTU catalyses the reduction of Zn^{2+} ions at mercury electrode in $NaClO_4$ solutions [11-13]. Quasireversible Zn^{2+} ion reduction in $NaClO_4$ solutions allows using this ion as a piloting one in studies of adsorption equilibrium at potentials outside the range of strong adsorption. The studied detergents belong to a biological detergents used to separate nucleic acids and proteins from their cellular structure. The detergents concentration was $7.5 \cdot 10^{-4}$ M .The chosen concentration is lower than detergents critical micellation point. Three detergents were chosen for the study: decanoyl-N-methylglucamide ($C_{17}H_{35}NO_6$) as a neutral detergent, sodium 1-decanesulfonate ($C_{10}H_{21}SO_3Na$) as an anionic detergent and octyltrimethylammonium bromide ($C_{11}H_{26}NBr$) as a cationic detergent. 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. A 1M $NaClO_4$ solution at pH 3 was used as a base electrolyte in these studies to protect the hydrolysis of Zn^{2+} ions. Sodium perchlorate is a suitable basic electrolyte because of its low tendency to form complexes.

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. Polarographic measurements and voltammetric experiments were performed employing the Autolab frequency response analyzer (Eco Chemie, Netherlands). The impedance measurements were carried out with 9121 FR analyser and 9131 Electrochemical Interface (Atlas-Solich, Gdańsk, Poland). The complex impedance data were collected at several frequencies in the range 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 $C_{10}H_{21}SO_3Na$, $C_{17}H_{35}NO_6$, $C_{11}H_{26}NBr$, TMTU, and $NaClO_4$ (Fluka) were used without any further purification. Studies of the catalytic activity of TMTU were carried out in

the concentration range from $3\cdot10^{-4}$ M to 0.05 M. The maximum TMTU concentration was limited by its solubility. 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

The electroreduction of Zn^{2+} ions at a mercury electrode in 1M $NaClO_4$ solution in the presence of studied organic substances result in a single well defined dc polarographic wave. A change in the organic substance concentration affects the limited diffusion current insignificantly. Approximate diffusion coefficients of Zn^{2+} ions in the examined solutions were calculated using the Ilkovič equation [14] for diffusion controlled limiting current.

The polarographic wave of Zn^{2+} in 0.1M KNO_3 with a Zn^{2+} diffusion coefficient, D_{ox} = $6.9\cdot10^{-6}$ $cm^2\cdot s^{-1}$ at 298K was used as a standard [15]. The analogous value for Zn in mercury, D_{red} = $1.67\cdot10^{-5}$ $cm^2\cdot s^{-1}$ was also selected from the literature [16]. The obtained value of D_{ox} for Zn^{2+} in 1 M $NaClO_4$ is $6.6\cdot10^{-6}$ $cm^2\cdot s^{-1}$. Addition of $7.5\cdot10^{-4}$ M of detergents: neutral, anionic and cationic into Zn^{2+} solution changes D_{ox} values to $6.5\cdot10^{-6}$ $cm^2\cdot s^{-1}$, $6.9\cdot10^{-6}$ $cm^2\cdot s^{-1}$, and $6.8\cdot10^{-6}$ $cm^2\cdot s^{-1}$, respectively. The D_{ox} values were determined from the limiting current, which depends on the viscosity of solution, a composition of zinc aquacomplex and on adsorption of studied organic substances.

The values of reversible potentials of the half wave, $E^r_{1/2}$ and formal potential, E^0_f were calculated on the basis of voltammetric measurements. Figures 1 to 3 show the cyclic voltammetric curves for studied systems. Analysis of these curves allow on qualitative estimation of the Zn^{2+} ions electroreduction kinetics in the presence of studied organic substances on the basis of difference between anodic and cathodic peak potentials (Table 1). The strongest inhibitor of Zn^{2+} ions reduction is cationic detergent, in its presence ΔE has maximal value of 512 mV, neutral detergent is weaker inhibitor. Anionic detergent accelerates electroreduction of Zn^{2+} ions on mercury electrode. Introduction of TMTU into solutions with detergent decreases an inhibiting action of cationic and neutral detergent gradually. Maximal concentration of TMTU in the presence of each tested detergents causes similar acceleration of Zn^{2+} reduction, significantly stronger than in the absence of detergent. Cyclic volammetric curves presented on Figures 1-3 show that TMTU influences on current of anodic and cathodic peaks in greater extend than the used detergents.

Table 1. Values of differences between potentials of anodic and cathodic peaks, ΔE and formal potentials, E_f^0 versus Ag/AgCl for systems: $5\cdot10^{-3}$ M Zn^{2+} in 1 M $NaClO_4$ + $7.5\cdot10^{-4}$ M detergent + increased concentrations of TMTU. The values of ΔE and E_f^0 for Zn^{2+} in 1 M $NaClO_4$ are 0.065 V and -0.962 V respectively.

	$C_{17}H_{35}NO_6$		$C_{10}H_{22}SO_3Na$		$C_{11}H_{26}NBr$	
10^2 c_{TMTU} / M	ΔE / V	$-E_f^0$ / V	ΔE / V	$-E_f^0$ / V	ΔE / V	$-E_f^0$ / V
0.00	0.298	0.973	0.052	0.959	0.512	1.010
0.03	0.264	0.974	0.048	0.956	0.411	1.020
0.05	0.264	0.974	0.044	0.956	0.379	1.021
0.10	0.250	0.981	0.038	0.957	0.373	1.029
0.30	0.214	0.984	0.038	0.957	0.325	1.041
0.50	0.184	0.988	0.036	0.958	0.305	1.048
1.00	0.093	0.966	0.038	0.957	0.054	0.949
2.00	0.041	0.96	0.034	0.955	0.040	0.950
3.00	0.037	0.956	0.038	0.954	0.040	0.950
4.00	0.042	0.956	0.038	0.956	0.038	0.951
5.00	0.036	0.955	0.038	0.957	0.038	0.951

For quasireversible Zn^{2+} ions reduction, the reversible potential of the half wave, $E_{1/2}^r$ was determined using equation (1) [17]:

$$E_{1/2}^r = \frac{E_{pc} + E_{pa}}{2} \tag{1}$$

where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively.
From the values of reversible half wave potentials, the standard formal potentials, E_f^0 were calculated using the equation (2):

$$E_f^0 = E_{1/2}^r + \frac{RT}{nF}\ln\left(\frac{D_{ox}}{D_{red}}\right)^{1/2} \tag{2}$$

For irreversible Zn^{2+} ions reduction, the values of E_f^0 were calculated from equation 3:

$$E_f^0 = \frac{1}{2}\left[E_{p_a/4} + E_{p_c/4} + \frac{\left(E_{p_a/4} + E_{p_c/4}\right) - \left(E_{3p_a/4} + E_{3p_c/4}\right)}{g-1}\right] \tag{3}$$

where:

$$g = \left[\left(E_{3p_a/4} - E_{3p_c/4}\right) / \left(E_{p_a/4} - E_{p_c/4}\right)\right]$$

$E_{p_a/4}, E_{p_c/4}$, $E_{3p_a/4}, E_{3p_c/4}$ are potentials at ¼ of anodic and cathodic peak height and at ¾ of anodic and cathodic peak height respectively.

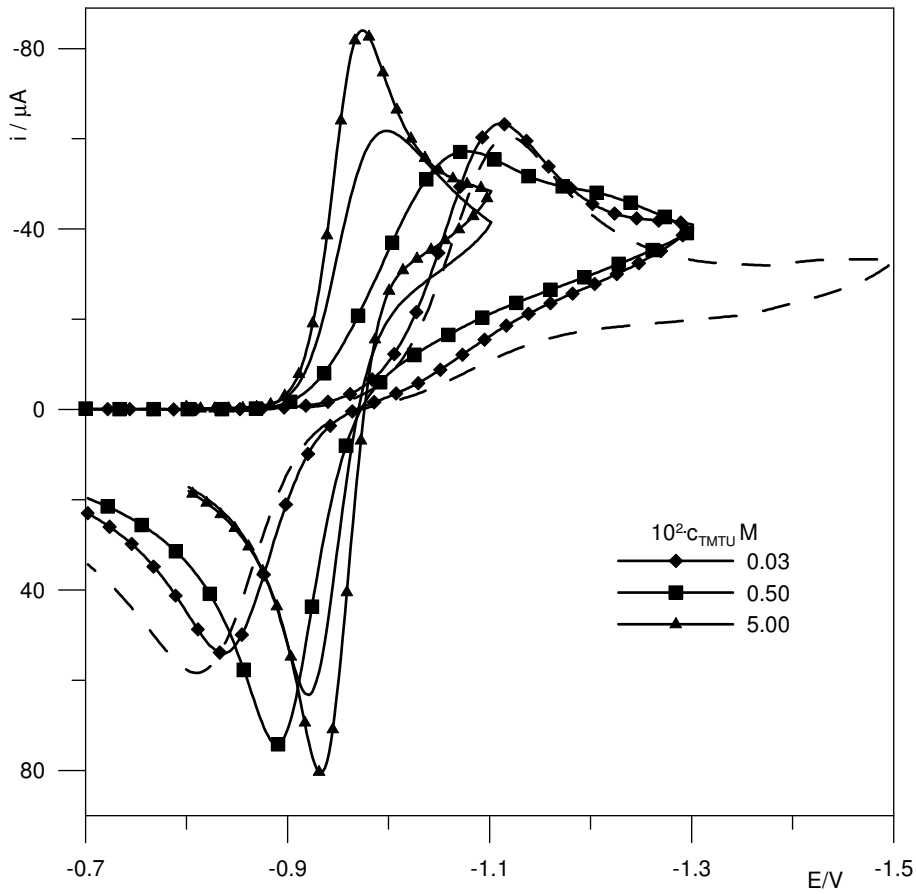

Fig. 1. Cyclic voltammetric curves for Zn^{2+}/Zn(Hg) at the scan rate 0.1 $V \cdot s^{-1}$ in 1 M $NaClO_4$ (continous line), with addition of $7.5 \cdot 10^{-4}$ M $C_{17}H_{35}NO_6$ (dashed line) and with addition of various TMTU concentrations as in figure legend.

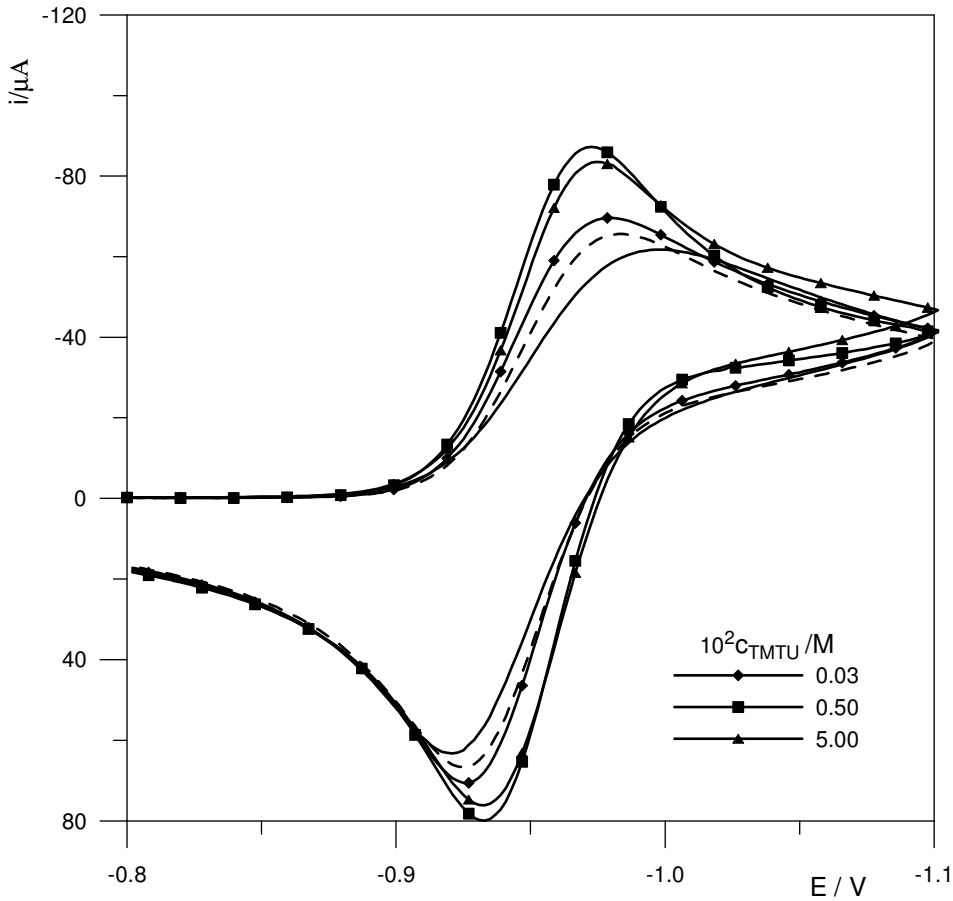

Fig. 2. Cyclic voltammetric curves for $Zn^{2+}/Zn(Hg)$ at the scan rate 0.1 $V \cdot s^{-1}$ in 1 M $NaClO_4$ (continous line), with addition of $7.5 \cdot 10^{-4}$ M $C_{10}H_{22}SO_3Na$ (dashed line) and with addition of various TMTU concentrations as in figure legend.

The strongest changes of E^0_f values appeared in solutions containing cationic detergent. For TMTU concentration of 0.01M skipped change of E^0_f and ΔE appeared, which was the result of sudden change in the structure of adsorption layer. The values of the apparent rate constant, were obtained from the charge-transfer resistance [18] as a function of dc potential. The impedance data were analyzed by fitting to the expressions valid in the case of Randles equivalent circuit [19, 20]. The decreased values of charge transfer resistance in the presence of TMTU demonstrate unequivocally the catalytic influence of TMTU.

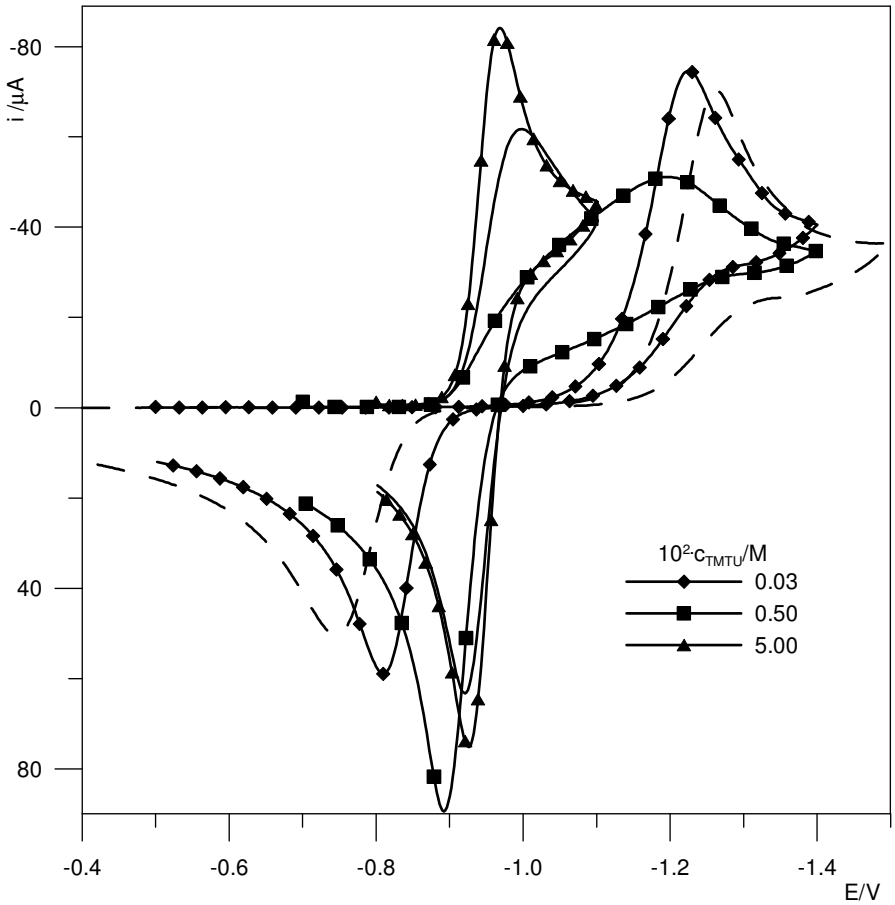

Fig. 3. Cyclic voltammetric curves for Zn^{2+}/Zn(Hg) at the scan rate 0.1 $V \cdot s^{-1}$ in 1 M $NaClO_4$ (continous line), with addition of $7.5 \cdot 10^{-4}$ M $C_{11}H_{26}NBr$ (dashed line) and with addition of various TMTU concentrations as in figure legend.

The dependencies ln k_s^{app} = f(E) in Figures 4-6 confirm observations made based on cyclic voltammetric curves. The acquitance of E_f^0 values allowed on determination of apparent standard rate constants, k_s^{app} .

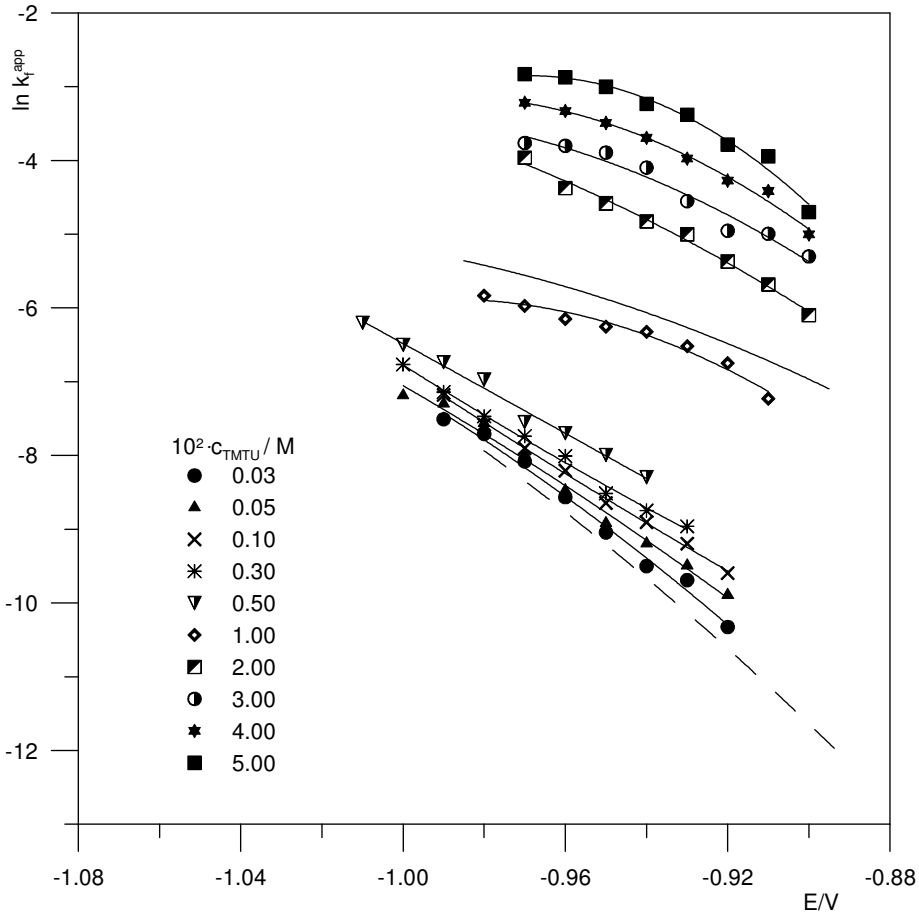

Fig. 4. Potential dependence of the natural logarithm of apparent rate constants of Zn^{2+} reduction in 1M $NaClO_4$ (continous line), with addition of $7.5 \cdot 10^{-4}$ M $C_{17}H_{35}NO_6$ (dashed line) and with addition of various TMTU concentrations as in figure legend.

Figure 7 shows the changes of k_s^{app} values in the function of TMTU concentration. In the presence of TMTU even at lowest concentration the significant increase in k_s^{app} value is noted in the solution containing cationic detergent. The analysis of the intersection of the line (a) or (g) indicates that compensation inhibiting and accelerating effects takes place for the concentration ratio TMTU: $C_{17}H_{35}NO_6$ = 15.7 and for ratio TMTU: C_{11} H_{26} NBr = 6.7. The obtained results point that TMTU eliminates easier the inhibiting effect caused by cationic detergent in comparison with neutral detergent. This effect not only refers to the compensation of inhibition and acceleration but also

to the whole range of TMTU concentrations used in the study. The anionic detergent acceleration effect and inhibiting effect of the cationic detergent are based on the electrostatic interaction of electrode surface with aqua Zn^{2+} ions. However the neutral detergents inhibiting effect is connected with electrode surface blocking for Zn^{2+} ions. Distinct inhibition mechanism of Zn^{2+} ions electroreduction by neutral and cationic detergent may by the cause of different kinetics of transfer electrons in the presence of TMTU and those detergents.

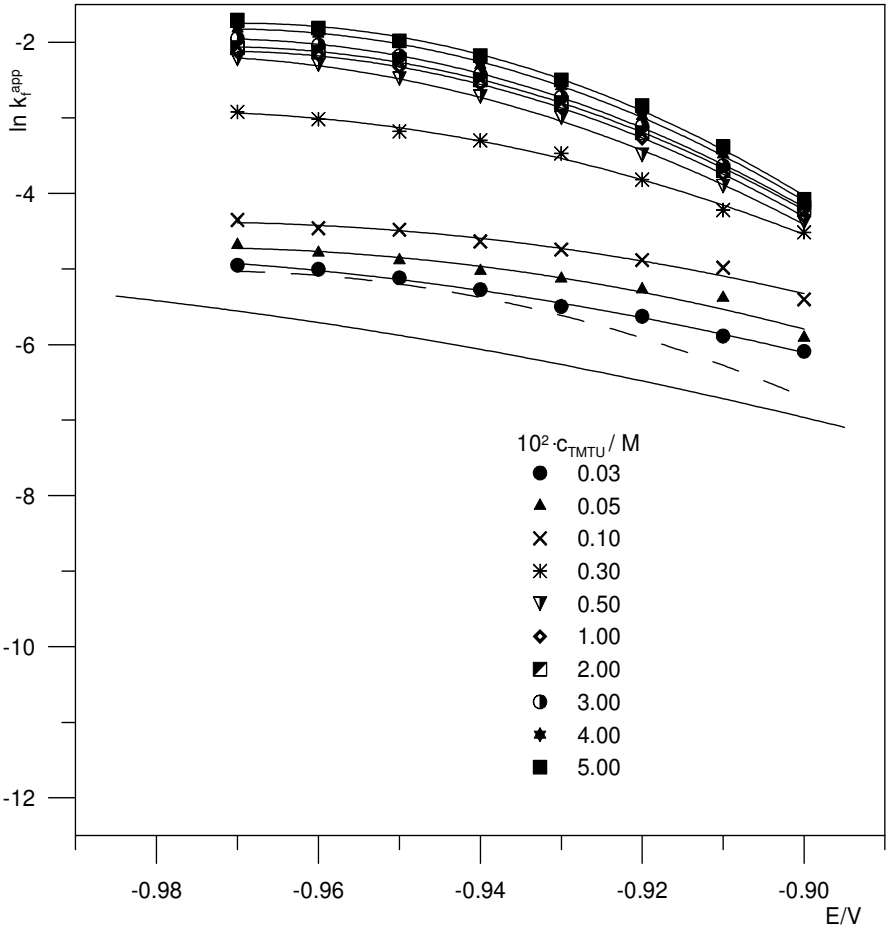

Fig. 5. Potential dependence of the natural logarithm of apparent rate constants of Zn^{2+} reduction in 1M $NaClO_4$ (continous line), with addition of $7.5 \cdot 10^{-4}$ M $C_{10}H_{22}SO_3Na$ (dashed line) and with addition of various TMTU concentrations as in figure legend.

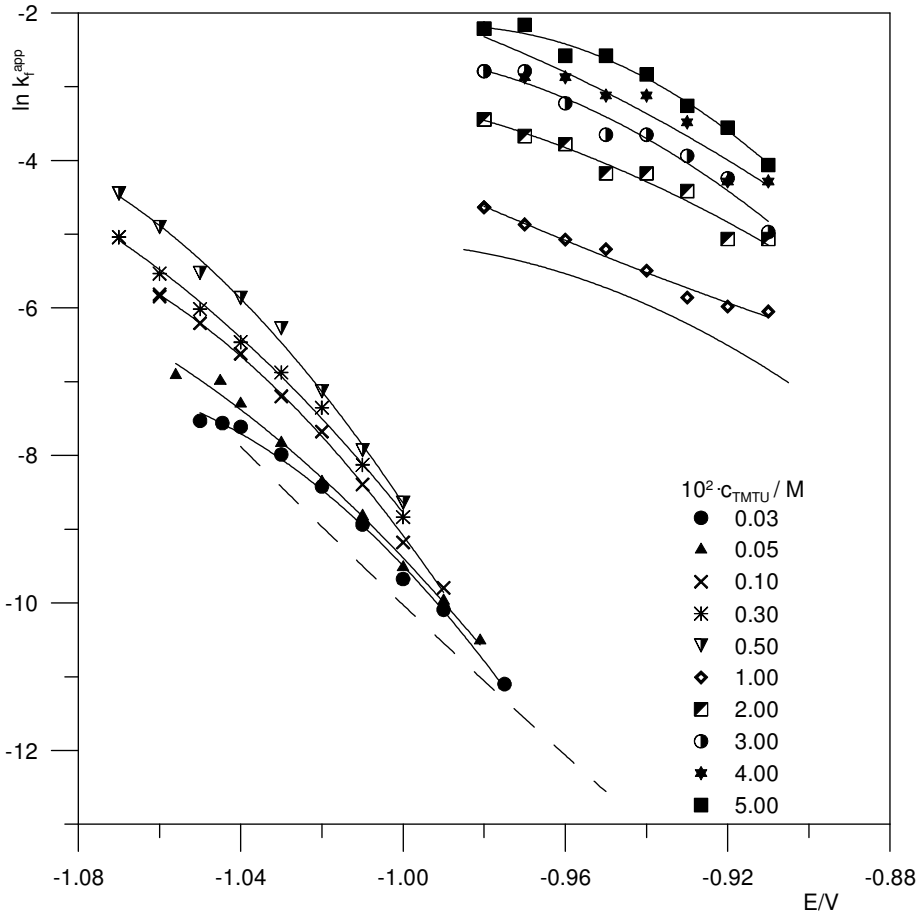

Fig. 6. Potential dependence of the natural logarithm of apparent rate constants of Zn^{2+} reduction in 1M $NaClO_4$ (continous line), with addition of $7.5 \cdot 10^{-4}$ M $C_{11}H_{26}NBr$ (dashed line) and with addition of various TMTU concentrations as in figure legend.

4. CONCLUSIONS

The kinetic studies of Zn^{2+} electroreduction as a piloting ion in the equilibrium of adsorption allow a direct, quality adsorption description of the two organic substances for potentials distant from potentials close to zero charge potential. The qualitative conclusions concerning the kinetic changes of Zn^{2+} reduction derived from measurements by cyclic voltammetry found a clear confirmation in the obtained standard rate constant values. Higher acceleration of Zn^{2+} reduction caused by TMTU in the detergents presence than in the

absence of detergent may result from a weaker hydration of electrode surface in the detergent presence.

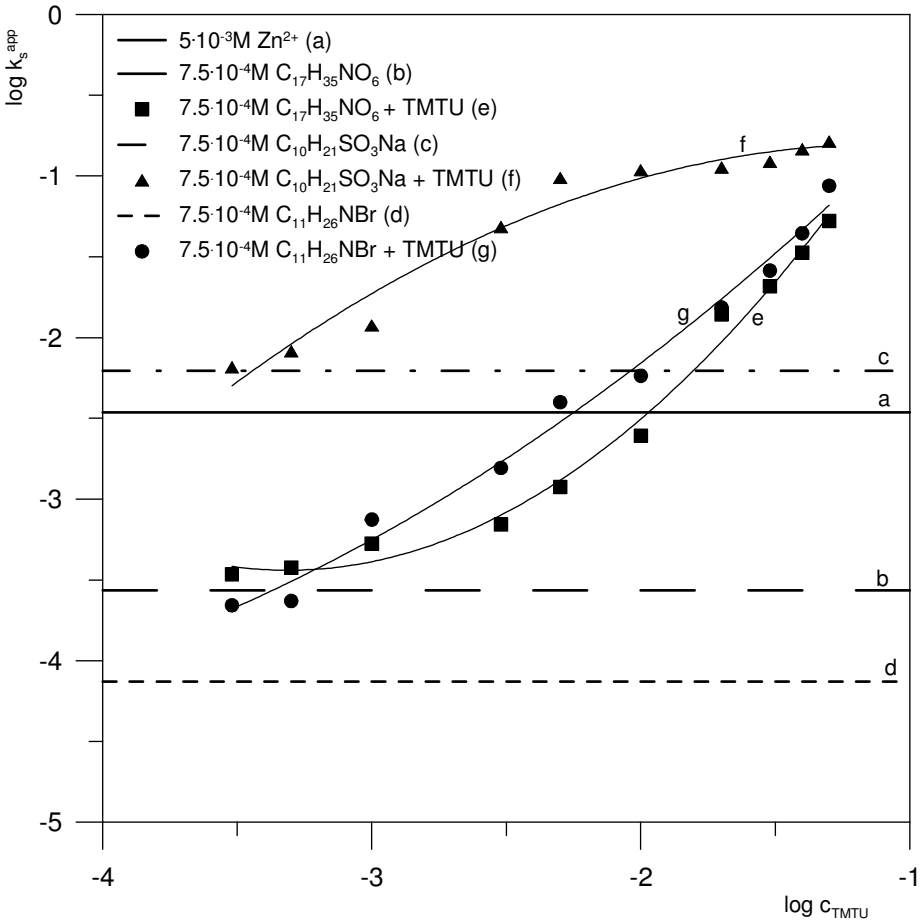

Fig. 7. Logarithmic dependence of the apparent standard rate constants, k_s^{app} on TMTU concentration for Zn^{2+} in 1 M $NaClO_4$ (a) + $7.5\cdot10^{-4}$ M detergent: $C_{10}H_{21}SO_3Na$ (b), $C_{17}H_{35}NO_6$ (c) and $C_{11}H_{26}NBr$ (d).

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