

**ADSORPTION OF IODIDE ION FROM AQUEOUS NaI-NaClO₄-
BUTAN-1-OL AT THE MERCURY-ELECTROLYTE INTERFACE**Jadwiga SABA^{1,*}, Kazimierz SYKUT, Jolanta NIESZPOREK and Jan SZARAN²*Faculty of Chemistry, M. Curie-Skłodowska University, 20031 Lublin, Poland;**e-mail: ¹ jsaba@hermes.umcs.lublin.pl, ² jszar@hermes.umcs.lublin.pl*

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Properties of the adsorption layers $\Gamma\text{-ClO}_4^- \text{-H}_2\text{O}$ and $\Gamma\text{-ClO}_4^- \text{-H}_2\text{O}$ -butan-1-ol on the mercury electrode were described using adsorption and kinetic parameters for the Zn(II) ion reduction. The systems were characterized by the measurements of differential capacity, zero charge potential and surface tension at this potential. The data were analysed to obtain the surface pressure and the charge due to specific adsorption of Γ^- ions as a function of charge and concentration of Γ^- ions. The standard Gibbs energy of adsorption ΔG_{ad}^0 and parameter B obtained from the virial isotherm were compared. The rate constants of Zn(II) ion reduction as an ion affecting the adsorption equilibrium were determined.

Key words: Mixed adsorption layer; Electroreduction Zn(II) ions; Polarography; Electrochemistry.

Specific adsorption of anions on a mercury electrode has been studied in detail for a number of aqueous solutions¹⁻³. Earlier studies of mixed adsorption of two organic substances described inverse influence on kinetics of Zn(II) ions electroreduction and showed that coadsorption takes place in the most cases⁴⁻⁷. The obtained results inspired replacement of the accelerating organic substance by the polarizable Γ^- ions which accelerate the Zn(II) electroreduction⁸⁻¹⁰ and are adsorbed on the mercury surface¹.

Studies of adsorption of Γ^- ions in the presence of thiourea¹¹ showed the decrease in Γ^- adsorption energy accompanied by the diminishing repulsive interaction between adsorbed Γ^- ions. This effect was explained by the ion desorption from the mercury electrode surface. In KBr solution depending on the choice of electrical variable, thiourea causes either increase in surface excess of Br^- ions (at $E = \text{const}$) or its decrease (at $\sigma_{\text{M}} = \text{const}$), particularly for $\sigma_{\text{M}} > 0$ (ref.¹²).

In the case of coadsorption of butan-1-ol and Cl^- , Br^- or ClO_4^- , a distinct decrease of the interaction among butan-1-ol molecules adsorbed on the

mercury electrode is observed¹³. Consequently the decrease of the differential capacity peak according to the Damaskin theory¹⁴ takes place.

On the basis of the theory describing coadsorption of ions and organic molecules¹⁵, it was stated that the values of Cl^- , Br^- , ClO_4^- and NO_3^- ion surface excesses increase with the increase of butan-1-ol concentration¹⁶. For I^- ions, however, these values do not depend on the butan-1-ol concentration. The increase in surface excesses of the above mentioned ions is caused by the attractive interaction between the molecules of butan-1-ol and anions as well as by a weaker interaction of OH groups with mercury in the presence of these anions.

The studies of ethane-1,2-diol adsorption in the presence of F^- , Cl^- , Br^- or I^- ions¹⁷ showed that the values of zero charge potential E_z shift with the increase in its concentration towards positive potentials. The shift is the largest for F^- ions and the smallest for I^- ions. The obtained results confirm explicitly that the adsorbed ethane-1,2-diol dipoles are oriented with their positive ends towards the mercury surface. Decrease of the surface tension in the whole range of potentials is associated with a certain dependence of the Gibbs energy of adsorption ΔG^0 on the electrode charge. It was also shown that the ethane-1,2-diol adsorption is accompanied by the removal of water dipoles but not of anions from the mercury surface.

This paper presents the study of butan-1-ol (BU) and I^- ions coadsorption in NaClO_4 solution of constant ionic strength. The advantages of ionic adsorption study at the mercury-solution interface at constant ionic strength have already been fully discussed^{1,18}.

BU was chosen because of its known adsorption properties on mercury^{16,19-21}. Due to the lack of literature data about I^- ions adsorption in solutions composed from $x \text{ M I}^- + (1 - x) \text{ M NaClO}_4$ (x denotes the concentration between 0.01 and 0.80 mol l⁻¹), the I^- ion adsorption parameters are presented.

EXPERIMENTAL

Analytical-grade reagents NaI, NaClO_4 and butan-1-ol (Merck) were used without further purification. Water and mercury were triply distilled. Electrolyte solutions were deoxygenated using nitrogen passed through vanadous sulfate solution.

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

The double layer capacity of DME was measured at 800 Hz using the 9121 FR Analyser and 9131 Electrochemical Interface (Atlas Sollich, Gdańsk). No significant frequency de-

pendence of the measured capacity was observed. The potential of zero charge E_z was measured for each solution by the method of streaming mercury electrode²². The interfacial tension between mercury and the mixed electrolyte solutions at E_z was measured with a conventional maximum-bubble-pressure capillary electrometer described earlier²³.

The studies of Zn(II) ion reduction kinetics were carried out with a polarograph PA-4 (Laboratorní přístroje, Prague) and EG & G PARC Instrument model 388 and 270 employing a static mercury drop electrode (SMDE) manufactured by Laboratorní přístroje, Prague. Kinetic data were obtained by the 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 Zn(II) reduction. The ohmic resistance of the electrolyte solution was obtained as the real impedance component at frequency of 10 kHz and a potential outside the faradaic region. The approximate diffusion coefficients of Zn(II) in the examined solutions were calculated from limiting currents using the Ilković equation. The polarographic wave of Zn(II) in 0.1 M KNO₃ with the value of the Zn(II) diffusion coefficient $D = 6.9 \cdot 10^{-6}$ cm² s⁻¹ (ref.²⁴) was used as a standard. The diffusion coefficient of zinc in mercury required for further calculations was taken from the literature²⁵ as equal to $1.67 \cdot 10^{-5}$ 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 NaClO₄ and NaClO₄ + 0.55 M BU aqueous solutions. As follows from the comparison of Figs 1 and 2 the I⁻

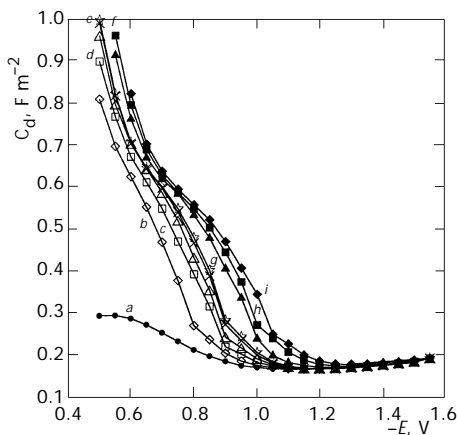


FIG. 1

Differential capacity for a mercury electrode in aqueous solution of x M NaI + $(1 - x)$ M NaClO₄ as a function of potential. Values of x : a 0, b 0.01, c 0.03, d 0.05, e 0.08, f 0.1, g 0.3, h 0.5, i 0.8

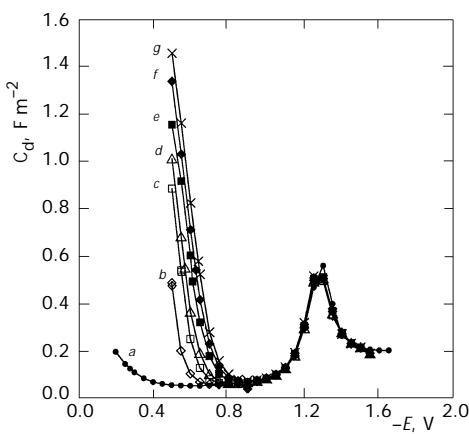


FIG. 2

Differential capacity for a mercury electrode in aqueous solution of x M NaI + $(1 - x)$ M NaClO₄ + 0.55 M butan-1-ol as a function of potential. Values of x : a 0, b 0.01, c 0.05, d 0.1, e 0.3, f 0.5, g 0.8

ion adsorption causes the capacity increase relative to the basic electrolyte. However, the potential range in which the increase takes place is much broader in 1 M NaClO₄ solution, compared to the solution containing BU. Besides, the characteristic capacitance hump appearing in finite system is more distinct at higher I⁻ ion concentrations. A similar hump observed in the solutions x M NH₄Br + (0.5 - x) M NH₄F does not appear³ in the presence of 0.55 M BU; similarly in ethanol²⁶ and methanol²⁷ solutions of I⁻ ions. At about -1.30 V the BU desorption peak (Fig. 2) does not change in the presence of I⁻ ions. It is believed that in this potential area the adsorption layer is modified mainly by BU molecules but not by I⁻ ions contrary to of $E > -0.90$ V range of 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 M NaI + (1 - x) M NaClO₄ solution and with an addition of 0.55 M BU. The increase in I⁻ ion concentration from 0 to 0.8 mol l⁻¹ causes a shift of E_z towards more negative potentials as it is usual for the adsorption of anions, but $dE_z/d(\log c_{I^-})$ coefficient (ca -0.078 V) is higher than that for alkali-metal salts with specifically adsorbed anions (approximately 2.3 RT/F) (ref.²⁸). This indicates significant contribution of the I⁻ ion potential to the potential drop across the inner layer. In the presence of BU, E_z values are a bit higher. Parallel courses of linear dependences of E_z with the increase of I⁻ ion concentration in the solutions with BU and without BU indicate removal of water molecules by adsorption of I⁻ ions, not by BU molecules. In the case of solutions without BU the E_z values were obtained also from back integration of capacity-potential plots starting from the potential -1.55 V. These values were in a good agreement with E_z determined using the

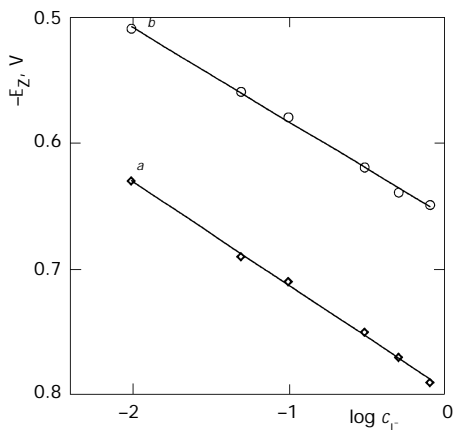


FIG. 3
Dependence of E_z on I⁻ ion concentration for systems: a x M NaI + (1 - x) M NaClO₄, b x M NaI + (1 - x) M NaClO₄ + 0.55 M BU

streaming electrode. An agreement was also found between the values of interfacial tension obtained from the electrocapillary measurements and from twice integrated capacity-potential curves.

The surface pressure curves at each value of the electrode charge were derived using methods proposed by Parsons²⁹, in terms of the function $\xi^+ = \gamma + qE^+$, where γ is the surface tension and E^+ is the potential related to the reference electrode. The surface pressure (Φ) for specifically adsorbed ions was derived from relation $\Phi = \xi^+ - \xi_0^+$, where ξ_0^+ refers to the solutions: 1 M NaClO₄ or 1 M NaClO₄ + 0.55 M BU and ξ^+ to the mixed electrolyte of x M NaI + $(1 - x)$ M NaClO₄ or x M NaI + $(1 - x)$ M NaClO₄ + 0.55 M BU. In Fig. 4 the dependence of surface pressure on the $\ln x$ for I⁻ ions in 1 M NaClO₄ (4a) or 1 M NaClO₄ + 0.55 M BU (4b) is shown. Positive values Φ were obtained in absence of BU for $-6 \leq q_M \leq +1 \mu\text{C cm}^{-2}$. In the presence of BU the range of electrode charge is much smaller (-3 to $0 \mu\text{C cm}^{-2}$). The range of q_M charges for adsorption of various ions on the mercury electrode in solutions of NaF is much broader. Thus, the results obtained in this paper should be associated with low adsorption of ClO₄⁻ ions³⁰ and additionally with BU adsorption. A narrow range of potentials for which the positive Φ values were obtained indicates adsorption equilibria in I⁻-ClO₄⁻-H₂O and I⁻-ClO₄⁻-H₂O-BU systems (Figs 1 and 2). In the latter case, the potential range in which I⁻ ions cause a decrease in differential capacity is more narrow.

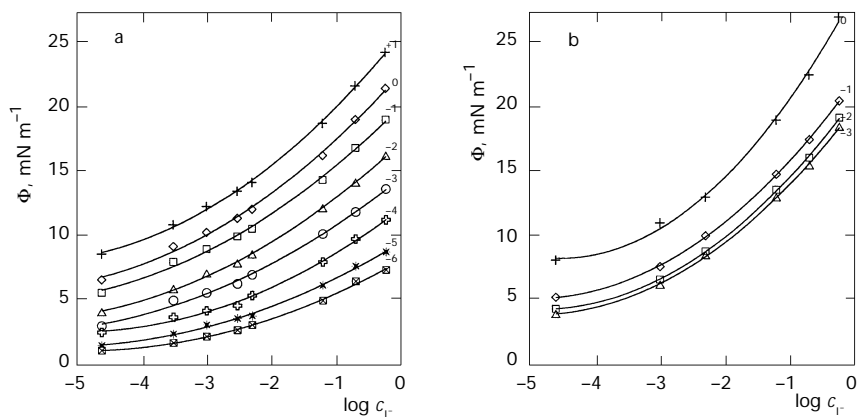


FIG. 4

Plots of the surface pressure due to I⁻ ions adsorbed on the mercury electrode from solutions: a x M NaI + $(1 - x)$ M NaClO₄ and b x M NaI + $(1 - x)$ M NaClO₄ + 0.55 M BU as a function of $\ln x$, the electrode charges (q_M in 10^{-2} C m^{-2}) indicated at each curve

The charge q_{ad} specific adsorption of Γ^- ions in solutions of constant ionic strength was determined using the method proposed earlier^{1,18}:

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

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 Fig. 5. The shapes of the isotherms of Fig. 5a represent straight lines, typical for adsorption of some anions. In the presence of 0.55 M BU (Fig. 5b) the isotherms do not have a linear course. At the same time a double increase of q_{ad} values is observed for $c_{\Gamma^-} \geq 0.3 \text{ mol l}^{-1}$ in the presence of BU. For $c_{\Gamma^-} 0.3 > \text{mol l}^{-1}$ q_{ad} is much lower than in the solution not containing BU. This synergism can result from much smaller hydration of mercury electrode surface in presence of BU molecules, resulting in easier adsorption of Γ^- ions as sufficiently high concentration. A similar effect was observed for adsorption of *p*- and *m*-toluidine in 1 M NaClO_4 and in presence of polyethylene glycol^{31,32}.

The adsorption of Γ^- ions may be described by a simple virial isotherm shown in Fig. 6. Values of the 2D second virial coefficient (B) were calculated from the slopes of lines in Fig. 6 and the corresponding values of standard Gibbs energy of adsorption ΔG_{ad}^0 were obtained from the intercepts of

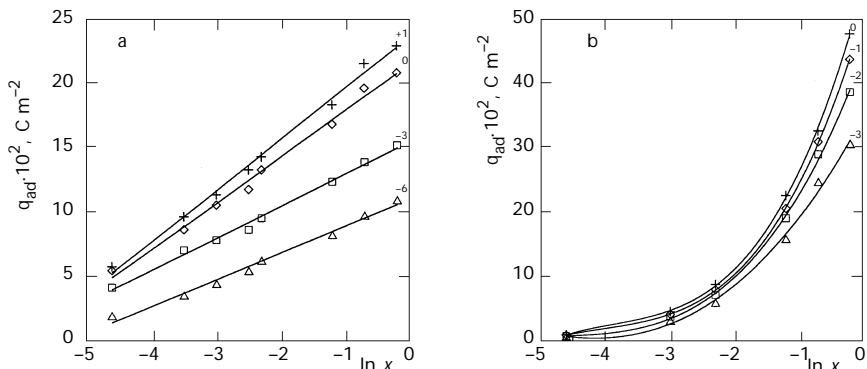


FIG. 5

The adsorbed charge density due to specific adsorption of Γ^- ions from solutions: a $x \text{ M NaI} + (1 - x) \text{ M NaClO}_4$ and b $x \text{ M NaI} + (1 - x) \text{ M NaClO}_4 + 0.55 \text{ M BU}$ as a function of $\ln x$. The electrode charges (q_M in 10^{-2} C m^{-2}) are indicated at each curve

these lines for $q_{\text{ad}} = 0$ (using the standard conditions corresponding to 1 mol I⁻ bulk concentration and x mol cm⁻² surface concentration). As follows from Fig. 6a, ΔG_{ad}^0 in absence BU remains practically equal to about -96.6 kJ mol⁻¹ for electrode charge $-3 \leq q_{\text{M}} \leq +1$ $\mu\text{C cm}^{-2}$. At higher negative charges it decreases to -93.2 kJ mol⁻¹, however, in solution containing BU (Fig. 6b), ΔG_{ad}^0 increases from -88.9 to -90.0 kJ mol⁻¹ for $-3 \leq q_{\text{M}} \leq 0$ $\mu\text{C cm}^{-2}$. In turn, the values of B in x M NaI + (1 - x) M NaClO₄ increase from 1.18 to 2.08 nm² per ion while the electrode charge changes from +1 to -6 $\mu\text{C cm}^{-2}$. In presence of 0.55 M BU, $B = 0.1$ nm² per ion. Much lower repulsive interaction between adsorbed I⁻ in BU solutions indicates a favourable effect of BU molecules on I⁻ ion adsorption compared with H₂O. This fact is confirmed by higher q_{ad} for sufficiently high concentration of I⁻ ions in solutions with BU compared with x M NaI + (1 - x) M NaClO₄ solutions.

The change in the potential drop across the inner layer $\Phi^{\text{M}-2}$ at the constant charge gives more information about the double-layer structure. The value of $\Phi^{\text{M}-2}$ was calculated by subtracting the potential E_z (in the absence of I⁻) and the potential of the outer Helmholtz plane Φ^{2-s} (calculated from the diffusion layer theory³³) from the measured electrode potential. The plots of $\Phi^{\text{M}-2}$ vs surface charge q_{ad} of specifically adsorbed I⁻ ions at constant electrode charge q_{M} are shown in Fig. 7. A linear dependence of $\Phi^{\text{M}-2}$ vs q_{ad} is obtained for all studied systems (Figs 7a and 7b). Different slopes of the $\Phi^{\text{M}-2}$ vs q_{ad} plots indicate the orientation of water molecules in the elec-

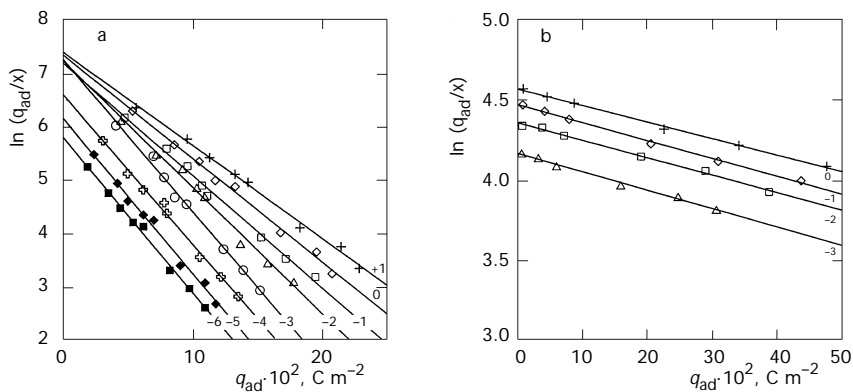


FIG. 6

Linear test of the virial isotherm for systems a) x M NaI + (1 - x) M NaClO₄ and b) x M NaI + (1 - x) M NaClO₄ + 0.55 M butan-1-ol. The electrode charges (q_{M} in 10^{-2} C m⁻²) indicated at each line

tric filed of the electrode and the change of dipol contribution to Φ^{M-2} (ref.³⁴). In solutions containing BU (Fig. 7b), changes of straight line slopes are small. Thus the influence of water dipoles on Φ^{M-2} is small and can be associated with the earlier suggested weaker hydration of the electrode surface in the presence of adsorbed BU molecules.

According to Grahame³⁵ the distance ratio $(x_2 - x_1)/x_2$ was calculated, where x_1 and x_2 are the distances of the inner (IHP) and outer (OHP) Helmholtz planes from the electrode, respectively, using the integral capacities ratio method:

$$\frac{q_M K^i}{q_{ad} K^i} = \frac{\varepsilon_2^i (x_2 - x_1)}{\varepsilon_{2,1}^i x_2} \quad (2)$$

Here, $q_M K^i$ is the integral capacity at the constant electrode charge and $q_{ad} K^i$ is the integral capacity of the condenser formed by the metal and the outer Helmholtz plane: $q_M K^i$ is obtained from the intercept and $q_{ad} K^i$ as the reciprocal slope of the lines in Fig. 7. Symbols ε_2^i and $\varepsilon_{2,1}^i$ represent the electric permittivities between metal and OHP and between IHP and OHP, respectively. As a rule, it is assumed that $\varepsilon_2^i = \varepsilon_{2,1}^i$. In Table I the distance ratios for Γ^- ions in the studied systems are collected. It should be noticed that $(x_2 - x_1)/x_2$ is significantly larger for Γ^- ions in the BU-free solution compared to those in the presence of BU. This difference can be explained by the weaker adsorption of Γ^- ions in the presence of BU and thus, the Γ^- ions may easily

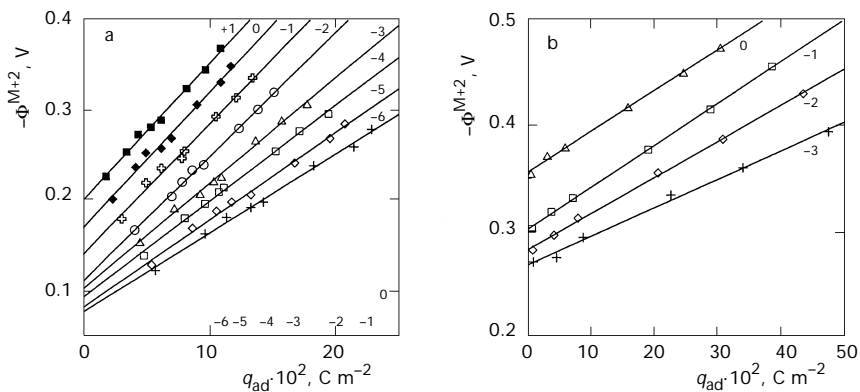


FIG. 7

Potential drop across the inner region vs the amount of specifically adsorbed Γ^- ions for systems: a x M NaI + $(1 - x)$ M NaClO₄ and b x M NaI + $(1 - x)$ M NaClO₄ + 0.55 M BU at constant electrode charges (q_M in 10^{-2} C m⁻²)

move away from the metal³⁶. It means that x_1 is larger in the presence of BU and, consequently, the distance ratio is lower. Variation in the electric permittivity of the inner layer ϵ^i in the presence of adsorbed I^- ions also seems probable.

The results concerning I^- ions adsorption presented earlier provide information about the structure of the adsorption layer but they cover a range of strong adsorption potential of I^- ions and BU molecules. The studies on kinetics of Zn(II) ion reduction as a driving ion broaden this range.

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

Diffusion coefficients of Zn(II) ion decrease from $6.6 \cdot 10^{-6}$ to $3.4 \cdot 10^{-6}$ $\text{cm}^2 \text{s}^{-1}$ with the increase of I^- ion concentration. In presence of 0.55 M BU the value of $2.2 \cdot 10^{-6}$ $\text{cm}^2 \text{s}^{-1}$ is reached. Therefore, the difference between the half-wave reversible potential $E_{1/2}^r$ and the formal potential E_f^0 for Zn(II) ion reduction in studied mixtures was from -6 to -13 mV.

Values of E_f^0 changed from -0.987 to -0.992 V in x M NaI + $(1 - x)$ M NaClO₄. In presence of 0.55 M BU they changed from -0.991 to -1.000 V. The similar changes of E_f^0 values in x M NaI + $(1 - x)$ M NaClO₄ solutions as well as in presence of BU indicate the lack of stable complexes Zn(II)- I^- in the solution.

Figure 8 presents a logarithmic dependence of k_s^{app} for Zn(II) ions reduction on concentration of I^- ions. Introducing I^- ions into the Zn(II) solution

TABLE I

Integral capacities of the double layer region and distance ratios $(x_2 - x_1)/x_2$ for the I^- ions in the studied systems

x M NaI + $(1 - x)$ M NaClO ₄				x M NaI + $(1 - x)$ M NaClO ₄ + 0.55 M BU		
q_M	$q_M K^i$	$q_{ad} K^i$	$(x_2 - x_1)/x_2$	$q_M K^i$	$q_{ad} K^i$	$(x_2 - x_1)/x_2$
0	98	115	0.85	91	350	0.26
-1	86	99	0.87	53	284	0.17
-2	72	87	0.83	27	248	0.11
-3	48	74	0.65	20	248	0.08
-4	40	71	0.56	-	-	-
-5	37	66	0.56	-	-	-
-6	34	64	0.53	-	-	-

accelerates the electroreduction. A noticeable k_s^{app} increase is observed from $c_{\text{I}^-} > 0.03 \text{ mol l}^{-1}$. At the maximum concentration of I^- ions $k_s^{\text{app}} = 3.1 \cdot 10^{-2} \text{ cm s}^{-1}$. In solutions containing 0.55 M BU, k_s^{app} increases from $6.5 \cdot 10^{-5}$ to $4.5 \cdot 10^{-4} \text{ cm s}^{-1}$. In these solutions the compensating effect on inhibition is not observed at the maximum I^- concentration and the more so on acceleration of Zn(II) electroreduction. The effects were observed in systems where accelerating organic substances were used^{4,5,7,31,32}. The presented results indicate the partial compensation of BU inhibiting effect on Zn(II) reduction by I^- ions, however its complete elimination was not observed. Iodide ion adsorption at the potential of Zn(II) ion reduction is weaker compared to BU. Similarities in $\log k_s^{\text{app}} = f(\log c_{\text{I}^-})$ in the $x \text{ M NaI} + (1-x) \text{ M NaClO}_4$ solution in presence and in absence of BU (Fig. 8) allow to state that the mechanism of Zn(II) ion reduction is based just on formation of ion pairs Zn(II)- I^- on the mercury electrode surface. Using the chronocoulometry Zn(II) adsorption induced by I^- ions was excluded³⁷. Absence of the inhibiting effect at sufficiently large I^- ions concentration does not allow us to determine the composition of mixed adsorption layer from the ratio $c_{\text{BU}}/c_{\text{I}^-}$, however, it is possible to find domination of BU adsorption.

CONCLUSIONS

The results can be summarized as follows:

BU molecules have a main effect on the structure of the mixed layer in the presence of 0.55 M BU.

Parallel courses of the linear plots E_z vs $\log c_{\text{I}^-}$ in absence and in presence of 0.55 M BU indicate replacement of water molecules but not BU molecules by adsorbing I^- ions.

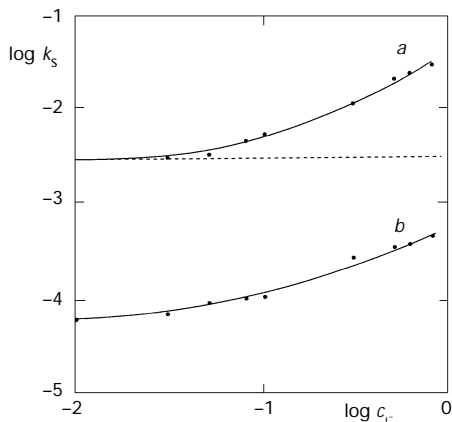


FIG. 8

Plots of $\log k_s^{\text{app}}$ for the (Hg) Zn ($5 \cdot 10^{-3} \text{ mol l}^{-1}$) /Zn(II) ($5 \cdot 10^{-3} \text{ mol l}^{-1}$) couple vs $\log c_{\text{I}^-}$ for systems: *a* $x \text{ M NaI} + (1-x) \text{ M NaClO}_4$, *b* $x \text{ M NaI} + (1-x) \text{ M NaClO}_4 + 0.55 \text{ M BU}$. The dashed line denotes $k_s^{\text{app}} = 3.31 \cdot 10^{-3} \text{ cm s}^{-1}$ for the Zn(II) in 1 M NaClO₄

Adsorption isotherms q_{ad} vs $\ln x$ are linear for adsorption of Γ^- ions in absence of BU but not linear if BU is present. The values q_{ad} are lower at $c_{\Gamma^-} < 0.3 \text{ mol l}^{-1}$ and almost twice higher at $c_{\Gamma^-} \geq 0.3 \text{ mol l}^{-1}$ in solutions with BU addition. This may be caused by lower hydration of the electrode surface due to BU adsorption.

The values of standard Gibbs energy of adsorption, ΔG_{ad}^0 , of Γ^- ions obtained from virial isotherm are slightly lower in solutions containing BU. Also, the 2D second virial coefficient is much lower than in absence of BU. This indicates that adsorbed BU molecules compensate repulsive interaction of Γ^- ions, which can lead to the increase of q_{ad} in $c_{\Gamma^-} \geq 0.3 \text{ mol l}^{-1}$.

The significant decrease in distance ratios $(x_2 - x_1)/x_2$ for Γ^- ions in presence of BU can be explained by the weaker adsorption of Γ^- , which can move easily away from the metal surface (increase of x_1).

Weaker adsorption of Γ^- ions compared with BU and the similarity of mechanism of Zn(II) ion reduction in presence of Γ^- ions and BU molecules was indicated.

REFERENCES

1. Dutkiewicz E., Parsons R.: *J. Electroanal. Chem.* **1966**, 11, 100.
2. Fawcett W. R., McCarrick T. A.: *J. Electrochem. Soc.* **1976**, 123, 1325.
3. Hills G. J., Reeves R. M.: *J. Electroanal. Chem.* **1975**, 42, 355.
4. Saba J.: *Electrochim. Acta* **1994**, 39, 711.
5. Saba J.: *Collect. Czech. Chem. Commun.* **1994**, 60, 1457.
6. Saba J.: *Collect. Czech. Chem. Commun.* **1996**, 61, 999.
7. Saba J.: *Electrochim. Acta* **1996**, 41, 297.
8. Koryta J.: *Electrochim. Acta* **1962**, 6, 67.
9. Randles J. E. B., Sommerton K. W.: *Trans. Faraday Soc.* **1952**, 48, 951.
10. Molodov A. N., Losiew W. W.: *Elektrokhimiya* **1965**, 1, 53.
11. Damaskin B. B., Polanovskaya N. S.: *Elektrokhimiya* **1988**, 24, 485.
12. Polanovskaya N. S., Damaskin B. B.: *Elektrokhimiya* **1986**, 22, 706.
13. Damaskin B. B., Survila A. A., Rybalka L. E.: *Elektrokhimiya* **1967**, 3, 927.
14. Damaskin B. B.: *Usp. Khim.* **1965**, 34, 1764.
15. Damaskin B. B., Frumkin A. N., Borovaya N. A.: *Elektrokhimiya* **1972**, 8, 807.
16. Borovaya N. A., Damaskin B. B.: *Elektrokhimiya* **1972**, 8, 1529.
17. Trasatti S.: *J. Electroanal. Chem.* **1970**, 28, 257.
18. Hurwitz H. D.: *J. Electroanal. Chem.* **1965**, 10, 35.
19. Moncelli M. R., Foresti M. L., Guidelli R.: *J. Electroanal. Chem.* **1990**, 295, 225.
20. Damaskin B. B., Survila A. A., Rybalka L. E.: *Elektrokhimiya* **1967**, 3, 146.
21. Lipkowski J., Galus Z.: *J. Electroanal. Chem.* **1975**, 61, 11.
22. Grahame D. C., Coffin E. M., Cummings J. T., Poth M. A.: *J. Am. Chem. Soc.* **1952**, 74, 1207.
23. Schiffrin D. J.: *J. Electroanal. Chem.* **1969**, 23, 168.
24. Turnham D. S.: *J. Electroanal. Chem.* **1965**, 10, 19.

25. Furman N. S., Cooper W. Ch.: *J. Am. Chem. Soc.* **1950**, 72, 5667.
26. Fawcett W. R., Rocha Filho R. C.: *J. Chem. Soc., Faraday Trans.* **1992**, 88, 1143.
27. Garnish J. D., Parsons R.: *Trans. Faraday Soc.* **1967**, 34, 1754.
28. Minc S., Jurkiewicz-Herbich M.: *J. Electroanal. Chem.* **1972**, 34, 351.
29. Parsons R.: *Trans. Faraday Soc.* **1959**, 55, 999.
30. Fawcett W. R., Rocha Filho R. C., Doubova L. M.: *J. Chem. Soc., Faraday Trans.* **1991**, 87, 2967.
31. Saba J.: *Monatsh. Chem.* **1997**, 128, 1.
32. Saba J.: *Gazz. Chim. Ital.* **1997**, 127, 53.
33. Grahame D. C.: *Chem. Rev.* **1947**, 41, 441.
34. Parsons R., Payne R.: *Z. Phys. Chem.* **1975**, 98, 9.
35. Grahame D. C.: *J. Am. Chem. Soc.* **1958**, 80, 4201.
36. Payne R.: *J. Phys. Chem.* **1965**, 69, 4113.
37. Anderson F. C., Barcalay D. J.: *Anal. Chem.* **1968**, 40, 1971.