ORIGINAL PAPER

The influence of tetramethylthiourea on a two-step Zn^{2+} ion electroreduction in concentrated $NaClO_4$ solutions

Jolanta Nieszporek

Abstract A two-step Zn^{2+} ion reduction was estimated at the dropping mercury electrode in 2, 3, and 4 mol dm^{-3} $NaClO_4$ with the addition of tetramethylthiourea using an impedance method at wide potential and frequency ranges. With increasing tetramethylthiourea and $NaClO_4$ concentrations the $k_{s_1}^t$ and $k_{s_2}^t$ values increased, achieving their maximum values at the highest concentrations of tetramethylthiourea in 3 and 4 mol dm^{-3} $NaClO_4$ solutions. The catalytic effect of tetramethylthiourea at its lowest employed concentration increased with increasing $NaClO_4$ concentration.

Keywords Electroreduction of Zn^{2+} ions ·
Tetramethylthiourea · Catalytic activity ·
True rate constants

Introduction

It is well known that 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 electrode reaction rate, in either the accelerating or inhibiting sense. Studies devoted to these reactions can be helpful in developing practical applications, such as corrosion- and photocorrosion-resistant metals and semiconductors as well as metal electrodeposition regulation. From the literature it is known that thiourea and its alkyl derivatives catalyze electroreduction of several cations: In^{3+} [1], H_3O^+ [2], Bi^{3+} [3], Cd^{2+} [4], and Zn^{2+} [3, 5–8]. According to Ikeda and coworkers [7], the standard rate constant for Zn^{2+} reduction is controlled by the inner-layer permittivity. This effect has been explained in terms of the solvent reorganization energy. Unstable Zn^{2+}–adsorbate complexes, mediating the electron exchange, are localized inside the adsorption layer.

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 catalyzed by tetramethylthiourea (TMTU) [9]. The base electrolyte concentration influences the degree of Zn^{2+} ion aquacomplexes and electrode surface hydration and hence the depolarizer electroreduction kinetics. Sluyters and coworkers [10] indicated that increasing the $NaClO_4$ concentration from 0.2 to 7 mol dm^{-3} causes an increase of the true standard rate constant for Zn^{2+} ion reduction, but for $NaClO_4$ concentrations ≥ 1 mol dm^{-3} the effect on the two-step Zn^{2+} ion electroreduction in the presence of TMTU has already been reported [9]. The authors showed that the catalytic activity of TMTU is related to both electron-transfer steps and decreases in the order: $1 > 0.5 > 0.1$ mol dm^{-3} $NaClO_4$. Because the relation between the Zn^{2+} ion electroreduction rate and the base electrolyte concentration is different in the presence and absence of TMTU, a test on the influence of concentrated $NaClO_4$ solutions on the acceleration of Zn^{2+} electroreduction by TMTU was conducted. The choice of $NaClO_4$ solution resulted from the fact that ClO_4^- ions cause the strongest disruption in water structure [11]. Moreover, the perchlorate anion is not specifically adsorbed in the potential region where Zn^{2+} ions are reduced [12]. Additionally, the perchlorate ion has low tendency to form complexes, and its double-layer data are available in the literature [12–15].

J. Nieszporek (✉)
Faculty of Chemistry, Maria Curie-Skłodowska University,
M. Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland
e-mail: jolan@poczta.umcs.lublin.pl

Results and discussion

Polarographic measurements

The present study shows that Zn^{2+} ion electroreduction at a mercury electrode in $NaClO_4$ solutions in the presence of tetramethylthiourea results in a single, well-defined direct-current (DC) polarographic wave. A change in the basic electrolyte concentration affects the limited diffusion current insignificantly. The approximate diffusion coefficients for Zn^{2+} ions in the examined solutions were calculated using the Ilkovič equation for diffusion-controlled limiting current.

The polarographic wave of Zn^{2+} in 0.1 mol dm^{-3} KNO_3 with a Zn^{2+} diffusion coefficient $D_{ox} = 6.9 \times 10^{-6}$ cm^2 s^{-1} at 298 K was used as a standard [16]. The analogous value for Zn in mercury, $D_{red} = 1.67 \times 10^{-5}$ cm^2 s^{-1}, was also selected from the literature [17]. The obtained D_{ox} values increase with increasing TMTU concentration, in 2 mol dm^{-3} $NaClO_4$ ranging from 6.06×10^{-6} to 7.00×10^{-6} cm^2 s^{-1}, in 3 mol dm^{-3} $NaClO_4$ from 5.72×10^{-6} to 6.95×10^{-6} cm^2 s^{-1}, and in 4 mol dm^{-3} $NaClO_4$ from 4.68×10^{-6} to 5.65×10^{-6} cm^2 s^{-1}. The decrease of D_{ox} with increasing $NaClO_4$ concentration in the absence of TMTU can result from the viscosity increase of the solutions. The zinc-aquo complex hydration number in the studied range of $NaClO_4$ concentrations is 19.6 [10]. The D_{ox} increase in the presence of TMTU may be linked to the hydration number decrease.

The reversible potential of the half-wave ($E_{1/2}^{r}$) of Zn^{2+} ion reduction was determined by cyclic voltammetry method using Eq. 1 [18]

$$E_{1/2}^{r} = \frac{E_{pc} + E_{pa}}{2}, \tag{1}$$

where E_{pc} and E_{pa} are potentials of the cathode or anode peak, respectively.

Figure 1 shows voltammetric curves of the Zn^{2+} electroreduction in 2 mol dm^{-3} $NaClO_4$ with and without addition of TMTU.

The decreased difference in the cathodic and anodic peak potentials (ΔE) of Zn^{2+} electroreduction with increasing TMTU concentration reveals the catalytic effect of TMTU on the studied process. This effect is strongest for the highest concentration of $NaClO_4$, and the values of ΔE decrease in the order: 2 < 3 < 4 mol dm^{-3} $NaClO_4$. With increasing TMTU concentration the $E_{1/2}^{r}$ values remain approximately constant. This led to the conclusion that the Zn^{2+}–TMTU complexes formed in the solution are very unstable. It is worth noting that, with increasing $NaClO_4$ concentration, the $E_{1/2}^{r}$ values decrease to a similar degree in the presence or absence of TMTU. From the
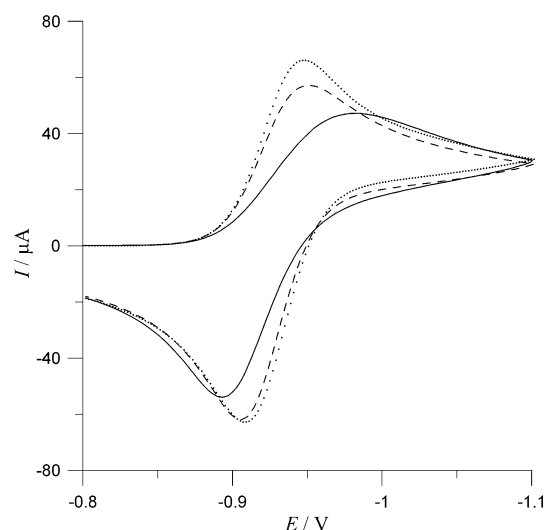

Fig. 1 Cyclic voltammetric curves for the Zn^{2+}/Zn (Hg) system in 2 mol dm^{-3} $NaClO_4$ at scan rate of 0.1 V s^{-1} in the presence of tetramethylthiourea: *solid line* 0 mol dm^{-3}, *dashed line* 5×10^{-4} mol dm^{-3}, and *dotted line* 4×10^{-2} mol dm^{-3}

reversible half-wave potential values the standard formal potential E_{f}^{0} was calculated using the following equation:

$$E_{f}^{0} = E_{1/2}^{r} + \frac{RT}{nF} \ln \left(\frac{D_{ox}}{D_{r}} \right)^{1/2}. \tag{2}$$

Double-layer analysis

The calculations of the double-layer parameters for the adsorption are based on the data from the differential capacity–potential curves obtained experimentally for all studied concentrations of TMTU [19]. The potentials of the outer Helmholtz plane (OHP), Φ_2, were derived assuming the validity of the Gouy–Chapman–Stern theory [20]

$$\Phi_2 = 0.0514 \sinh^{-1} \left(\frac{\sigma^m + \sigma^i}{11.73 c^{1/2}} \right), \tag{3}$$

where c is the bulk concentration of $NaClO_4$, σ^m is the charge density on the electrode, and σ^i is the charge density of specifically adsorbed ClO_4^- ions (taken from [13]).

Table 1 presents σ^m electrode charge density values, outer Helmholtz plane (OHP) potentials, Φ_2, and respective Φ^r values for used TMTU and $NaClO_4$ concentrations. The Φ_2 values are practically independent of $NaClO_4$ concentration, but the Φ^r values become less negative with increasing concentration of the base electrolyte.

The potential in the reaction plane, Φ^r, can be calculated by subtracting the diffuse-layer potential:

$$\Phi^r = \Phi^{OHP} = E - \Phi_2. \tag{4}$$

Aramata and Delahay [21] proved that the hydrated Zn^{2+} ion is larger than the Na^+ ion, and therefore the plane of closest approach for Zn^{2+} is farther from the electrode

Table 1 Charge densities (10^2 σ^m/C m^{-2}), potentials of the outer Helmholtz plane (Φ_2/V), and potentials in the reaction plane (Φ^r/V) as a function of TMTU and NaClO$_4$ concentration at formal potentials of the Zn^{2+} ion reduction

c_{TMTU} (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	9.77	0.038	0.950	9.50	0.038	0.943	8.21	0.039	0.924
3×10^{-4}	8.61	0.038	0.940	9.00	0.038	0.933	7.92	0.039	0.914
5×10^{-4}	8.50	0.038	0.940	8.60	0.038	0.933	7.34	0.039	0.914
1×10^{-3}	8.25	0.039	0.940	8.27	0.038	0.933	6.89	0.040	0.914
3×10^{-3}	7.94	0.039	0.940	7.61	0.039	0.933	5.11	0.041	0.914
5×10^{-3}	7.43	0.039	0.940	5.32	0.040	0.932	4.51	0.041	0.914
1×10^{-2}	4.99	0.039	0.940	4.85	0.040	0.932	4.03	0.042	0.914

than the OHP, resulting in overestimation of the Frumkin effect.

Andreu et al. [10] proved that the reaction plane is 0.28 nm farther from the electrode, which corresponds to the diameter of one H$_2$O molecule, d_{H_2O}. The potential at the reaction location can be determined [22] from:

$$\Phi^r = \Phi^{OHP+0.28\ nm}$$
$$= E + \frac{4RT}{F}\tanh^{-1}\left[\tanh\left|\frac{F\Phi_2}{4RT}\right|\exp(-\kappa d_{H_2O})\right] \quad (5)$$

at 298 K:

$$\kappa = (3.29 \times 10^7)zc^{1/2}, \quad (6)$$

where c is the bulk z:z electrolyte concentration in mol dm^{-3}, and κ is given in cm^{-1} [23].

The relative surface excess of TMTU presented in Fig. 2a–c was obtained according to the Gibbs adsorption isotherm:

$$\Gamma' = \frac{1}{RT}\left(\frac{\partial\Phi}{\partial\ln c}\right)_\sigma, \quad (7)$$

where c is the bulk concentration of TMTU, Φ is the surface pressure, $\Phi = \Delta\xi$, $\xi = \gamma + \sigma E$ is the Parsons auxiliary function [24], γ is the surface tension, σ is the electrode charge, E is the electrode potential, and $\Delta\xi = \xi_0 - \xi$ (where ξ_0 and ξ are the values of the Parsons auxiliary function for the base electrolyte and for the solution containing TMTU, respectively).

By using Eq. 7 it should be assumed that the mean TMTU and NaClO$_4$ activity coefficients do not vary with the change in TMTU concentration. The presented relationships in Fig. 2a–c are linear and depend insignificantly on the potential. For higher concentrations of TMTU (from 3×10^{-3} to 1×10^{-2} mol dm^{-3}) the values of Γ' increase with increasing NaClO$_4$ concentration. This effect is similar to those observed for the following concentrations: 0.1, 0.5, and 1 mol dm^{-3} NaClO$_4$ [19], and confirms that,

under less hydrated electrode surface conditions, due to a larger ClO$_4^-$ ion concentration, it is easier to adsorb TMTU molecules onto the electrode surface.

The rate of electroreduction

Complex impedance data were collected at 36 frequencies ranging from 15 to 100,000 Hz within the Faradaic potential region at 10-mV intervals. Figure 3a–c presents the dependencies between the real Z' and the imaginary Z'' part of the cell impedance [$Z'' = f(Z')$] for Zn^{2+} ion electroreduction in 2, 3, and 4 mol dm^{-3} NaClO$_4$ in the absence of TMTU and with the addition of TMTU.

The decreased values of the charge-transfer resistance R_{ct} in the presence of TMTU show the catalytic effect of TMTU on Zn^{2+} electroreduction. Even the lowest TMTU concentration causes a distinct decrease of charge-transfer resistance, the most distinct one in 4 mol dm^{-3} NaClO$_4$. With decreasing NaClO$_4$ concentration the changes also decrease. The impedance data were analyzed by fitting using Randles' equivalent circuit [25, 26], described in terms of ohmic resistance (R_Ω), double-layer capacitance (C_d), charge-transfer resistance (R_{ct}), and Warburg coefficient (σ). In agreement with the well-known irreversibility of Zn^{2+} reduction it was generally found that $R_{ct} \gg \sigma\omega^{-1/2}$. Consequently, the charge-transfer resistance was obtained with greater accuracy than the Warburg coefficient. The k_f values were computed from R_{ct} values as a function of DC potential [10]

$$R_{ct} = \frac{RT}{n^2F^2c_0k_f}\frac{a_0/k_f + 1 + r_s\exp(b)}{\alpha a_0/k_f + r_s\exp(b)}, \quad (8)$$

where

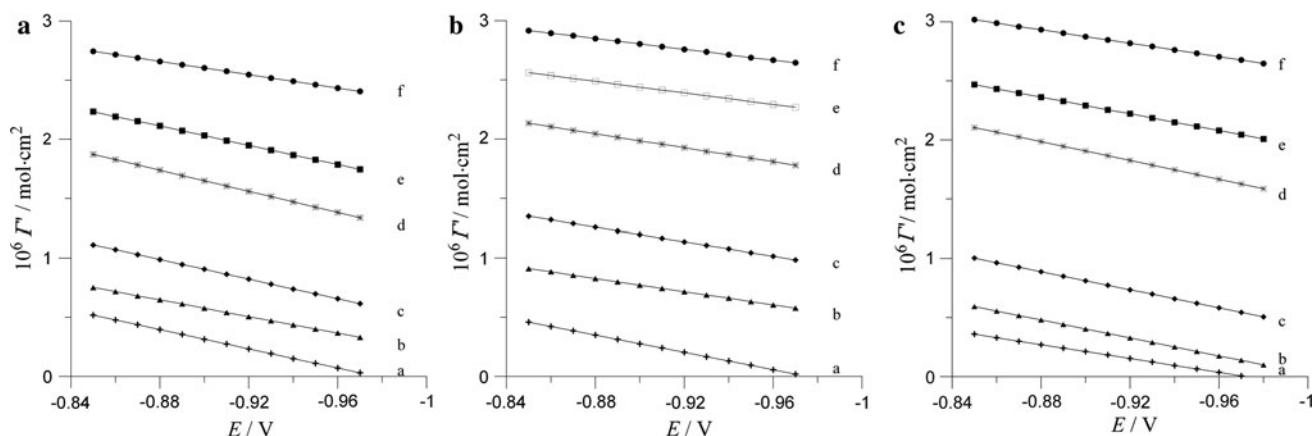$$a_0 = D_0^{1/2}(3\pi t/7)^{-1/2} + D_0r_0^{-1}, \quad (9)$$

Fig. 2 **a** Relative surface excess Γ' of TMTU versus E in 2 mol dm^{-3} NaClO$_4$ at varied concentrations of TMTU: (*a*) 3×10^{-4} mol dm^{-3}, (*b*) 5×10^{-4} mol dm^{-3}, (*c*) 1×10^{-3} mol dm^{-3}, (*d*) 3×10^{-3} mol dm^{-3}, (*e*) 5×10^{-3} mol dm^{-3}, and (*f*) 1×10^{-2} mol dm^{-3}.

b Relative surface excess Γ' of TMTU versus E in 3 mol dm^{-3} NaClO$_4$ at varied concentrations of TMTU as indicated in **a**. **c** Relative surface excess Γ' of TMTU versus E in 4 mol dm^{-3} NaClO$_4$ at varied concentrations of TMTU as indicated in **a**
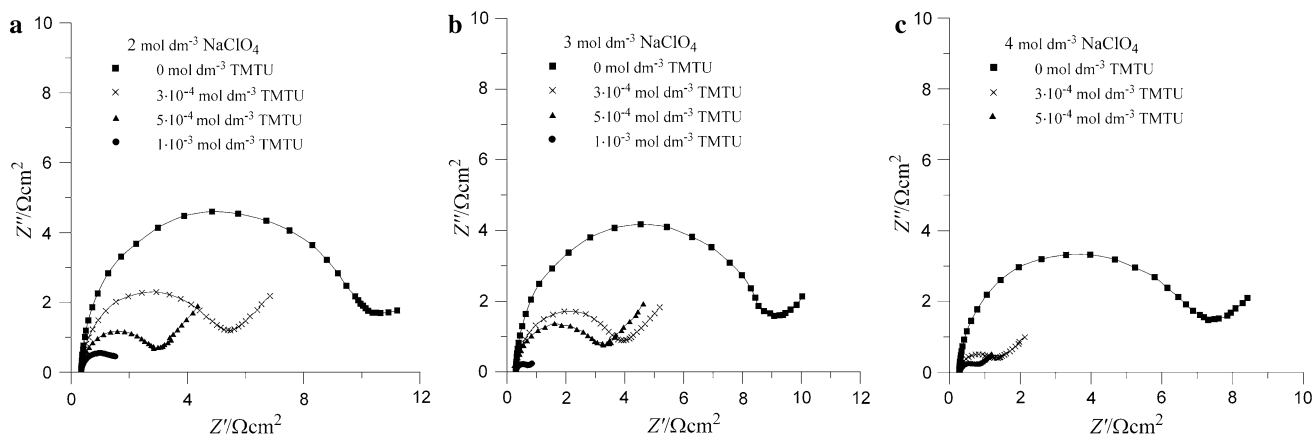

Fig. 3 **a** Impedance diagrams measured at E_f^0 for the electroreduction of Zn^{2+} ions in 2 mol dm^{-3} NaClO$_4$ at varied concentrations of TMTU. **b** Impedance diagrams measured at E_f^0 for the electroreduction of Zn^{2+} ions in 3 mol dm^{-3} NaClO$_4$ at varied concentrations of

TMTU. **c** Impedance diagrams measured at E_f^0 for the electroreduction of Zn^{2+} ions in 4 mol dm^{-3} NaClO$_4$ at varied concentrations of TMTU

$$r_s = \frac{r_0 + (3\pi t D_0/7)^{1/2}}{r_0 - (3\pi D_R/7)^{1/2}}, \tag{10}$$

$$b = (nF/RT)(E - E_{1/2}^r), \tag{11}$$

$$\alpha = -(RT/nF)(d \ln k_f/dE). \tag{12}$$

In these equations t is the drop lifetime, r_0 is the drop radius at that time, and c_0 is the bulk concentration of reactant while $c_R = 0$ in the experiments.

The rate constants for the forward reaction, k_f, obtained in the solutions of constant NaClO$_4$ concentration and various TMTU concentrations at the standard potential, confirm the catalytic activity of TMTU with increasing concentration. The accelerating activity of TMTU is observed in the whole range of potentials. This effect is larger in the more negative potential region.

The true rate constants, k_f^t, can be obtained from Eq. 13 [22]

$$k_f(\Phi^r) = k_f^t(\Phi^r) \exp\left[-(E - \Phi^r)\frac{nF}{RT}\right]. \tag{13}$$

Figure 4a–c shows the potential dependence of the true rate constants k_f^t of Zn^{2+} ion electroreduction calculated at OHP + 0.28 nm, obtained at various TMTU concentrations.

The k_f^t values increase with increasing TMTU concentration, achieving their highest values in 4 mol dm^{-3} NaClO$_4$. The accelerating effect due to TMTU concentration is stronger at the highest negative potentials. Similar behavior is observed in more dilute NaClO$_4$ solutions: 0.1, 0.5, and 1 mol dm^{-3} [9]. Simultaneously the obtained values of k_f^t for Zn^{2+} ion electroreduction in 2, 3, and
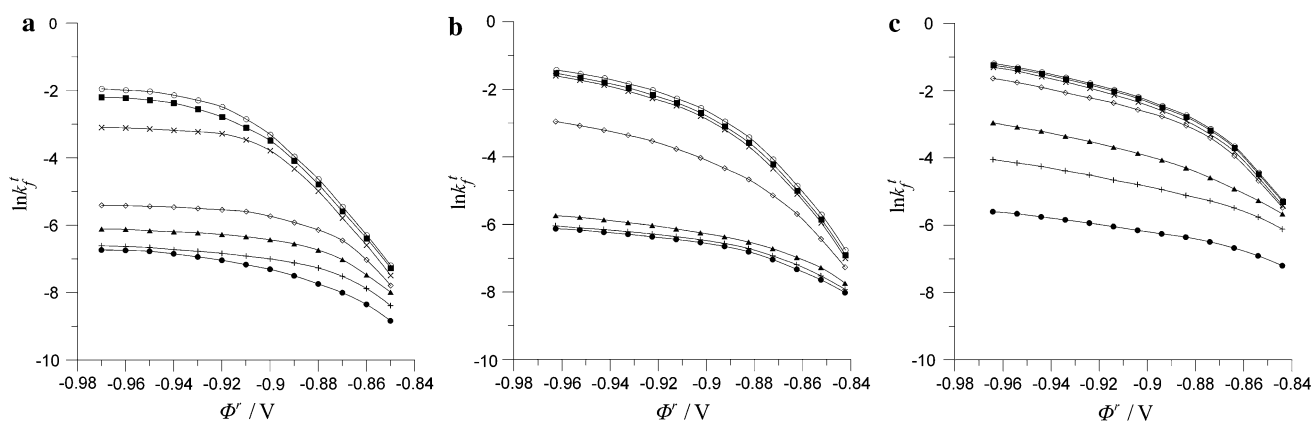
Fig. 4 **a** Potential dependence of the true rate constants of the Zn^{2+} ion reduction in 2 mol dm^{-3} NaClO$_4$ at various TMTU concentrations: 0 mol dm^{-3} (*filled circles*), 3×10^{-4} mol dm^{-3} (*pluses*), 5×10^{-4} mol dm^{-3} (*filled triangles*), 1×10^{-3} mol dm^{-3} (*open diamonds*), 3×10^{-3} mol dm^{-3} (*times*), 5×10^{-3} mol dm^{-3} (*filled squares*), and 1×10^{-2} mol dm^{-3} (*open circles*). **b** The potential dependence of the true rate constants of the Zn^{2+} ion reduction in 3 mol dm^{-3} NaClO$_4$ at varied concentrations of TMTU as indicated in **a**. **c** The potential dependence of the true rate constants of the Zn^{2+} ion reduction in 4 mol dm^{-3} NaClO$_4$ at varied concentrations of TMTU as indicated in **a**

4 mol dm^{-3} NaClO$_4$ are distinctly higher than in dilute solutions. With increasing concentration of the base electrolyte the k_f^t values increases in the order: $0.1 < 0.5 < 1 < 2 < 3 < 4$ mol dm^{-3} NaClO$_4$.

It has recently been shown [9] that a linear relationship exists between the rate constant of Zn^{2+} electroreduction and the relative surface excess of TMTU. This indicates active complex formation between Zn^{2+} and TMTU, which facilitates electroreduction transfer across the inner layer. In contrast to earlier studied systems [9], in 2, 3, and 4 mol dm^{-3} NaClO$_4$ a linear relationship between the rate constant of Zn^{2+} electroreduction and the relative surface excess of TMTU does not exist, which indicates that active complexes between Zn^{2+} and TMTU are not present in the systems described herein.

The relations $k_f^t = f(\Phi^r)$ are not rectilinear, and the slope of the curves changes with the potential and the concentrations of TMTU. This nonlinear dependence indicates the two-stage character of the mechanism of the electroreduction of Zn^{2+} ions in the studied solutions.

By analyzing the dependencies $k_f^t = f(\Phi^r)$ and $\Gamma' = f(E)$ we may assume that, with increasing TMTU concentration in 2 mol dm^{-3} NaClO$_4$, the k_f^t value remains in the same qualitative relationship with the Γ' value. The Γ' and k_f^t values rise distinctly in 3×10^{-3} mol dm^{-3} TMTU concentration. In 3 mol dm^{-3} NaClO$_4$, this tendency is not so distinct. The weakest relationship between the k_f^t and Γ' values was observed in 4 mol dm^{-3} NaClO$_4$.

Assuming that charge transfer proceeds via two consecutive one-electron transfer steps [10, 22], the first electron transfer is rate determining ($k_1^t = k_f^t$) at the most negative potentials. At more positive potentials, the overall rate is determined by both steps simultaneously:

$$\frac{1}{k_f^t} = \frac{1}{k_1^t} + \frac{K_1}{k_2^t}, \tag{14}$$

where K_1 is the formal equilibrium constant of the first stage.

By using the above relationship and adopting the experimental data $\ln k_f^t = f(\Phi^r)$, the values of the true standard rate constants $k_{s_1}^t$ corresponding to the values E_0^f and the constants $k_{s_1}^t$ and $k_{s_2}^t$ were determined. The constants $k_{s_1}^t$ and $k_{s_2}^t$ characterize the first electron-transfer stage and the second electron-exchange stage, respectively.

Table 2 shows the values of the corrected individual rate constants of Zn^{2+} electroreduction at various NaClO$_4$ and TMTU concentrations. The obtained $k_{s_1}^t$ and $k_{s_2}^t$ values for Zn^{2+} ion reduction in the absence of TMTU are in agreement with the literature data [10, 22]. With increasing TMTU and NaClO$_4$ concentrations the $k_{s_1}^t$ and $k_{s_2}^t$ values increase, achieving their maximum values at the highest concentrations of TMTU in 3 and 4 mol dm^{-3} NaClO$_4$ solutions. In each of the studied systems a much larger increase in $k_{s_1}^t$ values compared with $k_{s_2}^t$ values was observed with TMTU concentration increase. This effect is different from the results obtained for 0.1, 0.5, and 1 mol dm^{-3} NaClO$_4$ [9] concentrations. Also the $k_{s_1}^t$ and $k_{s_2}^t$ values in the presence of TMTU obtained for 2, 3, and 4 mol dm^{-3} NaClO$_4$ are unquestionably higher than in more dilute NaClO$_4$ solutions.

The effectiveness of the acceleration of the Zn^{2+} ion electroreduction process in the studied systems can be expressed by the ratio between a_1, for the first electron-transfer stage, and a_2, for the second electron-exchange stage:

Table 2 Corrected individual rate constants of Zn^{2+} ion electroreduction extrapolated to E_f^0 for various concentrations of NaClO$_4$ and TMTU; $k_{s_1}^t$, $k_{s_2}^t$ (cm s^{-1})

c_{TMTU} (mol dm^{-3})	2 mol dm^{-3} NaClO$_4$		3 mol dm^{-3} NaClO$_4$		4 mol dm^{-3} NaClO$_4$	
	$10^2 k_{s_1}^t$	$10^1 k_{s_2}^t$	$10^2 k_{s_1}^t$	$10^1 k_{s_2}^t$	$10^2 k_{s_1}^t$	$10^1 k_{s_2}^t$
0	0.151	0.740	0.198	0.764	0.267	0.765
3×10^{-4}	0.165	0.891	0.205	1.380	1.050	2.650
5×10^{-4}	0.210	1.450	0.265	2.310	2.840	6.440
1×10^{-3}	0.432	3.120	3.610	9.660	10.60	14.50
3×10^{-3}	4.500	7.340	13.70	17.40	13.80	17.70
5×10^{-3}	10.20	12.70	15.10	19.20	15.40	20.00
1×10^{-2}	13.00	19.8	16.50	23.00	16.70	23.70

$$a_1 = \frac{k_{s_1}^{t(c_{max})}}{k_{s_1}^{t(c_0)}}, \tag{15}$$

$$a_2 = \frac{k_{s_2}^{t(c_{max})}}{k_{s_2}^{t(c_0)}}, \tag{16}$$

where the true standard rate constants $k_{s_1}^{t(c_0)}$ and $k_{s_2}^{t(c_0)}$ characterize the first electron-transfer stage and the second electron-exchange stage, respectively, obtained in the absence of TMTU, and the true standard rate constants $k_{s_1}^{t(c_{max})}$ and $k_{s_2}^{t(c_{max})}$ characterize the first electron-transfer stage and the second electron-exchange stage, respectively, obtained for maximum 1×10^{-2} mol dm^{-3} TMTU concentration. The values of a_1 and a_2 parameters obtained for 2, 3, and 4 mol dm^{-3} NaClO$_4$ are presented in Table 3.

The presented a_1 and a_2 value parameters in Table 3 point out the fact that the maximum catalytic effect depends in a different degree on NaClO$_4$ concentration. In the case of the first electron transfer the catalytic effect decreases with increasing NaClO$_4$ concentration. This is undoubtedly related to a different degree of Zn^{2+} ion hydration. This may be confirmed by the fact that the Γ' values for TMTU increase with increasing NaClO$_4$ concentration, so the electrode surface state does not seem to be responsible in a dominant way for the acceleration effect. In the case of the second electron transfer, the catalytic effect only increases slightly with increasing NaClO$_4$ concentration. This suggests that Zn^{1+} aqua ions composition practically does not depend on NaClO$_4$ concentration.

Table 3 Values of the parameters a_1 and a_2 for various NaClO$_4$ concentrations

c_{NaClO_4}(mol dm^{-3})	a_1	a_2
2	86.09	26.76
3	83.33	30.10
4	62.55	30.98

Conclusions

1. A two-step Zn^{2+} ion reduction process is clearly seen in concentrated NaClO$_4$ solutions, in the presence and absence of TMTU.
2. Maximum increases in $k_{s_1}^t$ and $k_{s_2}^t$ were clearly higher in concentrated NaClO$_4$ solutions in comparison with more dilute NaClO$_4$ solutions [9].
3. Analysis of $k_{s_1}^t$ values as a function of TMTU concentration showed a distinct influence of NaClO$_4$ concentration. Maximum increases of $k_{s_1}^t$ obtained for 2 and 3 mol dm^{-3} NaClO$_4$ were comparable, whereas in 4 mol dm^{-3} NaClO$_4$ they were distinctly lower.
4. While in dilute NaClO$_4$ solutions there was a distinct increase in the acceleration effect of $k_{s_1}^t$ and $k_{s_2}^t$ values [9], in the currently studied systems the maximum increase of the $k_{s_2}^t$ value practically did not depend on the concentration of the base electrolyte. This may be the result of a similar Zn^{1+} aquaion composition.
5. There is no quantitative relationship between the increasing Γ' values for TMTU with increasing NaClO$_4$ concentration and the changes in the $k_{s_1}^t$ and $k_{s_2}^t$ values. This may suggest that, in the Zn^{2+} ion electroreduction acceleration mechanism triggered by TMTU, the electrode surface state plays a less important role in comparison with the Zn^{2+} aquaion composition.

Experimental

Solutions were prepared from freshly double-distilled water and Fluka analytical-grade chemicals. The adsorption and catalytic activity studies were carried out in the TMTU concentration range from 3×10^{-4} to 0.05 mol dm^{-3} in NaClO$_4$ solutions of the following concentrations: 2, 3, and 4 mol dm^{-3}.

Zinc perchlorate was prepared by dissolving ZnO in small excess of perchloric acid. Optimal accuracy was

achieved by maintaining the Zn^{2+} concentration around 0.005 mol dm^{-3}. In order to avoid hydrolysis of Zn^{2+}, this excess of perchloric acid was chosen to make the final solution 0.001 mol dm^{-3} with respect to H^{+} concentration. Solutions were deaerated using nitrogen, which was also passed over the solution during measurements.

All measurements were carried out at 298 ± 0.1 K. Polarographic, voltammetric, and differential capacity measurements were performed by employing an Autolab frequency-response analyzer (Eco Chemie, The Netherlands). Impedance measurements were carried out by using a 9121FR analyzer and 9131 electrochemical interface (Atlas-Sollich, Gdańsk, Poland). Experiments were performed in a three-electrode cell with a dropping mercury electrode as a working electrode (MTM, Poland), Ag/AgCl as a reference electrode, and a platinum spiral as an auxiliary electrode.

References

1. Kazarov A, Losharev MA (1967) Elektrokhimiya 3:681
2. Meures K, Gierst R (1971) Collect Czech Chem Commun 36:389
3. Damaskin BB, Afanasev BN (1977) Elektrokhimiya 13:1099
4. Souto RM, Sluyters-Rehbach M, Sluyters JH (1986) J Electroanal Chem 201:3
5. Sykut K, Saba J, Marczewska B, Dalmata G (1984) J Electroanal Chem 178:295
6. Sykut K, Dalmata G, Nowicka B, Saba J (1978) J Electroanal Chem 90:299
7. Ikeda O, Watanabe K, Taniguchi Y, Tamura H (1984) Bull Chem Soc Jpn 57:3363
8. Dalmata G (1994) Collect Czech Chem Commun 59:1931
9. Nieszporek J, Gugała D, Sieńko D, Fekner Z, Saba J (2004) Bull Chem Soc Jpn 73:77
10. Andreu R, Sluyters-Rehbach M, Remijnse AG, Sluyters JH (1982) J Electroanal Chem 134:101
11. Koryta J, Dvorak J, Bohackova V (1980) Elektrochemia. PWN, Warszawa, p 30
12. Parsons R, Payne R (1975) Z Phys Chem 98:9
13. Wroblowa H, Kovac Z, Bockris JOM (1965) Trans Faraday Soc 61:1523
14. Damaskin BB, Frumkin AN, Ivanov VF, Melekhova NI, Khonina VF (1968) Elektrokhimiya 4:1336
15. Payne R (1966) J Phys Chem 70:204
16. Turnham DS (1965) J Electroanal Chem 10:19
17. Stromberg AG (1952) Dokl Akad Nauk USSR 85:831
18. Galus Z (1979) Elektroanalityczne metody wyznaczania stałych fizykochemicznych, Warszawa, p 250
19. Sieńko D, Gugała-Fekner D, Nieszporek J, Fekner Z, Saba J (2009) Collect Czech Chem Commun 74:1309
20. Mohilner DM (1966) Electroanalytical chemistry. In: Bard AJ (ed), Marcel Dekker, New York, vol 1, p 241
21. Aramata A, Delahay P (1964) J Phys Chem 68:880
22. Perez M, Baars A, Zevenhuizen SJM, Sluyters-Rehbach M, Sluyters JH (1995) J Electroanal Chem 397:87
23. Bard AJ, Faulkner LR (2001) Electrochemical methods fundamentals and applications, Wiley, p 548
24. Parsons R (1961) Proc R Soc A 261:79
25. Sluyters-Rehbach M, Sluyters JH (1970) Electroanalytical chemistry. In: Bard AJ (ed) Marcel Dekker, New York, vol 4, p 1
26. Sluyters-Rehbach M, Sluyters JH (1984) Comprehensive treatise of electrochemistry. In: Yeager E, Bockris JOM, Conway BE, Sarangapani S (eds) Plenum Press, New York, vol 9, p 177