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Original Scientific Article

The Influence of *tert*-Butanol on a Two-step Zn^{2+} Ion Electroreduction in Concentrated $NaClO_4$ Solutions

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Abstract. The two-step reduction of Zn^{2+} ions at the dropping mercury electrode in 2, 3, and 4 mol dm^{-3} $NaClO_4$ with the addition of *tert*-butanol, using the impedance method in wide potential and frequency ranges was examined. An inhibiting influence of *tert*-butanol is shown in the used experimental systems, which increases with the rise of the base electrolytes concentration. This effect caused by $NaClO_4$ concentration change is probably linked with the electrodes surface and the Zn^+ aquaion composition change. (doi: 10.5562/cca1726)

Keywords: *tert*-butanol, Zn^{2+} electroreduction, inhibition, adsorption, true rate constants

INTRODUCTION

Adsorption at the electrode/electrolyte solution interface plays an important role in the study of electrode kinetics. The presence of adsorbed nonelectroactive species can have a drastic influence on the rate of an electrode reaction, either in an accelerating or a inhibiting sense. The organic adsorbates inhibiting effect on various inorganic cations electroreduction is generally known.[1,2] Quasi-reversible electrode processes are the most suitable for the studies on the influence of organic compounds because they enable standard rate constant measurements in a wide range of quantities. The Zn^{2+} ion is such a model reactant. Electroreduction of Zn^{2+} ions on the mercury electrode is a typical example of a reaction controlled both by diffusion and charge transfer. In the literature several papers discuss[3–8] the possibility of a mechanism with two single electron transfers.

The Zn^{2+} ion electroreduction at a mercury electrode in $NaClO_4$ as the base electrolyte is an example of an electrode reaction which is inhibited by *tert*-butanol (TB).[9] The base electrolyte concentration influences the degree of Zn^{2+} ion aquacomplexes and electrode surface hydration and hence on the depolarizer electroreduction kinetics. The influence of $NaClO_4$ concentration on Zn^{2+} electroreduction in presence of *tert*-butanol was investigated recently but it concerned diluted solutions.[9] The present paper is a continuation of this problem referring to 2, 3, and 4 mol dm^{-3} $NaClO_4$. The results obtained are a compilation of *tert*-butanol adsorption and Zn^{2+} ions kinetic electroreduction parameters in the presence of *tert*-butanol. In the supporting electrolytes concentrated solutions the Zn^{2+} ions undergo a two step reduction where the inhibition effect of Zn^{2+} ion reduction is the strongest in 4 mol dm^{-3} $NaClO_4$. The results obtained from the kinetic studies of this process permitt a qualitative description of the adsorption-desorption balance of *tert*-butanol in Zn^{2+} ions potential reduction range in $NaClO_4$, so in an area distant from maximum adsorption potential.

EXPERIMENTAL

The experiments were performed in a three-electrode cell with a dropping mercury electrode made by MTM Poland as a working electrode, Ag/AgCl as a reference electrode and a platinum spiral as an auxiliary electrode. The reference electrode was fitted with a Luggin capillary probe. The capillary was filled with the cell solution. The impedance measurements were carried out with a 9121FR Analyzer and 9131 electrochemical interface (Atlas-Sollich, Gdańsk, Poland). The complex impedance data were collected at 36 frequencies ranging from 15 to 50000 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.

I dedicate this paper in loving memory of my father Zdzisław Flaga to honor his unconditional love and never ending support throughout my whole life.

Table 1. Charge densities ($10^2\sigma^m$ / Cm^{-2}) potentials of the outher Helmholtz plane (Φ_2 / V) and potentials in the reaction plane (Φ^r / V) as a function of *tert*-butanol and NaClO4 concentration at potentials: –0.96 V in 2 mol dm^{-3} NaClO$_4$, –0.94 V in 3 mol dm^{-3} NaClO$_4$ and –0.93 V in 4 mol dm^{-3} NaClO$_4$ above values of potentials are close to E_f^0 of Zn^{2+} ion reduction

c_{TB} / mol dm^{-3}	2 mol dm^{-3} NaClO$_4$			3 mol dm^{-3} NaClO$_4$			4 mol dm^{-3} NaClO$_4$		
	$-\sigma^m$	$-\Phi_2$	$-\Phi^r$	$-\sigma^m$	$-\Phi_2$	$-\Phi^r$	$-\sigma^m$	$-\Phi_2$	$-\Phi^r$
0	8.70	0.0384	0.950	8.49	0.0383	0.933	8.37	0.0384	0.924
0.01	8.74	0.0384	0.950	8.77	0.0381	0.933	8.45	0.0383	0.924
0.03	8.64	0.0384	0.950	8.69	0.0381	0.933	8.03	0.0387	0.924
0.05	7.93	0.0386	0.950	7.25	0.0389	0.933	7.52	0.0391	0.924
0.08	6.77	0.0388	0.950	6.32	0.0394	0.932	5.81	0.0404	0.924
0.09	7.10	0.0387	0.950	6.12	0.0395	0.932	5.38	0.0407	0.924
0.10	6.68	0.0388	0.950	6.58	0.0393	0.932	3.99	0.0415	0.924
0.20	6.44	0.0388	0.950	4.72	0.0401	0.932	3.80	0.0416	0.924
0.30	4.68	0.0390	0.950	3.92	0.0403	0.932	3.87	0.0415	0.924
0.40	4.61	0.0390	0.950	3.95	0.0403	0.932	3.76	0.0416	0.924
0.50	4.41	0.0391	0.950	4.02	0.0403	0.932	3.65	0.0417	0.924

Polarographic measurements and voltammetric experiments were performed employing the Autolab frequency response analyzer (Eco Chemie, Netherlands).

Chemicals of analytical grade were used from Fluka. Optimal accuracy was achieved by maintaining the Zn^{2+} concentration around 0.005 mol dm^{-3}. Solutions of *tert*-butanol were prepared to cover the range from 0.01 to 0.5 mol dm^{-3} in NaClO$_4$ solutions. The hydrolysis of Zn^{2+} was suppressed by maintaining the solutions at pH = 3.

The solutions were deaerated using nitrogen. This gas was passed over the solution during the measurements. Water and mercury were distilled twice. Measurements were carried out at 298.0 ± 0.1 K.

RESULTS AND DISCUSSION

Double Layer Analysis

The double layers parameter calculations for the adsorption were based on the data from differential capacity-potential curves obtained experimentally for several concentrations of *tert*-butanol in NaClO$_4$ solutions of the following concentrations: 2 mol dm^{-3}, 3 mol dm^{-3} and 4 mol dm^{-3}.[10]

The curves $C = f(E)$ obtained in NaClO$_4$ solutions with the addition of increasing *tert*-butanol 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 –0.3 V to –1.1 V. The shape of the respective differential capacity curves obtained in the used concentrations of NaClO$_4$ is similar to the mentioned above potential range. The differences concern only the desorption peaks heights, which decrease in the following order: 4 mol dm^{-3} > 3 mol dm^{-3} > 2 mol dm^{-3} NaClO$_4$.

In order to calculate the potential profile in the diffuse double layer it is necessary to estimate the charge density, σ^i, of specifically adsorbed $\mathrm{ClO_4^-}$ ions as a function of the charge density on the electrode, σ^m. Data of the specifically adsorbed charge σ^i of $\mathrm{ClO_4^-}$ were taken from the Parsons and Payne study.[11] It was assumed, as in Reference 12, that the amount of specific $\mathrm{ClO_4^-}$ adsorption is the same for HClO$_4$ and NaClO$_4$ at the same concentration and charge density. The potentials of the outer Helmholtz plane (OHP), Φ_2, were derived in the usual manner assuming the validity of the Gouy-Chapman-Stern theory:[13]

$$\Phi_2 = 0.0514\sinh^{-1}\left(\frac{\sigma^m + \sigma^i}{11.73c^{1/2}}\right) \qquad (1)$$

where c is the bulk concentration of NaClO$_4$.

Table 1 collects the electrode charge densities σ^m and the potentials of the outer Helmholtz plane Φ_2 pertaining to the Zn^{2+} ions electroreduction potentials for various NaClO$_4$ and *tert*-butanol concentrations. Electrode surface charge, σ^m, takes on higher values with the increase of *tert*-butanol concentration. This is consistent with the change of zero charge potential in the presence of *tert*-butanol. The Φ_2 values however slightly depend on *tert*-butanol concentration like in the presence of tetramethylthiourea.[14] Similar Φ_2 potential changes in the case of chemisorption of tetramethylthiourea and physical *tert*-butanol adsorption suggest a mainly $\mathrm{ClO_4^-}$ ions input to Φ_2 values. Earlier it was argued that the plane of the closest approach to Zn^{2+} is more remote from the electrode than the outer Helmholtz plane.[15] Andreu *et al.*[7] proved that the reaction plane is 0.28 nm further from the electrode, which corresponds to the diameter of one water molecule d_{H_2O}. The potential in the reaction plane Φ^r can be calculated[8] by

$$\Phi^r = E\kappa d \frac{4RT}{F}\tanh^{-1}\left[\tanh\left|\frac{F\Phi_2}{4RT}\right|\exp(-\quad {}_{H_2O})\right] \quad (2)$$

where κ is the double-layer thickness parameter expressed in cm^{-1} and 298 K is equal to[16]

$$\kappa = (3.29\times10^7)zc^{1/2} \quad (3)$$

where c is the bulk z:z electrolyte concentration in mol dm^{-3}. The calculated Φ^r values are collected in Table 1. They practically do not depend on tert-butanol concentration but with the increase of $NaClO_4$ shift in the direction of less negative potentials.

Figure 1 shows the relative surface excess of *tert*-butanol plotted at constant $NaClO_4$ concentration versus Φ^r the potential. In the range of Zn^{2+} reduction potentials the relative surface excess, Γ', of *tert*-butanol distinctly increases with the increasing *tert*-butanol and $NaClO_4$ concentration. Such Γ' value changes with $NaClO_4$ concentration increase clearly point (as in the case of tetramethylthiourea[14]) to a facilitated *tert*-butanol adsorption on a less hydrated electrode surface in the presence of higher quantities of ClO_4^- ions. In all studied systems two areas of change for the Γ' value in the Φ^r function can be distinguished. The first area in which the obtained dependence $\Gamma' = f(\Phi^r)$ has a nearly linear character apply to concentrations from 0.01 mol dm^{-3} to 0.1 mol dm^{-3} *tert*-butanol. The second area of higher *tert*-butanol concentrations from 0.2 mol dm^{-3} to 0.5 mol dm^{-3} the $\Gamma' = f(\Phi^r)$ dependencies loose their linear character and the observed Γ' shifts more clearly depend on the Φ^r potential as well as on the *tert*-butanol concentration.

Polarographic and Voltammetric Measurements

The approximate diffusion coefficients of Zn^{2+} in the examined solution were calculated using the Ilkovič equation for a diffusion-controlled limiting current. The polarographic wave of Zn^{2+} in 0.1 mol dm^{-3} KNO_3 with a value of $D_{ox} = 6.9\times10^{-6}$ cm^2 s^{-1} for the Zn^{2+} diffusion coefficient was used as a standard.[17] The D_{ox} values in the 2, 3, and 4 mol dm^{-3} $NaClO_4$ change with an increase of *tert*-butanol concentration ranging from 6.06×10^{-6} cm^2 s^{-1} to 5.75×10^{-6} cm^2 s^{-1}, from 5.72×10^{-6} cm^2 s^{-1} to 4.9×10^{-6} cm^2 s^{-1} and from 4.68×10^{-6} cm^2 s^{-1} to 3.93×10^{-6} cm^2 s^{-1}. The decrease of D_{ox} values for Zn^{2+} ions in the absence of *tert*-butanol, with $NaClO_4$ concentration increase results from much stronger solution viscosity. The addition of the highest *tert*-butanol concentration generaly decreases the D_{ox} values.

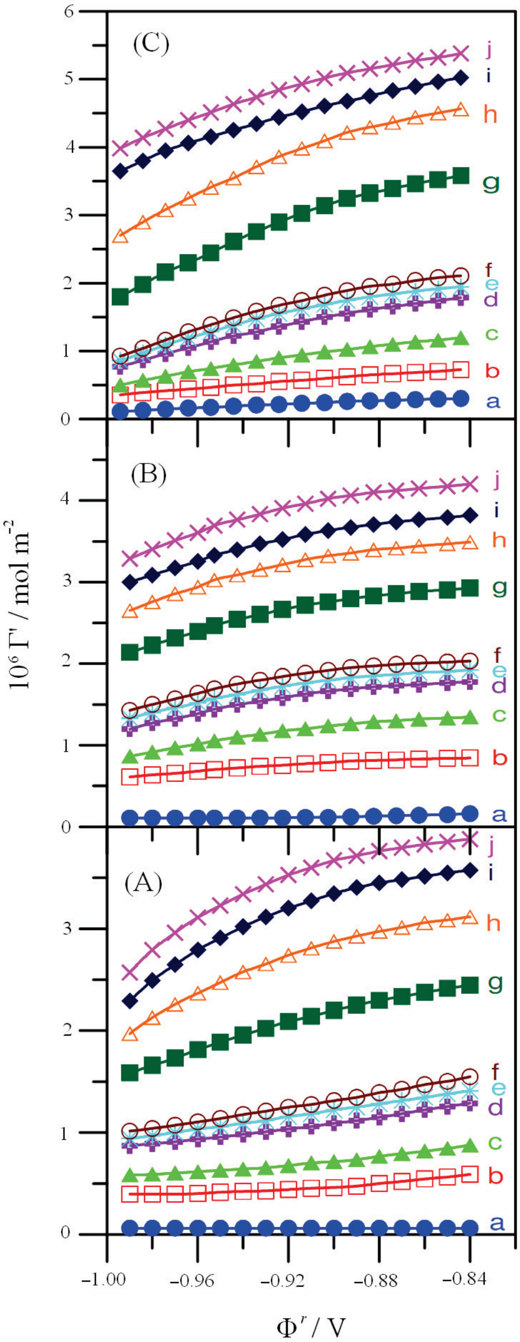

Figure 1. Relative surface excess Γ' of *tert*-butanol *vs*. Φ^r at varied concentrations of *tert*-butanol: (a) 0.01mol dm^{-3}, (b) 0.03 mol dm^{-3}, (c) 0.05 mol dm^{-3}, (d) 0.08 mol dm^{-3}, (e) 0.09 mol dm^{-3}, (f) 0.1 mol dm^{-3}, (g) 0.2 mol dm^{-3}, (h) 0.3 mol dm^{-3}, (i) 0.4 mol dm^{-3}, (j) 0.5 mol dm^{-3} and varied concentrations of $NaClO_4$: (A) 2 mol dm^{-3}, (B) 3 mol dm^{-3}, (C) 4 mol dm^{-3}.

The reversible potentials of the half wave $E^r_{1/2}$ of the Zn^{2+} ions reduction were estimated from the cyclic voltammetric curves[17] with the reproducibility ±0.002 V, using the sweep rates of 0.005 to 0.1 V s^{-1}

Table 2. The ΔE value of the potential differences of the anode and cathode peak in 2, 3, and 4 mol dm^{-3} $NaClO_4$ in the presence of different amounts of *tert*-butanol

c_{TB} / mol dm^{-3}	ΔE / V		
	$c(NaClO_4)$ / mol dm^{-3}		
	2	3	4
0	0.091	0.084	0.067
0.01	0.091	0.086	0.069
0.03	0.093	0.086	0.071
0.05	0.097	0.089	0.082
0.08	0.109	0.097	0.145
0.09	0.109	0.105	0.171
0.10	0.110	0.107	0.191
0.20	0.141	0.187	0.260
0.30	0.223	0.248	0.328
0.40	0.264	0.302	0.355
0.50	0.299	0.322	0.371

$$E^r_{1/2} = \frac{E_{pc} + E_{pa}}{2} \tag{4}$$

where E_{pc} and E_{pa} are cathode and anode peak potentials respectively.

In the studied $NaClO_4$ concentrations the increase in *tert*-butanol concentration does not cause significant $E^r_{1/2}$ value changes. These small $E^r_{1/2}$ changes in the studied electrolytes can be linked to the liable adsorption balance of *tert*-butanol in the potential range of Zn^{2+} ions reduction.[10] In this potential range *tert*-butanol desorption peaks start to form.

Figure 2 shows voltammetric curves of Zn^{2+} electroreduction in 2, 3, and 4 mol dm^{-3} $NaClO_4$ with and without the addition of *tert*-butanol. A distinct decrease of the anodic peak current, the strongest in 4 mol dm^{-3} $NaClO_4$ should be noticed. In the case of Zn^{2+} ions reduction acceleration by tetramethylthiourea[14] an increase of anodic and cathodic peak currents takes place.

From the results presented in Table 2 it can be stated that the base electrolyte concentration increase was accompanied by the decrease of ΔE values for Zn^{2+} ions electroreduction attesting an acceleration of the electroreduction process. This tendency continued in $c \leq$ 0.05 mol dm^{-3} *tert*-butanol solutions. The introduction of higher amounts of *tert*-butanol caused a strong inhibition of Zn^{2+} ions in 4 mol dm^{-3} $NaClO_4$ which is confirmed by the highest ΔE values. The observed effects correspond with the Γ' values for *tert*-butanol (Figure 1).

The Rate of Electroreduction

The complex impedance data were collected at 36 frequencies. Figure 3 shows some examples of impedance diagrams for the electroreduction of Zn^{2+} ions in 3 mol dm^{-3} $NaClO_4$ with the addition of *tert*-butanol. The Z' and Z'' measurements accuracy was about 2 %. Just as in the diluted $NaClO_4$ solutions[9] the increased values of the charge-transfer resistance in the presence of *tert*-butanol demonstrate unequivocally the inhibiting influence of *tert*-butanol. Even a 0.09 mol dm^{-3} *tert*-butanol concentration causes a distinct increase of charge-transfer resistance, the most distinct in 4 mol dm^{-3} $NaClO_4$.

The charge-transfer resistance values were used to determine the apparent rate constants k_f values.[7] The details are described elsewhere.[19,20] The k_f values obtained for the solutions of a constant $NaClO_4$ concentration and varying concentrations of *tert*-butanol indicate an inhibiting *tert*-butanol influence on the Zn^{2+} electroreduction in the studied systems.

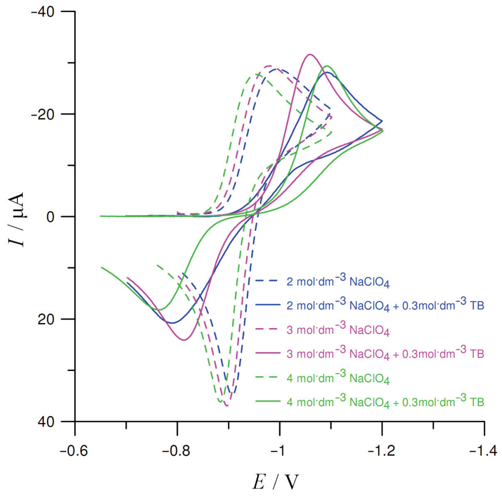

Figure 2. Cyclic voltammetric curves for the Zn^{2+}/Zn(Hg) system in 2, 3, and 4 mol dm^{-3} $NaClO_4$ at a scan rate 0.1 V s^{-1} in the absence and in the presence of 0.3 mol dm^{-3} *tert*-butanol.

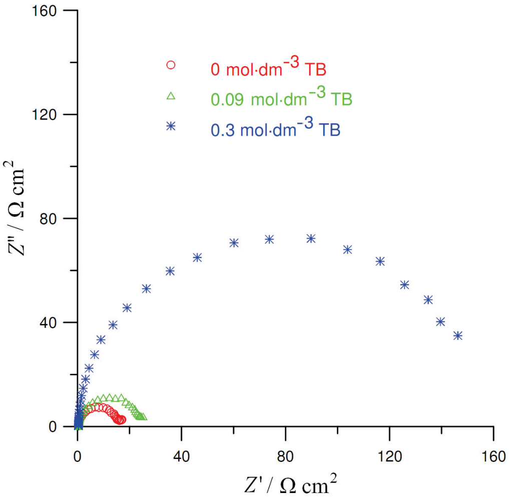

Figure 3. Impedance diagrams measured at E^0_f for the electroreduction of Zn^{2+} in 3 mol dm^{-3} $NaClO_4$ and in the presence of *tert*-butanol.

Table 3. The coefficient of determination R^2 values which characterize the linear regression quality in cases where the dependence $\ln k_f^t = f(\Phi^r)$ is rectilinear

c_{TB} / mol dm^{-3}	R^2		
	c(NaClO$_4$) / mol dm^{-3}		
	2	3	4
0.20	-	-	0.9909
0.30	-	0.9976	0.9863
0.40	0.9981	0.9984	0.9857
0.50	0.9705	0.9958	0.9861

Based on the command of the k_f and Φ^r values true rate constants were appointed based on the dependence

$$k_f(\Phi^r) = k_f^t(\Phi^r)\exp\left\{-(E-\Phi^r)\frac{nF}{RT}\right\} \qquad (5)$$

Figure 4 shows the potential dependence of the true rate constants k_f of Zn^{2+} ion electroreduction calculated at OHP + 0.28 nm, obtained at various *tert*-butanol concentrations.

In some cases the dependence $\ln k_f^t$ *vs*. Φ^r seems to be linear. Then to characterize the regression quality a coefficient of determination, R^2 was used. In this case, the R^2coefficient of determination is a statistical measure of how well the regression line approximates the real data points. An R^2 of 1.0 indicates that the regression line perfectly fits with the data making it easy to evaluate the quality of the fit. Table 3 shows the values of R^2 for the cases when experimental points were adjusted by linear function. It can be seen, that the use of higher *tert*-butanol concentration: $c \geq 0.4$ mol dm^{-3} in the case of 2 mol dm^{-3} NaClO$_4$, $c \geq 0.3$ mol dm^{-3} in the case of 3 mol dm^{-3} NaClO$_4$ and $c \geq 0.2$ mol dm^{-3} in the case of 4 mol dm^{-3} NaClO$_4$ results in rectilinear dependencies $\ln k_f^t = f(\Phi^r)$. In this case it was nearly impossible to determine a constant rate of individual transfer stages consecutive electrons during Zn^{2+} ions electroreduction on a mercury electrode. This effect could probably be explained by the Zn^{2+} ions electroreduction irreversibility in the presence of a substantial amount of *tert*-butanol. The strong irreversibility of the studied process did not allow two separate electron transfer stages.

For lower *tert*-butanol concentrations the relations $\ln k_f^t = f(\Phi^r)$ are not rectilinear, and the slope of the curves changes with the potential and the *tert*-butanol concentrations. This nonlinear dependence indicates a two-step character of Zn^{2+} ions electroreduction mechanism in the studied solutions. This multistep mechanism is determined by the following properties:

1. A two one-electron transfer processes (mechanism EE),[21]
2. A slow transfer of zinc cation through the double layer with two distinct steps to a site at the interface where a metal ion reactant is adsorbed (mechanism IA),[21,22]
3. A chemical step followed by electron transfer (mechanism CE). The chemical step is assumed to involve loss or exchange of a ligand, which could be a solvent molecule.[23] On the basis of the kinetic analysis we cannot detect the presence of chemical reactions[24]
4. An ion transfer step followed by an electron transfer (mechanism IE).[23]

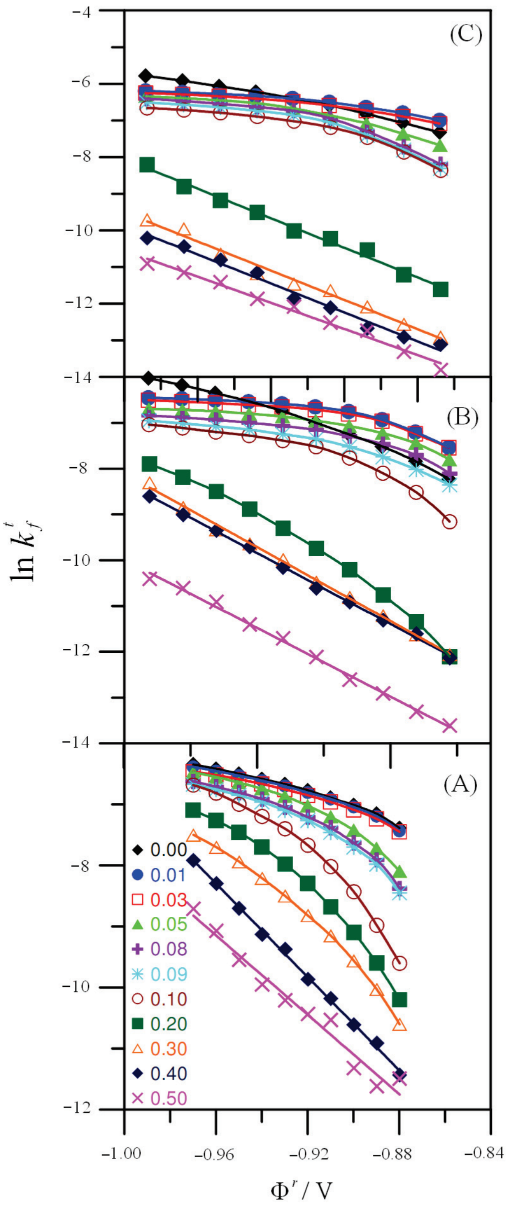

Figure 4. Potential dependence of the true rate constants of the Zn^{2+} ion reduction in (A) 2 mol dm^{-3} NaClO$_4$, (B) 3 mol dm^{-3} NaClO$_4$ and (C) 4 mol dm^{-3} NaClO$_4$ at various tert-butanol concentrations (mol dm^{-3}) indicated under A.

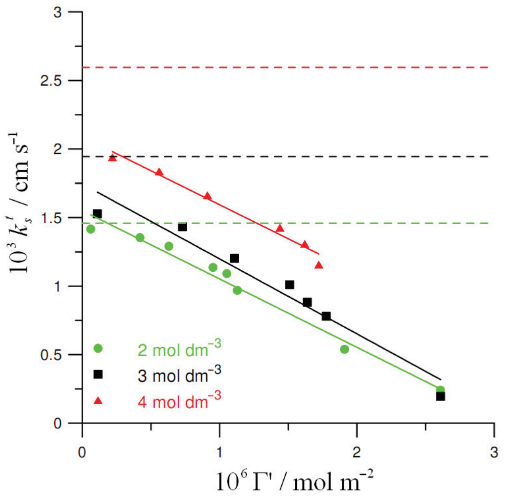

Figure 5. The true standard rate constants k_s^t for the Zn^{2+} reduction vs. the relative surface excess of *tert*-butanol in 2, 3, and 4 mol dm^{-3} $NaClO_4$. The dashed lines denote k_s^t values in the absence of *tert*-butanol.

As the dependence on Figure 4 shows the introduction of the lowest *tert*-butanol concentrations to the studied systems caused a Zn^{2+} electroreduction rate decrease. This *tert*-butanol inhibiting effect is the clearest at less negative potentials and increases with the rise of *tert*-butanol concentration.

It is assumed that for the studied systems which obtained non-linear dependencies $\ln k_f^t = f(\Phi^r)$ the charge transfer takes place *via* two-consecutive one electron transfer steps.[7,8] The first electron transfer is rate determining ($k_1^t = k_f^t$) at the most negative potentials. At less negative potentials, the overall rate is determined by both steps simultaneously

$$\frac{1}{k_f^t} = \frac{1}{k_1^t} + \frac{K_1}{k_2^t} \qquad (6)$$

where K_1 is the formal equilibrium constant of the first stage. The balance constants for each of the electron transfer stages were connected with a Nernstian-like potential dependence.[7] By using the above relationship and adopting the experimental data $\ln k_f^t = f(\Phi^r)$, the true standard rate constants k_s^t values corresponding to the values E_f^0 and the values of constants k_{s1}^t and k_{s2}^t were determined. The constants k_{s1}^t and k_{s2}^t characterize the first electron transfer stage and the second electron-exchange stage, respectively. The individual standard rate constant values of the Zn^{2+} electroreduction in 2, 3, and 4 mol dm^{-3} $NaClO_4$, corrected for the double layer effects are: $k_{s1}^t = 1.51\times10^{-3}$ cm s^{-1} and $k_{s2}^t = 7.40\times10^{-2}$ cm s^{-1}; $k_{s1}^t = 1.98\times10^{-3}$ cm s^{-1} and $k_{s2}^t = 7.64\times10^{-2}$ cm s^{-1}; $k_{s1}^t = 2.67\times10^{-3}$ cm s^{-1} and $k_{s2}^t = 7.65\times10^{-2}$ cm s^{-1}, respectively. These values systematically grow with the increase of $NaClO_4$ concentration and correspond with the literature data.[7,8]

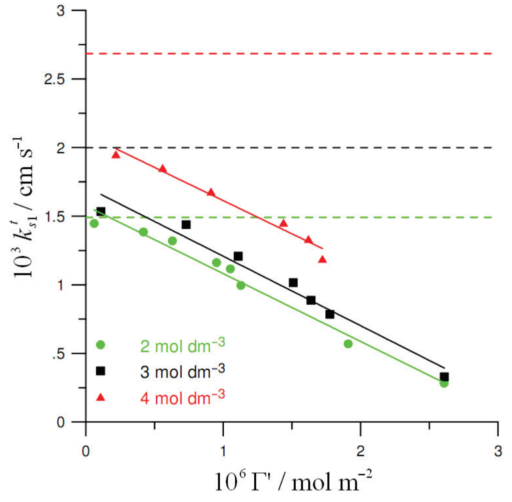

Figure 6. The individual true standard rate constants k_{s1}^t for the Zn^{2+} reduction *vs*. the relative surface excess of *tert*-butanol in 2, 3, and 4 mol dm^{-3} $NaClO_4$. The dashed lines denote k_{s1}^t values in the absence of tert-butanol.

Figures 5–7 present the k_s^t, k_{s1}^t and k_{s2}^t values dependence versus surface concentration of *tert*-butanol which lead to the following conclusions:

- In all of the studied systems an inhibiting *tert*-butanol influence is observed on the first electron transfer stage. The $k_s^t = f(\Gamma')$ and $k_{s1}^t = f(\Gamma')$ dependencies have a similar character. k_s^t and k_{s1}^t value shifts are analogical in the $NaClO_4$ concentration function as in the *tert*-butanol concentration. In all the base electrolytes studied, the rectilinear almost parallel dependences $k_s^t = f(\Gamma')$, $k_{s1}^t = f(\Gamma')$ are observed. The k_s^t and k_{s1}^t value change comparison for *tert*-butanol concentrations $c \leq 0.1$ mol dm^{-3} follows that Zn^{2+} ions reduction inhibition effect is comparable in 3 and 4 mol dm^{-3} solutions of $NaClO_4$ and stronger than in 2 mol dm^{-3}.
- In the case of the second electron transfer in a 2 mol dm^{-3} $NaClO_4$ the lowest *tert*-butanol concentration caused his inhibition. In a 3 mol dm^{-3} $NaClO_4$ to fully exercise the *tert*-butanol inhibition effect a 0.2 mol dm^{-3} is needed and in a 4 mol dm^{-3} $NaClO_4$ a 0.09 mol dm^{-3} *tert*-butanol concentration. The $k_{s2}^t = f(\Gamma')$ dependences are also linear. Only in the case of a 2 mol dm^{-3} $NaClO_4$ this dependence concerns inhibition. For 3 and 4 mol dm^{-3} $NaClO_4$ this effect occurs only for the highest *tert*-butanol concentrations, due to the fact that the lowest *tert*-butanol concentrations cause a significant increase of the k_{s2}^t value. Higher *tert*-butanol concentrations cause a linear decrease of the k_{s2}^t values, which for suitably low *tert*-butanol concentrations are higher in comparison with the k_{s2}^t values obtained in *tert*-butanols absence. The surpris-

Table 4. The true standard rate constant k_s^t of Zn^{2+} ion electroreduction extrapolated to the E_f^0 for various concentrations of $NaClO_4$ and *tert*-butanol

c_{TB} / mol dm^{-3}	$10^3 k_s^t$ / cm s^{-1}		
	$c(NaClO_4)$ / mol dm^{-3}		
	2	3	4
0.00	1.459	1.944	2.595
0.01	1.416	1.528	1.938
0.03	1.354	1.432	1.836
0.05	1.291	1.202	1.662
0.08	1.136	1.010	1.426
0.09	1.091	0.882	1.307
0.10	0.969	0.780	1.156
0.20	0.539	0.196	0.152
0.30	0.241	0.107	0.052
0.40	0.100	0.103	0.040
0.50	0.052	0.020	0.024

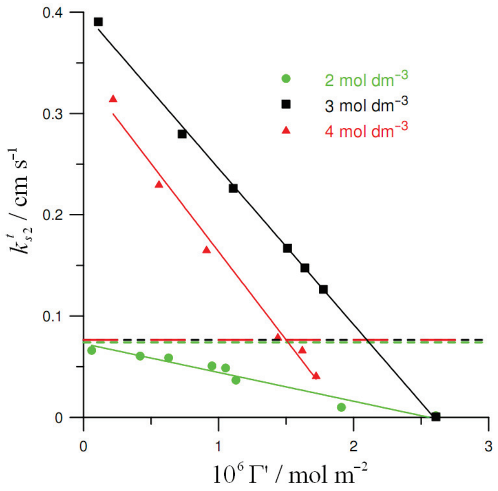

Figure 7. The individual true standard rate constants k_{s2}^t for the Zn^{2+} reduction *vs.* the relative surface excess of *tert*-butanol in 2, 3, and 4 mol dm^{-3} $NaClO_4$. The dashed lines denote k_{s2}^t values in the absence of *tert*-butanol.

ing accelerating effect of the second electrons transfer in concentrated $NaClO_4$ solutions in the presence of small *tert*-butanol concentrations is linked with the Zn^+ aquaion structure. In 3 and 4 mol dm^{-3} $NaClO_4$ solutions the Zn^+ ion is less hydrated. The electrodes surface is also less hydrated for example for a 0.1 mol dm^{-3} *tert*-butanol concentration at E_f^0 potential the Γ' values are 1.1×10^{-6}, 1.8×10^{-6} and 1.7×10^{-6} mol m^{-2} w 2, 3, and 4 mol dm^{-3} $NaClO_4$, respectively.

- For *tert*-butanol maximum concentration only the k_s^t values (Table 4) could have been determined. At the highest *tert*-butanol concentration used 0.5 mol dm^{-3} the highest inhibiting effect was observed in a 4 mol dm^{-3} $NaClO_4$. The k_s^t value for this concentration decreases over 100 times in relation to the k_s^t value determined in the absence of-*tert*-butanol , in a 3 mol dm^{-3} $NaClO_4$ over 90 times, and in a 2 mol dm^{-3} about 30 times. In reference to the results obtained from diluted $NaClO_4$ solutions[9] it can be said that the *tert*-butanol inhibiting effect increases in the following order:0.1 mol dm^{-3} < 0.5 mol dm^{-3} < 1.0 mol dm^{-3} < 2.0 mol dm^{-3} < 3.0 mol dm^{-3} < 4.0 mol dm^{-3} $NaClO_4$.

CONCLUSIONS

From the presented results it can be stated that:

1. Slight $E_{1/2}^r$ value shifts in all the studied systems 2 mol dm^{-3}, 3 mol dm^{-3} and 4 mol dm^{-3} $NaClO_4$ may be the result of a weak *tert*-butanol adsorption in the Zn^{2+} ion reduction potential region.
2. Determination of constant rate stages of Zn^{2+} ions electroreduction was possible in solutions with lower *tert*-butanol concentrations for which $\Gamma' = f(\Phi^r)$ dependencies had a generally linear character whereas the $\ln k_f^t = f(\Phi^r)$ dependence was non-linear. In higher *tert*-butanol concentrations responsible for the strong Zn^{2+} ions reduction irreversibility process $\ln k_f^t = f(\Phi^r)$ dependencies were linear and did not permit the determination of constant rate stages.
3. The analysis of the true rate constant k_s^t depending on *tert*-butanol and the base electrolytes concentration as well as the work[9] results allows to conclude that the strongest inhibiting effect at the highest *tert*-butanol concentration occurs in a 4 mol dm^{-3} $NaClO_4$. The *tert*-butanol inhibiting effect increases in the order: 0.1 mol dm^{-3} < 0.5 mol dm^{-3} < 1.0 mol dm^{-3} < 2.0 mol dm^{-3} < 3.0 mol dm^{-3} < 4.0 mol dm^{-3} $NaClO_4$.
4. The rectilinear and parallel dependences $k_{s1}^t = f(\Gamma')$ suggest that the used $NaClO_4$ concentrations do not influence the first electron transfer mechanism. From the $k_{s2}^t = f(\Gamma')$ and $\Gamma' = f(c)$ dependences it follows that the Zn^+ aquaions and the hydration degree composition has a clear influence on the second electrode transfer mechanism.

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