ADSORPTION OF BUTYL ACETATE ON MERCURY ELECTRODE AND ITS EFFECT ON ELECTROREDUCTION OF Zn CATIONS

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Adsorption of butyl acetate on the mercury electrode in 1 M, 0.5 M or 0.1 M $NaClO_4$ is described. Differential capacity curves obtained in these solutions for various butyl acetate concentrations point to the strongest decrease in capacity in 0.1 M $NaClO_4$ for the smallest concentration of the ester tested. At the same time the heights of desorption peaks in the solutions tested decrease in the following order: 1 M > 0.5 M > 0.1 M $NaClO_4$. The obtained results show dynamic competitive adsorption in the ClO_4^-–H_2O–ester system. In all the systems studied the zero charge potential values determined with a streaming electrode are shifted towards positive potential with increasing ester concentration. These results suggest that the polar molecule of the ester adsorbs on the mercury electrode with its hydrophobic end while hydrophilic ester group is directed towards the solution. The values of the relative surface excess obtained in the range of potentials where the strong adsorption occurs, virtually do not depend on the base electrolyte concentration. The values of the Gibbs energy of adsorption ΔG^0 determined from the Frumkin isotherm have also similar values at base concentrations of the electrolyte tested. The values of interaction constant A are radically different: the adsorbed molecules undergo repulsive force in 1 M $NaClO_4$, whereas in 0.5 M and 0.1 M $NaClO_4$ they are under weak attraction. In the range of more negative potentials, the adsorption layer was investigated following the kinetics of the reduction of Zn^{++} as a pilot ion. It was stated that the concentration of the base electrolyte fundamentally affects the process: the inhibition of butyl acetate decreases in the order 1 M > 0.5 M > 0.1 M $NaClO_4$.
Keywords: Electrochemistry; Adsorption; Butyl acetate; Mercury electrode; Zinc; Polarography.

Surface-active agents are widely used in cathodic reduction of metals and alloys and also as inhibitors of corrosion because adsorption of organic molecules on the electrode surface plays an important role in the kinetics of electrochemical reactions. Studies on such reactions give information concerning mechanism of electron transfer in heterogenous processes. These processes may also serve as simple models of ion transport in biologi-

cal membranes. Thermodynamic methods are often used for calculating adsorption parameters of organic compounds on the mercury electrode. The resulting adsorption parameters provide information about the configuration of adsorbed molecule as well as about intermolecular interactions in the adsorption layer. The mercury dropping electrode is chosen for such studies due to the fact that the electrode is ideally polarized; therefore, the mercury electrode reflects well thermodynamic dependences. Butyl acetate has been under investigation in the field of anticorrosive protecting coatings for over 20 years. Incorporation of the ester in silicate-based vehicles for storage-stable zinc-rich coating compositions[1] or preparation of metallic films by electrodeposition at the interface between two liquid phases[2] motivates the study of the adsorption and inhibition action of the ester. The effects of surfactants on the reduction of Zn(II) cations has been studied in the past. It was stated that the mechanism of this process does not change in the presence of amyl alkohol[3], butanol[4] and in the presence of ethanol, acetone and tetrahydrofurane[5]. Kůta and Smoler explained the inhibition of various cations electroreduction by blocking with polyvinyl alkohol. As the result of studies about the inhibition of cathodic reduction of Zn(II) cations by amyl alkohol, butanol and hexanol it was stated that the mechanism of inhibition can be attributed to competitive adsorption of activated complex, solvent and inhibitor molecules[7]. The inhibition can be well described by three different model equations originated from Flory–Huggins, Frumkin or Blomgren–Bockris adsorption isotherms for activated complex based on a statistical analysis. Earlier studies on the influence of various esters on polarographic reduction of Zn(II), Cd(II) and Cu(II) cations show that half-wave potentials shift a few hundred millivolts towards negative potentials, which confirms the inhibiting influence of esters on the above electrode processes[8]. It was stated that the studied esters are stable in 0.5 M Na_2SO_4 solution and at pH ≤ 7 for at least several days. Differential capacity curves obtained in the above base electrolyte allowed the calculation of the potential of maximum adsorption for butyl acetate which equals –0.55 V. The shift of the zero charge potential equals 0.308 V towards positive potentials[9] when the coverage values range from $\Theta = 0$ to 1. The authors pointed out that the adsorption properties depend on molecular weight of the esters. Adsorption parameters are similar for isomeric esters such as butyl acetate and ethyl butyrate. In such cases, the adsorption region and potentials of desorption peaks are convergent.

The paper presents the results of studies on adsorption of butyl acetate (BA) in 1 M, 0.5 M or 0.1 M $NaClO_4$. The adsorption parameters were ob-

tained from the Frumkin isotherm. The kinetic parameters of Zn(II) cation electroreduction in the studied systems were determined.

EXPERIMENTAL

Measurements were carried out using a three-electrode cell containing a dropping or static mercury electrode, Ag/AgCl electrode with 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 double layer capacity was measured using the ac impedance technique at a frequency of 800 Hz with a 9121 Frequency Response Analyzer and 9131 electrochemical interface using an appropriate program (Atlas Sollich, Gdańsk, Poland). A controlled-growth mercury drop electrode (CGMDE) (MTM, Poland) was used. The capacitance was measured with an accuracy of ±0.2%. For the whole polarization range, capacitance dispersion was tested at five different frequencies between 200 and 2 000 Hz. In the potential range studied, no dispersion of capacitance was observed. The potential of zero charge E_z was measured using a streaming mercury electrode[10,11]. Interfacial tension γ at E_z was measured by the maximum bubble pressure method according to Schiffrin[12]. Polarographic measurements were carried out using a PA-4 polarograph (Laboratorní Přístroje, Prague, Czech Republic). Cyclic voltammetric experiments were carried out employing a model 270 electrochemical analysis system (EG&G PAR, Princeton, U.S.A.) and an IBM 486 PC equipped with a data interface. A static mercury drop electrode (SMDE) (Laboratorní Přístroje, Prague, Czech Republic) was used. The kinetic parameters for the reduction of Zn(II) cations were determined using the cyclic voltammetry technique (sweep rates from 0.005 to 0.1 V s^{-1}) with an accuracy of ±7%. Chemicals of analytical grade from Merck (Darmstadt, Germany) were used. Water and mercury were distilled twice. $Zn(NO_3)_2 \cdot 6H_2O$ from Fluka (Sigma–Aldrich, Steinheim, Switzerland) was used without further purification. The Zn(II) cations concentration in the solutions was $5 \cdot 10^{-3}$ mol l^{-1}. The concentrations of butyl acetate were 0.015–0.225 mol l^{-1}. Measurements were carried out at 298 ± 0.1 K. Solutions were deoxygenated using high-purity nitrogen. Nitrogen was passed over the solution during the measurements.

RESULTS AND DISCUSSION

Adsorption of Butyl Acetate

The differential capacity curves obtained in $NaClO_4$ solutions with the addition of increasing butyl acetate amounts are characterized by a significant decrease in differential capacity as compared with the basic electrolyte, typical for inhibitors. The potential range in which this decrease occurs extends from –0.1 to –1.2 V. Figure 1 presents the differential capacity curves obtained in 1 M $NaClO_4$ with addition of various amounts of butyl acetate. The shape of the respective differential capacity curves obtained in 0.5 M and 0.1 M $NaClO_4$ is similar as in the above mentioned potential range. The differences concern only the heights of desorption peaks, which decrease in

the following order: 1 M > 0.5 M > 0.1 M $NaClO_4$. The results obtained show dynamic competitive adsorption in the system: ClO_4^-–H_2O–butyl acetate. The capacity against the potential data dependences was numerically integrated from the E_z point. The relevant E_z and γ values are presented in Tables I and II, respectively.

The values of E_z in solutions of $NaClO_4$ without butyl acetate are shifted to negative potentials with increasing $NaClO_4$ concentrations, which confirms adsorption of ClO_4^- ions. An introduction of butyl acetate into the base solution causes a shift of E_z values to positive potentials. The maximum shift of E_z is approximately 0.3 V and is not dependent on the $NaClO_4$ concentration. The above results confirm the calculated data based on capacity values for $\Theta = 1$ presented in ref.[9]. The shift of E_z values with increasing butyl acetate concentration suggests that the polar molecules of the ester adsorb on the mercury electrode with hydrophobic side while the hydrophilic ester group is directed into the solution. In turn, the values of surface tension γ determined for E_z decrease with increasing butyl acetate concentration, the maximum decrease being observed in 1 M $NaClO_4$. Slight deviations in the monotonic changes in values of γ are in the range of accuracy of the method. The values of γ obtained by integration of the differential capacity curves were then used to calculate the surface pressure:

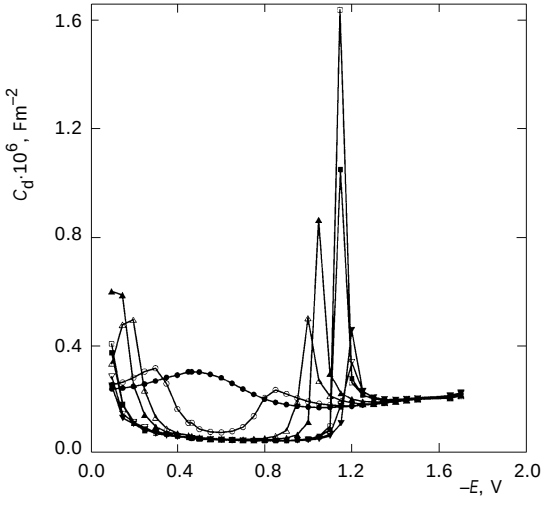

FIG. 1

Differential capacity curves of Hg/1 M $NaClO_4$ for different butyl acetate concentrations (in mol l^{-1}): 0 (●), 0.015 (○), 0.0225 (Δ), 0.0375 (▲), 0.06 (□), 0.075 (■), 0.15 (∇) and 0.225 (▼)

TABLE I
Potential of zero charge $-E_z$, V vs Ag/AgCl for different $NaClO_4$ and butyl acetate concentrations

c_{BA}, mol l^{-1}	c_{NaClO_4}, mol l^{-1}		
	1	0.5	0.1
0.000	0.4797	0.4548	0.4182
0.015	0.4471	0.3970	0.3868
0.023	0.4291	0.3800	0.3663
0.038	0.3700	0.3522	0.3208
0.060	0.2908	0.2920	0.2640
0.075	0.2500	0.2502	0.2222
0.150	0.1812	0.1601	0.1204
0.225	0.1760	0.1560	0.1112

TABLE II
Surface tension γ, mN m^{-1} for E_z in solutions containing various amounts of $NaClO_4$ and butyl acetate

c_{BA}, mol l^{-1}	c_{NaClO_4}, mol l^{-1}		
	1	0.5	0.1
0.000	423.0	425.0	425.0
0.015	422.0	422.4	423.0
0.023	422.1	421.8	421.0
0.038	420.5	420.5	420.5
0.060	417.3	416.6	419.2
0.075	415.4	416.0	417.3
0.150	410.2	409.6	410.0
0.225	403.2	408.3	409.3

$\Phi = \gamma_0 - \gamma$, where γ_0 is the value for supporting electrolyte, while γ is the value determined in the presence of butyl acetate. According to the Gibbs adsorption isotherm, the relative surface excess of butyl acetate is given by

$$\Gamma'_{BA} = -\frac{1}{RT}\left(\frac{\partial \Phi}{\partial \ln c_{BA}}\right)_E , \qquad (1)$$

where c_{BA} is the bulk concentration of ester. In Eq. (*1*) it is assumed that the mean activity coefficients of butyl acetate and $NaClO_4$ do not change with changing in butyl acetate concentration. Positive values of surface pressure Φ were obtained for 1 M, 0.5 M and 0.1 M $NaClO_4$ in the following potential ranges: –0.3 to –0.9 V, –0.2 to –0.8 V and –0.2 to –0.7 V, respectively. Subsequently for the above potential ranges, values of Γ' were calculated. Figure 2 presents the dependence of Γ' values obtained for studied concentrations of butyl acetate in the bulk as a function of electrode potential. Curves presented in Fig. 2 are parabolic-shaped. The maximum Γ' shifted from potential of E = –0.64 to –0.5 V with increasing butyl acetate concentration. The divergence of 50 mV from the potential of maximum adsorption presented in ref.[9] may be due to the employed 50 mV changes in electrode potential

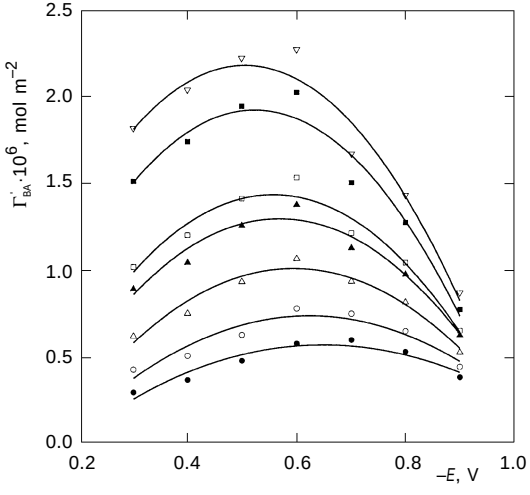

FIG. 2
Relative surface excess of butyl acetate in 1 M $NaClO_4$ as a function of electrode potential for different butyl acetate concentrations (in mol l^{-1}): 0.015 (●), 0.0225 (○), 0.0375 (Δ), 0.06 (▲), 0.075 (❐), 0.15 (■) and 0.225 (▽)

in the present study. The shape of curves in Fig. 2 shows competitive electrostatic interactions: organic molecules–water dipoles[13]. The respective dependences of Γ' calculated for 0.5 M and 0.1 M $NaClO_4$ are similar to those in Fig. 2 but in 0.1 M $NaClO_4$ solution the maximum is situated at the potential of –0.5 V. The adsorption of butyl acetate was further analyzed on basis of surface pressure data using the method previously developed by Parsons[14–16]. Individual surface pressure curves were superposed graphically by shifting them parallel to the log of butyl acetate concentration axis. It was stated that the interaction constant in the Frumkin isotherm, *i.e.*, the *A* parameter, varied with electrode potential. Therefore the constants of Frumkin isotherm were determined from the equation

$$\beta x = \left[\Theta / \left(1 - \Theta\right)\right] \exp\left(-2A\Theta\right), \qquad (2)$$

where *x* is the mole fraction of butyl acetate in solution, β is the adsorption coefficient, which is defined as exp $(-\Delta G^0/RT)$ and Θ is the surface coverage. The surface excess at saturation[8] is $3.14 \cdot 10^{-6}$ mol m^{-2}. Figures 3, 4 and 5 present the linear test of the Frumkin isotherm for 1 M, 0.5 M and 0.1 M

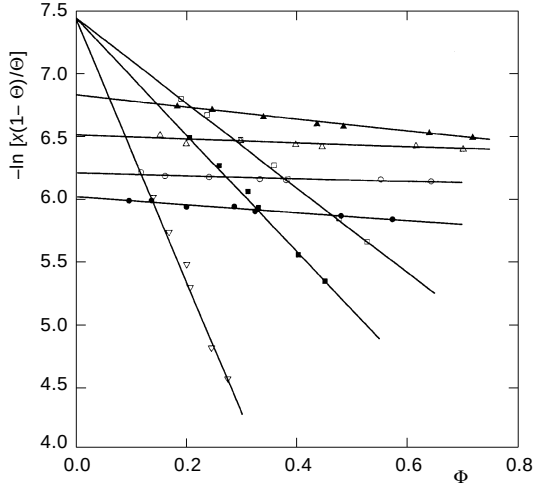

FIG. 3
Linear test of the Frumkin isotherm for 1 M $NaClO_4$. Electrode potentials (in V) are: –0.3 (●), –0.4 (○), –0.5 (△), –0.6 (▲), –0.7 (□), –0.8 (■) and –0.9 (▽)

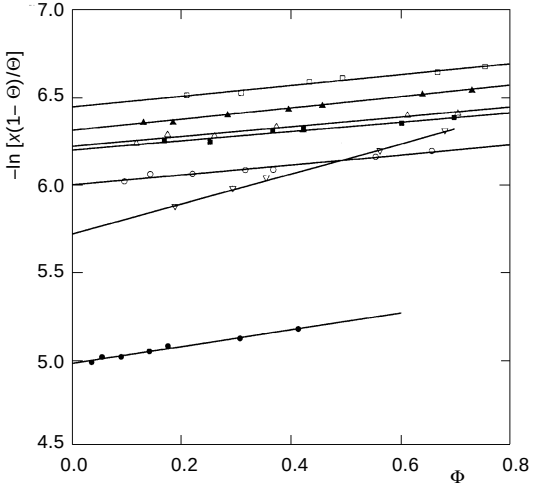

FIG. 4
Linear test of the Frumkin isotherm for 0.5 M $NaClO_4$. Electrode potentials (in V) are: –0.2 (●), –0.3 (○), –0.4 (Δ), –0.5 (▲), –0.6 (❒), –0.7 (■) and –0.8 (▽)

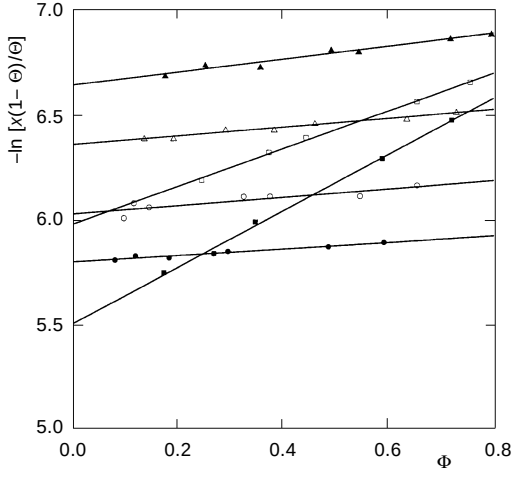

FIG. 5
Linear test of the Frumkin isotherm for 0.1 M $NaClO_4$. Electrode potentials (in V) are: –0.2 (●), –0.3 (○), –0.4 (Δ), –0.5 (▲), –0.6 (❒) and –0.7 (■)

$NaClO_4$, respectively. The values of parameter *A* calculated from the slopes of lines in Figs 3–5 and the corresponding values of standard Gibbs energy of adsorption ΔG^0 were determined by the extrapolation of lines of the dependence of ln $[(1 - \Theta)x/\Theta]$ *vs* Θ to the value $\Theta = 0$. As can be seen from Table III, repulsive interaction between adsorbed butyl acetate molecules appears only in 1 M $NaClO_4$. At more negative potentials, the repulsive effect is even stronger. In remaining systems, the molecules of butyl acetate are under a weak attraction. Weak adsorption of ClO_4^- ions undoubtedly influences such change of parameter *A*. At the same time the values of ΔG^0 are the highest in 1 M $NaClO_4$ solution. There is no direct dependence of Γ' value on the concentration of base electrolyte solution. This can be explained by the fact that adsorption is determined by the resultant of both parameter *A* and value of ΔG^0. Larger ΔG^0 values accompany the more repulsive interaction, whereas ΔG^0 decreases with increasing intermolecular attraction in butyl acetate.

Kinetics of Zn(II) Cations Reduction

The results presented earlier concerning butyl acetate adsorption provide information about the structure of the adsorption layer but they cover only

TABLE III
Comparison of Frumkin isotherm constants for $NaClO_4$ systems containing butyl acetate

E, V	1 M $NaClO_4$		0.5 M $NaClO_4$		0.1 M $NaClO_4$	
	$-\Delta G^0$, kJ mol^{-1}	*A*	$-\Delta G^0$, kJ mol^{-1}	*A*	$-\Delta G^0$, kJ mol^{-1}	*A*
–0.2	–	–	12.33	+0.24	14.34	+0.09
–0.3	14.86	–0.15	14.83	+0.13	14.96	+0.09
–0.4	15.38	–0.07	15.41	+0.13	15.78	+0.10
–0.5	16.10	–0.07	15.65	+0.13	16.50	+0.14
–0.6	16.86	–0.24	15.98	+0.13	14.81	+0.45
–0.7	18.48	–1.67	15.33	+0.13	13.65	+0.67
–0.8	18.48	–2.32	14.19	+0.40	–	–
–0.9	18.48	–5.24	–	–	–	–

the range of strong adsorption potential of this substance. The studies on kinetics of Zn(II) cation reduction as a piloting ion broaden this range. The course of cyclic voltammetric curves for Zn(II) cations electroreduction in the presence of increasing concentrations of butyl acetate shows a decrease in reversibility of the electrode process. Figure 6 presents such effect for 1 M $NaClO_4$ and selected concentrations of butyl acetate. In all tested systems an increase in butyl acetate concentration in the bulk causes an increase in potential difference between the cathodic peak potential E_K and the anodic peak potential E_A. For the maximal tested butyl acetate concentration 0.225 mol l^{-1}, the differences $E_K - E_A$ in solutions of 1 M, 0.5 M and 0.1 M $NaClO_4$ are –0.393, –0.415 and –0.331 V, respectively. As a result of our findings, it can be stated that the reversibility of Zn(II) cations electroreduction slightly decreases in 0.1 M $NaClO_4$, but in 1 M and 0.5 M $NaClO_4$ is comparable, because the differences $E_K - E_A$ are in the limits of accuracy of the method. Standard rate constants were calculated using the parameters characteristic of the voltammetric curves. The method of Nicholson[17] was employed to calculate kinetic parameters for quasi-reversible processes at lower butyl acetate concentrations. At higher butyl acetate concentrations, the rate constants were calculated on the basis of the theory of irreversible processes[18,19]. In all tested systems, the values of formal potentials E_f^0 moved slightly in the direction of negative potentials, maximally by 15 mV. With decreasing $NaClO_4$ concentration the range of butyl acetate concentrations in which E_f^0 values are stable is broadened. It should be

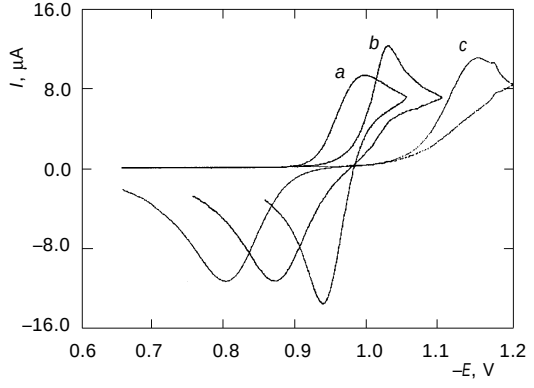

FIG. 6

Cyclic voltammetric curves for Zn(II) cation electroreduction in 1 M $NaClO_4$ in the presence of different butyl acetate concentrations (in mol l^{-1}): 0.0075 (*a*), 0.0375 (*b*) and 0.15 (*c*); sweep rate v = 0.2 V s^{-1}

noted that even the maximum used concentration of butyl acetate does not change the values of diffusion constants D_{ox} of Zn(II) cations. Figure 7 presents a logarithmic dependence of the standard rate constants k_s of Zn(II) cation reduction *vs* butyl acetate concentration. The dashed line denotes the value $k_s = 3.31 \cdot 10^{-3}$ cm s^{-1} for the Zn(II) cation electroreduction in 1 M $NaClO_4$ in the absence of butyl acetate. The respective values of k_s obtained in 0.5 M and 0.1 M $NaClO_4$ are as follows: $3.52 \cdot 10^{-3}$ and $3.20 \cdot 10^{-3}$ cm s^{-1}. The full points in Fig. 7 were calculated using the theory of irreversible processes. The remaining points scattered around the dashed line refer to k_s values calculated using the theory of quasi-reversible processes. As it can be seen from Fig. 7, the inhibition effect of butyl acetate on electroreduction of Zn(II) cations decreases in order: 1 M > 0.5 M > 0.1 M $NaClO_4$. The observed phenomenon is probably caused by "salting-out" effect. Consequently, the adsorption of butyl acetate at electrode potentials corresponding to E_f^0 is the weakest in 0.1 M $NaClO_4$ solution. The strongest adsorption of butyl acetate in 1 M $NaClO_4$ at the reduction potentials of Zn(II) ions reflects the differences between competitive adsorption in the systems: ClO_4^-–butyl acetate and H_2O–butyl acetate. The results outlined in the paper confirm strong adsorption of butyl acetate even at considerably negative electrode potentials. Slight attraction between molecules of butyl

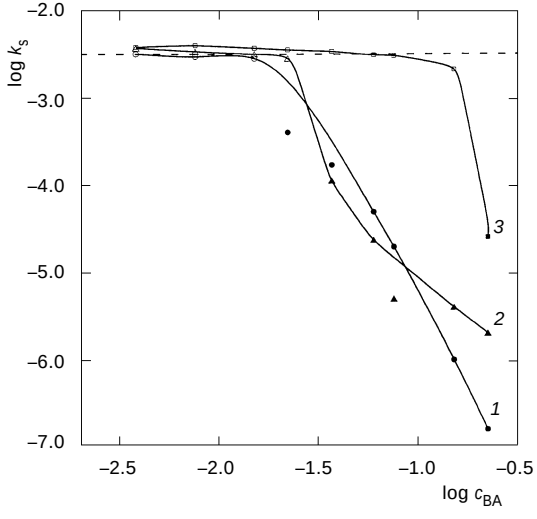

FIG. 7
Plots of log k_s for the (Hg)Zn/Zn(II) couple *vs* log c_{BA} for different $NaClO_4$ concentrations (in mol l^{-1}): 1 (*1*), 0.5 (*2*) and 0.1 (*3*). The dashed line denotes $k_s = 3.31 \cdot 10^{-3}$ cm s^{-1} for Zn(II)

acetate in some systems suggest the formation of tight adsorption layers, which explain the protective and inhibiting properties of the ester. At the same time we furnished evidence that the base electrolyte concentration does not influence the adsorption of butyl acetate in the region of its strong adsorption.

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