

On the Catalytic Effect of Thiolactams on the Electrochemical Reduction of Zn(II) Ions

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Summary. The electroreduction of Zn(II) ions in 1 M NaClO₄ in the presence of thiolactams has been studied by means of the faradaic impedance method in wide frequency ranges. The standard rate constants are found to be a linear function of the surface excesses of thiolactams. Catalytic activity of thiolactams increases in the following order: thiopyrrolidone, thiopiperidinone, thiocaprolactam; the enthalpies of activation decrease in this order. The differences in the catalytic activity of thiolactams result mainly from the double layer effect.

Keywords. Electroreduction of Zn(II) ions; Thiolactams; Catalytic activity.

Zum katalytischen Effekt von Thiolactamen auf die elektrochemische Reduktion von Zn(II)-Ionen

Zusammenfassung. Die Elektroreduktion von Zn(II)-Ionen in 1 M NaClO₄ in Gegenwart von Thiolactamen wurde mittels der *Faradayschen* Impedanzmethode über große Frequenzbereiche untersucht. Die Standardgeschwindigkeitskonstanten sind eine lineare Funktion der Überschußoberfläche der Thiolactame. Deren katalytische Aktivität steigt in der Reihenfolge Thiopyrrolidon – Thiopiperidinon – Thiocaprolactam; die Aktivierungsenthalpien sinken in der angegebenen Reihenfolge. Die Unterschiede in der katalytischen Aktivität der Thiolactame sind hauptsächlich auf den Doppelschichteffekt zurückzuführen.

Introduction

Electroreduction of Zn(II) ions on mercury is one of the electrode reactions most frequently studied. Only recently, interest has focused on the multistep character of its mechanism [1–6]. The electroreduction of Zn(II) ions occurs at various rates, depending on the nature of the supporting electrolyte. The rate of the electroreduction rises if the supporting electrolyte has a polarizable anion adsorbed on the mercury [7–10]. *Andreu et al.* [11] stated that J⁻ ions catalyze both steps of the electron transfer, but greater acceleration is achieved with the transfer of the first electron.

The electroreduction of Zn(II) ions is also accelerated by organic substances which meet the conditions determined by the cap-pair principle [12, 13]. Thiolactams meet these conditions. They adsorb on the mercury surface in the potential range of Zn(II) ion reduction [14] and possess a strongly polar thiocarbonyl group as well as a free pair of electrons which influence their chemical activity.

Thiolactams form various complexes with metals: ionic pair [15, 16], ternary mixed [17], and cationic [18] types. Simple thiolactam complexes are unstable and undergo decomposition with evolution of sulfides. Thiolactams are very interesting compounds because of their medicinal application as an important remedy in modern therapy as well as because of their technological importance.

This paper presents studies and comparisons of the catalytic activity of thiopyrrolidone, thiopiperidinone, and thiocaprolactam on the overall rate constants of the electroreduction of Zn(II) ions from 1 M NaClO₄ solutions.

Results and Discussion

The approximate diffusion coefficients of Zn(II) ions 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 M KNO₃ with the value of $D_{ox} = 6.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the Zn(II) ion diffusion coefficient at 298 K [21] was 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 thiolactams ($0 < c < 0.01 \text{ mol} \cdot \text{dm}^{-3}$) are minimally smaller than the value for 1 M NaClO₄ and vary in the range of $6.6\text{--}6.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Together with the value of the diffusion coefficient $D_R = 16.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for Zn in mercury [22, 23] this gives a value of 6 mV for the difference $E_{1/2r} - E_f$ between the reversible half wave potential and the formal potential at 298 K.

The reversible half wave potentials $E_{1/2r}$ of the reduction of Zn(II) ions were estimated from cyclic voltammetric curves [24] with a reproducibility of $\pm 0.002 \text{ V}$ using sweep rates from 0.005 to 0.01 V s⁻¹.

The complex cell impedance was obtained at 18 frequencies in the range from 100 to 10000 Hz. The ohmic resistance of the electrolyte solution was obtained as the real impedance component at a frequency of 10 kHz and at a potential outside the faradaic region. The activation polarization resistances R_A were determined for

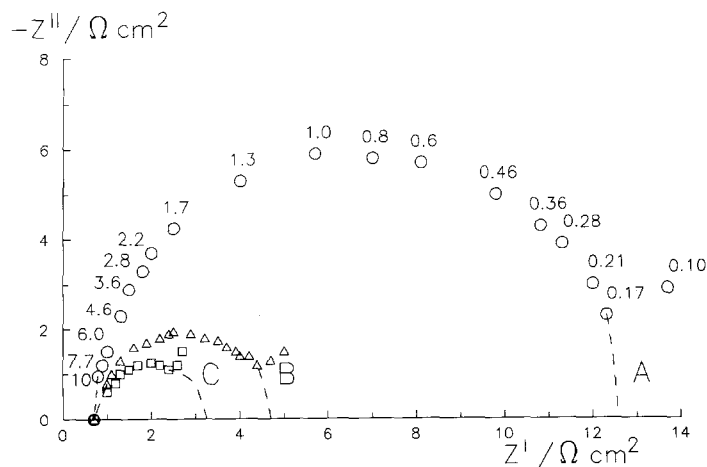


Fig. 1. Impedance diagrams measured at E_f for the electroreduction of Zn(II) ions in the presence of $0.001 \text{ mol} \cdot \text{dm}^{-3}$ thiopyrrolidone (A), thiopiperidinone (B), and thiocaprolactam (C); the numbers indicate the frequency in kHz

E_f and calculated from the dependence $Z' = f(\omega Z'')$ or $Z' = f(Z'')$ [25–27], where Z' is the real and Z'' the imaginary part of the cell impedance. The accuracy of measurements of Z' and Z'' was about 2%. Figure 1 presents some examples of impedance diagrams for the electroreduction of Zn(II) ions in the presence of 0.001 M thiolactams.

The reaction standard rate constants k_s were calculated according to equation 1 [26] where c is the concentration of depolarizer.

$$k_s = \frac{RT}{n^2 F^2 c R_A} \quad 1$$

Tables 1–3 present reversible half wave potentials, standard rate constants of the electroreduction of Zn(II) ions, and surface excesses at the formal potential in solutions of 1 M NaClO₄ at various concentrations of thiolactams.

Table 1. Values of reversible half wave potential ($E_{1/2r}$), standard rate constants (k_s) of the (Hg)Zn (1×10^{-3} mol·dm⁻³)/Zn(II)(1×10^{-3} mol·dm⁻³) system, and surface excesses at the potential E_f in 1 M NaClO₄ solutions at various concentrations of thiopyrrolidone. Data of the surface excesses were taken from Ref. [14]

$c \cdot 10^3$ (mol·dm ⁻³)	0	0.5	1	1.5	2	4	6	8	10
$-E_{1/2r}$ (V)	0.985	0.985	0.982	0.980	0.979	0.979	0.980	0.980	0.981
$k_s \cdot 10^3$ (cm·s ⁻¹)	3.3	4.5	5.5	7.5	10.0	12.0	13.2	14.5	16.3
$\Gamma \cdot 10^{10}$ (mol·cm ⁻²)	0	0.8	1.3	1.5	1.8	2.3	2.6	2.8	2.9

Table 2. Values of reversible half wave potential ($E_{1/2r}$), standard rate constants (k_s) of the (Hg)Zn (1×10^{-3} mol·dm⁻³)/Zn(II)(1×10^{-3} mol·dm⁻³) system, and surface excesses at the potential E_f in 1 M NaClO₄ solutions at various concentrations of thiopiperidinone. Data of the surface excesses were taken from Ref. [14]

$c \cdot 10^3$ (mol·dm ⁻³)	0	0.5	1	1.5	2	4	6	8	10
$-E_{1/2r}$ (V)	0.985	0.989	0.991	0.991	0.989	0.990	0.990	0.990	0.990
$k_s \cdot 10^3$ (cm·s ⁻¹)	3.3	9.7	17.5	19.5	23.0	34.1	44.0	47.0	49.3
$\Gamma \cdot 10^{10}$ (mol·cm ⁻²)	0	0.8	1.4	1.7	2.1	3.2	4.1	4.4	4.5

Table 3. Values of reversible half wave potential ($E_{1/2r}$), standard rate constants (k_s) of the (Hg)Zn (1×10^{-3} mol·dm⁻³)/Zn(II)(1×10^{-3} mol·dm⁻³) system, and surface excesses at the potential E_f in 1 M solutions NaClO₄ at various concentrations of thiocaprolactam. Data of the surface excesses were taken from Ref. [14]

$c \cdot 10^3$ (mol·dm ⁻³)	0	0.5	1	1.5	2	4
$-E_{1/2r}$ (V)	0.985	0.990	0.991	0.989	0.990	0.990
$k_s \cdot 10^3$ (cm·s ⁻¹)	3.3	13.6	27.3	35.0	41.0	59.3
$\Gamma \cdot 10^{10}$ (mol·cm ⁻²)	0	0.9	2.2	2.8	3.4	4.8

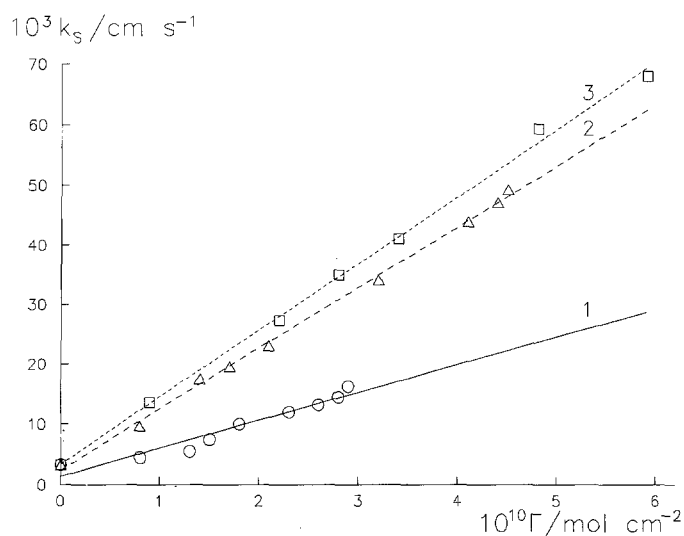


Fig. 2. Dependence of the standard rate constants for the Zn(Hg)/Zn(II) couple on the surface excess of thiopyrrolidone (1) thiopiperidinone (2), and thiocaprolactam (3) at the formal potential

$E_{1/2r}$ of Zn(II) ions electroreduction is shifted by *ca.* 5 mV towards positive potentials by thiopyrrolidone; thiopiperidinone and thiocaprolactam cause shifts of *ca.* 5 mV towards negative potentials. Such small changes of $E_{1/2r}$ indicate that no stable Zn-thiolactam complexes are present in the solutions; they are caused only by the influence of thiolactams on ϕ_2 .

The standard rate constants of the electroreduction of Zn(II) ions increased with rising concentration of thiolactams in the solution which indicated strong double layer effects. Figure 2 presents the dependence of the standard rate constant of the electroreduction of Zn(II) ions on the thiolactam surface excess at the formal potential. The linear dependence $k_s = f(\Gamma_{Ef})$ can be interpreted by the so-called bridging model [9] where the adsorbed species are assumed to facilitate the transfer of electrons across the inner layer. With an increasing number of CH_2 groups in the thiolactam molecules, the surface excesses of these compounds at the formal potential and their catalytic activity increase. It seems that the differences in the catalytic activity result mainly from double layer effects which is indicated by the rectilinear dependence $k_s = f(\Gamma_{Ef})$ (Fig. 2).

To find out whether or not Zn(II) ions can be accumulated in the surface layer by the interaction with the adsorbed thiolactams molecules, chronocoulometric measurements of the maximal charge (Q_d) of Zn(II) ions electroreduction as a function of the integration time (t_p) were performed in 0.001 M thiolactams in 1 M NaClO_4 . Q_d of the Zn(II) electroreduction process was measured at a potential of -1.05 V. The plot of Q_d vs. $t_p^{1/2}$ was linear and intersected the origin of coordinates after subtraction of the double layer charge recorded for blank solutions. It has to be pointed out that under such conditions, the cathodic reduction of Zn(II) ions is limited by diffusion and the induced adsorption of Zn(II) ions, if any, is within the limits of experimental error.

The effect of temperature (290–328 K) on Zn(II) ions electroreduction in the presence of 0.001 M thiolactams was also studied (Table 4). The small temperature coefficient of the limiting current values (1.08–1.4% per degree) for the polarographic reduction of Zn(II) ions in the presence of thiolactams indicates the diffusion – controlled nature of the wave.

Table 4. Effect of temperature on the polarographic limiting current (i_{lim}) of the electroreduction of $1 \times 10^{-3} M$ Zn(II) ions in $1 M$ NaClO₄ with addition of $1 \times 10^{-3} mol \cdot dm^{-3}$ thiolactam; values of the reversible half wave potentials $E_{1/2r}$ estimated from the cyclic voltammetric curves

temperature (K)	$i_{lim} \cdot 10^6$ (A)	temperature coefficient (percent \cdot degree ⁻¹)	$-E_{1/2r}$ (V)
thiopyrrolidone			
290	3.4	—	0.990
298	3.8	1.40	0.982
308	4.3	1.23	0.981
318	4.9	1.30	0.975
328	5.5	1.15	0.971
thiopiperidinone			
290	3.4	—	0.996
298	3.9	1.37	0.991
308	4.4	1.20	0.981
318	4.9	1.08	0.979
328	5.5	1.15	0.973
thiocaprolactam			
290	3.4	—	0.999
298	3.8	1.40	0.991
308	4.3	1.23	0.986
318	4.9	1.30	0.983
328	5.6	1.34	0.981

Thiolactams do not affect the temperature changes of Zn(II) ions diffusion coefficients. The observed positive shift in the reversible half wave potential with increasing temperature can be explained by considering the correlation between electrode kinetics and double-layer structure developed by *Frumkin* [28] and *Delahay* [29].

From the temperature dependence of the standard rate constants (Fig. 3), the enthalpies of activation (ΔH^\ddagger) were determined according to equation 2 [30].

$$\Delta H^\ddagger = 2.303R \cdot d(\lg k_s) / d\left(\frac{1}{T}\right) \quad 2$$

Enthalpies of activation are $35.4 \text{ kJ} \cdot \text{mol}^{-1}$, $26.0 \text{ kJ} \cdot \text{mol}^{-1}$, and $17.9 \text{ kJ} \cdot \text{mol}^{-1}$ in the presence of thiopyrrolidone, thiopiperidinone, and thiocaprolactam, respectively. *Hush* and *Blackledge* [1] determined ΔH^\ddagger for Zn(II) ions electroreduction at the Hg electrode at various concentrations of NaClO₄. They found that it was constant and equal to $42 \text{ kJ} \cdot \text{mol}^{-1}$. The decrease of enthalpies of activation confirms the catalytic activity of thiolactams. Thiocaprolactam is evidently the most effective one in accelerating the electroreduction of Zn(II) ions.

The present investigation provides a basis for more detailed studies on the influence of catalytic effects on the step character of the Zn(II) ions electroreduction

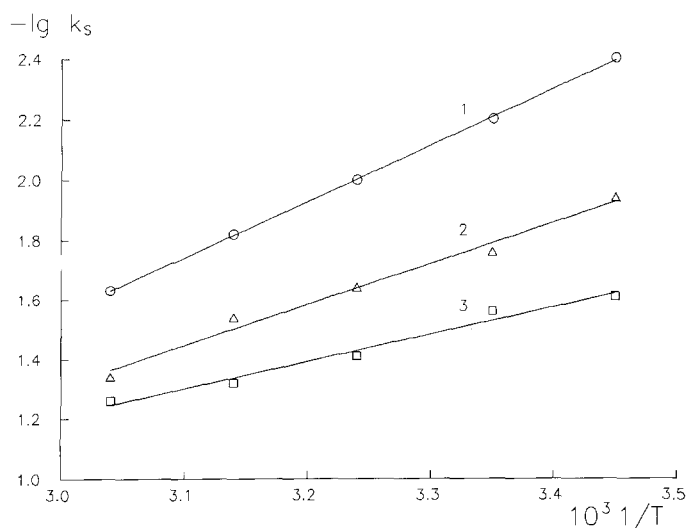


Fig. 3. Plot of $\lg k_s$ vs. $1/T$ for the electroreduction of Zn(II) ions in the presence of thio-pyrrolidone (1), thiopiperidinone (2), and thiocaprolactam (3)

process. These effects will possibly allow to determine the mechanism of the reduction process and the nature of the catalytic effect.

Experimental

The measurements were carried out with a polarograph PA-4 by Laboratorni Pstroje Prague and an EG and G PARC Instrument model 388 and 270 employing a static mercury drop electrode manufactured by Laboratorni Pstroje - Prague (the drop surface of the hanging electrode was 0.0133 cm^2). The reference electrode was a saturated calomel electrode with NaCl (SSCE) or Ag/AgCl; a platinum spiral was used as an auxiliary electrode. The reference electrode was equipped with a *Luggin* capillary probe. The capillary was filled with cell solution. The potentials are referred to the SSCE.

Solutions were made up from twice distilled water and analytical grade reagents (Merck). Zinc perchlorate was prepared by dissolving ZnO in a small excess of perchloric acid. Concentrations: Zn(II), $0.001 \text{ mol} \cdot \text{dm}^{-3}$; NaClO_4 , $1 \text{ mol} \cdot \text{dm}^{-3}$. The *pH* of the solutions was adjusted to 5.2. The preparation of thiolactams was accomplished according to a published procedure [20]. Lactams were commercially available (Merck). Measurements were made for 5–8 concentrations of thiolactams between 0.0005 and $0.01 \text{ mol} \cdot \text{dm}^{-3}$.

Solutions were deaerated by 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 $298 \pm 1 \text{ K}$.

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