

Catalytic Effect of 2,4- or 2,6-Diaminotoluene on the Electrochemical Reduction of Zinc(II) Ions

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Adsorption of 2,4 and 2,6-diaminotoluene on the mercury/1 mol dm⁻³ NaClO₄ interface was examined. The differential capacity, potential of zero charge of mercury and the interfacial tension at PZC were measured. Surface concentrations were calculated on the basis of these measurements.

Rate constants of Zn(II) ion electroreduction in 1 mol dm⁻³ NaClO₄ in the presence of 2,4- and 2,6-diaminotoluene were determined by a cyclic voltammetry method. The catalytic activity of 2,4-diaminotoluene was found to be much higher than that of 2,6-diaminotoluene due to different orientation of these isomers on the electrode surface. From the temperature dependence of rate constants, the enthalpies of activation of zinc electroreduction $\Delta H^\ddagger = 16.3 \text{ kJ mol}^{-1}$ in the presence of 2,6-diaminotoluene and $\Delta H^\ddagger \cong 0$ in the presence of 2,4-diaminotoluene were determined.

INTRODUCTION

It is widely known that the electroreduction of many metal ions at a mercury electrode is accelerated by the presence of adsorbed nonelectroactive species.¹⁻¹²

Two phenomena: the labile adsorption of the accelerating substance and the active complex generated on the electrode surface are simultaneously responsible for the catalytic effect.^{13,14,15}

Studies of the effect of toluene amino derivatives on the polarographic reduction of Zn(II) showed that toluidine and diaminotoluene isomers increased sw peaks of Zn(II) reduction in 1 mol dm⁻³ NaClO₄.¹⁶ As it follows from literature,^{17,18} various situations of -NH₂ group in the toluidine mole-

cule affect only insignificantly the adsorption properties. However, it was stated that *p*-toluidine showed almost twice greater catalytic activity on electroreduction of Zn(II) ions than *m*-toluidine, which was due to a more favourable distribution of the free-electron density in the *p*-toluidine molecule for complex generation.¹⁹

The aim of the paper is to investigate 2,4 and 2,6-diaminotoluene adsorption at the mercury/1 mol dm⁻³ NaClO₄ interface and to explain the effect of these substances on the mechanism and kinetics of Zn (II) ion electroreduction.

EXPERIMENTAL

Polarographic measurements were carried out using a PA-4 polarograph (Laboratori Pristroje).

A static mercury drop electrode (Laboratori Pristroje) (for the hanging electrode the drop surface was 0.01827 cm²) was used. The reference electrode was a saturated calomel electrode with NaCl (SSCE) or Ag/AgCl and the platinum spiral was used as an auxiliary electrode. The reference electrode was connected to the cell *via* a salt bridge filled with the cell solution. The potentials were referred to the SSCE. The differential capacity of the double layer was calculated from the data obtained at the frequency of 800 Hz with an impedance meter EIM-2 (manufactured by the Łódź University) with on-line computer control. A dropping mercury electrode constructed according to Randles²⁰ was used. The balance of the bridge was achieved after 6 s of drop growth. The time was 8 s and the flow rate 0.762 mg s⁻¹ at a mercury column height of 50 cm. The reproducibility of the average capacity measurements was ± 1% over a wide range of potentials. For the whole polarization range, the capacity dispersion was tested at five different frequencies between 295 and 1900 Hz. A small frequency dispersion occurred at potentials more positive than -0.5 V.

The potential of zero charge (PZC) was measured for each solution using the streaming mercury electrode.^{21,22} Interfacial tension at PZC was measured by the maximum bubble pressure following Schiffrin's method.²³

The kinetic parameters were determined using the cyclic voltammetric technique over a wide range of sweep rates (0.005 – 20 V s⁻¹) with a precision of ± 7% employing a Model 270 Electrochemical Analysis System (EG & G PAR). In addition to the kinetic studies on zinc(II) reduction, its coadsorption on the electrode was investigated by a single-step chronocoulometric method.

High-purity reagent grade (Merck) Zn(NO₃)₂ · 6H₂O was used. The Zn(II) concentration in the solutions was always 0.005 mol dm⁻³ and that of NaClO₄ 1 mol dm⁻³. The pH of 0.005 mol dm⁻³ Zn(II) in 1 mol dm⁻³ NaClO₄ solutions was adjusted to 5.2 by addition of concentrated HClO₄. The pH was measured with a pH-meter, type N 5122, Mera Elwro.

Analytical reagents grade 2,4-diaminotoluene (2,4 DAT) and 2,6-diaminotoluene (2,6 DAT) (Fluka) were used without further purification.

Measurements were made for eleven concentrations of 2,4 DAT or 2,6 DAT between 0.0005 mol dm⁻³ and 0.05 mol dm⁻³.

Solutions were deaerated using nitrogen which had been passed through a vanadous sulphate 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.

RESULTS AND DISCUSSION

Studies of 2,4 and 2,6 DAT Adsorption at the Mercury/1 mol dm⁻³ NaClO₄ Interface

Curves of the differential capacitance as a function of potential for five concentrations of 2,4 DAT and 2,6 DAT in 1 mol dm⁻³ NaClO₄ are shown in Figures 1, 2 and the coordinates of the PZC are given in Table I. The chief feature is a not large lowering of differential capacity from its value in the base electrolyte in the vicinity of maximum adsorption. At the zinc reduction potential, addition of 2,4 DAT or 2,6 DAT $c < 0.01$ mol dm⁻³ to the investigated solutions caused an increase in the differential capacity of the double layer; in the presence of higher concentrations of these isomers, a decrease of differential capacitance was observed. The curves of differential capacitance for 2,4 DAT and 2,6 DAT differ insignificantly.

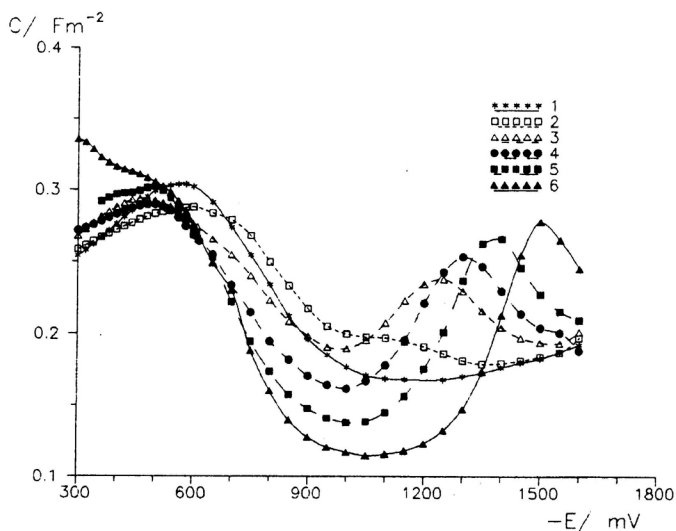


Figure 1. Differential capacitance of a mercury electrode in contact with 1 mol dm⁻³ NaClO₄ containing 2,4 DAT concentrations/mol dm⁻³. 1) 0; 2) 0.001; 3) 0.005; 4) 0.01; 5) 0.02; 6) 0.05.

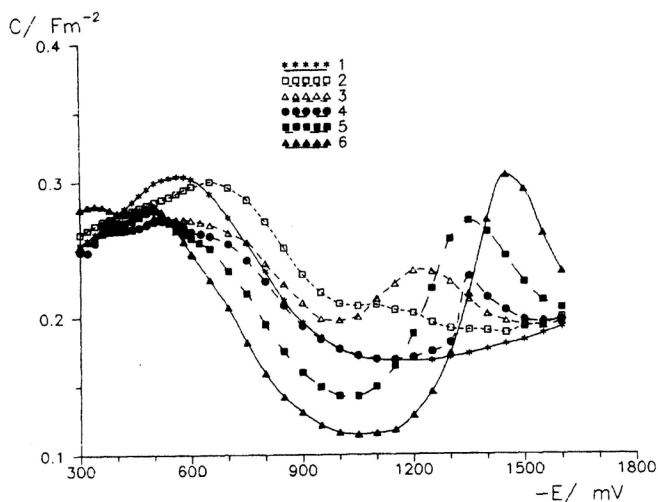


Figure 2. Differential capacitance of a mercury electrode in contact with 1 mol dm^{-3} NaClO_4 containing 2,6 DAT concentrations/ mol dm^{-3} . 1) 0; 2) 0.001; 3) 0.005; 4) 0.01; 5) 0.02; 6) 0.05.

The capacity curves were integrated twice and then differentiated with respect to the \ln of the concentration of DAT using a computer program similar to that described by Lawrence *et al.*²⁴ The corresponding adsorption isotherms are shown in Figures 3 and 4. The slope of the isotherms in-

TABLE I

Parameters of the PZC for solutions of 2,4 DAT or 2,6 DAT in 1 mol dm^{-3} NaClO_4

$c/\text{mol dm}^{-3}$	$-E_z/V$		$\gamma_{E_z}/\text{mN m}^{-1}$	
	2,4 DAT	2,6 DAT	2,4 DAT	2,6 DAT
0.0005	0.589	0.589	413.2	408.3
0.0010	0.600	0.600	408.3	404.6
0.0020	0.604	0.614	407.7	400.9
0.0050	0.610	0.625	404.0	397.9
0.0080	0.613	0.626	397.2	394.2
0.010	0.614	0.626	396.0	392.3
0.015	0.613	0.625	394.2	389.9
0.020	0.608	0.622	391.1	388.0
0.030	0.600	0.616	387.4	385.0
0.040	0.594	0.611	385.0	382.5
0.050	0.590	0.603	383.1	380.0

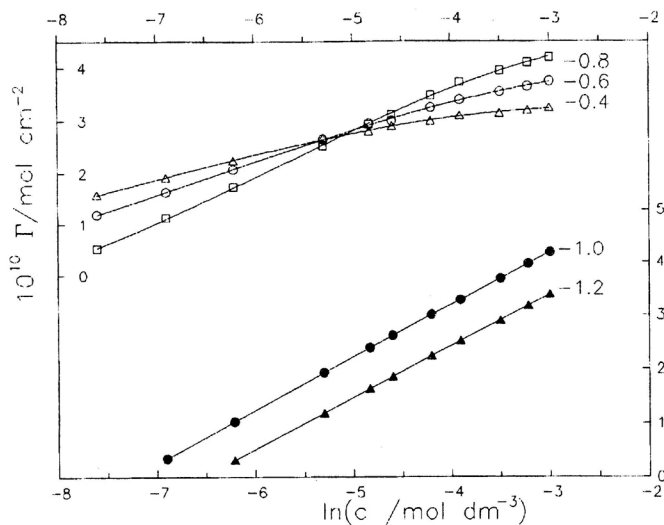


Figure 3. Surface concentration Γ of 2,4 DAT as a function of \ln concentration at constant electrode potential. The curves at potentials more positive than -0.8 V are displaced vertically for clarity.

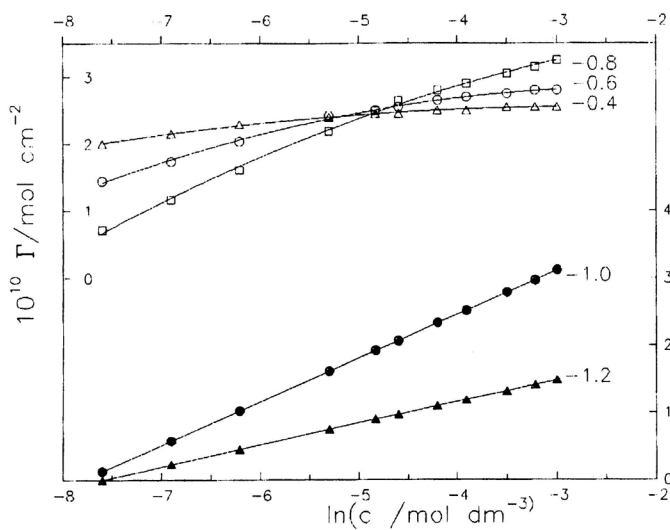


Figure 4. Surface concentration Γ of 2,6 DAT as a function of \ln concentration at constant electrode potential. The curves at potentials more positive than -0.8 V are displaced vertically for clarity.

creases with an increasing potential up to the region of the adsorption maxima, where it appears to become flatter, though it is in this region that the results are more dubious owing to the steep rise of the capacity curves, the possibility of coadsorption of the perchlorate ion.

In the potential range of Zn(II) reduction, surface concentrations of 2,4 DAT are larger than those of 2,6 DAT.

Table I includes the values of the PZC as well as the values of surface tension at PZC for $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ in the presence of various concentrations of 2,4 and 2,6 DAT. For dilute solutions of 2,4 or 2,6 DAT, the PZC shifts towards negative potentials, which is a regularity observed for aromatic compounds. This can be explained by the interaction between π electrons of evenly arranged rings and the mercury surface. At sufficiently high concentrations of 2,4 or 2,6 DAT, the molecules take a more vertical position and weaker interactions of π electrons with the mercury surface cause a shift of PZC towards the positive side. 2,6 DAT decreases the surface tension at PZC more than 2,4 DAT at the same concentration. This may be related to stronger mutual interactions between 2,6 DAT molecules adsorbed on mercury.

Chronocoulometric Search for Zn(II) Coadsorption

To find out whether or not Zn(II) can be accumulated in the surface layer by interaction with the adsorbed DAT molecules, chronocoulometric measurements of the maximal charge (Q_d) of Zn(II) electroreduction as a function of the integration time (t_p) were carried out in $0.005 \text{ mol dm}^{-3}$ 2,4 DAT or 2,6 DAT in $1 \text{ mol dm}^{-3} \text{ NaClO}_4$. The Q_d of Zn(II) electroreduction was measured at the potential equal to -1.05 V . The plot of Q_d versus $t_p^{1/2}$ was linear and crossed the origin of coordinates after subtraction of the double layer charge recorded for blank solutions. This indicates that under such conditions, the cathodic reduction of Zn(II) is limited by diffusion and the induced adsorption of Zn(II), if any, is within the limits of experimental error.

Studies of the Kinetics of Zn(II) Ion Reduction in $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ in the Presence of 2,4 DAT or 2,6 DAT

The approximate diffusion coefficients of Zn(II) in the examined solutions were calculated using the Ilkovic equation for a diffusion – controlled limiting current. The polarographic wave of Zn(II) in $0.1 \text{ mol dm}^{-3} \text{ KNO}_3$ with the value of the Zn(II) diffusion coefficient $D_{\text{ox}} = 6.9 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 298 K given in the literature²⁵ being used as a standard. The reproducibility of the results obtained was $\pm 5\%$. The values of Zn(II) ion diffusion coefficients in the presence of 2,4 DAT or 2,6 DAT ($0 < c < 0.05 \text{ mol dm}^{-3}$) are

minimally smaller than the values for $1 \text{ mol dm}^{-3} \text{ NaClO}_4$, and the change in the range $6.6 + 5.9 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The diffusion coefficients of zinc in mercury, required for the kinetic calculations, were taken from the literature.²⁶

The formal potentials E_f° of the reduction of Zn(II) were estimated from cyclic voltammetric curves²⁷ with reproducibility $\pm 0.002 \text{ V}$ using the sweep rates $0.005 - 0.02 \text{ V s}^{-1}$. The formal potential E_f° of Zn(II) ions in $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ was found to be -0.991 V . With a concentration increase of 2,4 DAT or 2,6 DAT, the values of E_f° are shifted towards positive potentials which is 10 mV at maximum concentrations. Small changes of E_f° show lack of Zn(II) stable complexes in the solution.

The standard rate constants of Zn(II) ions reduction were calculated from cyclic voltammetric measurements by the method described by Nicholson.²⁸ The cathodic transfer coefficient for the quasireversible process was determined on the basis of the dependence of the formal values αn_α on $1/\nu$.²⁷ The cathodic transfer coefficient for electroreduction Zn(II) ions increased with the concentration of the studied isomers from 0.23 to 0.29 in the presence of 0.05 mol dm^{-3} 2,6 DAT and 0.43 in the presence of 0.05 mol dm^{-3} 2,4 DAT.

Figure 5 presents the dependence of the standard rate constant k_s of Zn(II) ions reduction on the surface concentration of 2,4 DAT or 2,6 DAT at the formal potential.

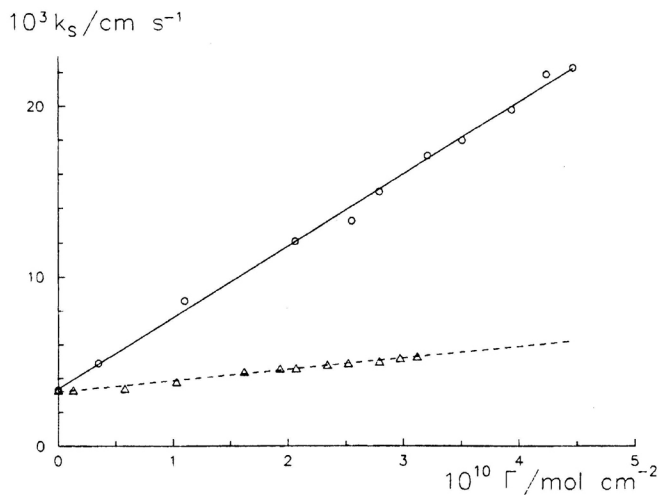


Figure 5. Dependence of standard rate constants for the Zn(Hg)/Zn(II) couple on surface concentration of 2,4 DAT (solid line) and 2,6 DAT (dotted line) at the formal potential.

A linear relationship between the rate constant of an electrochemical reaction and the surface concentration of some adsorbed species could be interpreted in terms of the so-called bridging model,¹ in which it is assumed that the adsorbed species facilitates the transfer of electrons across the inner layer.

k_s values of Zn(II) ion electroreduction in the presence 2,4 DAT or 2,6 DAT change according to:

$$k_s = k_s^0 + A\Gamma_{\text{Ef}} \quad (1)$$

where k_s^0 is the standard rate constant of Zn(II) ion electroreduction in 1 mol dm^{-3} NaClO_4 ; Γ_{Ef} is the surface concentration of 2,4 DAT or 2,6 DAT at the formal potential. The values of A equal $42.5 \cdot 10^6$ and $6.3 \cdot 10^6$ for 2,4 DAT and 2,6 DAT, respectively. They represent a comparative measure of catalytic activities of these isomers.

The catalytic activity of 2,4 DAT is higher than that of 2,6 DAT. Indeed, adsorption of 2,4 DAT in the range of Zn(II) reduction potentials is slightly greater but it is not likely that it would cause such catalytic activity differentiation. Possibilities of various vertical arrangements of 2,4 and 2,6 DAT molecules on the electrode surface should be taken into account. Undoubtedly, 2,4 DAT molecules are oriented with a hydrophobic group towards the electrode. Surrounding the $-\text{CH}_3$ group with two hydrophilic $-\text{NH}_2$ groups points to the situation of 2,6 DAT molecule with these groups towards the solution. Such extremely different situations of 2,4 and 2,6 DAT molecules can be responsible for their different catalytic activity.

Temperature changes of the rate constants of Zn(II) ions electroreduction in the presence of $0.005 \text{ mol dm}^{-3}$ 2,4 or 2,6 DAT in the range 290 – 328 K were studied. The results are collected in Table II. From the temperature dependence of rate constants, the enthalpies of ΔH^\ddagger were determined from the relationship.²⁹

TABLE II

Temperature dependence of the standard rate constant of Zn(II) electroreduction in 1 mol dm^{-3} NaClO_4 + $0.005 \text{ mol dm}^{-3}$ 2,4 or 2,6 DAT

Temperature/K	$\log k_s/\text{cm s}^{-1}$	
	2,4 DAT	2,6 DAT
290	-1.96	-2.51
298	-1.92	-2.36
308	-1.94	-2.29
318	-1.95	-2.21
328	-1.97	-2.12

$$\Delta H^\ddagger = R \frac{d \ln k_s}{d \frac{1}{T}} \quad (2)$$

For electroreduction of Zn(II) in 1 mol dm⁻³ NaClO₄ in the presence of 0.005 mol dm⁻³ 2,6 DAT $\Delta H^\ddagger = 16.3 \text{ kJ mol}^{-1}$ but in the presence of 0.005 mol dm⁻³ 2,4 DAT $\Delta H^\ddagger \cong 0$.

The enthalpies of activation are apparent values, because, if catalysis by the adsorbed species does occur, there will be a contribution from the temperature dependence of the amount adsorbed and possibly of the orientation effect.

Hush *et al.*³⁰ determined ΔH^\ddagger for Zn(II) electroreduction at the Hg electrode at various concentrations of NaClO₄. They found that it was constant and equal to 42 kJ mol⁻¹.

The decrease of energy activation confirms the DAT catalytic activity. DAT molecules adsorbed on the electrode react much stronger with Zn(II) ions than water molecules, forming an active complex undergoing reduction more readily than an aquaion.

Lack of temperature dependence of the rate constant for Zn(II) electroreduction in the presence of 2,4 DAT can be connected with the process under entropy control.

A similar effect was observed by Taraszewska *et al.*³¹ for Zn(II) reduction in H₂O + 0.9 mol dm⁻³ NaClO₄ + 20% DMSO mixture, which was accounted for by strong solvation of zinc ions in these mixtures as well as by Randles *et al.*³² for complexes of Cu(II) with ethylenediamine.

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SAŽETAK

Katalitički utjecaj 2,4- i 2,6-diaminotoluena na elektrokemijsku redukciju iona Zn(II)

Grażyna Dalmata

Istražena je adsorpcija 2,4- i 2,6-diaminotoluena na površinu živine elektrode u 1 M otopini NaClO₄. Površinska koncentracija adsorbiranih molekula izračunana je na osnovi mjerenja diferencijalnog kapaciteta, potencijala nultog naboja i površinske napetosti žive pri tom potencijalu. Cikličkom voltammetrijom izmjerene su konstante brzine elektoredukcije iona Zn(II) na živinoj elektrodi u 1 M otopini NaClO₄ u prisutnosti 2,4- i 2,6-diaminotoluena. Zbog različite orijentacije adsorbiranih molekula na površini elektrode, 2,4-diaminotoluen je katalitički mnogo aktivniji od 2,6-diaminotoluena. Na osnovi ovisnosti konstanti brzine o temperaturi, određene su aktivacijske entalpije elektoredukcije Zn(II) u prisutnosti 2,6-diaminotoluena ($\Delta H^\ddagger = 16.3$ kJ/mol) i 2,4-diaminotoluena ($\Delta H^\ddagger \cong 0$).