The Influence of tert-Butanol on a Two-step Zn$^{2+}$ Ion Electroreduction in Concentrated NaClO$_4$ Solutions

Jolanta Nieszporek

Department of Analytical Chemistry and Instrumental Analysis, Faculty of Chemistry, Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland

(E-mail: jolan@poczta.umcs.lublin.pl)

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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.

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 nonselective adsorbs 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. Electrodereaction 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 permit 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-Solich, 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 Zdzislaw Flaga to honor his unconditional love and never ending support throughout my whole life.
Table 1. Charge densities \((10^2 \sigma^m / \text{Cm}^2)\) potentials of the outer Helmholtz plane \((\Phi_2 / V)\) and potentials in the reaction plane \((\Phi' / V)\) as a function of tert-butanol and NaClO4 concentration at potentials: -0.96 V in 2 mol dm\(^{-3}\) NaClO4, -0.94 V in 3 mol dm\(^{-3}\) NaClO4 and -0.93 V in 4 mol dm\(^{-3}\) NaClO4 above values of potentials are close to \(E^o\) of Zn\(^{2+}\) ion reduction.

<table>
<thead>
<tr>
<th>(c_{\text{TB}} / \text{mol dm}^{-3})</th>
<th>2 mol dm(^{-3}) NaClO4</th>
<th>3 mol dm(^{-3}) NaClO4</th>
<th>4 mol dm(^{-3}) NaClO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma^m)</td>
<td>(-\Phi_2)</td>
<td>(-\Phi')</td>
<td>(-\Phi_2)</td>
</tr>
<tr>
<td>0</td>
<td>8.70</td>
<td>0.0384</td>
<td>0.950</td>
</tr>
<tr>
<td>0.01</td>
<td>8.74</td>
<td>0.0384</td>
<td>0.950</td>
</tr>
<tr>
<td>0.03</td>
<td>8.64</td>
<td>0.0384</td>
<td>0.950</td>
</tr>
<tr>
<td>0.05</td>
<td>7.93</td>
<td>0.0386</td>
<td>0.950</td>
</tr>
<tr>
<td>0.08</td>
<td>6.77</td>
<td>0.0388</td>
<td>0.950</td>
</tr>
<tr>
<td>0.09</td>
<td>7.10</td>
<td>0.0387</td>
<td>0.950</td>
</tr>
<tr>
<td>0.1</td>
<td>6.68</td>
<td>0.0388</td>
<td>0.950</td>
</tr>
<tr>
<td>0.2</td>
<td>6.44</td>
<td>0.0388</td>
<td>0.950</td>
</tr>
<tr>
<td>0.3</td>
<td>4.68</td>
<td>0.0390</td>
<td>0.950</td>
</tr>
<tr>
<td>0.4</td>
<td>4.61</td>
<td>0.0390</td>
<td>0.950</td>
</tr>
<tr>
<td>0.5</td>
<td>4.41</td>
<td>0.0391</td>
<td>0.950</td>
</tr>
</tbody>
</table>

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 NaClO4 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 NaClO4 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 NaClO4 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 NaClO4 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\(^{-3}\) NaClO4.

In order to calculate the potential profile in the diffuse double layer it is necessary to estimate the charge density, \(\sigma^m\), of specifically adsorbed ClO\(_4^-\) ions as a function of the charge density on the electrode, \(\sigma^m\). Data of the specifically adsorbed charge \(\sigma'\) of ClO\(_4^-\) were taken from the Parsons and Payne study.\(^{11}\) It was assumed, as in Reference 12, that the amount of specific ClO\(_4^-\) adsorption is the same for HClO\(_4\) and NaClO4 at the same concentration and charge density. The potentials of the outer Helmholtz plane (OHP), \(\Phi_2\), were derived in the usual manner assuming the validity of the Gouy-Chapman-Stern theory.\(^{13}\)

\[
\Phi_2 = 0.0514 \sinh^{-1} \left( \frac{\sigma^m + \sigma'}{11.73c_{\text{TB}}} \right) 
\]

where \(c\) is the bulk concentration of NaClO4.

Table 1 collects the electrode charge densities \(\sigma^m\) and the potentials of the outer Helmholtz plane \(\Phi_2\) pertaining to the Zn\(^{2+}\) ions electroreduction potentials for various NaClO4 and tert-butanol concentrations. Electrode surface charge, \(\sigma^m\), 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 \(\Phi_2\) values however slightly depend on tert-butanol concentration like in the presence of tetramethylthiourea.\(^{14}\) Similar \(\Phi_2\) potential changes in the case of chemisorption of tetramethylthiourea and physical tert-butanol adsorption suggest a mainly ClO\(_4^-\) ions input to \(\Phi_2\) 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.\textsuperscript{15} Andreu et al.\textsuperscript{7} proved that the reaction plane is 0.28 nm further from the electrode, which corresponds to the diameter of one water molecule $d_{w,0}$. The potential in the reaction plane $\Phi'$ can be calculated\textsuperscript{8} by

$$
\Phi' = E_{mK} - \frac{4RT}{F} \tanh^{-1} \left[ \tanh \left( \frac{F\Phi_0}{4RT} \right) \exp \left( - \frac{\kappa d}{RT} \right) \right]
$$

(2)

where $\kappa$ is the double-layer thickness parameter expressed in cm$^{-1}$ and 298 K is equal to $167 1/2(3.29 \times 10^{-7})z_c$\textsuperscript{16}

(3)

where $c$ is the bulk z:z electrolyte concentration in mol dm$^{-3}$. The calculated $\Phi'$ 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 $\Phi'$ the potential. In the range of Zn$^{2+}$ reduction potentials the relative surface excess, $\Gamma'$, of tert-butanol distinctly increases with the increasing tert-butanol and NaClO$_4$ concentration. Such $\Gamma'$ value changes with NaClO$_4$ concentration increase clearly point (as in the case of tetramethylthiourea\textsuperscript{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 $\Gamma'$ value in the $\Phi'$ function can be distinguished. The first area in which the obtained dependence $\Gamma' = f(\Phi')$ 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 $\Gamma' = f(\Phi')$ dependencies loose their linear character and the observed $\Gamma'$ shifts more clearly depend on the $\Phi'$ 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 $D_{ox} = 6.9 \times 10^{-6}$ cm$^2$ s$^{-1}$ for the Zn$^{2+}$ diffusion coefficient was used as a standard.\textsuperscript{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 $6.06 \times 10^{-6}$ cm$^2$ s$^{-1}$ to $5.75 \times 10^{-6}$ cm$^2$ s$^{-1}$, from $5.72 \times 10^{-6}$ cm$^2$ s$^{-1}$ to $4.93 \times 10^{-6}$ cm$^2$ s$^{-1}$ and from $4.68 \times 10^{-6}$ cm$^2$ s$^{-1}$ to $3.93 \times 10^{-6}$ 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 solu-

![Figure 1. Relative surface excess $\Gamma'$ of tert-butanol vs. $\Phi'$ 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 $E'_{1/2}$ of the Zn$^{2+}$ ions reduction were estimated from the cyclic voltammetric curves\textsuperscript{17} with the reproducibility $\pm 0.002$ V, using the sweep rates of 0.005 to 0.1 V s$^{-1}$.
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

<table>
<thead>
<tr>
<th>$c_{TB}$ / mol dm$^{-3}$</th>
<th>$\Delta E$ / V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 (NaClO$_4$) / mol dm$^{-3}$</td>
</tr>
<tr>
<td>0</td>
<td>0.091</td>
</tr>
<tr>
<td>0.01</td>
<td>0.091</td>
</tr>
<tr>
<td>0.03</td>
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</tr>
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</tr>
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</tr>
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<td>0.264</td>
</tr>
<tr>
<td>0.50</td>
<td>0.299</td>
</tr>
</tbody>
</table>

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 $E_{1/2}$ value changes. These small $E_{1/2}$ 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. 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 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 $\Gamma$ 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 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. The details are described elsewhere. 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 $E_f^0$ for the electroreduction of Zn$^{2+}$ in 3 mol dm$^{-3}$ NaClO$_4$ and in the presence of tert-butanol.
Based on the command of the $k_f$ and $\Phi'$ values true rate constants were appointed based on the dependence

$$
\ln (k_f') = \Phi' \exp \left\{-\frac{nF(E-\Phi')}{RT} \right\}
$$

(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 $\ln k_f'$ vs. $\Phi'$ seems to be linear. Then to characterize the regression quality a coefficient of determination, $R^2$ was used. In this case, the $R^2$ coefficient 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 $\ln k_f' = f(\Phi')$. 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 $\ln k_f' = f(\Phi')$ 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),

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),

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.

4. An ion transfer step followed by an electron transfer (mechanism IE).

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

<table>
<thead>
<tr>
<th>$c_{TB}$/ mol dm$^{-3}$</th>
<th>$c$(NaClO$_4$)/ mol dm$^{-3}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>0.20</td>
<td>-</td>
<td>0.9909</td>
</tr>
<tr>
<td>0.30</td>
<td>-</td>
<td>0.9976</td>
</tr>
<tr>
<td>0.40</td>
<td>0.9981</td>
<td>0.9847</td>
</tr>
<tr>
<td>0.50</td>
<td>0.9705</td>
<td>0.9861</td>
</tr>
</tbody>
</table>

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.
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 least negative potentials and increases with the rise of tert-butanol concentration.

It is assumed that for the studied systems which obtained non-linear dependencies $\ln k'_1 = f(\Phi')$ the charge transfer takes place via two-consecutive one electron transfer steps.\(^7\) The first electron transfer is rate determining ($k'_1 = k'_f$) at the most negative potentials. At less negative potentials, the overall rate is determined by both steps simultaneously.

\(\frac{1}{k'_f} = \frac{1}{k'_1} + \frac{1}{k'_{i2}}\) \hspace{1cm} (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 $\ln k'_1 = f(\Phi')$, the true standard rate constants $k'_1$ values corresponding to the values $E^\circ_{1/2}$ and the values of constants $k'_{i1}$ and $k'_{i2}$ were determined. The constants $k'_{i1}$ and $k'_{i2}$ 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: 

- $k'_{i1} = 1.51 \times 10^{-3}$ cm s$^{-1}$ and $k'_{i2} = 7.40 \times 10^{-2}$ cm s$^{-1}$; 
- $k'_{i1} = 1.98 \times 10^{-3}$ cm s$^{-1}$ and $k'_{i2} = 7.64 \times 10^{-2}$ cm s$^{-1}$; 
- $k'_{i1} = 2.67 \times 10^{-3}$ cm s$^{-1}$ and $k'_{i2} = 7.65 \times 10^{-2}$ cm s$^{-1}$, respectively. These values systematically grow with the increase of NaClO$_4$ concentration and correspond with the literature data.\(^7,8\)

Figures 5–7 present the $k'_1$, $k'_{i1}$, and $k'_{i2}$ 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 $k'_1 = f(\Gamma')$ and $k'_{i1} = f(\Gamma')$ dependencies have a similar characteristic. $k'_1$ and $k'_{i1}$ value shifts are analogous in the NaClO$_4$ concentration function as in the tert-butanol concentration. In all the base electrolytes studied, the rectilinear almost parallel dependencies $k'_1 = f(\Gamma')$, $k'_{i1} = f(\Gamma')$ are observed. The $k'_1$ and $k'_{i1}$ 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 $k'_{i2} = f(\Gamma')$ 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 $k'_{i2}$ value. Higher tert-butanol concentrations cause a linear decrease of the $k'_{i2}$ values, which for suitably low tert-butanol concentrations are higher in comparison with the $k'_{i2}$ values obtained in tert-butanol absence. The surpris-
ing accelerating effect of the second electrons transfer in concentrated NaClO₄ solutions in the presence of small tert-butanol concentrations is linked with the Zn⁺ aquation structure. In 3 and 4 mol dm⁻³ NaClO₄ 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 \( E_{\text{pol}} \) potential the \( \Gamma' \) 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 NaClO₄, respectively.

For tert-butanol maximum concentration only the \( k'_i \) 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 NaClO₄. The \( k'_i \) value for this concentration decreases over 100 times in relation to the \( k'_i \) value determined in the absence of tert-butanol, in a 3 mol dm⁻³ NaClO₄ over 90 times, and in a 2 mol dm⁻³ about 30 times. In reference to the results obtained from diluted NaClO₄ solutions 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 NaClO₄.

### CONCLUSIONS

From the presented results it can be stated that:

1. Slight \( E_{\text{pol}} \) value shifts in all the studied systems 2 mol dm⁻³, 3 mol dm⁻³ and 4 mol dm⁻³ NaClO₄ may be the result of a weak tert-butanol adsorption in the Zn⁺⁺ ion reduction potential region.
2. Determination of constant rate stages of Zn⁺⁺ ions electroreduction was possible in solutions with lower tert-butanol concentrations for which \( \Gamma' = f(\Phi') \) dependencies had a generally linear character whereas the \( \ln k'_i = f(\Phi') \) dependence was non-linear. In higher tert-butanol concentrations responsible for the strong Zn⁺⁺ ions reduction irreversibility process \( \ln k'_i = f(\Phi') \) dependencies were linear and did not permit the determination of constant rate stages.
3. The analysis of the true rate constant \( k'_i \) depending on tert-butanol and the base electrolytes concentration as well as the work⁹ results allows to conclude that the strongest inhibiting effect at the highest tert-butanol concentration occurs in a 4 mol dm⁻³ NaClO₄. 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 NaClO₄.
4. The rectilinear and parallel dependences \( k'_i = f(\Gamma') \) suggest that the used NaClO₄ concentrations do not influence the first electron transfer mechanism. From the \( k'_{i2} = f(\Gamma') \) and \( \Gamma' = f(\epsilon) \) dependencies it follows that the Zn⁺⁺ aquations and the hydration degree composition has a clear influence on the second electrode transfer mechanism.

### REFERENCES


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