

KINETICS AND MECHANISM OF Zn(II) ION ELECTROREDUCTION IN THE PRESENCE OF VETRALAN

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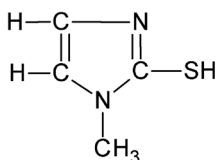
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The two-step reduction of Zn(II) ions at a dropping mercury electrode in 1 M NaClO₄ with addition of vetranal was examined using dc polarography, cyclic voltammetry and impedance measurements. Small changes of reversible potential of half-wave, $E_{1/2}^r$, values indicate that the Zn(II)–vetranal complexes formed in the solution are very unstable. A stepwise character of electron transfer in the Zn(II) ion reduction was established. The catalytic activity of vetranal is stronger in the first step of electron transfer than in the second one. The linear dependence of the true rate constant for the forward reaction, k_f' , of Zn(II) electroreduction versus relative surface excess, Γ' , of vetranal at a given potential in the reaction plane, Φ^f , was interpreted in terms of a “bridging model”.

Keywords: Catalytic activity; Zinc(II) electroreduction; Vetranal; Rate constants; Mercury electrode.

The electrochemical reduction of Zn(II) in NaClO₄ solution at the mercury electrode is one of the most frequently studied reactions in electrochemistry. It is known that the electroreduction of Zn(II) is accelerated by the presence of adsorbed nonelectroactive species containing sulfur atom^{1–9}. Presumably, in the acceleration process two simultaneous phenomena play an important role: the adsorption of an organic substance at the electrode surface and the formation of an active complex between the depolarizer ions and the organic substance adsorbed at the mercury electrode¹⁰. The electroreduction of Zn(II) at the mercury electrode is a typical example of a reaction controlled by both diffusion and charge transfer. Often, the kinetics of Zn(II) reduction is assumed to proceed simply via a simultaneous two-electron transfer described by only one rate constant. Andreu et al.¹¹ suggested a more complex mechanism of Zn(II) electroreduction in which two one-electron transfer steps were preceded by a partial desolvation of the re-

agents although the desolvation reactions were not rate-determining. Sodium perchlorate is a suitable base electrolyte because of its low tendency to form complexes and because the double layer data needed are available from the literature¹²⁻¹⁵. Vetranal (1-methylimidazole-2-thiol) is the thio-urea derivative.



Vetranal is a biologically active compound, which inhibits normal interactions of iodine and peroxidase with thyroglobulin to form thyroxine and triiodothyronine (two thyroid hormones). Vetranal is prescribed as a drug named methimazole, mainly to treat hyperthyroidism, but sometimes it causes severe side effects. It is interesting to find the influence of the cyclic structure of vetranal on the kinetics and mechanism of Zn(II) electroreduction at a mercury electrode in comparison with thiourea and its alkyl derivatives. The electroreduction of Zn(II) in 1 M NaClO₄ solution at a mercury electrode in the presence of vetranal is assumed 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 steps would change with the potential. Furthermore, as the reaction involves charged reactants in the double layer, double layer effects¹⁶ are expected to be important in these processes.

EXPERIMENTAL

The 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. The optimal accuracy was achieved by maintaining the Zn(II) ions concentration at around 0.005 M. Studies of the adsorption and catalytic activity were carried out at the vetranal concentration from 1×10^{-4} to 2.5×10^{-2} M in 1 M NaClO₄. Analytical grade reagents: vetranal (Sigma) and NaClO₄ (Fluka) were used without any purification. The solutions containing vetranal were prepared immediately before each measurement. Hydrolysis of Zn(II) was suppressed by maintaining the solutions used at pH 3. Water and mercury were distilled twice prior to use. All the measurements were carried out at 298 ± 0.1 K under nitrogen atmosphere. The solutions were deaerated prior to use with nitrogen.

Polarographic measurements and voltammetric experiments were performed employing the Autolab frequency response analyzer (Eco Chemie, Netherlands). The impedance measu-

rements were carried out with a 9121 FR analyzer and 9131 Electrochemical Interface (Atlas-Sollich, Gdańsk, Poland).

The complex impedance data were collected at 36 frequencies ranging from 100 to 100,000 Hz within the Faradaic potential region with 10 mV intervals. The ohmic resistance of the electrolyte solution was obtained at a potential outside the Faradaic region.

RESULTS

The electroreduction of Zn(II) at a mercury electrode in 1 M NaClO₄ in the presence of vetranal results in a single well-defined dc polarographic wave. Approximate diffusion coefficients of Zn(II) ion (D_{ox}) in the examined solutions were calculated using the Ilkovič equation for diffusion-controlled limiting current. The polarographic wave of Zn(II) in 0.1 M KNO₃ with a Zn(II) diffusion coefficient $D_{\text{ox}} = 6.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 298 K was used as a standard¹⁷. The analogous value for Zn in mercury $D_{\text{red}} = 1.67 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, was also selected from the literature¹⁸. The obtained D_{ox} values increase with an increase in vetranal concentration from 6.6×10^{-6} to $7.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The D_{ox} values were determined from the limiting current, which depends on the viscosity of solution, the composition of zinc aqua complex and on adsorption of vetranal. The reversible half-wave potentials, $E_{1/2}^r$, of the Zn(II) ion reduction were estimated from cyclic voltammetric curves with the reproducibility $\pm 0.002 \text{ V}$ using the sweep rates 0.005–0.1 V s⁻¹ and Eq. (1):

$$E_{1/2}^r = \frac{E_{\text{pc}} + E_{\text{pa}}}{2} \quad (1)$$

where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively.

Figure 1 shows voltammetric curves of the Zn(II) electroreduction in 1 M NaClO₄ with addition of vetranal. The values of cathodic peak potentials of Zn(II) shift to 29 mV towards less negative potentials with increased vetranal concentration. Simultaneously, potentials of anodic peak shift to 12 mV towards more negative potentials. The potential difference $\Delta E = E_{\text{pa}} - E_{\text{pc}}$ decreases with an increase in vetranal concentration from 84 to 40 mV. These changes in ΔE values evidence that the reversibility of Zn(II) electroreduction increases.

The values of the apparent rate constant, k_f , were obtained from the charge-transfer resistance R_{ct} ¹¹ as a function of the dc potential. The impedance data were analyzed by fitting to the expressions valid in the case of Randles equivalent circuit^{19,20}. The precision of determined R_{ct} values was

$\pm 5\%$. The decreased values of R_{ct} in the presence of vetranal demonstrate unequivocally the catalytic influence of vetranal.

DISCUSSION

The values of $E_{1/2}^r$ calculated from Eq. (1) shift by 10 mV towards less negative potentials. It was concluded, therefore, that the Zn(II)–vetranal complexes formed in the solution are very unstable²¹. From the values of reversible half-wave potentials, the standard formal potentials, E_f^o , were calculated using Eq. (2):

$$E_f^o = E_{1/2}^r + \frac{RT}{nF} \ln \left(\frac{D_{ox}}{D_{red}} \right)^{1/2} \quad (2)$$

The obtained values of E_f^o change from -0.967 to -0.957 mV with increased vetranal concentration.

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 the studied concentrations of vetranal¹⁶. The potentials of the outer Helmholtz plane (OHP), Φ_2 , were derived assuming the validity of the Gouy–Chapman–Stern theory²²:

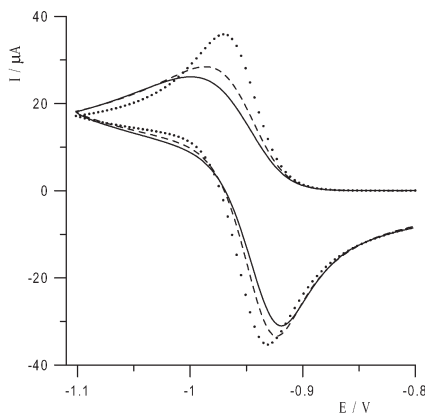


FIG. 1
Cyclic voltammetric curves for the Zn(II)/Zn(Hg) system in 1 M NaClO₄ at a scan rate of 0.1 V s⁻¹ in the presence of vetranal (in M): 0 (solid line), 5 × 10⁻⁴ (dashed line) and 1.0 × 10⁻² (dotted line)

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

where c is the bulk concentration of NaClO_4 , σ^m is the charge density on the electrode, σ^i is the charge density of specifically adsorbed ClO_4^- ions (taken from ref.¹⁴).

Table I lists the σ^m and Φ_2 values pertaining to the potentials of the electroreduction of Zn(II) ion. The Φ_2 values presented in Table I are comparable with the Φ_2 values obtained in 1 M NaClO_4 for tetramethylthiourea in a similar range of concentrations⁶. The potential in the reaction plane, Φ^r , can be calculated by subtracting the diffuse layer potential:

$$\Phi^r = \Phi^{\text{OHP}} = E - \Phi_2 \quad (4)$$

Aramata and Delahay²¹ proved that the hydrated Zn(II) ion is larger than the Na(I) ion and, therefore, the plane of the closest approach for Zn(II) is farther from the electrode than the OHP. Andreu et al.¹¹ proved that the reaction plane is 0.28 nm farther from the electrode. This distance corresponds to the diameter of one water molecule, $d_{\text{H}_2\text{O}}$. The potential Φ^r can be determined from ref.²³:

TABLE I

Charge densities $10^2 \sigma^m$ (in C m^{-2}), potentials of the outer Helmholtz plane Φ_2 and potentials in the reaction plane Φ^r as a function of vetranal concentration at potential -0.96 V close to the formal potential of the Zn(II) ion reduction

$10^3 c_{\text{vetranal}}, \text{ M}$	$-\sigma^m$	$-\Phi_2, \text{ V}$	$-\Phi^r, \text{ V}$
0	10.2	0.045	0.933
0.1	9.8	0.045	0.933
0.5	9.4	0.044	0.933
1.0	9.3	0.044	0.933
2.5	9.2	0.044	0.933
5.0	8.9	0.044	0.934
7.5	8.5	0.043	0.934
10.0	8.4	0.043	0.934

$$\Phi^r = \Phi^{\text{OHP}+0.28\text{nm}} = E + \frac{4RT}{F} \tanh^{-1} \left[\tanh \left(\frac{F\Phi_2}{4RT} \right) \exp(-\kappa d_{\text{H}_2\text{O}}) \right] \quad (5)$$

where $\kappa = (3.29 \times 10^7)zc^{1/2}$ at 298 K, c is the bulk z : z electrolyte concentration in M, κ^{24} is given in cm^{-1} .

The relative surface excess of vetranal presented in Fig. 2 was obtained according to the Gibbs adsorption isotherm:

$$\Gamma' = \frac{1}{RT} \left(\frac{\partial \Phi}{\partial \ln c} \right)_\sigma \quad (6)$$

where c is the bulk concentration of vetranal, Φ is the surface pressure: $\Phi = \Delta\xi$, $\xi = \gamma + \sigma E$ is the Parsons auxiliary function²⁵, where γ is the surface tension, σ is the electrode charge, E is the electrode potential, $\Delta\xi = \xi_0 - \xi$ (ξ_0 and ξ are the values of the Parsons auxiliary functions for base electrolyte and for the solution containing vetranal, respectively).

In writing Eq. (6) it is assumed that the mean activity coefficients of vetranal and NaClO_4 do not change with the change in vetranal concentration. The presented relationships in Fig. 2 are linear and depend insignificantly on the potential.

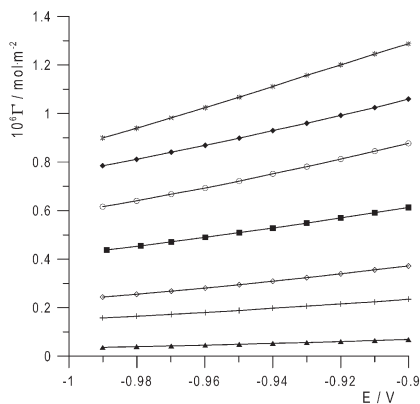


FIG. 2
Relative surface excess Γ' of vetranal versus E at various vetranal concentrations (in M): 1×10^{-4} (▲), 5×10^{-4} (+), 1×10^{-3} (◇), 2.5×10^{-3} (■), 5×10^{-3} (○), 7.5×10^{-3} (◆), 1×10^{-2} (*) in the bulk

The obtained values of Γ' for vetranal at the potentials of Zn(II) ion electroreduction are approximately twice lower than analogous values obtained for tetramethylthiourea⁶. This is probably a result of stronger repulsive interaction between adsorbed vetranal molecules.

The rate constants for the forward reaction, k_f , obtained for various vetranal concentrations at the mean dc potential indicate an increase in the catalytic vetranal activity with an increase in its concentration. This increase in k_f values occurs up to the 1×10^{-2} M vetranal concentration. Above this concentration, the k_f values do not change dramatically. The analysis of the $k_f = f(E)$ dependence allows to state that the catalytic effect attributed to vetranal is independent of the electrode potential. It should be emphasized that the inhibitory effect of *tert*-butyl alcohol on the reduction of Zn(II) ion is stronger at less negative potentials⁶.

The true rate constant, k_f^t , can be obtained from Eq. (7)²³:

$$k_f(\Phi^r) = k_f^t(\Phi^r) \exp\left[-(E - \Phi^r) \frac{nF}{RT}\right] \quad (7)$$

The values of the true rate constants of electroreduction of Zn(II) ion plotted as natural logarithm of the true rate constant, $\ln k_f^t$, obtained at various concentrations of vetranal as a function of the potential, Φ^r , are presented in Fig. 3.

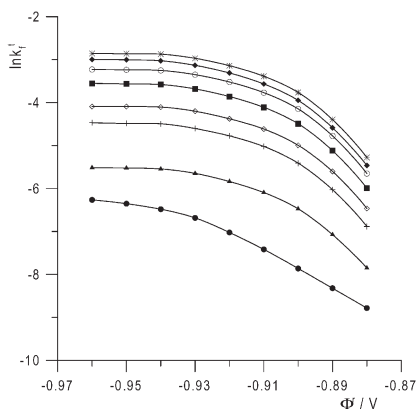


FIG. 3

The potential dependence of the true rate constants of the Zn(II) reduction in 1 M NaClO₄ at various vetranal concentrations (in M): 0 (●), 1×10^{-4} (▲), 5×10^{-4} (+), 1×10^{-3} (◇), 2.5×10^{-3} (■), 5×10^{-3} (○), 7.5×10^{-3} (◆), 1×10^{-2} (*) in the bulk

The non-rectilinear $\ln k_f^t = f(\Phi^r)$ dependences confirm a step character of electrons transfer in Zn(II) ion reduction¹¹. The slopes of the obtained curves change with the potential and concentration of vetranal. The k_f^t values increase with an increase in vetranal concentration and achieve the highest values for 1×10^{-2} M vetranal. The catalytic effect of vetranal can be illustrated in the system k_f^t vs Γ' at a given Φ^r (Fig. 4). These plots were constructed using the curves $\Gamma' = f(\Phi^r)$ and $\ln k_f^t = f(\Phi^r)$.

The obtained straight lines have the point of intersection on the horizontal axis at the value Γ' of vetranal, -0.25×10^{-6} mol m⁻². It seems that the k_f^t values of Zn(II) electroreduction in the presence of vetranal change according to the equation obtained by Souto et al.²⁶:

$$k_f^t(\Phi^r)/k_f^{0,t}(\Phi^r) = 1 + B\Gamma' \quad (8)$$

where $k_f^{0,t}$ denotes the true rate constant determined in the absence of vetranal. The value of $B = 4.0 \times 10^6$ mol⁻¹ m² is a comparative measure of the catalytic activity of vetranal in the studied system. A linear relationship between the rate constant of electrochemical reduction and the surface excess of vetranal could be interpreted in terms of a "bridging model"²⁷ in which it is assumed that the adsorbed species facilitated the transfer of electrons across the inner layer. This is the evidence for some active complex formation.

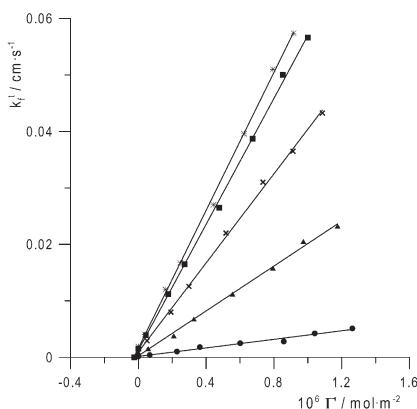


FIG. 4

The true rate constants of Zn(II) ion electroreduction versus the relative surface excess of vetranal at constant Φ^r indicated for each line (in V): -0.88 (●), -0.90 (▲), -0.92 (×), -0.94 (■), -0.96 (*)

From the dependence of $\ln k_f^t = f(\Phi^r)$ (Fig. 3), the values of the true standard rate constants, k_s^t , corresponding to the values of E_f^o and the constants k_{s1}^t and k_{s2}^t characterizing the first step of the first electron transfer and the second step of the second electron exchange were determined^{11,12,17}. Table II presents the individual standard rate constants of the Zn(II) electroreduction at various concentrations of vetranal.

The values of the true individual standard rate constants of the electroreduction of Zn(II) ions in 1 M NaClO₄ are in agreement with the literature data^{11,23}. The electrochemical reduction of Zn(II) ion in 1 M NaClO₄ is controlled by the rate of the first electron transfer also in the presence of vetranal. The obtained values of k_{s1}^t and k_{s2}^t show that the first electron transfer step is catalyzed more strongly with vetranal than the second step. Similar results were obtained with thiourea⁹, 1,3-dimethylthiourea, 1,3-diethylthiourea, 1,3-diisopropylthiourea and 1,3-dibutylthiourea⁴. For the system NaClO₄-tetramethylthiourea, the k_{s2}^t increase to a greater extent than k_{s1}^t values. This is probably due to the presence of two CH₃ groups at nitrogen atoms responsible for the formation of active complex Zn(II)-tetramethylthiourea. It should be emphasized that catalytic activity of vetranal on the electroreduction of Zn(II) ion is stronger than that of tetramethylthiourea. For distinct by smaller Γ' values of vetranal, the values of k_{s1}^t increase faster but the values of k_{s2}^t increase similarly to changes of these quantities in the presence of tetramethylthiourea. Including the formation of an active complex between Zn(II) ion and vetranal, it can be stated that

TABLE II
Corrected individual rate constants of Zn(II) ion electroreduction extrapolated to the E_f^o for various concentrations of vetranal

$10^3 c_{\text{vetranal}}, \text{ M}$	$10^3 k_{s1}^t, \text{ cm s}^{-1}$	$10^2 k_{s2}^t, \text{ cm s}^{-1}$
0	1.50	3.70
0.1	4.08	5.23
0.5	11.0	6.41
1.0	16.1	19.4
2.5	27.3	37.8
5.0	38.0	43.2
7.5	48.2	51.3
10.0	56.7	60.2

the reduction of Zn(II) with the first electron leads to the active complex still partly hydrated, but reduction of Zn(I) with the second electron gives the completely dehydrated active complex.

CONCLUSIONS

The present studies have clearly shown that the electroreduction of Zn(II) is accelerated by vetranal. This is demonstrated by the decrease in the potential differences between the cathodic and anodic peaks on the cyclic voltammetric curves. From the $k_f = f(E)$ dependence it appears that the catalytic effect of vetranal is practically independent of the electrode potential. It was also stated that both transfers (of first and second electron) are accelerated by vetranal, however, the first step is catalyzed more strongly. The obtained linear dependences of k_f^l values on the relative surface excess Γ' of vetranal at $\Phi^F = \text{const}$ confirm the formation of an active complex of the adsorbed vetranal and Zn(II) ion. The shape of the k_f vs E dependence indicates the multistep mechanism:

- slow transfer of Zn(II) cations through the double layer where the metal ions are adsorbed as active complexes (mechanism IA)^{28,29}
- fast chemical steps involve loss or exchange of water molecule followed by electron transfer (mechanism CE)³⁰
- two one-electron transfer steps (mechanism EE)²⁸.

The presented strong catalytic effect of vetranal on Zn(II) electroreduction broadens our knowledge of its influence on kinetics of reactions associated with the presence of metal ions in organisms when vetranal is prescribed as a drug, and could help to explain its severe side effects.

SYMBOLS

D_{ox}	diffusion coefficient of Zn(II) ion
D_{red}	diffusion coefficient of zinc in mercury
$E_{1/2}^{\circ}$	reversible potential of the half-wave
E_{pa}	anode peak potential
E_{pc}	cathode peak potential
E_f°	standard formal potential
k_f	apparent rate constant
k_f^l	true rate constant
k_s^l	true standard rate constant
k_{s1}^l	true standard rate constant characterizing the first step of the first electron transfer
k_{s2}^l	true standard rate constant characterizing the second step of the second electron transfer
Φ_2	potential of the outer Helmholtz plane

Φ^r	potential in the reaction plane
Γ^r	relative surface excess of vetranal
σ^m	charge density on the electrode

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