

Effect of diaminotoluene isomers on Zn(II) ions
electroreduction in the perchlorate solutions at varied water
activities

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The reduction of Zn(II) ions in the presence of the diaminotoluene isomers has been studied in the perchlorate solutions at varied water activity.

The hydration number of the Zn(II) ions in the solutions was obtained from the shift of $E_{1/2}$ with water activity.

The results obtained allow to isolate the following stages in the mechanism of catalytic action of the diaminotoluene isomers on the Zn(II) ions electroreduction in sodium perchlorate:

- fast dehydration of Zn(II) ions and formation of the active complex Zn(II) – diaminotoluene,
- slow transfer of the first electron,
- fast loss of the remaining water molecules and formation of the active complex Zn(I) – diaminotoluene,
- slow transfer of the second electron.

1. INTRODUCTION

Biologically zinc is one of the most important metals. Its enzymes are present in a great number of body cells and the hydrolysis of zinc ions might significantly influence their activity. Hydrolytic reactions may also influence other reactions of zinc ions in water solutions, particularly those which are conducted at low acidity. Therefore some additional data on zinc ions

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electroreduction in solution at varied water activities and also in the presence of organic substances would be useful for both fields inorganic – and biochemistry.

Various workers have reported the effect of non-complexing electrolyte concentration on the kinetic parameters of the electrode reaction of zinc ions. In several papers [1-7] the observed increase in the reaction rate with dilution of supporting electrolyte was interpreted on the basis of the Frumkin theory [8] as an effect of the increased potential drop across the diffuse double layer.

Aramata et al. [3] and Tanaka et al. [9] from their studies in 0.1 – 1.0 mol dm⁻³ NaClO₄ concluded that change in the concentration of supporting electrolyte varies the value of the standard rate constant even after correction of the Frumkin type is made. However in the case of concentrated supporting electrolyte solutions the results have indicated a slight increase in the reduction rate with concentration [4-7,10,11].

Jindal et al. [12] studied the electrochemical kinetic parameters for the reduction of Zn(II) ions in concentrated supporting electrolytes consisting of sodium, ammonium, lithium, magnesium nitrates and sodium perchlorate. The rate parameter decreases with increase of radius of the alkali-metal cations present in the electrolyte and with increase of the cation charge of the electrolytes in solution of the same ionic strength. It also decreases, passes through a minimum and then increases with the increase in the concentration of any of the supporting electrolytes. The initial decrease is ascribed to the Frumkin double layer effect but the latter increase has been explained in terms of the change in the activity of water around the electrode.

Andreu et al. [13] studied electroreduction of Zn(II) ions in NaClO₄ at varied water activity. They concluded that the Zn(II) reduction proceeds according to a CECE mechanism, where C stands for a fast desolvation step and E for a rate-determining electron transfer. It was also found that identifying the reaction plane with the outer Helmholtz plane led to an overestimation of the Frumkin correction and that supposing the reaction plane to be situated 0.28 nm more remote from the electrode gave a good result.

The electroreduction of Zn(II) ions is accelerated by the presence of adsorbed nonelectroactive species [14-19]. The catalytic organic substance always contains sulfur or nitrogen atoms with electron pairs capable of forming coordinate bonds. In the mechanism of organic substance catalytic action on the Zn(II) ions electroreduction process it is assumed that the catalyzing organic substance forms on the electrode surface complexes with Zn(II) ions which intermediate in the transfer of electrons.

A direct detection of substitution reaction of active complexes is impossible due to its greater rate compared with the electron transfer rate. If the constant of Zn(II) ions dehydration rate is comparable with the constant of Cd(II) ions dehydration rate which is 1.43 cm⁻¹, then individual stages of the electron

transfer are almost 1000 and 100 times more slowly [20]. The evidence for formation of Zn(II) ions complexes with the catalyzing substance on the electrode surface is the rectilinear dependence of the constants of Zn(II) ions electroreduction rate on the surface excesses of the catalyzing substances [21]. The evidence for formation of active Zn(II) – catalyzing substance complexes can be also reduction of Zn(II) ions hydration number in the presence of the catalyzing substance.

This paper presents the studies of the effect of 2,6-, 2,4- and 3,4-diaminotoluene (2,6-DAT; 2,4-DAT; 3,4-DAT) on Zn(II) ions electroreduction in NaClO₄ solution at varied water activity with the aim of better understanding the reaction mechanism and nature of the catalytic effect.

2. EXPERIMENTAL

The measurements were performed using a three-electrode cell containing a dropping or static mercury electrode, a saturated calomel electrode with NaCl (SSCE) and a 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 double-distilled water and Fluka p.a. chemicals. The solution of $1 \cdot 10^{-3}$ mol dm⁻³ Zn(II) was prepared by dissolving ZnO in a small excess of perchloric acid. The supporting electrolyte was 1 - 5 mol dm⁻³ NaClO₄ and special care was taken that the pH of the solutions was close to 5. Analytical reagents grade 2,6-DAT; 2,4-DAT and 3,4-DAT (Aldrich) were used without further purification. The concentrations of DAT were chosen to be 1,5 and $10 \cdot 10^{-3}$ mol dm⁻³. Only freshly prepared solutions of DAT were used. The solutions were deaerated using nitrogen which had been passed through a vanadous sulfate solution and presaturated with the investigated solution. This gas was passed over the solution during the measurements. Measurements were carried out at 298 ± 1 K.

The impedance measurements were carried out with the Atlas-Sollich (Gdańsk, Poland) 9121 FR Analyzer and the 9131 Electrochemical Interface. DC polarograms were obtained using a PA-4 polarograph by Laboratorni Pstroje (Prague, Czech). Cyclic chronovoltammetric curves were taken using Model 270 analysis system AG & G PARC employing a static mercury drop electrode manufactured by Laboratorni Pstroje.

3. RESULTS AND DISCUSSION

The diffusion coefficients D_0 of Zn(II) ions and the reversible half wave potentials $E_{1/2r}$ of the reduction of Zn(II) ions. The electroreduction of Zn(II) ions at a mercury electrode in the 1 – 5 mol dm⁻³ solution of NaClO₄ with the addition of 2,6-DAT; 2,4-DAT or 3,4-DAT results in a single well defined DC polarographic wave. From the limiting current in the DC polarograms the diffusion coefficient D_0 of Zn(II) ions was derived. The details are described elsewhere [22]. The diffusion coefficient $D_R = 1.67 \cdot 10^{-5}$ cm² s⁻¹ for Zn in mercury was selected from literature [23].

By extrapolation of the reversible part of the wave to $\ln[I/I_d - I] = 0$ in the $\ln[I/I_d - I]$ vs E plot [1] was obtained a first estimate of $E_{1/2r}$. $E_{1/2r}$ were estimated from cyclic voltammetric curves [24] at a polarization rate of 0.005 – 0.02 V s⁻¹ with the reproducibility of ± 0.002 V. The optimal values of $E_{1/2r}$ were selected from the DC potential dependence of charge – transfer resistance [25]. Table 1 presents D_0 values of Zn(II) ions and $E_{1/2r}$ of Zn(II) ions electroreduction in 1 – 5 mol dm⁻³ NaClO₄. These values are in good agreement with literature data [13]. The values of D_0 and $E_{1/2r}$ obtained at various isomers DAT concentrations are tabulated in Table 2. The values of Zn(II) ion diffusion coefficients in the presence of isomers DAT are smaller than the values for NaClO₄. With a concentration increase of isomers DAT the values of $E_{1/2r}$ are shifted towards positive potentials in 1 and 2 mol dm⁻³ NaClO₄. In 3 – 5 mol·dm⁻³ NaClO₄ the values of $E_{1/2r}$ are shifted towards negative potentials which is 6 – 24 mV at 0.010 mol·dm⁻³ DAT in 5 mol·dm⁻³ NaClO₄. Small changes of $E_{1/2r}$ show lack of stable Zn(II) complexes in the solution.

Tab. 1. Values of the water activity (a_w)^x diffusion coefficients (D_0) and reversible half wave potentials ($E_{1/2r}$) of Zn(II) ions in 1 – 5 mol dm⁻³ NaClO₄

Concentration NaClO ₄ (mol dm ⁻³)	a_w	$10^6 D_0$ (cm ² s ⁻¹)	$-E_{1/2r}$ (V)
1	0.966	6.5	0.986
2	0.928	6.1	0.975
3	0.885	5.5	0.959
4	0.834	5.1	0.948
5	0.776	4.6	0.930

x Values of the water activity (a_w) were taken from literature [26,27]

Tab. 2. Values of diffusion coefficients (D_o), reversible half wave potentials ($E_{1/2r}$) of Zn(II) ions in 1 – 5 mol dm⁻³ NaClO₄ at the applied concentrations of DAT isomers

	$10^6 D_o$ (cm s ⁻¹)	$-E_{1/2r}$ (V)	$10^6 D_o$ (cm s ⁻¹)	$-E_{1/2r}$ (V)	$10^6 D_o$ (cm s ⁻¹)	$-E_{1/2r}$ (V)
Concentration (mol dm ⁻³)	0.001		0.005		0.010	
NaClO ₄	2,6 DAT					
1	6.0	0.982	5.9	0.979	5.7	0.980
2	5.3	0.973	5.1	0.970	5.3	0.970
3	4.9	0.961	4.7	0.961	4.9	0.961
4	4.5	0.948	4.4	0.950	4.3	0.950
5	4.3	0.932	4.2	0.937	4.1	0.936
	2,4 DAT					
1	6.2	0.979	6.1	0.975	6.0	0.970
2	5.2	0.971	5.2	0.967	5.1	0.965
3	5.1	0.960	4.9	0.958	4.8	0.957
4	4.5	0.947	4.3	0.947	4.2	0.948
5	4.4	0.932	4.1	0.934	4.2	0.936
	3,4 DAT					
1	5.9	0.986	5.8	0.982	5.8	0.981
2	5.2	0.978	5.0	0.976	4.9	0.976
3	4.9	0.970	4.8	0.969	4.6	0.970
4	4.6	0.959	4.5	0.959	4.2	0.962
5	4.2	0.948	4.2	0.949	4.1	0.954

Determination of Zn(II) ions hydration numbers. For the quasireversible reduction of Zn(II) ions on the mercury electrode



The electrode potential is described by the dependence

$$E = E_f^\circ + \frac{RT}{nF} \ln \frac{a_{\text{Zn(II)}}}{a_{\text{Zn}}(a_w)^m} \quad (2)$$

where

$$E_f^\circ = E_{1/2r} + \frac{RT}{nF} \ln \left(\frac{D_o}{D_R} \right)^{1/2} \quad (3)$$

$a_{\text{Zn(II)}}$ is the activity of Zn(II) ion in the solution,

a_{Zn} is the activity of zinc in the amalgam,

a_w is the activity of water in the solution.

At the constant relation $a_{\text{Zn(II)}}/a_{\text{Zn}}$ the dependence $E_f^0 = f(\ln a_w)$ is a straight line of the $-m RT/nF$ inclination. The determined hydration number of Zn(II) ions in $1 - 5 \text{ mol dm}^{-3} \text{ NaClO}_4$ is 19.4. This value is in agreement with the hydration number determined by Andreu et al. [13] as well as Stokes and Robinson [26]. Table 3 presents the hydration numbers of Zn(II) ions in $1 - 5 \text{ mol} \cdot \text{dm}^{-3} \text{ NaClO}_4$ in the presence of the studied isomers DAT. The addition of $0.005 - 0.01 \text{ mol dm}^{-3}$ isomers DAT to the NaClO_4 solutions does not affect density. It is assumed that the isomers DAT in the range of studied concentrations do not affect water activity in the perchlorate solutions.

Tab. 3. The hydration number of the Zn(II) ions in $1 - 5 \text{ mol dm}^{-3} \text{ NaClO}_4$ at varied concentrations of the DAT isomers

Concentration of DAT (mol dm^{-3})	Hydration number			
	0	0.001	0.005	0.010
2,6 DAT	19.4	17.1	16.3	15.6
2,4 DAT	19.4	16.4	15.0	14.1
3,4 DAT	19.4	14.0	11.7	9.7

As follows from Table 3 Zn(II) ions hydration numbers decrease with the increase of the isomers DAT concentration. Activity of the isomers DAT in the decrease of Zn(II) ions hydration number increases in the series 2,6-DAT; 2,4-DAT; 3,4-DAT and it is undoubtedly connected with their complexing properties.

The rate of electroreduction of Zn(II) ions in $1 - 5 \text{ mol dm}^{-3} \text{ NaClO}_4$ in the presence of $0.005 \text{ mol dm}^{-3}$ isomers of DAT. The complex impedance data were collected at 21 frequencies in the range $200 - 50\,000 \text{ Hz}$ within the faradaic potential region with 10 mV intervals. The frequency analysis was performed in the usual way [25]. The values of the apparent rate constant k_f were obtained from the charge – transfer resistance. The details are described elsewhere [16,17].

The values of the apparent rate constants of electroreduction of Zn(II) ions in $1 - 5 \text{ mol dm}^{-3} \text{ NaClO}_4$ in the presence of $0.005 \text{ mol dm}^{-3}$ isomers of DAT plotted as $\ln k_f$ as a function of the potential E are presented in Figures 1 – 3.

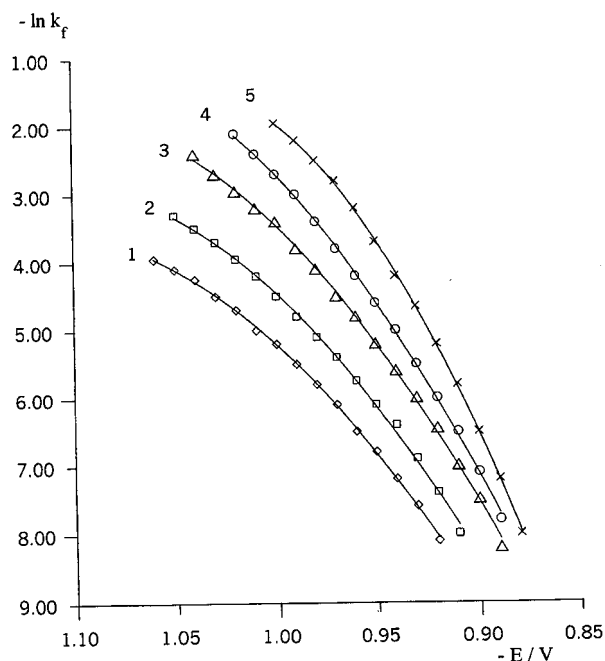


Fig. 1. The potential dependence of the apparent rate constant of the Zn(II) reduction in NaClO_4 in the presence of $0.005 \text{ mol dm}^{-3}$ 2,6-diaminotoluene. The molarity of NaClO_4 is indicated with each curve

From the curves in Figures 1 – 3 it follows:

- the dependences $\ln k_f = f(E)$ are not rectilinear and the slope of the curves changes with the potential and the concentrations of NaClO_4 ,
- the values k_f increase with the increasing concentration of NaClO_4 (decreasing of water activity).

The general shape of these plots is difficult to explain in terms of a single-step electrode reaction. Such a course of the dependences $k_f = f(E)$ indicates a multistage character of Zn(II) ions reduction in NaClO_4 in the presence of the DAT isomers.

These stages must include:

- charge transfer steps in which there are exchanged single electron between the electrode and the reactant without modification of the coordination shell,
- chemical stages connected with the change of interactions with water, sodium perchlorate, DAT isomers or electrode excluding the charge transfer,
- displacement through the electric field of the interphase.

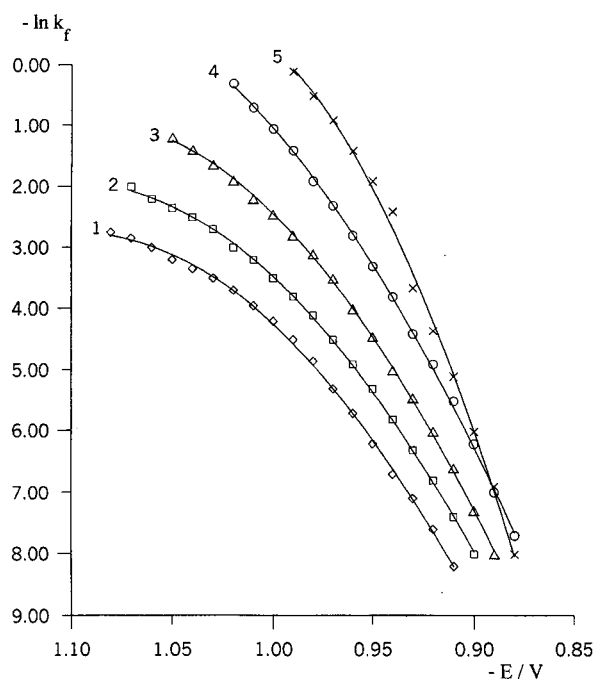


Fig. 2. The potential dependence of the apparent rate constant of the Zn(II) reduction in NaClO_4 in the presence of $0.005 \text{ mol dm}^{-3}$ 2,4-diaminotoluene. The molarity of NaClO_4 is indicated with each curve

Assuming that the charge transfer proceeds via two consecutive one-electron transfer steps [13,29] the first electron transfer is rate determining $k_f = k_1$ at the most negative potentials. At more positive potentials the overall rate is determined by both steps simultaneously

$$\frac{1}{k_f} = \frac{1}{k_1} + \frac{K_1}{k_2} \quad (4)$$

Figures 3 and 4 present individual rate constants of Zn(II) ions electroreduction extrapolated to the E_f^0 plotted against the water activity.

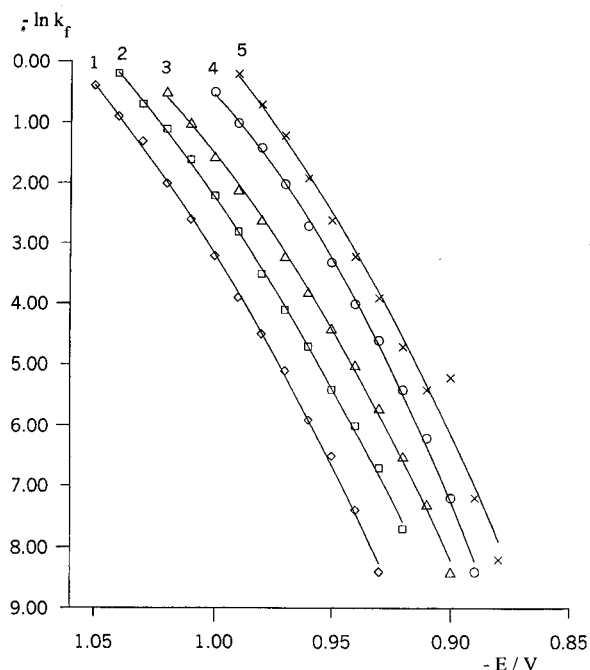


Fig. 3. The potential dependence of the apparent rate constant of the Zn(II) reduction in NaClO_4 in the presence of $0.005 \text{ mol dm}^{-3}$ 3,4-diaminotoluene. The molarity of NaClO_4 is indicated with each curve

The sharp rise of $\ln k_{s1}$ and k_{s2} on dilution can be explained in terms of the Frumkin effect [3,10,12], while its increase in a concentration range where the diffuse layer must be strongly compressed (and thus the Frumkin effect is of minor influence) indicates the presence of a preceding dehydration step [6,7,12].

It appears that the k_{s1} and k_{s2} values trends to a constant value independent of electrolyte concentration. The course of these dependences suggests that most hydration water is removed before transfer of the second electron. The earlier studies showed that the values k_{s1} and k_{s2} increase with the increasing concentration of the studied DAT isomers [18] and the rate constants are a linear function of the surface excesses [17,22]. This indicates formation of active complexes on the electrode surface making the electron transfer easier. Lack of the data concerning adsorption of the DAT isomers on mercury does not allow to estimate the potential of the reaction plane and to determine the true rate constants. It is possible only to predict that the reaction planes for transfer of successive electrons do not coincide with OHP.

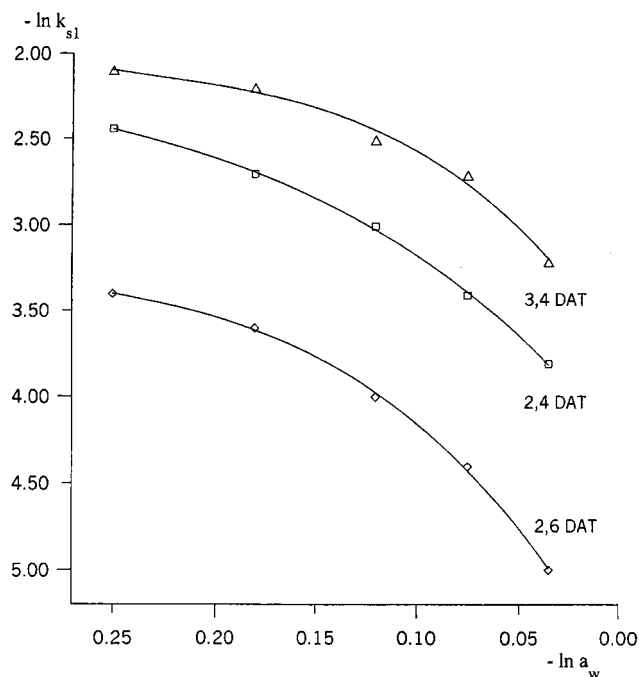


Fig. 4. The individual standard rate constants k_{s1} of the Zn(II) reduction in NaClO_4 in the presence of $0.005 \text{ mol dm}^{-3}$ 2,6-; 2,4- or 3,4-diaminotoluene plotted against the water activities

The studies allow to isolate the following stages in the mechanism of catalytic action of the DAT isomers on the Zn(II) ions electroreduction in sodium perchlorate:

- fast dehydration of Zn(II) ions and formation of the active complex Zn(II) – DAT,
- slow transfer of the first electron,
- fast loss of the remaining water molecules and formation of the active complex Zn(I) – DAT,
- slow transfer of the second electron.

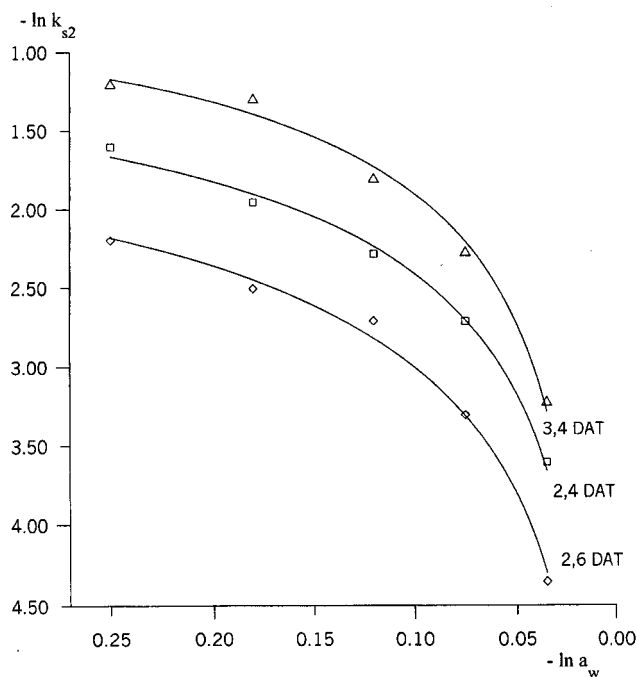


Fig. 5. The individual standard rate constants k_{s2} of the Zn(II) reduction in NaClO_4 in the presence of $0.005 \text{ mol dm}^{-3}$ 2,6-; 2,4- or 3,4-diaminotoluene plotted against the water activities

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