

Properties of the Mixed Polyethyleneglycoles-iodide Ions Adsorption Layers on a Mercury Electrode

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Adsorption of a mixture of I^- ions and polyethyleneglycoles of molecular weights 400 (PEG 400) and 10 000 (PEG 10 000) on a mercury electrode from $NaClO_4$ solution of constant ionic strength is described. Parallel courses of linear dependences of the potential of zero charge with the increase of I^- ion concentration in the solutions with PEG and without PEG indicate removal of water molecules by adsorption of I^- ions and not PEG molecules. The standard Gibbs energy of adsorption $\Delta_{ad}G^0$ and parameter B obtained from the virial isotherm do not depend on PEG 10 000 concentration. This can be associated with the full coverage of the electrode surface with its molecules already at a concentration of 10^{-4} mol dm^{-3} . For PEG 400, a dependence of adsorption parameters on its concentration was observed. Lower repulsive interaction between the adsorbed I^- ion in PEG solutions indicates a favourable effect of PEG molecules on I^- ion adsorption compared with H_2O . The values of rate constants k_s^{app} of Zn^{2+} ion reduction as a piloting ion were determined. Acceleration of the processes inhibited by PEG 400 or PEG 10 000 by I^- ions is based on formation of ion pairs $Zn^{2+}-I^-$ on the mercury surface. Kinetic measurements confirm stronger adsorption of PEG 10 000 compared with PEG 400.

Key words: electrochemistry, adsorption of I^- ions, inhibition of Zn^{2+} reduction, coadsorption, mixed adsorption layers.

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INTRODUCTION

Adsorption studies of different substances on a mercury electrode enable a closer insight into the electrical structure of the double layer^{1,2} and its effect on the electrode processes.³ Earlier studies on the acceleration of the electroreduction of Zn^{2+} ions by some organic substances^{4,5} have enabled to choose pairs of organic substances causing inhibiting or accelerating effects on the above mentioned reduction process. The obtained results inspired replacement of the accelerating organic substance by polarizable I^- ions that accelerate the Zn^{2+} electroreduction⁶⁻⁸ and are adsorbed on the mercury surface.⁹

Studies of adsorption of I^- ions in the presence of thiourea¹⁰ revealed a decrease in I^- adsorption energy accompanied by the diminishing repulsive interaction between the adsorbed I^- ions. On the basis of the theory describing coadsorption of ions and organic molecules,¹¹ it was stated that the values of Cl^- , Br^- , ClO_4^- and NO_3^- ion surface excesses increase with the increase of 1-butanol concentration.¹² For I^- ions, however, these values do not depend on the 1-butanol (BU) concentration. The increase in surface excesses of the above mentioned ions is caused by attractive interaction between the molecules of 1-butanol and anions as well as by a weaker interaction of OH groups with mercury in the presence of these anions.

This paper presents the results of studies on coadsorption of polyethyleneglycoles of mean molecular weight: 400 (PEG 400) or 10 000 (PEG 10 000) as typical inhibitors of electrode processes¹³ and I^- ions. Polyethyleneglycols are nonionic surfactants, readily soluble in water,¹⁴ frequently used as inhibitors of corrosion¹⁵ as well as in the processes of metal electrodeposition.¹⁶ In aqueous solutions, polyethyleneglycoles occur in the helical form. The helix structure and hydrogen bonds between ether atoms of PEG oxygen and water are responsible for the unlimited solubility of PEG in water.¹⁷ According to Kjellander,¹⁷ the PEG chain forms a spiral in which five monomers correspond to one twist and the spiral slip is 47 nm. This distance and the distance of 28.8 nm between the closest ether atoms in the chain correspond perfectly to the distance between oxygen atoms in the hexagonal water lattice (47 and 28.5 nm).¹⁸ The coadsorption of I^- ions and PEG molecules described in the paper was studied from NaClO_4 solution of constant ionic strength: $x \text{ mol dm}^{-3} \text{I}^- + (1 - x) \text{ mol dm}^{-3} \text{NaClO}_4$ (x denotes the concentration between 0.01 and 0.8 mol dm^{-3}). Concentrations of PEG were constant: $1 \times 10^{-4} \text{ mol dm}^{-3}$ or $5 \times 10^{-4} \text{ mol dm}^{-3}$. Advantages of the ionic adsorption study at the mercury-solution interface at constant ionic strength have already been fully discussed.^{9,19} The results presented in the paper concern the adsorption parameters of I^- ions and kinetic parameters of Zn^{2+} ions reduction in the PEG- I^- mixture.

EXPERIMENTAL

Analytical-grade reagents NaI, NaClO₄, PEG 400 and PEG 10 000 (Merck) were used without further purification. Water and mercury were triply distilled. Electrolyte solutions were deoxygenated using nitrogen passed through water.

A three-electrode cell, containing a dropping mercury electrode (DME) as working electrode, a saturated calomel electrode (SCE) with sodium chloride and a platinum spiral were used, as the reference and counter electrodes, respectively. The reference electrode was connected to the cell *via* a salt bridge filled with the cell solution.

The double layer capacity of DME was measured at 800 Hz using the 9121 FR Analyzer and 9131 Electrochemical Interface (Atlas Sollich, Gdańsk). No significant frequency dependence of the measured capacity was observed. The potential of zero charge E_z was measured for each solution by the method of streaming mercury electrode.²⁰ The interfacial tension between mercury and the mixed electrolyte solutions at E_z was measured with a conventional maximum bubble-pressure capillary electrometer described earlier.²¹

The studies of Zn²⁺ ion reduction kinetics were carried out with polarograph PA-4 (Laboratorni Pstroje, Prague) and EG&G PARC Instrument model 388 and 270 employing a static mercury drop electrode (SMDE) manufactured by Laboratorni Pstroje, Prague. Kinetic data were obtained by impedance or cyclic voltammetric measurement over a wide range of sweep rates (0.005–5 V s⁻¹). The complex cell impedance was measured at different frequencies in the range from 100 to 25 000 Hz at the formal potential of Zn²⁺ reduction. The ohmic resistance of the electrolyte solution was obtained as the real impedance component at a frequency of 10 kHz and a potential outside the faradaic region. Approximate diffusion coefficients of Zn²⁺ in the examined solutions were calculated from limiting currents using the Ilković equation. The polarographic wave of Zn²⁺ in 0.1 mol dm⁻³ KNO₃ with the value of the Zn²⁺ diffusion coefficient $D = 6.9 \times 10^{-6}$ cm² s⁻¹ (Ref. 22) was used as a standard. The diffusion coefficient of zinc in mercury required for further calculations was taken from the literature²³ as being equal to 1.67×10^{-5} cm² s⁻¹. Measurements were carried out in solutions of pH = 5 at 298 ± 1 K.

RESULTS AND DISCUSSION

Figures 1 and 2 present the dependence of the double layer differential capacity on the electrode potential for I⁻ ions in the aqueous solutions: x mol dm⁻³ NaI + (1 - x) mol dm⁻³ NaClO₄ + 5×10^{-4} mol dm⁻³ PEG 400 and x mol dm⁻³ NaI + (1 - x) mol dm⁻³ NaClO₄ + 5×10^{-4} mol dm⁻³ PEG 10 000, respectively. It follows from the comparison of Figures 1 and 2 that the I⁻ ion adsorption causes the capacity increase compared to the basic electrolyte (curve a) in the range of potentials: $E > -1.10$ V for PEG 400 and $E > -1.00$ V for PEG 10 000.

In the presence of PEG, the characteristic capacitance hump for I⁻ ions appearing in 1 mol dm⁻³ NaClO₄ does not appear similarly in ethanol²⁴ or

methanol²⁵ solutions of I^- ions. The occurrence of this hump results mainly from changes in the electrostatic interactions between adsorbed molecules. At about -1.60 V, the PEG 400 desorption peak appears (Figure 1), which does not change in the presence of I^- ions. It is believed that in the potential range of $E < -1.10$ V for PEG 400 and $E < -1.00$ V for PEG 10 000 the adsorption layer is modified mainly by PEG molecules but not the I^- ion contrary to more positive potentials. The capacity–potential plots were numerically integrated from E_z . Figure 3 presents the changes in E_z in relation to I^- ion concentration for $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4$ solution (line a) and with an addition of PEG. The increase in I^- ion concentration from 0 to 0.8 mol dm^{-3} causes a shift of E_z towards more negative potentials, as it is usual for the adsorption of anions, but the $dE_z/d(\log c_{I^-})$ coefficient (*ca.* -0.078 V) is higher than that for alkali-metal salts with specifically adsorbed anions (approximately $2.3 RT/F$).²⁶ This indicates a significant contribution of the I^- ion adsorption to the potential drop across the inner layer. In the presence of BU, E_z values are slightly higher. Parallel courses of linear dependences of E_z with the increase of I^- ion concentration in the solutions with PEG and without PEG indicate removal of water molecules by adsorp-

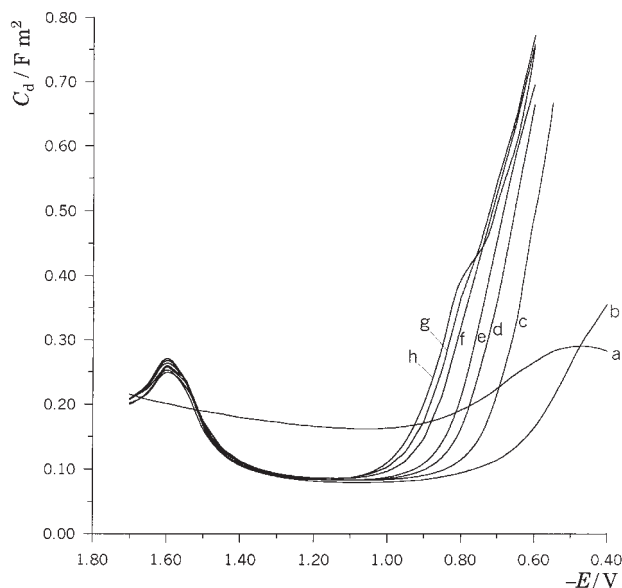


Figure 1. Differential capacity for a mercury electrode in aqueous solutions of $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ (a) and $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4 + (5 \times 10^{-4}) \text{ mol dm}^{-3} \text{ PEG 400}$ as a function of potential.

Values of x : b) 0, c) 0.01, d) 0.05, e) 0.1, f) 0.3, g) 0.5, h) 0.8.

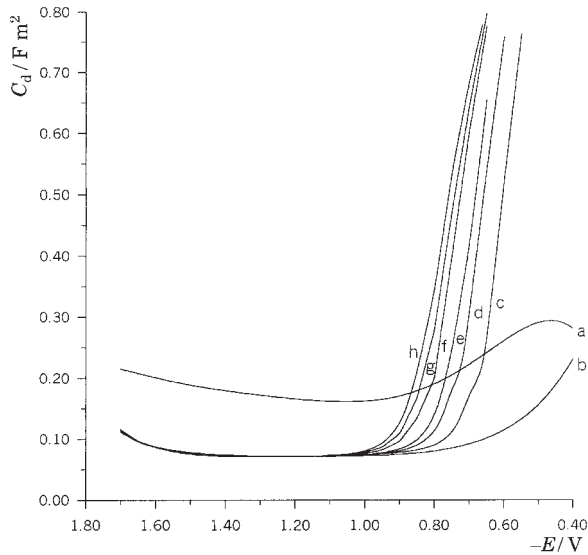


Figure 2. Differential capacity for a mercury electrode in aqueous solutions of $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ (a) and $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4 + (5 \times 10^{-4}) \text{ mol dm}^{-3} \text{ PEG 10 000}$. Values of x as indicated in Figure 1.

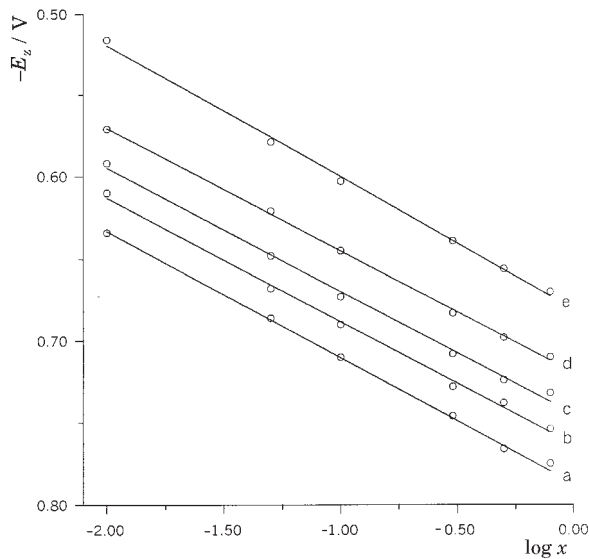


Figure 3. Dependence of E_z on I^- ion concentration for systems: a) $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4$ and in the presence of, b) $1 \times 10^{-4} \text{ mol dm}^{-3} \text{ PEG 400}$, c) $5 \times 10^{-4} \text{ mol dm}^{-3} \text{ PEG 400}$, d) $1 \times 10^{-4} \text{ mol dm}^{-3} \text{ PEG 10 000}$, e) $5 \times 10^{-4} \text{ mol dm}^{-3} \text{ PEG 10 000}$.

tion of Γ^- ions and not PEG molecules. The surface pressure curves at each value of the electrode charge (q_M) were derived using the methods proposed by Parsons,²⁵ in terms of the function $\xi^+ = \gamma + qE^+$, where γ is the surface tension, E^+ is the potential related to the reference electrode. The surface pressure (Φ) for specifically adsorbed ions was derived from the relation $\Phi = \xi^+ - \xi_o^+$, where ξ_o^+ refers to the solutions: 1 mol dm⁻³ NaClO₄ + determined constant concentration of PEG 400 or PEG 10 000 and ξ^+ to the mixed electrolyte of x mol dm⁻³ NaI + (1 - x) mol dm⁻³ NaClO₄ + PEG. Figure 4 shows the dependence of surface pressure on the $\ln x$ for Γ^- ions in NaClO₄ + 5×10^{-4} mol dm⁻³ PEG 400 (a) or NaClO₄ + 5×10^{-4} mol dm⁻³ PEG 10 000 (b) solutions. Positive values Φ were obtained for the studied systems:

x mol dm⁻³ NaI + (1 - x) mol dm⁻³ NaClO₄ + 1×10^{-4} mol dm⁻³ PEG 400:
 $-4 \leq q_M \leq +3 \mu\text{C cm}^{-2}$,

x mol dm⁻³ NaI + (1 - x) mol dm⁻³ NaClO₄ + 5×10^{-4} mol dm⁻³ PEG 400:
 $-6 \leq q_M \leq +3 \mu\text{C cm}^{-2}$,

x mol dm⁻³ NaI + (1 - x) mol dm⁻³ NaClO₄ + 1×10^{-4} mol dm⁻³ PEG 10 000:
 $-5 \leq q_M \leq +1 \mu\text{C cm}^{-2}$,

x mol dm⁻³ NaI + (1 - x) mol dm⁻³ NaClO₄ + 5×10^{-4} mol dm⁻³ PEG 10 000:
 $-7 \leq q_M \leq 0 \mu\text{C cm}^{-2}$.

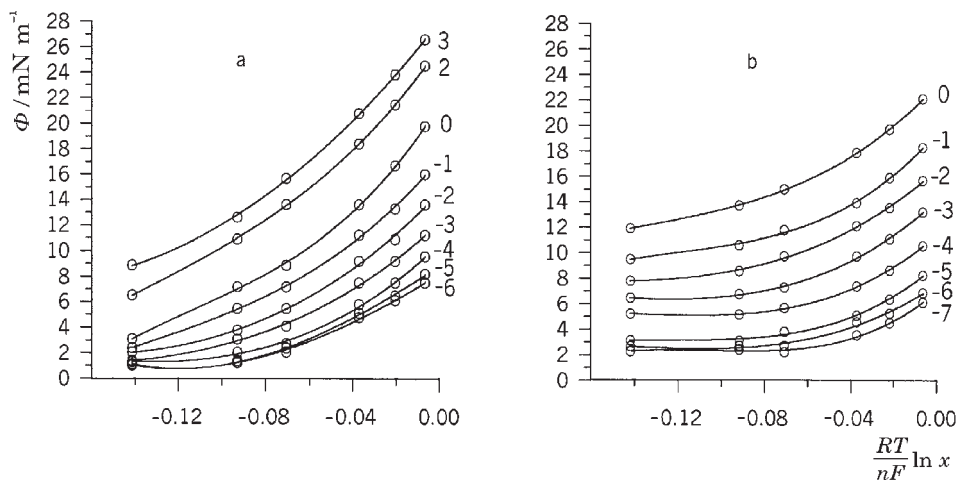


Figure 4. Plots of the surface pressure due to Γ^- ions adsorbed on the mercury electrode from solutions: a) x mol dm⁻³ NaI + (1 - x) mol dm⁻³ NaClO₄ + (5×10^{-4}) mol dm⁻³ PEG 400 and b) x mol dm⁻³ NaI + (1 - x) mol dm⁻³ NaClO₄ + (5×10^{-4}) mol dm⁻³ PEG 10 000 as a function of $\ln x$; electrode charges (q_M in 10^{-2} C m⁻²) are indicated by each curve.

The range of q_M charges for adsorption of various ions on the mercury electrode in the solutions of NaF is much broader. Thus, the results obtained in this paper should be associated with low adsorption of ClO_4^- ions²⁷ and additionally with PEG adsorption. A narrow range of potentials for which the positive Φ values were obtained indicates adsorption equilibria in I^- - ClO_4^- - H_2O -PEG 400 and I^- - ClO_4^- - H_2O -PEG 10 000 systems (Figures 1 and 2). In the studied solutions containing PEG, the potential range in which I^- ions cause an increase in differential capacity is narrower than in the NaF solution.⁹

The charge q_{ad} specific adsorption of I^- ions in the solutions of constant ionic strength was determined using the method proposed earlier:^{9,19}

$$q_{\text{ad}} = -\frac{F}{RT} \left(\frac{\partial \xi^+}{\partial \ln x} \right)_{q_M, T, c_{\text{PEG}}} \quad (1)$$

The variation in activity coefficients with concentration was assumed to be negligible. The q_{ad} vs. $\ln x$ plots at constant charge are presented in Figure 5. The obtained isotherms do not have a linear course in contrast to the adsorption isotherms of some anions which are straight lines. The q_{ad} values obtained in the presence of PEG 400 are approximated q_{ad} in the absence of PEG 400,²⁸ however, in the presence of PEG 10 000 they are slightly lower than in the solution not containing PEG 10 000. The adsorp-

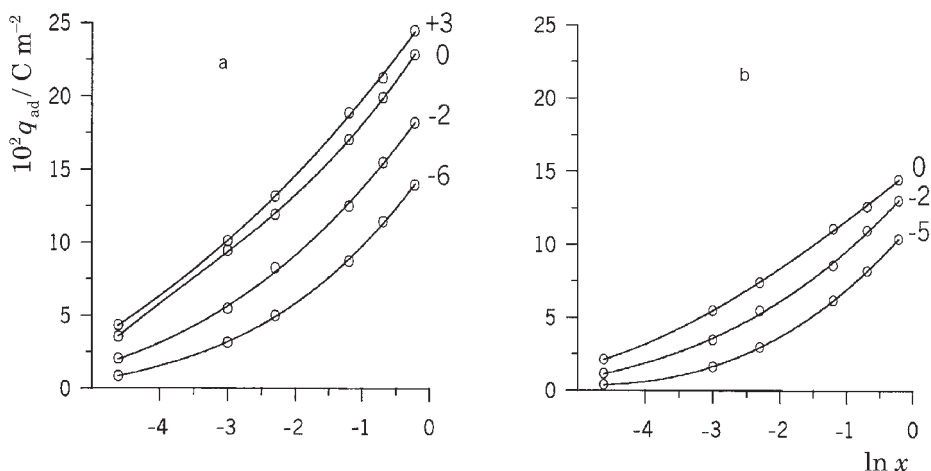


Figure 5. The adsorbed charge density due to specific adsorption of I^- ions from solutions: a) $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4 + (5 \times 10^{-4}) \text{ mol dm}^{-3} \text{ PEG 400}$ and b) $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4 + (5 \times 10^{-4}) \text{ mol dm}^{-3} \text{ PEG 10 000}$ as a function of $\ln x$. Electrode charges (q_M in 10^{-2} C m^{-2}) are indicated by each curve.

tion of Γ^- ions may be described by a simple virial isotherm²⁹ shown in Figure 6. Values of the 2D second virial coefficient (B) were calculated from the slopes of lines in Figure 6 and the corresponding values of standard Gibbs energy of adsorption $\Delta_{\text{ad}}G^\circ$ were obtained from the intercepts of these lines for $q_{\text{ad}} = 0$ (using the standard conditions corresponding to 1 mol dm^{-3} bulk concentration and 1 ion cm^{-2} on the surface). As follows from Figure 6 and the corresponding dependences $\ln(q_{\text{ad}}/x)$ vs. q_{ad} for $1 \times 10^{-4} \text{ mol dm}^{-3}$ PEG $\Delta_{\text{ad}}G^\circ$ values depend on q_M and PEG 400 concentration: in the solutions containing $1 \times 10^{-4} \text{ mol dm}^{-3}$ PEG 400 or $5 \times 10^{-4} \text{ mol dm}^{-3}$ PEG 400 $\Delta_{\text{ad}}G^\circ$ values increase from -95.1 to $-96.9 \text{ kJ mol}^{-1}$ and from -89.8 to $-94.8 \text{ kJ mol}^{-1}$ respectively, when q_M increases. In the case of PEG 10 000, $\Delta_{\text{ad}}G^\circ$ values practically do not depend on PEG 10 000 concentration and change from -87.1 to $-96.8 \text{ kJ mol}^{-1}$. In turn, the values of B depend on PEG 400 concentration and are constant in the studied q_M range for $5 \times 10^{-4} \text{ mol dm}^{-3}$ PEG 400: $B = 0.92 \text{ nm}^2 \text{ ion}^{-1}$, however, in the $1 \times 10^{-4} \text{ mol dm}^{-3}$ PEG 400 systems B is $1.34 \text{ nm}^2 \text{ ion}^{-1}$ for $q_M \geq 0 \text{ } \mu\text{C cm}^{-2}$ while $q_M < 0 \text{ } \mu\text{C cm}^{-2}$ B increases from 1.56 to $1.72 \text{ nm}^2 \text{ ion}^{-1}$. In the solutions containing PEG 10 000, the B values do not depend on PEG 10 000 concentration and increase from 0.76 to $1.12 \text{ nm}^2 \text{ ion}^{-1}$ while q_M increases. As follows from the presented adsorption parameters, Γ^- ions adsorption energy in the studied systems is lower than in the absence of PEG.²⁸ An exception is the solution containing $1 \times 10^{-4} \text{ mol dm}^{-3}$ PEG 400. Lower repulsive interaction between the adsorbed Γ^- ion in PEG solutions indicates a favourable effect of PEG molecules on Γ^- ion ad-

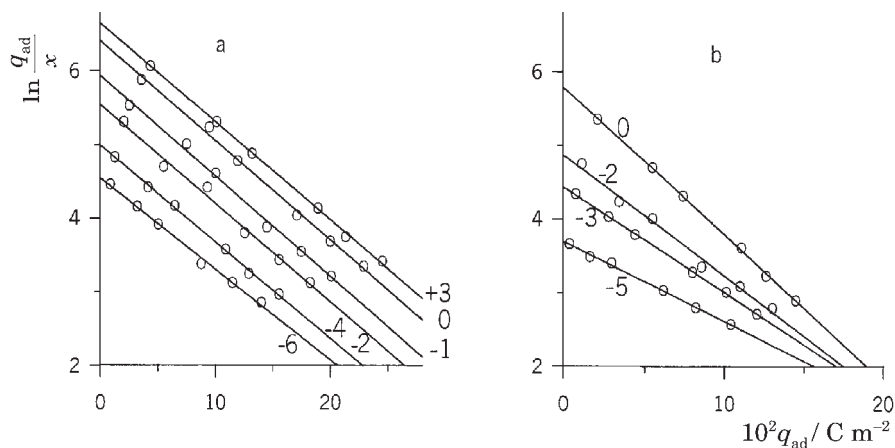


Figure 6. Linear test of the virial isotherm for systems: a) $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4 + (5 \times 10^{-4}) \text{ mol dm}^{-3} \text{ PEG 400}$ and b) $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4 + (5 \times 10^{-4}) \text{ mol dm}^{-3} \text{ PEG 10 000}$. Electrode charges (q_M in 10^{-2} C m^{-2}) are indicated by each line.

sorption compared with H_2O . Independence of adsorption parameters of PEG 10 000 concentration can be associated with the full coverage of the electrode surface with its molecules already at the concentration of $1 \times 10^{-4} \text{ mol dm}^{-3}$.

The change in the potential drop across the inner layer Φ^{M-2} at constant charge gives further information about the double layer structure. The value of Φ^{M-2} was calculated by subtracting potential E_z (in the absence of Γ^-) and the potential of the outer Helmholtz plane Φ^{2-s} (calculated from the diffusion layer theory)³⁰ from the measured electrode potential. The plots of Φ^{M-2} vs. surface charge q_{ad} of specifically adsorbed Γ^- ions at constant electrode charge q_M are shown in Figure 7. A linear dependence of Φ^{M-2} vs. q_{ad} was obtained for all studied systems (Figures 7a and b). Changes of straight line slopes are small; especially in the presence of PEG 10 000 the plots are almost parallel lines. Thus, the influence of water dipoles on Φ^{M-2} is small and can be associated with the weaker hydration of the electrode surface in the presence of adsorbed PEG molecules.

The results concerning Γ^- ions adsorption presented earlier provide information about the structure of the adsorption layer but they cover a range of strong adsorption potential of Γ^- ions and PEG molecules. Studies on the kinetics of Zn^{2+} ion reduction as a piloting ion broaden this range.

The values required to determine the rate constant (k_s^{app}) of Zn^{2+} ion reduction in the studied systems changed as follows:

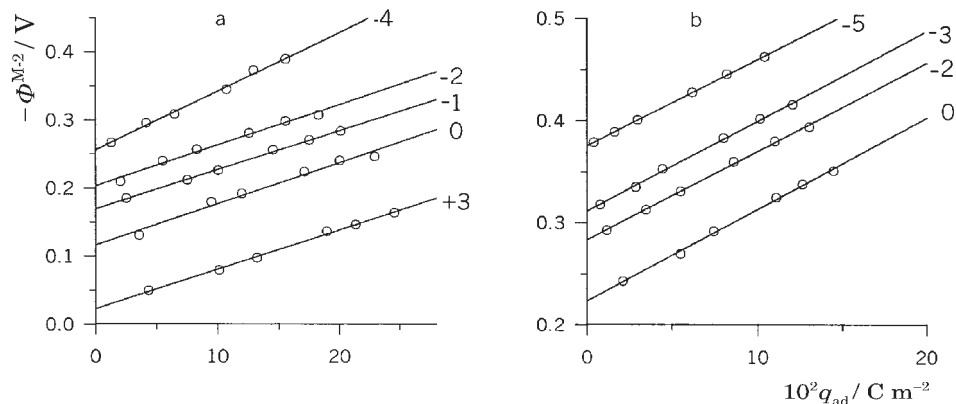


Figure 7. Potential drop across the inner region vs. the amount of specifically adsorbed Γ^- ions for systems: a) $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4 + (5 \times 10^{-4}) \text{ mol dm}^{-3} \text{ PEG 400}$ and b) $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4 + (5 \times 10^{-4}) \text{ mol dm}^{-3} \text{ PEG 10 000}$ at constant electrode charges (q_M in 10^{-2} C m^{-2}).

Diffusion coefficients of Zn^{2+} ion decrease from $6.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ to $3.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ with the increase of I^- ion concentration. Therefore, the difference between the half wave reversible potential $E_{1/2}^r$ and the formal potential E_f^0 for Zn^{2+} ion reduction was from -6 mV to -13 mV .

The E_f^0 values changed from -1.017 to -0.960 V and from -1.100 V to -1.129 V in the presence of PEG 400 or PEG 10 000, respectively. Thus, introducing a larger amount of I^- ions into the solutions containing PEG 400 causes a shift of E_f^0 values to the potentials at which reduction of Zn^{2+} ions takes place in the absence of PEG 400. However, in the solutions containing PEG 10 000, similar effects are not observed in the presence of larger amount of I^- ions.

Figure 8 presents a logarithmic dependence k_s^{app} for Zn^{2+} ions reduction on the concentration of I^- ions. Introduction of I^- ions into the Zn^{2+} solution accelerates the electroreduction. At the maximum concentration of I^- in the

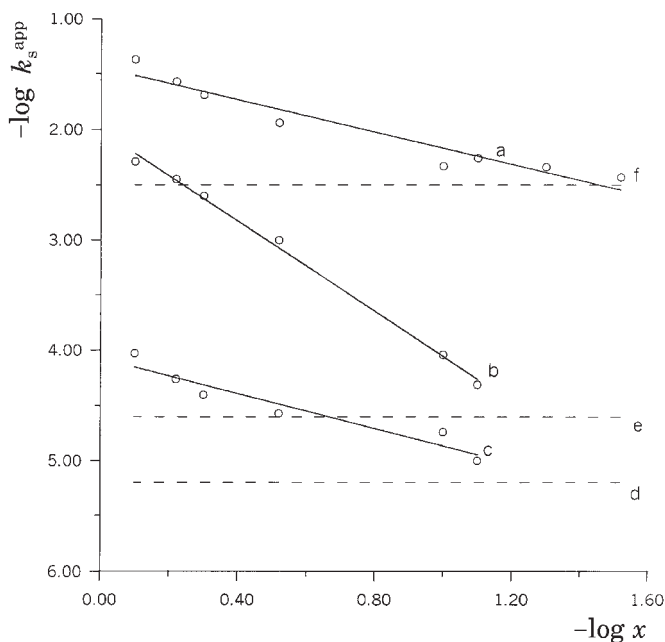


Figure 8. Plots of $\log k_s^{\text{app}}$ for the (Hg) Zn ($5 \times 10^{-3} \text{ mol dm}^{-3}$) / Zn^{II} ($5 \times 10^{-3} \text{ mol dm}^{-3}$) couple vs. $\log x$ for systems: a) $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4$, b) $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4 + (5 \times 10^{-4}) \text{ mol dm}^{-3} \text{ PEG 400}$, c) $x \text{ mol dm}^{-3} \text{ NaI} + (1-x) \text{ mol dm}^{-3} \text{ NaClO}_4 + (5 \times 10^{-4}) \text{ mol dm}^{-3} \text{ PEG 10 000}$. Dashed lines denote: d) $k_s^{\text{app}} = 6.9 \times 10^{-6} \text{ cm s}^{-1}$ for $1 \text{ mol dm}^{-3} \text{ NaClO}_4 + (5 \times 10^{-4}) \text{ mol dm}^{-3} \text{ PEG 10 000}$, e) $k_s^{\text{app}} = 2.3 \times 10^{-5} \text{ cm s}^{-1}$ for $1 \text{ mol dm}^{-3} \text{ NaClO}_4 + (5 \times 10^{-4}) \text{ mol dm}^{-3} \text{ PEG 400}$, f) $k_s^{\text{app}} = 3.31 \times 10^{-3} \text{ cm s}^{-1}$ for $1 \text{ mol dm}^{-3} \text{ NaClO}_4$.

absence of PEG, $k_s^{\text{app}} = 3.1 \times 10^{-2} \text{ cm s}^{-1}$ (curve a). In the solutions containing 1×10^{-4} or $5 \times 10^{-4} \text{ mol dm}^{-3}$ PEG 400, k_s^{app} increases from $2.7 \times 10^{-5} \text{ cm s}^{-1}$ to $4.8 \times 10^{-3} \text{ cm s}^{-1}$ or from $2.3 \times 10^{-5} \text{ cm s}^{-1}$ to $3.6 \times 10^{-3} \text{ cm s}^{-1}$, respectively. In these solutions, the compensation of inhibiting and accelerating effects takes place and at the maximal concentrations of I⁻ ions, a slight acceleration of Zn²⁺ ions reduction process is observed (curve b). In the presence of PEG 10 000, $k_s^{\text{app}} = 6.9 \times 10^{-6} \text{ cm s}^{-1}$ and does not depend on the concentration, which is, undoubtedly, due to a large coverage of the electrode surface with a monolayer that is not very tight. The k_s^{app} values obtained in the I⁻ ion and PEG 10 000 mixtures do not depend on the concentration of the second component ther. In these solutions, the compensating effect of inhibition is not observed at the maximum I⁻ ion concentration (curve c).

A slightly different course of $\log k_s^{\text{app}}$ vs. $\log x$ dependence for PEG 400 compared with PEG 10 000 can be the evidence of different structures of mixed adsorption layers PEG 400-I⁻ and PEG 10 000-I⁻. Adsorption of I⁻ ions in the presence of PEG 400 molecules proceeds more readily than in the presence of PEG 10 000 molecules, making Zn²⁺ ions reduction easy. This fact is confirmed also by the changes of E_f^0 values. Acceleration of the processes inhibited by PEG 400 or PEG 10 000 by I⁻ ions is based on formation of ion pairs Zn²⁺-I⁻ on the mercury surface. Using chronocoulometry, Zn²⁺ adsorption induced by I⁻ ions was excluded.³¹

Kinetic measurements confirm stronger adsorption of PEG 10 000 compared with PEG 400, as suggested earlier on the basis of adsorption measurements.

Earlier studies of the mixed adsorption layers of PEG-*m*-toluidine,³² PEG-*p*-toluidine,³³ PEG-thiourea³⁴ on a mercury electrode showed stronger adsorption of both toluidine isomers and thiourea in the presence of PEG compared with I⁻ ion adsorption as indicated by $\Delta_{\text{ad}}G^0$ values. This is associated with the more efficient elimination of inhibition of Zn²⁺ ions electroreduction by PEG with toluidine isomers and thiourea than with I⁻ ions.

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SAŽETAK

Svojstva adsorbiranih slojeva smjese polietilenglikol-jodidni ioni na živinoj elektrodi

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Opisana je adsorpcija smjese iona I^- i polietilenglikola molekulske mase 400 (PEG 400) i 10 000 (PEG 10 000) na živinoj elektrodi iz otopine $NaClO_4$ konstantne ionske jakosti. Paralelni tokovi linearne ovisnosti potencijala nultog naboja s porastom koncentracije iona I^- u otopini s PEG i bez PEG ukazuju na uklanjanje

molekule vode adsorpcijom iona I⁻ bez PEG molekula. Standardna Gibbsova energija adsorpcije $\Delta_{\text{ad}}G^{\circ}$ i parametar B dobiven iz virialne izoterme ne ovisi o koncentraciji PEG 10 000. To se povezuje s potpunim prekrivanjem površine elektrode s molekulama PEG već pri koncentraciji od 10^{-4} mol dm⁻³. Opažena je i ovisnost adsorpcijskih parametara o koncentraciji PEG 400. Manje međusobno odbijanje adsorbiranog iona I⁻ u otopini PEG ukazuje na povoljniji utjecaj molekula PEG na adsorpciju iona I⁻ s obzirom na H₂O.

Određene su vrijednosti konstante brzine reakcije k_s^{app} redukcije iona Zn²⁺ kao modelnog iona. Ubrzanje procesa usporenog s PEG 400 ili PEG 10 000 i I⁻ ionima temelji se na nastajanju ionskog para Zn²⁺-I⁻ na površini žive. Kinetička mjerenja potvrđuju jaču adsorpciju PEG 10 000 s obzirom na PEG 400.