

## THE INFLUENCE OF DIAMINOTOLUENE ISOMERS ON THE TWO-STEP ELECTROREDUCTION OF Zn(II) IONS IN ACETATE BUFFERS AT DIFFERENT ACIDITIES

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The influence of diaminotoluene isomers on the two-step reduction of Zn(II) ions on the mercury electrode in acetate buffers at different acidities was examined. It was stated that 2,4- and 2,6-diaminotoluene inhibit the electroreduction process of Zn(II) ions, while 3,4-diaminotoluene, in dependence on pH of acetate buffer, can act as inhibitor or catalyst. The differences in activity of these isomers result mainly from their complex formation properties. The catalytic activity of 3,4-diaminotoluene is associated with removing of the coordinated water molecules from the hydration sphere of Zn(II) ions and with the formation of active complexes on the electrode surface. This reaction controls the total rate of the process. The active complexes participate in consecutive electron transfer. Both steps of electron transfer are catalysed by 3,4-diaminotoluene.

**Keywords:** Electrochemistry; Electrochemical reduction; Zinc; Acidity; Inhibition; Catalysis; Rate constants; 3,4-Diaminotoluene.

Zinc is one of the most important metals from the biological point of view. Although only a small amount of zinc about 15 mg per day is necessary for the proper functioning of living organisms, this element is indispensable almost in all chemical processes taking place in their cells. Zinc has an influence on the hormone secretion and enzyme production. Also it controls the adequate level of cholesterol. It is also responsible for proper functioning of brain, glands, and the formation of bones.

Electrochemical reduction of Zn(II) ions is one of the most frequently studied reactions in electrochemistry. Mechanism and kinetics of Zn(II) ions electroreduction were studied in relation to the kind of supporting electrolyte, the solvent or an added inhibitor or catalyst.

It is well known that the electroreduction of Zn(II) ions at a mercury electrode is accelerated in the presence of adsorbed nonelectroactive species<sup>1-4</sup>. The importance of this effect can be deduced from the compilation of stan-

standard rate constants made by Tamamushi and Tanaka<sup>5,6</sup> for many electrode reactions and compositions of supporting electrolytes.

Various models have been published<sup>7-14</sup> describing specific interactions in the inner double layer between the adsorbed species and the reactant in an electrode reaction. However, interpretation of experimental results in terms of such a model cannot be done only by correlation of double layer data with the standard rate constant. The reason is the increasing evidence<sup>15-21</sup> that the electroreduction of Zn(II) ions proceeds *via* elementary reaction steps, by single-electron transfer chemical conversions. Each of these steps may be influenced individually by the double layer structure.

It was found earlier<sup>22,23</sup> that the catalysis of the reduction of Zn(II) ion in NaClO<sub>4</sub> with adsorbed isomers of diaminotoluene (DAT), 2,4-, 2,6- or 3,4-diaminotoluene, can be described in terms of an EE mechanism (two successive rate-determining electron transfers). It was concluded that the studied isomers catalyse the first electron transfer; the rate of the second electron transfer changes insignificantly. The differences in the catalytic activity of the isomers indicate the complex character of the catalysis mechanism<sup>24</sup>. The experiments in the presence of diaminotoluene isomers with basic properties have been made in unbuffered media. In this media, the acid-base equilibria at the electrode surface are ill-defined and may change in the course of the experiment. Protonation of diaminotoluenes can effect both adsorption of diaminotoluene and acid-base catalysis of the hydration-dehydration process.

This paper presents the study of the influence of 2,4-, 2,6- and 3,4-diaminotoluene (2,4-, 2,6-, 3,4-DAT) on the electroreduction of Zn(II) ions in acetate buffers at pH 3–5.6. As Zn(II) ions do not form strong complexes with acetates, acetate buffer seems to be a suitable supporting electrolyte for presented experiments.

## EXPERIMENTAL

The measurements were performed using a three-electrode cell containing dropping mercury or hanging mercury drop electrode, saturated Ag|AgCl (NaCl) reference electrode and platinum as an auxiliary electrode. The reference electrode was equipped with a Luggin capillary probe. The capillary was filled with the cell solution.

Solutions were prepared from fresh, doubly distilled water and analytical grade chemicals. High-purity reagent grade (Merck) Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was used. The Zn(II) concentration in solutions was always  $1 \times 10^{-3}$  mol dm<sup>-3</sup>. The supporting electrolyte was acetate buffers in the range of pH 3–5.6. Acetate buffers were prepared according to Walpole<sup>25</sup> from 0.2 mol dm<sup>-3</sup> CH<sub>3</sub>COOH and 0.2 mol dm<sup>-3</sup> CH<sub>3</sub>COONa. Analytical reagent-grade 2,6-, 2,4- and 3,4-DAT (Aldrich) were used without further purification. The concentrations of the DAT were  $1 \times 10^{-5}$  and  $1 \times 10^{-2}$  M, respectively. Only freshly prepared solutions of DAT were used. The

solutions were deaerated with nitrogen passed through a vanadous sulfate solution and pre-saturated with the investigated solution. The nitrogen gas passed over the solution during the measurements. Measurements were carried out at  $298 \pm 1$  K.

DC polarograms were obtained using a polarograph PA-4 (Laboratorní Přístroje, Prague). Square-wave (SW) and cyclic voltammetric (CV) measurements were performed using a PAR Model 384B and Model 270 electrochemical analyser.

The values of the differential double layer capacity in acetate buffers in the presence of isomers of DAT were measured at a frequency of 800 Hz. The reproducibility of the average capacity measurements was  $\pm 1\%$  over the wide range of potentials. For the whole polarization range, the capacity dispersion was tested at five different frequencies between 200 and 2000 Hz. In the potential range studied, no dispersion of the capacitance was observed.

The complex impedance data were collected at 21 frequencies in the range from 200 to 50 000 Hz with 10 mV potential intervals. The frequency analysis was performed in usual way<sup>26,27</sup>. The values of apparent rate constants  $k_f$  were obtained with the precision  $\pm 5\%$  from the charge-transfer resistance<sup>20</sup>. The details are described elsewhere<sup>28</sup>.

The solution pH was measured with a pH-meter CPC-551 (Elmetron).

## RESULTS AND DISCUSSION

### *Voltammetric Measurements*

The polarographic wave of the reduction of Zn(II) ions in acetate buffers is well-defined. The wave height depends neither on pH in the range 3–5.6 nor on the concentration of the examined DAT isomers in the range  $5 \times 10^{-5}$ – $1 \times 10^{-2}$  mol dm<sup>-3</sup>. The diffusion coefficient  $D_{\text{ox}}$  of Zn(II) ions was derived from the limiting current in the polarograms. The details are described elsewhere<sup>22</sup>. The diffusion coefficient of Zn(II) ions in acetate buffers in the pH range 3–5.6 was found to be  $6.18 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>. The presence of 3,4-DAT in acetate buffers does not cause any changes in diffusion coefficients of Zn(II) ions. The limiting current of the electroreduction of Zn(II) ions in acetate buffers and in acetate buffers with addition of DAT isomers is dependent on the height of a mercury reservoir, which points to the absence of the catalytic control of the described process, it does not exclude participation of a catalytic process in the electrode reaction.

Square-wave polarograms display well-defined peaks of the electroreduction of Zn(II) ions in acetate buffers. Peaks are decreasing in presence of 2,4- or 2,6-DAT (acetate buffers pH 3–5.6). This effect is further pronounced with the rise in the concentration of examined isomers. In the presence of 3,4-DAT the heights of peaks of Zn(II) electroreduction decrease or increase, depending on pH of acetate buffer. Figure 1 presents changes of peak current (SW) of the electroreduction of Zn(II) ions in acetate buffers (pH 3–5.6) as a function of 3,4-DAT concentration. In acetate buffers of pH 3 and 3.6,

an addition of 3,4-DAT results in a decrease in Zn(II)-reduction peak. At pH 4.2–5.6, the electroreduction of Zn(II) yields peaks increasing with rising 3,4-DAT concentration. For 3,4-DAT concentrations higher than  $1 \times 10^{-3}$  M, the parameter affecting the peak height is pH of the solution.

The influence of pH on the electroreduction of Zn(II) ions results also from the course of cyclic voltammetric curves (Fig. 2a). Together with increasing pH, the difference between cathodic and anodic peak potentials decreases, which indicates the rise of the process reversibility. Simultaneously, voltammetric curves of the electroreduction of Zn(II) ions in acetate buffers are shifted towards negative potentials. This suggests that different forms of depolarisers are present in the solution; hydrated  $\text{Zn}^{2+}$ ,  $[\text{ZnOH}]^+$  or  $[\text{ZnCH}_3\text{COO}]^+$  should be mentioned here. The voltammetric curves clearly point to the inhibiting properties of 3,4-DAT in acetate buffer of pH 3 (Fig. 2b), whereas its catalytic activity in acetate buffer of pH 5 is hard to notice (Fig. 2c). The conclusion concerning the rise of the reversibility for the electroreduction of Zn(II) ions in the presence of 3,4-DAT can be reached by analysing the difference between potentials of cathodic and anodic peaks ( $\Delta E_{c-a}$ ) as a function of potential sweep rate ( $v$ ). The influence of sweep rate on the difference between peak potentials in acetate buffer of pH 5 containing 3,4-DAT is presented in Fig. 3. In the absence of 3,4-DAT,  $\Delta E_{c-a} \approx 43\text{--}190$  mV for the potential sweep rates  $v = 10\text{--}1000$  mV s $^{-1}$ . In the presence of 3,4-DAT,  $\Delta E_{c-a}$  is significantly less dependent on  $v$ . A slight change in  $\Delta E_{c-a}$  indicates that the process is little dependent on the poten-

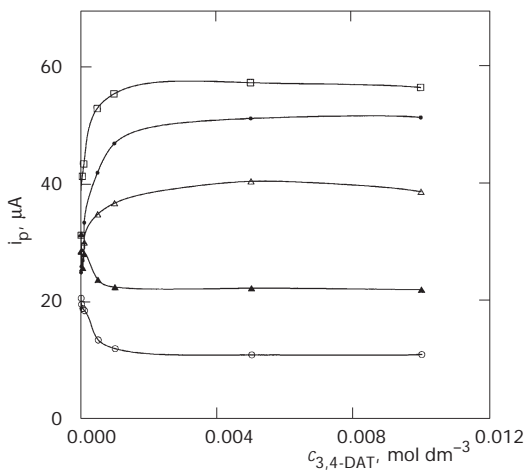


FIG. 1

Dependence of SW peak current of  $1 \times 10^{-3}$  mol dm $^{-3}$  Zn(II) ions in acetate buffers of pH 3 (○), 3.6 (▲), 4.2 (△), 5 (●), 5.6 (□) on 3,4-DAT concentration

tial sweep rate. It is well known that this occurs when the total rate of the process is controlled by a chemical reaction. Calculations of kinetic parameters were based on the theoretical equations of Nicholson and Shain for flat electrodes<sup>29,30</sup> which may be used with a slight error for spherical electrodes fulfilling the condition  $r^2v \geq 10^{-4}$  (refs<sup>31,32</sup>) ( $r$  is electrode radius). Thus, for the electrode of  $r = 0.065$  cm and sweep rate  $v = 0.05$  V s<sup>-1</sup>, the value of  $r^2v = 2.1 \times 10^{-4}$  resulted. The required condition is thus fulfilled. The standard rate constant  $k_s$  was determined using Nicholson's method, which relates the function  $\Psi$  with  $k_s$  by

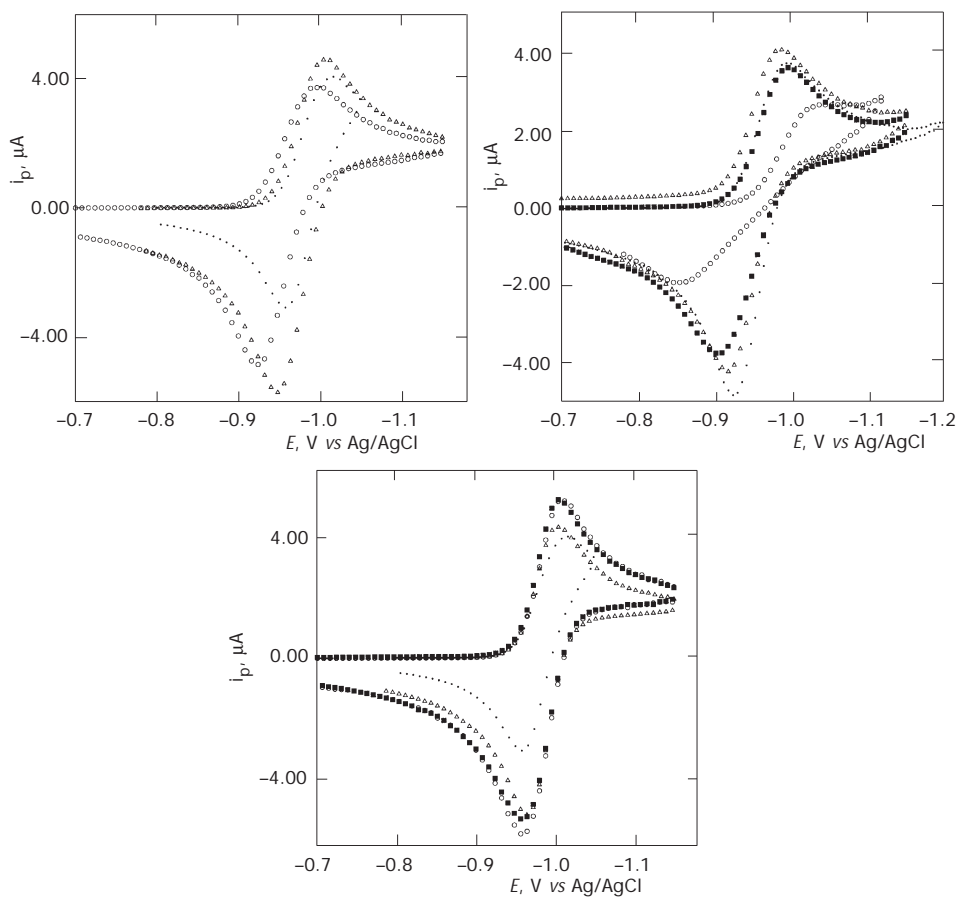


FIG. 2

Cyclic voltammogram of  $1 \times 10^{-3}$  mol dm<sup>-3</sup> Zn (II). Scan rate 100 mV s<sup>-1</sup>,  $f = 120$  Hz,  $\Delta E = 20$  mV. a In acetate buffers of pH 3 (○), 4.2 (△), 5 (●). b In acetate buffer of pH 3 with various concentrations of 3,4-DAT (mol dm<sup>-3</sup>): 0 (●),  $5 \times 10^{-5}$  (△),  $1 \times 10^{-3}$  (■),  $1 \times 10^{-2}$  (○). c In acetate buffer of pH 5 with various concentrations of 3,4-DAT as indicated in Fig. 2b

$$\Psi = \left( \frac{D_{\text{ox}}}{D_{\text{red}}} \right)^{\alpha/2} \frac{k_s (RT)^{1/2}}{(\Pi n F v D_{\text{ox}})^{1/2}}, \quad (1)$$

where  $D_{\text{ox}}$  is the diffusion coefficient of Zn(II) ions in supporting electrolyte,  $D_{\text{red}}$  is the diffusion coefficient for zinc in mercury,  $\alpha$  is the cathodic transfer coefficient, and  $n$ ,  $F$ ,  $R$  and  $T$  have their usual meanings.

The cathodic transfer coefficient for quasireversible process was determined using the dependence of the formal values  $\alpha n_{\alpha}$  on  $1/v$  (ref.<sup>33</sup>). The formal potential  $E_f^0$  was fixed at polarization rate of  $v = 0.005 \text{ V s}^{-1}$  using the equation

$$E_f^0 = \frac{1}{2} \left\{ E_{a/4} + E_{c/4} + \left[ \frac{(E_{a/4} + E_{c/4}) - (E_{3a/4} + E_{3c/4})}{g - 1} \right] \right\}, \quad (2)$$

where

$$g = \frac{(E_{3a/4} - E_{3c/4})}{(E_{a/4} - E_{c/4})},$$

$E_a$  and  $E_c$  are the peak potential of the anodic curve and that of the cathodic curve on the cyclic voltammogram.

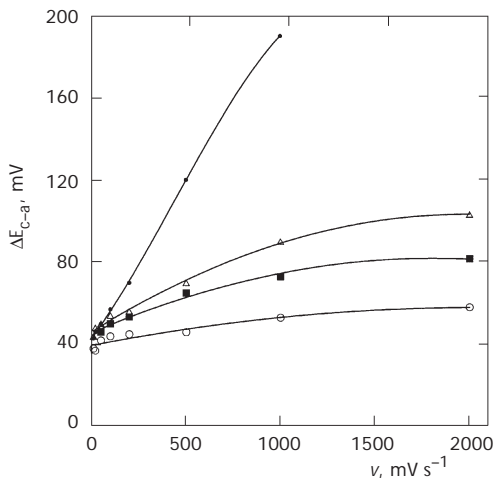


FIG. 3

Influence of polarization rate on the difference between potentials of cathodic and anodic peaks ( $\Delta E_{c-a}$ ) for the Zn(II)/Zn(Hg) couple in acetate buffer (pH 3) with various concentrations of 3,4-DAT (mol dm<sup>-3</sup>): 0 (●),  $5 \times 10^{-5}$  (△),  $1 \times 10^{-4}$  (■),  $1 \times 10^{-5}$  (○)

The kinetic data were obtained with the accuracy 7%. All kinetic parameters are presented in Table I as an average calculated from four measurements.

In acetate buffer solutions of pH 3, the formal potential  $E_f^0$  of Zn(II) electroreduction is shifted *ca* 8 mV towards positive potentials in presence of 3,4-DAT. At higher pH values, the changes of  $E_f^0$  are minimal indicating that no stable Zn-3,4-DAT complexes are present in the solutions. The standard rate constants of the electroreduction of Zn(II) ions decreased with rising concentration of 3,4-DAT in acetate buffer of pH 3. In acetate buffers of pH 4.2 and pH 5, the values of  $k_s$  passed *via* maximum with rising 3,4-DAT concentration. It is worth noting that in the case of all examined 3,4-DAT concentrations the standard rate constants rise with increasing pH.

### Impedance Measurements

Differential capacitance of a mercury electrode in contact with acetate buffers of pH 3, 4.2 and 5, containing  $1 \times 10^{-2}$  mol dm<sup>-3</sup> 3,4-DAT, is presented in Fig. 4. The influence of pH and 3,4-DAT on the course of differential double layer capacity curves is visible mainly in the range of zero charge potentials. At potentials of Zn(II) reduction, the influence of pH on differential capacity is negligible. The differential capacity is risen by 3,4-DAT in acetate buffer of pH 5, while at lower pH, changes of the differential capacity are insignificant. The course of  $C_d = f(E)$  curves in acetate buffers in the presence of 2,4- or 2,6-DAT actually do not differ from those presented in Fig. 4.

TABLE I

Kinetic parameters of electrode reactions of zinc in acetate buffers (pH 3, 4.2 and 5) and with addition of 3,4-DAT (voltammetric method)

Concentration of 3,4-DAT mol dm <sup>-3</sup>	$-E_f^0$ , V			$k_s \times 10^3$ , cm s <sup>-1</sup>		
	pH 3	pH 4.2	pH 5	pH 3	pH 4.2	pH 5
0	0.963	0.982	0.992	3.40	4.38	5.90
$5 \times 10^{-5}$	0.954	0.979	0.989	3.38	5.69	7.30
$1 \times 10^{-3}$	0.957	0.984	0.990	1.92	11.87	13.65
$5 \times 10^{-3}$	0.957	0.982	0.989	1.38	8.67	15.10
$1 \times 10^{-2}$	0.954	0.980	0.989	1.30	6.65	9.70

Values of apparent rate constants of electroreduction of Zn(II) ions in acetate buffer of pH 5 at various 3,4-DAT concentrations as a function of the mean DC potential are shown in Fig. 5. The dependences  $\ln k_f = f(E)$  are not linear and their slope changes with the potential and concentration of

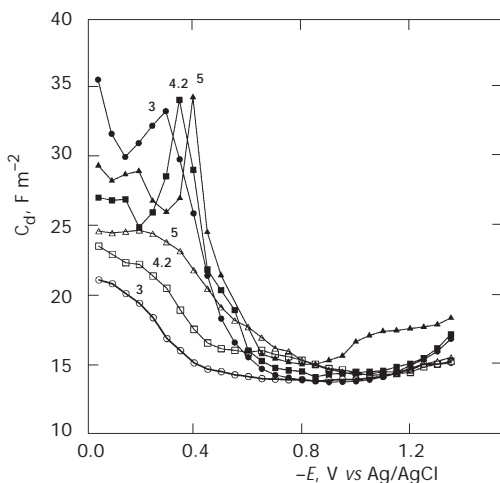


FIG. 4

Differential capacity-potential curves of mercury in acetate buffers of pH 3 (○), 4.2 (□), 5 (△) and in the presence of  $1 \times 10^{-2} \text{ mol dm}^{-3}$  3,4-DAT in acetate buffers of pH 3 (●), 4.2 (■), 5 (▲)

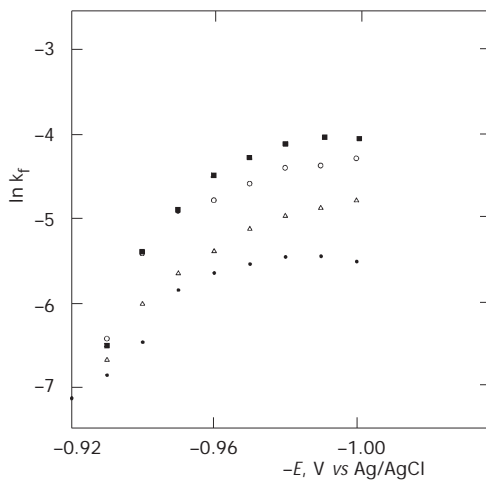


FIG. 5

Potential dependence of the electroreduction rate constant for  $1 \times 10^{-3} \text{ mol dm}^{-3}$  Zn(II) in acetate buffer (pH 5) with various concentration of 3,4-DAT (M): 0 (●),  $5 \times 10^{-5}$  (△),  $1 \times 10^{-3}$  (■),  $1 \times 10^{-2}$  (○)



3,4-DAT. The nonlinearity can be explained assuming that electrons are transferred successively also in the presence of 3,4-DAT. The catalytic activity of 3,4-DAT is higher at negative potentials and seems to be absent in the region of less negative potentials. At most negative potentials, the first electron transfer is the rate determining ( $k_f = k_1$ ), while at less negative potentials, the overall rate is determined simultaneously by both steps<sup>20,26</sup>. Table II presents values of the rate constants of the electroreduction of Zn(II) ions extrapolated to the formal potential  $E_f^0$  in acetate buffers of pH 3, 4.2 and 5, and in the presence of 3,4-DAT.

The values of standard rate constants determined by impedance measurements are consistent with those determined by voltammetric measurements. The values of rate constants of electroreduction of Zn(II) ions decrease with increasing 3,4-DAT concentration in acetate buffer of pH 3, whereas in acetate buffers of pH 4.2 and 5 the rate constant values pass the maximum. The maximum is shifted towards higher concentrations of 3,4-DAT as pH is rising. The character of  $k_s$ ,  $k_{s1}$  and  $k_{s2}$  changes as functions of 3,4-DAT concentration is similar. However, the dramatic drop of  $k_{s2}$  value after its maximum was reached should be noticed. The rate decrease at the highest examined 3,4-DAT concentrations is without doubt, associated with limited accessibility of the mercury electrode surface blocked by adsorption. This is particularly important for the second electron transfer, which is related to the amalgam formation.

TABLE II

Standard rate constants and individual rate constants of the electroreduction of Zn(II) ions extrapolated to the  $E_f^0$  in acetate buffers (pH 3, 4.2 and 5) at various concentrations of 3,4-DAT (impedance method)

Concentration of 3,4-DAT mol dm <sup>-3</sup>	pH 3			pH 4.2			pH 5		
	$k_s \times 10^3$	$k_{s1} \times 10^3$	$k_{s2} \times 10^2$	$k_s \times 10^3$	$k_{s1} \times 10^3$	$k_{s2} \times 10^2$	$k_s \times 10^3$	$k_{s1} \times 10^3$	$k_{s2} \times 10^2$
	cm s <sup>-1</sup>								
0	3.2	3.8	2.0	4.0	4.6	3.0	4.7	5.2	5.0
$5 \times 10^{-5}$	3.1	4.0	1.5	5.1	5.6	5.7	7.4	8.6	5.3
$1 \times 10^{-3}$	1.8	2.2	1.4	11.2	12.1	15.0	16.5	18.0	19.8
$5 \times 10^{-3}$	1.5	1.7	1.3	5.2	6.1	3.6	18.3	20.0	21.5
$1 \times 10^{-2}$	1.4	1.6	1.2	4.0	5.2	1.7	11.6	16.1	4.2

## CONCLUSIONS

Both the hydrogen ion and 3,4-DAT concurrently are rate determining factors for the Zn(II) electroreduction process in acetate buffers. The rise in  $H^+$  concentration causes inhibition of the electrode process. This fact is certainly associated with higher hydration of Zn(II) ions and the necessity of dehydration before the electron exchange. As pH is rising, the concentration of weaker hydrated  $Zn(OH)^+$  is rising as well. The catalytic effect of 3,4-DAT must be associated with its ability to displace coordinated water from the inner hydration shell by establishing a bond to the zinc central ion. Introduction of 3,4-DAT to the coordination sphere of the aqua-ion increases the rate of displacement of the remaining water molecules.

It was pointed out that dehydration of the zinc hydrocomplexes becomes the rate-determining step of Zn(II) reduction. Labilization of the hydration sphere plays a key role in all ligand catalysed reductions of metal ions<sup>34</sup>. As 3,4-DAT forms a complex with zinc on the electrode surface, it displaces coordinated water, which proceeds gradually with increasing 3,4-DAT concentration in the solution. This reaction occurs preferentially at the electrode surface where the local 3,4-DAT concentration is rised due to adsorption. It was found that 2,4- and 2,6-DAT inhibit the electroreduction of Zn(II) ions in acetate buffers. Such behaviour is a primary consequence of blocking the electrode surface by these isomers. It should be noted that the differences in catalytic activity of these isomers result mainly from their complex formation properties. The presence of amine groups in 3,4-DAT in *ortho*-position creates optimum conditions for the formation of stable complex connections, whereas there are no significant differences in adsorption of the studied isomers on the mercury electrode.

The active complexes participate probably in consecutive electron transfer process. Nevertheless, it seems that the composition of these complexes is diversified, which follows from the Marcus theory predicting the change of ion sheath after partial loss of charge. The rate of the second electron transfer is also associated with the availability of electrode surface, which is very important in the amalgam formation. At pH 3 the two nitrogen atoms in the amino groups of 3,4-DAT are protonated, and hence no complexation can take place with the Zn(II) ions. The presence of DAT at the electrode surface under that condition can only hinder the electron transfer. With buffers of higher pH the complex formation proceeds up to the point when the electrode surface is completely covered by the adsorbed ligand, which then turns into a hindering surfactant.

Comparing the influence of 3,4-DAT on the electroreduction of Zn(II) ions in 1 mol dm<sup>-3</sup> NaClO<sub>4</sub> acidified by 0.001 mol dm<sup>-3</sup> HClO<sub>4</sub> and in the acetate buffer, it should be pointed that the process rate is higher in perchlorates, also in solutions without 3,4-DAT (ref.<sup>35</sup>). This is probably associated with stronger adsorption of acetate ions on the mercury compared with the adsorption of perchlorate ions.

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