# The Effect of $NaClO_4$ Concentration on the Two-Step Electroreduction of $Zn^{2+}$ Ions in the Presence of Tetramethylthiourea[#]

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The dependence of the two-step reduction of $Zn^{2+}$ ions on $NaClO_4$ and TMTU concentration at the dropping mercury electrode was examined. The catalytic activity of TMTU is related to both electron transfer steps and decreases in the order: 1 M $NaClO_4$ > 0.5 M $NaClO_4$ > 0.1 M $NaClO_4$. In each of the studied systems there was observed a much larger increase in the $k_{s2}^{t}$ values compared to the $k_{s1}^{t}$ values when the concentration of TMTU was increased. A linear relationship between the rate constant of the electroreduction of $Zn^{2+}$ and the relative surface excess of TMTU indicates the formation of a bridge between $Zn^{2+}$ and TMTU which facilitates the transfer of electrons across the inner layer.

The behaviour of water at the electrode–solution interface is a fundamental interest in electrochemistry because water is an essential component of electrochemical systems. The role of water molecules in studies of the adsorption of organic substances and kinetics of electroreduction of inorganic depolarizers is very often neglected.

From the literature it is known that thiourea *N*,*N′*-dialkylthioureas[1–3] and tetramethylthiourea (TMTU)[3] catalyse the reduction of $Zn^{2+}$ ions at mercury electrodes even at low coverages of previously mentioned substances. The electrode process of the $Zn^{2+}/Zn(Hg)$ reduction seems to proceed in the adsorption layer. It has been found that one of the interfacial properties susceptible to a large change with adsorbates is the permittivity of the adsorption layer or the inner-layer permittivity. For a thin adsorption layer with lower permittivity than that in the solution bulk, Afanasiev and Damaskin[4] treated the above effect as the work involved in transferring a reacting ion from the solution bulk into the structured surface layer. Ikeda et al.[3] have treated this effect simply as the work for the activation of $Zn^{2+}$ in the adsorption layer.

This work is part of a broader project concerned with the influence of water activity on the structure of the mercury/TMTU, $H_2O$, $ClO_4^-$ interface and the structure of the $Zn^{2+}$–$H_2O$, TMTU complex. Another reason for the choice of TMTU is based on the expectation that the vertical orientation of thiourea due to metal–sulfur interactions[5] may change with the possibility of metal–hydrophobic group interactions.[6]

The electroreduction of $Zn^{2+}$ ions on the mercury electrode is a typical example of a reaction controlled by both diffusion and charge transfer. Often, the kinetics of $Zn^{2+}$ reduction is assumed to proceed simply via a simultaneous two-electron transfer described by only one rate constant. However, in several literature sources the possible validity of a mechanism with two one-electron transfers is discussed.[7–12] The electroreduction of $Zn^{2+}$ ions from 1 M, 0.5 M, and 0.1 M $NaCl_4$ solutions at a mercury electrode in the presence of TMTU is supposed to involve two consecutive one-electron transfer steps in the overall reaction. Since the kinetics of the electron transfer steps would be potential dependent, the nature of the rate controlling the steps would change with the potential. Furthermore, as the reaction involves charged reactants in the double layer, double layer effects are expected to be important in these processes.

Sodium perchlorate is a suitable basic electrolyte because of its low tendency to form complexes and because the double layer data needed are available from the literature.[13–16]

## 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.

Polarographic measurements were carried out using a polarograph PA-4 (Laboratorni Pristroje, Prague, Czech. Republic). Voltammetric experiments were performed employing a Model 270 Electrochemical Analysis System AG&G PARC. The impedance measurements were carried out with a 9121FR Analyzer and 9131 Electrochemical Interface of Atlas-Sollich (Gdańsk, Poland). Optimal accuracy was achieved by maintaining the $Zn^{2+}$ concentration around 0.005 M. Studies of the adsorption and catalytic activity were carried out in the TMTU concentration range of $3 \times 10^{-4}$ M to 0.05 M in $NaClO_4$ solutions of the following concentrations: 0.1 M, 0.5 M, and 1 M. The solutions containing TMTU were prepared using Fluka analytical grade chemicals before each measurement. The zinc perchlorate solution was prepared by dissolving ZnO in a small excess of perchloric acid. In order to avoid hydrolysis of $Zn^{2+}$, this excess of perchloric acid was chosen to make the final solution 0.001 M with respect to $H^+$ concentration.

Water and mercury were distilled twice. Measurements were carried out at $298 \pm 0.1$ K. The solutions were deaerated using nitrogen. This gas was passed over the solution during the measurements.

## Results and Discussion

**Double Layer Analysis.** The calculations of the double layer parameters for the adsorption are based on the data from the

Published on the web January 13, 2004; DOI 10.1246/bcsj.77.73

differential capacity–potential curves obtained experimentally for all studied concentrations of TMTU.[17] In order to calculate the potential profile in the diffuse double layer it is necessary to estimate the charge density, $\sigma^{\mathrm{i}}$, of specifically adsorbed $\mathrm{ClO_4^-}$ ions as a function of the charge density on the electrode, $\sigma^{\mathrm{m}}$. Data of the specifically adsorbed charge $\sigma^{\mathrm{i}}$ of $\mathrm{ClO_4^-}$ were taken from the study of Parsons and Payne.[13] It was assumed, as in Ref. 18, that the amount of specific $\mathrm{ClO_4^-}$ adsorption is the same for HClO$_4$ and NaClO$_4$ at the same concentration and the same 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:[19]

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

where $c$ is the bulk concentration of NaClO$_4$. The values of $\sigma^{\mathrm{i}}$ were taken from Ref. 15 and were extrapolated for the 0.1 M NaClO$_4$ solution and for $\sigma^{\mathrm{m}} < -0.08\ \mathrm{C\,m^{-2}}$.

Table 1 lists exemplary $\sigma^{\mathrm{m}}$ and $\Phi_2$ values pertaining to the potentials of the electroreduction of Zn$^{2+}$ ions for the various NaClO$_4$ and TMTU concentrations. The $\Phi_2$ values presented in Table 1 become less negative with an increase in NaClO$_4$ concentration, which is consistent with Ref. 19. In turn, the increase in NaClO$_4$ concentration causes the values $\Phi^{\mathrm{r}}$ to become increasingly negative due to the presence of a larger number of $\mathrm{ClO_4^-}$ ions on the electrode surface.

To calculate the potential in the reaction plane, $\Phi^{\mathrm{r}}$, it was assumed that the reaction takes place at the OHP, where the potential can be calculated by substracting the diffuse layer potential:

$$\Phi^{\mathrm{r}} = \Phi^{\mathrm{OHP}} = E - \Phi_2. \tag{2}$$

Aramata and Delahay[20] proved that the hydrated Zn$^{2+}$ ion is larger than the Na$^+$ ion, and therefore the plane of closest approach for Zn$^{2+}$ is further from the electrode than the OHP, resulting in an overestimation of the Frumkin effect.

Andreu et al.[11] proved that the reaction plane is 0.28 nm further from the electrode, which corresponds to the diameter of one H$_2$O molecule $d_{\mathrm{H_2O}}$. The potential at the reaction location can be determined[12] from:

$$\begin{aligned}\Phi^{\mathrm{r}} &= \Phi^{\mathrm{OHP+0.28nm}}\\ &= E + \frac{4RT}{F}\tanh^{-1}\left[\tanh\left|\frac{F\Phi_2}{4RT}\right|\exp(-\kappa d_{\mathrm{H_2O}})\right],\end{aligned} \tag{3}$$

at 298K:

$$\kappa = (3.29 \times 10^7)zc^{1/2}, \tag{4}$$

where: $c$ is the bulk z:z electrolyte concentration in M and $\kappa$ is given in cm$^{-1}$.[21]

The data obtained from the integration of differential capacity curves were then used to calculate the Parsons' auxiliary function, $\xi = \gamma + \sigma E$, and the surface pressure, $\Phi = \Delta\xi = \xi^0 - \xi$, where $\gamma$ is the surface tension and $\xi^0$ is the mean value of the supporting electrolyte without TMTU.[5,22] According to the Gibbs adsorption isotherm, the relative surface excess of TMTU is given by:

$$\Gamma'_{\mathrm{TMTU}} = -\frac{1}{RT}\left(\frac{\partial\Phi}{\partial \ln c_{\mathrm{TMTU}}}\right)_{\sigma}, \tag{5}$$

where $c_{\mathrm{TMTU}}$ is the bulk concentration of TMTU.

In writing Eq. 4, it is assumed that the mean activity coefficients of TMTU and NaClO$_4$ do not change with the change in TMTU concentration.

Figure 1 presents the relative surface excess of TMTU plotted at constant NaClO$_4$ concentration versus the electrode potential, $E$. In all applied systems, the presented relationships are linear and depend insignificantly on the potential. For the three lowest concentrations of TMTU, the values $\Gamma'$ do not depend on the basic electrolyte concentration. For higher concentrations of TMTU the values $\Gamma'$ increase with an increase in NaClO$_4$ concentration. This effect confirms the easier adsorption of TMTU on to the electrode surface under less hydrated conditions due to a larger concentration of $\mathrm{ClO_4^-}$ ions.

**Polarographic Measurements.** The electroreduction of Zn$^{2+}$ ions at a mercury electrode in NaClO$_4$ solutions in the presence of TMTU results in a single well-defined dc polarographic wave (Fig. 2). A change in the basic electrolyte concentration affects the limited diffusion current insignificantly. Approximate diffusion coefficients of Zn$^{2+}$ ions in the examined solutions were calculated using the Ilković equation for diffusion controlled limiting current.

The polarographic wave of Zn$^{2+}$ in 0.1 M KNO$_3$ with a Zn$^{2+}$ diffusion coefficient $D_{\mathrm{ox}} = 6.9 \times 10^{-6}\ \mathrm{cm^2\,s^{-1}}$ at 298 K was used as a standard.[23] The analogous value for Zn in mercury, $D_{\mathrm{R}} = 1.67 \times 10^{-5}\ \mathrm{cm^2\,s^{-1}}$, was also selected from the literature.[24] In all studied systems, the $D_{\mathrm{ox}}$ values increase with an increase in TMTU concentration. In the 1 M NaClO$_4$ and 0.5 M NaClO$_4$, these changes are small, ranging from $6.6 \times 10^{-6}$ cm$^2$ s$^{-1}$ to $7.3 \times 10^{-6}$ cm$^2$ s$^{-1}$ and from $7.0 \times 10^{-6}$ cm$^2$ s$^{-1}$

Table 1. Charge Densities $10^2\ \sigma^{\mathrm{m}}/\mathrm{C\,m^{-2}}$, Potentials of the Outher Helmholtz Plane $\Phi_2$/V and Potentials in the Reaction Plane $\Phi^{\mathrm{r}}$/V as a Function of TMTU and NaClO$_4$ Concentration at Potential −0.96 V Close to the Formal Potential of the Zn$^{2+}$ Ion Reduction

| $c_{\mathrm{TMTU}}$/M | 1 M NaClO$_4$ | | | 0.5 M NaClO$_4$ | | | 0.1 M NaClO$_4$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $-\sigma^{\mathrm{m}}$ | $-\Phi_2$ | $-\Phi^{\mathrm{r}}$ | $-\sigma^{\mathrm{m}}$ | $-\Phi_2$ | $-\Phi^{\mathrm{r}}$ | $-\sigma^{\mathrm{m}}$ | $-\Phi_2$ | $-\Phi^{\mathrm{r}}$ |
| 0 | 10.2 | 0.045 | 0.933 | 9.9 | 0.060 | 0.931 | 9.2 | 0.086 | 0.902 |
| $3 \times 10^{-4}$ | 9.4 | 0.044 | 0.935 | 11.0 | 0.064 | 0.929 | 8.9 | 0.085 | 0.903 |
| $5 \times 10^{-4}$ | 8.7 | 0.043 | 0.934 | 10.5 | 0.062 | 0.930 | 9.0 | 0.085 | 0.903 |
| $1 \times 10^{-3}$ | 8.7 | 0.043 | 0.934 | 9.0 | 0.057 | 0.932 | 9.2 | 0.086 | 0.902 |
| $3 \times 10^{-3}$ | 9.3 | 0.044 | 0.933 | 8.0 | 0.054 | 0.934 | 7.0 | 0.075 | 0.908 |
| $5 \times 10^{-3}$ | 7.3 | 0.042 | 0.934 | 6.9 | 0.050 | 0.935 | 6.0 | 0.070 | 0.911 |
| $1 \times 10^{-2}$ | 5.9 | 0.040 | 0.935 | 5.7 | 0.046 | 0.937 | — | — | — |

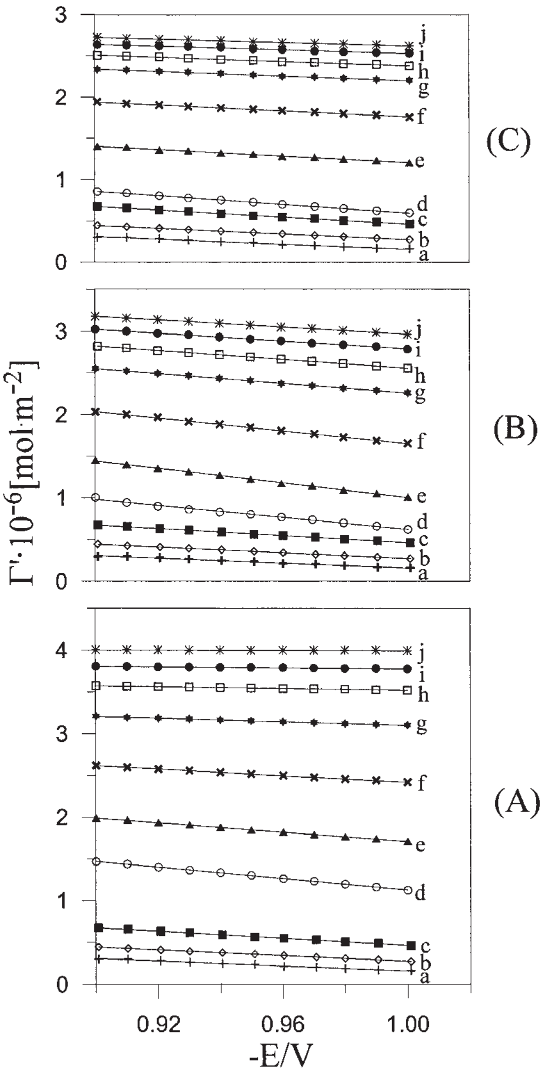

Fig. 1. Relative surface excess $\Gamma'$ of TMTU vs $E$ at varied concentrations of TMTU: (a) $3 \times 10^{-4}$ M, (b) $5 \times 10^{-4}$ M, (c) $1 \times 10^{-3}$ M, (d) $3 \times 10^{-3}$ M, (e) $5 \times 10^{-3}$ M, (f) $1 \times 10^{-2}$ M, (g) $2 \times 10^{-2}$ M, (h) $3 \times 10^{-2}$ M, (i) $4 \times 10^{-2}$ M, (j) $5 \times 10^{-2}$ M and varied concentrations of $NaClO_4$: (A) 1 M, (B) 0.5 M, (C) 0.1 M.

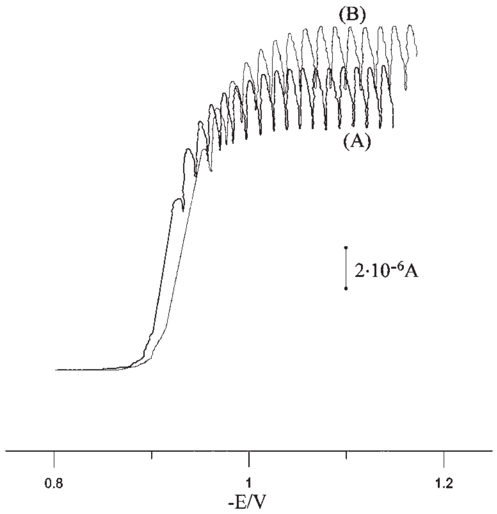

Fig. 2. Polarograms dc for $5 \times 10^{-3}$ M $Zn^{2+}$ in 1 M $NaClO_4$ (A) and 0.1 M $NaClO_4$ (B) in the presence of $5 \times 10^{-2}$ M TMTU.

to $7.9 \times 10^{-6}$ cm$^2$ s$^{-1}$, respectively. However, in the 0.1 M $NaClO_4$ solution, the maximum concentration of TMTU causes $D_{ox}$ to increase from $7.2 \times 10^{-6}$ cm$^2$ s$^{-1}$ to $9.9 \times 10^{-6}$ cm$^2$ s$^{-1}$.

The reversible potential of the half wave ($E^{r}_{1/2}$) was determined by the cyclic voltammetry method using Eq. 6:[25]

$$E^{r}_{1/2} = \frac{E_{pc} + E_{pa}}{2}, \tag{6}$$

where $E_{pc}$ and $E_{pa}$ are the cathode or anode peak potentials, respectively. In the 1 M $NaClO_4$, the increase in TMTU concentration does not change $E^{r}_{1/2}$, but in the 0.5 M $NaClO_4$ and 0.1 M $NaClO_4$ solutions the $E^{r}_{1/2}$ values shift towards more negative potentials, from $-0.967$ V to $-0.971$ V and from $-0.974$ V to $-0.995$ V, respectively. It was concluded, therefore, that the $Zn^{2+}$–TMTU complexes formed in the solution are very unstable.[26] From the reversible half wave potentials, the standard formal potentials, $E^{0}_{f}$, were calculated using the equation:

$$E^{0}_{f} = E^{r}_{1/2} + \frac{RT}{nF} \ln\left(\frac{D_{ox}}{D_{R}}\right)^{1/2}. \tag{7}$$

**The Rate of Electroreduction.** The complex impedance data were collected at 36 frequencies in the range from 100 Hz to 50000 Hz within the faradaic potential region at 10 mV intervals. The values of the apparent rate constant, $k_f$, were obtained from the charge-transfer resistance values[11] as a function of dc potential. Details are described elsewhere.[27–29]

The $k_f$ values obtained in the solutions of constant $NaClO_4$ concentration and various TMTU concentrations in the presence of the mean dc potential indicate an increase in the catalytic TMTU activity with an increase in its concentration. This increase in $k_f$ values occurs in 1 M $NaClO_4$ and 0.5 M $NaClO_4$ only up to the $1 \times 10^{-2}$ M TMTU concentration, but in 0.1 M $NaClO_4$ only up to the $5 \times 10^{-3}$ M TMTU concentration. Above these concentrations of TMTU the $k_f$ values do not change dramatically. The analysis of the $k_f = f(E)$ dependence allows us to distinguish two areas of potentials: at less negative potentials the increase in $k_f$ is much faster, but at more negative potentials it proceeds more slowly.

The true rate constant, $k^{t}_{f}$, can be obtained from Eq. 8:[12]

$$k_f(\Phi^{r}) = k^{t}_{f}(\Phi^{r}) \exp\left[-(\mathrm{E} - \Phi^{r}) \frac{nF}{RT}\right]. \tag{8}$$

The values of the true rate constants of electroreduction of $Zn^{2+}$ ions plotted as $\ln k^{t}_{f}$ obtained at various TMTU concentrations as a function of the potential, $\Phi^{r}$, are presented in Figs. 3 and 4. It follows from the presented dependences that:

1) a stage character of electrons transfer in $Zn^{2+}$ ions reduction is confirmed by the not rectilinear $\ln k^{t}_{f} = f(\Phi^{r})$ dependences.[11]
2) the slope of the curves changes with the potential and concentrations of TMTU and $NaClO_4$.
3) the accelerating effect due to the TMTU concentrations is stronger at the most negative potentials.

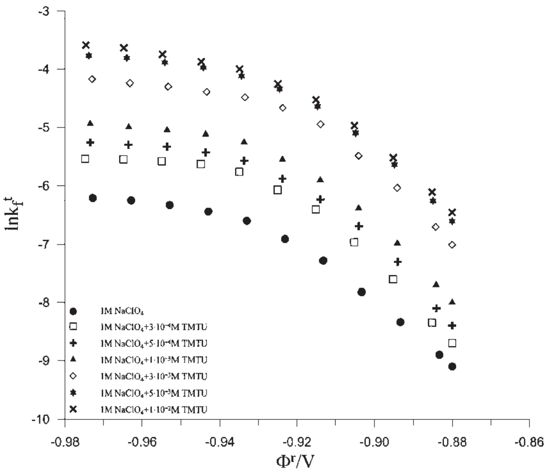

Fig. 3. The potential dependence of the true rate constants of the $Zn^{2+}$ reduction in 1 M $NaClO_4$ at various TMTU concentrations.

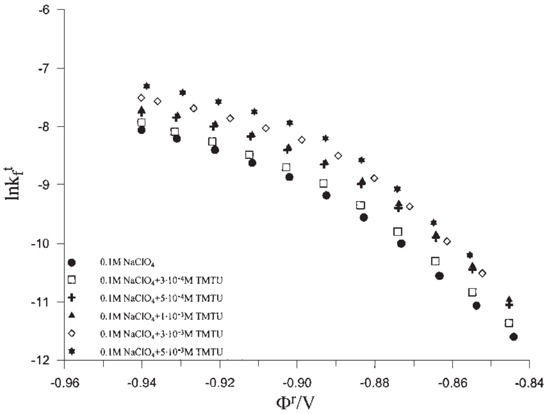

Fig. 4. The potential dependence of the true rate constants of the $Zn^{2+}$ reduction in 0.1 M $NaClO_4$ at various TMTU concentrations.

4) the $k_f^t$ values increase with an increase in the TMTU concentration and achieve the highest values in 1 M $NaClO_4$.
5) the acceleration of the reduction of $Zn^{2+}$ ions by TMTU is similar in 1 M $NaClO_4$ and 0.5 M $NaClO_4$, while in 0.1 M $NaClO_4$ this effect is much weaker.

The catalytic influence of TMTU can be better described by a $k_f^t$ versus $\Gamma'$ plot at a given $\Phi^r$ (see Figs. 5 and 6). These plots were constructed with the aid of the curves $\Gamma' = f(\Phi^r)$ and $\ln k_f^t = f(\Phi^r)$. Although there is some scatter, straight lines are indeed obtained. It seems that the $k_f^t$ values of $Zn^{2+}$ electroreduction in the presence of TMTU change according to Eq. 9:

$$k_f^t(\Phi^r)/k_f^{0,t}(\Phi^r) = 1 + B\Gamma', \tag{9}$$

where $k_f^{0,t}(\Phi^r)$ denotes the true rate constant determined at a certain potential in the absence of TMTU. Equation 9 was obtained earlier by Souto et al.,[26] who refer to the catalytic effect of thiourea on the electroreduction of $Cd^{2+}$ ions. The obtained straight lines (Figs. 5 and 6) have a point of intersection on the horizontal axis at "value" $\Gamma'$ of TMTU: $-0.20 \times 10^{-6}$ mol m$^{-2}$, $-0.26 \times 10^{-6}$ mol m$^{-2}$, and $-1.05 \times 10^{-6}$ mol m$^{-2}$ in 1 M $NaClO_4$, 0.5 M $NaClO_4$, and 0.1 M $NaClO_4$, respectively.

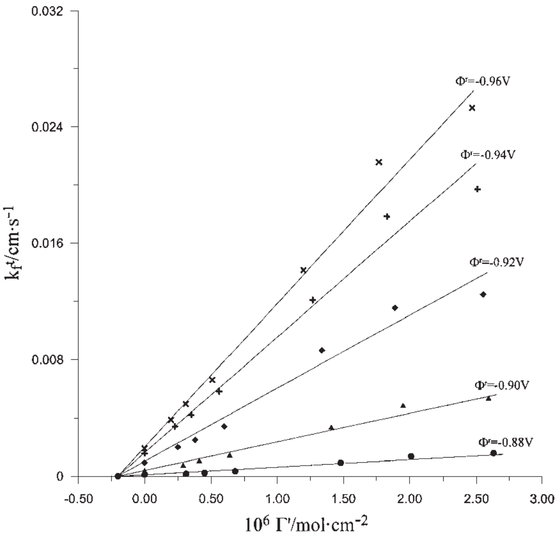

Fig. 5. The true rate constants of the $Zn^{2+}$ reduction versus the relative surface excess of TMTU at constant $\Phi^r$ indicated for each curve in 1 M $NaClO_4$.

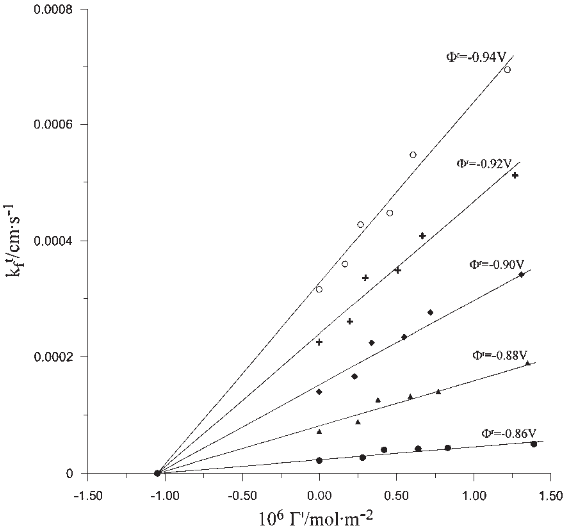

Fig. 6. The true rate constants of the $Zn^{2+}$ reduction versus the relative surface excess of TMTU at constant $\Phi^r$ indicated for each curve in 0.1 M $NaClO_4$.

The values of $B$: $5 \times 10^6$, $3.85 \times 10^6$, and $0.95 \times 10^6$, are comparative measures of the catalytic activities of TMTU in the observed systems. A linear relationship between the rate constant of the electroreduction of $Zn^{2+}$ and the relative surface excess of TMTU indicates the formation of active complex between $Zn^{2+}$ and TMTU, which facilitates the transfer of electrons across the inner layer.[30] This is the only evidence for active some complex formation. It seems that active complex formation is very fast, compared with the electron transfer, and that is why its detection is practically impossible. The results may suggest that bridging enhances the rate of all steps of the reduction mechanism of $Zn^{2+}$ ions.

From the dependence of $\ln k_f^t = f(\Phi^r)$ (Figs. 3 and 4), the values of the true standard rate constants $k_s^t$ corresponding to the values, $E_f^0$, and the constants $k_{s1}^t$ and $k_{s2}^t$ characterizing

Table 2. Corrected Individual Rate Constants of $Zn^{2+}$ Ion Electroreduction Extrapolated to the $E_f{}^0$ for Various Concentrations of $NaClO_4$ and TMTU; $k^t_{s1}$, $k^t_{s2}$/cm s$^{-1}$

| $c_{TMTU}$/M | 0.1 M $NaClO_4$ | | 0.5 M $NaClO_4$ | | 1 M $NaClO_4$ | |
|---|---|---|---|---|---|---|
| | $10^4\ k^t_{s1}$ | $10^4\ k^t_{s2}$ | $10^2\ k^t_{s1}$ | $10^2\ k^t_{s2}$ | $10^2\ k^t_{s1}$ | $10^2\ k^t_{s2}$ |
| 0 | 1.30 | 3.10 | 0.15 | 2.42 | 0.15 | 3.70 |
| $3 \times 10^{-4}$ | 1.49 | 3.97 | 0.23 | 3.39 | 0.35 | 8.00 |
| $5 \times 10^{-4}$ | 2.32 | 5.00 | 0.29 | 8.00 | 0.41 | 11.0 |
| $1 \times 10^{-3}$ | 2.44 | 6.23 | 0.48 | 15.6 | 0.52 | 18.0 |
| $3 \times 10^{-3}$ | 4.10 | 27.3 | 0.72 | 23.5 | 1.21 | 30.0 |
| $5 \times 10^{-3}$ | 5.48 | 36.4 | 1.14 | 28.1 | 1.81 | 44.2 |
| $1 \times 10^{-2}$ | 5.48 | 36.4 | 1.48 | 41.4 | 2.02 | 66.8 |

the first stage of the first electron transfer and the second stage of the second electron exchange, respectively, were determined.[11,13,23] The values of the individual standard rate constants of the electroreduction of $Zn^{2+}$ ions in 1 M $NaClO_4$, corrected for the double layer effects, are: $k^t_{s1} = 1.5 \times 10^{-3}$ cm s$^{-1}$ and $k^t_{s2} = 3.7 \times 10^{-2}$ cm s$^{-1}$. These values are in agreement with the literature data.[11,12]

Table 2 presents the values of the individual standard rate constants of the electroreduction of $Zn^{2+}$ at various concentrations of $NaClO_4$ and TMTU. The distinctly decreasing $k^t_{s1}$ and $k^t_{s2}$ values obtained in the 0.1 M $NaClO_4$ solution not including TMTU compared with the 0.5 M $NaClO_4$ and 1 M $NaClO_4$ solutions could be the result of strong hydration of the electrode surface in this solution due to stronger hydrogen bonds between water molecules. $ClO_4^-$ causes the strongest disruption in water structure.[31] However, their concentration in 0.1 M $NaClO_4$ is too small compared with that of the other applied basic electrolytes to observe any favourable effect on the kinetics of $Zn^{2+}$ ion electroreduction. Such properties of $ClO_4^-$ ions also promote the adsorption of TMTU, as can be seen in Fig. 1. As a result, the effect of $Zn^{2+}$ ion electroreduction acceleration by TMTU increases with increasing $NaClO_4$ concentration.

As follows from the presented values, the catalytic effect of TMTU on the electroreduction of $Zn^{2+}$ ions as a function of basic electrolyte concentration decreases in the order: 1 M $NaClO_4 >$ 0.5 M $NaClO_4 >$ 0.1 M $NaClO_4$. In each of the studied systems there is observed a much larger increase in the $k^t_{s2}$ values compared with the $k^t_{s1}$ values when the concentration of TMTU increases.

As follows from the literature data,[11] in aqueous $NaClO_4$ solutions between 0.2 M and 5 M $NaClO_4$, $Zn^{2+}$ ions have an effective hydration number of 19.6. As a result, the $k^t_{s1}$ and $k^t_{s2}$ values in 1 M $NaClO_4$ and 0.5 M $NaClO_4$ in the absence of TMTU are similar. Much lower values of these quantities obtained in 0.1 M $NaClO_4$ may result from a stronger hydration of $Zn^{2+}$ ions. A similar accelerating action of TMTU in 1 M $NaClO_4$ and 0.5 M $NaClO_4$, as well as the much smaller accelerating effect of TMTU in 0.1 M $NaClO_4$, indicates a lack of univocal relations between the determined kinetic parameters and the values $\Gamma'$ for TMTU.

The $\Gamma'$ values for TMTU decrease with decreasing concentration of $NaClO_4$, but these changes are insignificant. Moreover, for the highest concentrations of TMTU in the bulk of the solution, the $\Gamma'$ values decrease significantly, but the $k^t_{s1}$ and $k^t_{s2}$ values remain unchanged. It can be assumed that the composition of the active complex changes with the increasing $\Gamma'$ values, but only for $\Gamma' \leq 2.2 \times 10^{-6}$ mol m$^{-2}$. Above this value of $\Gamma'$, the complex composition remains stable and the determined kinetic parameters do not change, either.

The larger increase of the $k^t_{s2}$ value described earlier compared to $k^t_{s1}$ in the presence of TMTU can confirm the mechanism of $Zn^{2+}$ ion electroreduction described in the literature.[11] Including formation of an active complex with TMTU (suggested above), it can be stated that the reduction of $Zn^{2+}$ ion with the first electron refers to the active complex still partly hydrated, but reduction of the $Zn^+$ ion with the second electron refers to the completely dehydrated active complex.

Both dehydration and active complex formation stages as chemical stages are much faster than that of electron transfer, and their detection by means of available measuring techniques is impossible.

Additionally postulated in Ref. 3 is a mechanism of electrode process acceleration by organic substances connected with a confirmed larger permittivity of the surface adsorption layer. The values for electric permittivity of the inner layer, $\varepsilon_i$, obtained for $\Gamma'_{TMTU} = 1.5$ mol m$^{-2}$ and $\sigma^m = -0.06$ C m$^{-2}$ increase from 9.15 to 16.97 when the concentration of $NaClO_4$ increases from 0.1 M to 1.0 M.[17]

If a direct relation between the $\Gamma'$ values and the acceleration of $Zn^{2+}$ ion reduction is not found, then the values of the electrostatic parameters of the double layer determined indirectly point to such a dependence.

## Conclusions

From the presented results it can be concluded that:

1) a lack of evident changes of the $E^r_{1/2}$ value in the presence of TMTU indicates that the $Zn^{2+}$–TMTU complexes formed in the solution are very unstable.
2) a linear relationship between the rate constant of $Zn^{2+}$ ion electroreduction and the relative surface excess of $Zn^{2+}$ obtained in all studied systems indicates formation of an activated complex between $Zn^{2+}$ and TMTU on the electrode surface.
3) distinctly larger values of $k^t_{s2}$ compared to $k^t_{s1}$ indicate that transfer of the second electron connected with $Zn^+$ ion reduction proceeds more readily than transfer of the first electron due to the dehydrated form of the active $Zn^+$–TMTU complex.
4) The lowest rate of $Zn^+$ ion reduction in the 0.1 M $NaClO_4$ solution in both the presence and absence of TMTU may result from a more stable water structure both inside the solution and on the electrode surface due to a small num-

ber of $ClO_4^-$ ions. A more stable water structure would have an effect on the hydration extent of $Zn^{2+}$ ions and on the extent of TMTU adsorption.

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\# Dedicated to Professor K. Sykut on the occasion of his 80th birthday.

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