NUMERICAL SIMULATION OF ANODIC DISSOLUTION OF ZINC

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Abstract. *A mathematical model of anodic dissolution of zinc in organic solvents was developed. Numerical analysis is performed using this model to simulate the kinetics of the electrochemical reaction. The mechanism and kinetic of anodic dissolution of zinc were examined in protogenic (methanol) and aprotic (acetonitrile) solvents containing $LiClO_4$ as a basic electrolyte. Result of that research allowed to give the mechanism of anodic dissolution of zinc in anhydrous organic media. Desorption of intermediate product - Zn^+_{ad} occurring on energetically preference places of zinc surface (kinks, structural defects) plays a very important role in this mechanism. The desorption proceeds according to catalytic process similar to the Heusler mechanism for metals of iron group. Experimental investigation confirms the simulation results.*

Keywords: *Zinc, Anodic Dissolution, Numerical Simulation*
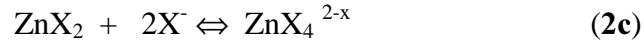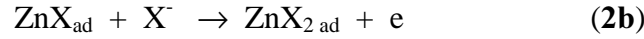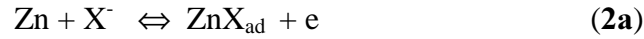
1. INTRODUCTION

The electrochemical dissolution and deposition of zinc has been intensive investigated in aqueous environments (Heusler et al., Harrison et al., Asakura, Wiart et al., Yu-Chi Chang, Jorne, Gerischer are some of the authors that can be mentioned). Simple model of dissolution and deposition bases on the two step mechanism according to the reactions:

$$Zn \xleftrightarrow{k_1} Zn^+_{ad} + e$$

(1a)

$$Zn^+_{ad} \xleftrightarrow{k_2} Zn^{+2} + e$$

(1b)

Reaction (1a) is very fast and the adsorbed intermediate product Zn^+_{ad} is present only on the metal surface (does not enter the solution). Reaction (1b) proceeds slowly and is always a rate determining step of the anodic dissolution or cathodic deposition. The complexing anions presented in the solution like OH^- (Yu-Chi Chang, 1984; Gerischer, 1953), CN^- (Gerischer, 1953), Cl^- (Cachet and Wiart, 1981), malonate (Heusler and Knoedler, 1973) take part in the charge transfer . Above mentioned mechanism is characterised by two anodic Tafel slopes

dE/dlogi equal 0.040 V (low overvoltage) and 0.120V (high overvoltage) and one cathodic Tafel slope -0.120V for stationary polarisation measurements (Heusler and Knoedler, 1973, Cachet and Wiart, 1981). The reaction order versus anion corresponding to above mentioned anodic slopes is equal 1.0 and 2.0 respectively and the electrochemical reactions with the participation of monovalent anion X^- can be presented as follows:

$$Zn + X^- \Leftrightarrow ZnX_{ad} + e \qquad\qquad (2a)$$

$$ZnX_{ad} + X^- \rightarrow ZnX_{2\,ad} + e \qquad\qquad (2b)$$

$$ZnX_2 + 2X^- \Leftrightarrow ZnX_4{}^{2-x} \qquad\qquad (2c)$$

More complicated model of electrochemical dissolution and deposition of zinc was proposed by Wiart (Cachet and Wiart, 1981&1988). Model takes into consideration two parallel paths with the participation of $Zn^+{}_{ad}$ intermediate. The intermediate product participates in catalytic reaction which is similar to the catalytic Heusler mechanism of iron dissolution (Allgaier and Heusler, 1975).

Mechanism of zinc dissolution in anhydrous organic solvents is similar to the mechanism in aqueous media (Banaś et al., 1986 and Biallozor and Bandura, 1987). However the stability of monovalent cations and than stability of adsorbed intermediate are in these solvents much higher than in aqueous environments (James, 1974; Parker et al. 1975; Parker, 1976, Gareao and Bonora, 1977; Banaś and Banaś , 1991). Therefore the strong inhibition of anodic and cathodic reactions could be expected in anhydrous organic electrolytes. In organic solvents the solubility of corrosion products is also lower than in aqueous solutions. Stability of surface species and mechanism of their desorption or dissolution play very important role in the electrochemical processes on zinc electrode in organic environments.
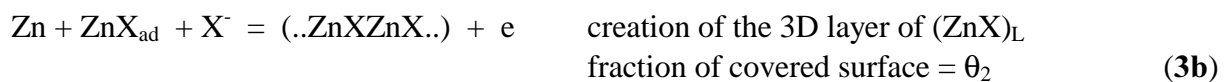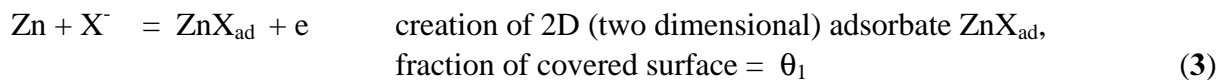
This work presents the *simulation model* of anodic dissolution of zinc which takes into account participation of two and three dimensional surface spaces in the electrochemical reactions on zinc electrode. Model have been verified experimentally in methanol and acetonitrile solutions of perchlorates and chlorates.

2. PRINCIPLES OF THE MODEL.

The mechanism of electrochemical reactions on zinc electrode in the solution containing X^- anion can be presented as the composition of consecutive and parallel steps.
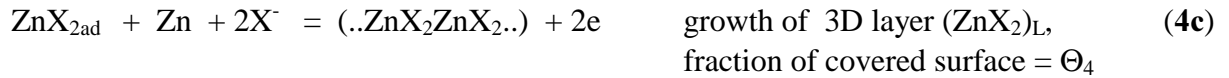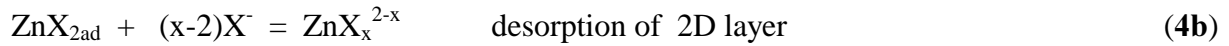
Three groups of reactions can be distinguished in the presented model:

Group I - the creation of low valence product Zn^+

$Zn + X^- = ZnX_{ad} + e$ creation of 2D (two dimensional) adsorbate ZnX_{ad},
fraction of covered surface $= \theta_1$ (3)

$ZnX_{ad} + (x-1)X^- = ZnX_x{}^{1-x}$ desorption of intermediate ZnX_{ad} (3a)

$Zn + ZnX_{ad} + X^- = (..ZnXZnX..) + e$ creation of the 3D layer of $(ZnX)_L$
fraction of covered surface $= \theta_2$ (3b)

$(ZnX)_L + (x-1)X^- = ZnX_x{}^{1-x}$ dissolution of 3D layer   (3c)

Reaction (3) is very fast and correspond to the equilibrium condition. Reaction 3a and 3c are chemical reaction leading to dissolution of 2D and 3D layers respectively. The monovalent cations Zn^+, co-ordinated by anions X^- (ZnX_x^{1-x}) are the soluble product of these reactions. Reaction 1b is the reaction of growth of 3D (three-dimensional) layer. Electrical field limits the growth of this layer across the layer.

Group II - the creation of Zn^{+2} compounds

$$ZnX_{ad} + X^- = ZnX_{2\,ad} + e \qquad \text{creation of adsorbed 2D layer } ZnX_{2ad} \qquad \text{(4a)}$$
$$\text{fraction of covered surface} = \theta_3$$

$$ZnX_{2ad} + (x-2)X^- = ZnX_x^{2-x} \qquad \text{desorption of 2D layer} \qquad \text{(4b)}$$

$$ZnX_{2ad} + Zn + 2X^- = (..ZnX_2ZnX_2..) + 2e \qquad \text{growth of 3D layer } (ZnX_2)_L, \qquad \text{(4c)}$$
$$\text{fraction of covered surface} = \Theta_4$$
$$(ZnX_2)_L + (x-2)X^- = ZnX_x^{2-x} \qquad \text{dissolution of 3D layer} \qquad \text{(4d)}$$
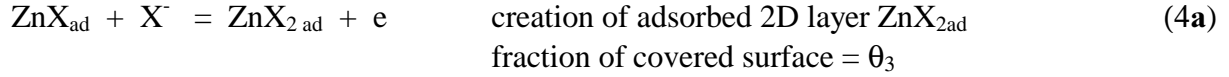
Reaction 4a is a charge transfer reaction - oxidation of Zn^+ to Zn^{+2}. This reaction is slow (comparing to the reaction 3) and determines very often the rate of overall reaction of metal dissolution. Analogous to the reactions 3a and 3c the reaction's 4b and 4d present chemical dissolution of 2D and 3D layers. Reaction 4c describes the growth of 3D layer.

Group III - desorption of intermediate Zn^+ as a result of catalytic reaction

$$Zn^*ZnX_{ad} + (x-1)X^- = Zn^* + ZnX_x^{2-x} + e \qquad \text{(5)}$$
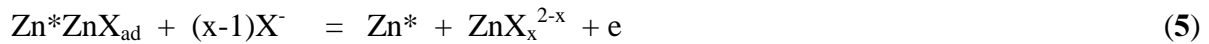
Reaction (5) is a catalytic oxidation reaction proceeding on "active " places of metal surface Zn^* (structural imperfections - kinks, dislocations etc.). This mechanism has been described for metals of iron group by Heusler (Heusler, 1963; Allgaier and Heusler, 1975). Our experiences show that also "soft" metals such as Zn, Cu can dissolve according to this mechanism when dissolution proceeds in the solvents with low dielectric permitivity. In these solvents the negligible energetic differences on metal surface play very important role in dissolution mechanism (Banaś, 1995).
The partial faradaic currents corresponding to the reactions presented in the model can be described by the kinetic equations:

Group I

$$i_1 /F = k_1^+(1-\theta_1-\theta_2-\theta_3-\theta_4)[X^-] - k_1^-\theta_1 \qquad \text{(6)}$$

$$i_{1a}/F = k_{1a}^+\theta_1[X^-]^{x-1} - k_{1a}^-(1-\theta_1-\theta_2-\theta_3-\theta_4)[ZnX_x^{1-x}] \qquad \text{(6a)}$$

$$i_{1b}/F = k_{1b}^+\theta_1[X^-] - k_{1b}^-\theta_2 \qquad \text{(6b)}$$

$$i_{1c}/F = k_{1c}^+\theta_2[X^-]^{x-1} - k_{1c}^-(1-\theta_1-\theta_2-\theta_3-\theta_4)[MeX_x^{1-x}] \qquad \text{(6c)}$$

where:
$$k_1^+ = k_1^{0+}\exp(\alpha FE/RT), \quad k_1^- = k_1^{0-}\exp\{-(1-\alpha)FE/RT\}$$

$$k_{1b}{}^+ = k_{1b}{}^{0+} \exp(aE), \quad k_{1b}{}^- = k_{1b}{}^{0-} \exp(-aE)$$

k_{1a}, k_{1c} - rate constants of chemical reactions (dissolution and growth of the layer - complexation and precipitation)

Group II

$$i_{2a}/F = k_{2a}{}^+ \theta_1[X^-] - k_{2a}{}^- \theta_3 \tag{7a}$$

$$i_{2b}/F = k_{2b}{}^+ \theta_3[X^-]^{x-2} - k_{2b}{}^-(1-\theta_1-\theta_2-\theta_3-\theta_4)[ZnX_x{}^{2-x}] \tag{7b}$$

$$i_{2c}/F = k_{2c}{}^+ \theta_3[X^-]^2 - k_{2c}{}^- \theta_4 \tag{7c}$$

$$i_{2d}/F = k_{2d}{}^+ \theta_4[X^-]^{x-2} - k_{2d}{}^-(1-\theta_1-\theta_2-\theta_3-\theta_4)[ZnX_x{}^{2-x}] \tag{7d}$$

where:

$$k_{2a}{}^+ = k_{2a}{}^{0+}\exp(\alpha FE/RT), \quad k_{2a}{}^- = k_{2a}{}^{0-}\exp\{-(1-\alpha)FE/RT\}$$
$$k_{2b}{}^+ = k_{2b}{}^{0+}\exp(aE), \quad k_{2b}{}^- = k_{2b}{}^{0-}\exp(-aE)$$

k_{2b}, k_{2c} rate constants of chemical reactions (complexation - dissolution of the layer and precipitation - growth of the layer).

Group III

$$i_3 = k_3{}^+ [Zn^*]\theta_1[X^-]^{x-1} - k_3{}^-(1-\theta_1-\theta_2-\theta_3-\theta_4)[Zn^*][ZnX_x{}^{2-x}] \tag{8}$$

where:

$$k_3{}^+ = k_3{}^{0+} \exp(\alpha FE/RT), \quad k_3{}^- = k_3{}^{0-} \exp\{-(1-\alpha)FE/RT\}$$
$$[Zn^*] = \pm[Zn^{*0}]\exp(FE/RT)$$

The rate of formation of a surface compound is given by the expression $\beta d\theta/dt$ where θ is a surface coverage ($0 \le \theta \le 1$) and β is a coefficient corresponding to the concentration of surface compound expressed in mol/cm^2. The ideal smooth surface has a value of β equal $2*10^{-9}$ mol/cm^2. For the stationary condition (surface coverage does not change with the time) the $\beta d\theta/dt$ is equal zero. At this condition the following equations present the rate of formation of surface compounds during the electrochemical reactions 6-8:

$$\beta d\theta_1/dt = k_1^+(1-\theta_1-\theta_2-\theta_3-\theta_4)[X^-] - k_1^-\theta_1 - k_{1a}^+\theta_1[X^-]^{x-1} + k_{1a}^-(1-\theta_1-\theta_2-\theta_3-\theta_4)[X^-][ZnX_x^{1-x}]$$
$$- k_{1b}^+\theta_1[X^-] + k_{1b}^-\theta_2 - k_{2a}^+\theta_1[X^-] + k_{2a}^-\theta_3 - k_3^+[Zn^*]\theta_1[X^-]^{x-1} +$$
$$k_3^-[Zn^*](1-\theta_1-\theta_2-\theta_3-\theta_4)[ZnX_x^{2-x}] = 0 \tag{9a}$$

$$\beta d\theta_2/dt = k_{1b}^+\theta_1[X^-] - k_{1b}^-\theta_2 - k_{1c}^+\theta_2[X^-]^{x-1} + k_{1c}^-[ZnX_x^{1-x}] = 0 \tag{9b}$$

$$\beta d\theta_3/dt = k_{2a}^+\theta_1[X^-] - k_{2a}^-\theta_3 - k_{2b}^+\theta_3[X^-]^{x-2} + k_{2b}^-(1-\theta_1-\theta_2-\theta_3-\theta_4)[ZnX_x^{2-x}] -$$
$$k_{2c}^+\theta_3[X^-]^2 + k_{2c}^-\theta_4 = 0 \tag{9c}$$

$$\beta d\theta_4/dt = k_{2c}^+\theta_3[X^-]^2 - k_{2c}^-\theta_4 + k_{2d}^-(1-\theta_1-\theta_2-\theta_3-\theta_4)[ZnX_x^{2-x}] - k_{2d}^+\theta_4[X^-]^{x-2} = 0 \tag{9d}$$

From these equations we can obtain the fraction of coverage of the surface as a function of potential "E", rate constants "k^0", concentration of anions $[X^-]$, concentration of soluble zinc complexes $[ZnX_x^{2-x}]$ and concentration of active surface atoms $[Zn^*]$:

$$\theta = f(k_1^{\ 0}, k_2^{\ 0}, k_3^{\ 0}, k_4^{\ 0}, [X^-], [ZnX_x^{1-x}], [ZnX_x^{2-x}], [Zn^*], E)$$

The total coverage of surface is a sum of partial coverages: $\theta_T = \Sigma \theta_j$.
The current of the overall electrochemical reaction $\mathbf{i_T}$ is a superposition of partial currents 6-8. Superposition proceeds according to the following rules:

$$i_T = \Sigma i_j \quad \text{for the parallel reactions,}$$

$$i_T^{-1} = \Sigma i_j^{-1} \text{ for consecutive reactions.}$$

The total current corresponding to the electrochemical dissolution and deposition of zinc according to the presented model is given by the equation:

$$i_T = \frac{i_1 i_{1a} + \dfrac{i_1 i_{1b} i_{ic}}{i_{1b} + i_{1c}} + \dfrac{i_1 i_{2a} i_{2b} i_{2c} + i_1 i_{2a} i_{2b} i_{2d} + i_1 i_{2a} i_{2c} i_{2d}}{i_{2a} i_{2c} + i_{2a} i_{2d} + i_{2b} i_{2c} + i_{2b} i_{2d} + i_{2c} i_{2d}} + i_1 i_3}{i_1 + i_{1a} + \dfrac{i_{1b} i_{ic}}{i_{1b} + i_{1c}} + \dfrac{i_{2a} i_{2b} i_{2c} + i_{2a} i_{2b} i_{2d} + i_{2a} i_{2c} i_{2d}}{i_{2a} i_{2c} + i_{2a} i_{2d} + i_{2b} i_{2c} + i_{2b} i_{2d} + i_{2c} i_{2d}} + i_3} \tag{10}$$

Presented model of electrochemical dissolution and deposition of zinc contains some simplifications. We assume that total electrochemical current is superposition only partial faradaic currents and capacitive currents are negligible. This assumption seems be plausible because the surface compounds show "salt - like" structure and rather high conductivity. We assume also that the growth of the thin 3D layer proceeds in course of solid state reaction and is determined by the electrical field across the layer (high field conductivity), as in Young, 1961.

3. MATHEMATICAL MODEL

For the mathematical modelling of the problem stationary conditions will be considered, assuming intermediary adsorption products to occur according to Langmuir isotherms, which can be represented by the equations of the previous section (9a – 9b).

From these equations one can obtains the surface fractions (θ_1, θ_2, θ_3, θ_4) as functions of the "k" constants, the soluble species concentration in the solution (anion $[X^-]$, metal complex $[ZnX_x^{1-x}]$, $[ZnX_X^{2-x}]$), and the potential E:

$$\theta = f(k_1, k_2, k_3, k_4, [X^-], [ZnX_x^{1-x}], [ZnX_x^{2-x}], E)$$

Using the temporal derivatives of θ ($\beta d\theta/dt$) and equating to zero, the equation can be solved for the surface fractions θ_1, θ_2, θ_3 and θ_4, through a linear system $\mathbf{A}\theta\text{-}\mathbf{b} = \mathbf{0}$, or $\mathbf{A}\theta = \mathbf{b}$, where $\mathbf{A}$ is a matrix of known components which depend on the electrochemical reactions constants given for the problem, θ is the solution vector sought and $\mathbf{b}$ the right hand side vector, also known and also dependent on the process constants.
This way a system will be obtained of the form:

$$\begin{bmatrix} A_{11} & A_{12} & A_{13} & A_{14} \\ A_{21} & A_{22} & A_{23} & A_{24} \\ A_{31} & A_{32} & A_{33} & A_{34} \\ A_{41} & A_{42} & A_{43} & A_{44} \end{bmatrix} \begin{Bmatrix} \theta_1 \\ \theta_2 \\ \theta_3 \\ \theta_4 \end{Bmatrix} = \begin{Bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \end{Bmatrix}$$

The system of linear equations will be solved by Gaussian Elimination (Barroso, 1987; Press et al., 1992) with back-substitution and partial pivoting, since this is a simple procedure and the problem is relatively small.

3.1 Gaussian elimination with back-substitution

Gaussian Elimination is performed using triangular decomposition. This method reduces the matrix of the system into an upper triangular matrix, containing zeros in all places below the diagonal. Initially the matrix and the right hand side vector are assembled in an augmented matrix, thus, to obtain the upper triangular matrix, linear operations between lines are performed in such a way as to obtain zeros below the diagonal. After the first column is taken care the program proceeds to the next column (and the second line) and the procedure is repeated until the lines are finished. Once the triangular matrix is obtained the system can be solved directly starting at the last equation (last line) and substituting the results back to the first line. Back-substitution allows for a fast solution of the system, since θ_4 is obtained directly as

$$\theta_4 = \frac{b_4}{A_{44}},$$

and θ_3 and others are obtained from the system substituting this θ_4 value in the previous equation, and successively as follows:

$$\theta_i = \frac{1}{A_{ii}} \left[b_i - \sum_{j=i+1}^{N} A_{ij} x_j \right],$$

where N is the order of the matrix, in our case 4.

3.2 Partial pivoting

For the elimination to be possible it is necessary that the diagonal element be non-zero, since the coefficients of the process will be divided by these elements. If a zero pivot is found it is necessary to change rows (or columns) to avoid such a nuisance. This can also happen for numerical methods for small values for the pivot, which can generate large round-off errors. One way to avoid this problem is to adopt partial pivoting, in which the lines (or columns) of the augmented matrix are exchanged in such a way as to put the desirable (non-zero) pivot on the diagonal, working always with the lines below the pivot in such a way not to alter the lines above it which have already been constructed. It has been suggested the column exchange as an optional procedure, but this technique is more computationally expensive than the row exchange (Press et al., 1992). For the same reason the technique of total pivoting is not popular.

With the found θ values it is possible to obtain the partial currents using the kinetic equations of the electrochemical reactions involved in the process of anodic dissolution of Zinc, and presented in the groups I, II, and III. The partial currents allow the computation of the total current, as mentioned in the previous section.

This model aids in the computation of the surface fractions θ and partial currents, as well as the total current, for each value of the potential E. Using the computational tool the vary the potential E it is possible to assemble a database that, with the aid of a plotting software, can be used to manufacture the I x E and θ x E charts that will be presented further.

3. SIMULATION OF CONSECUTIVE MECHANISM

The consecutive process of zinc dissolution proceeds according to the bolded path on the scheme presented underline:
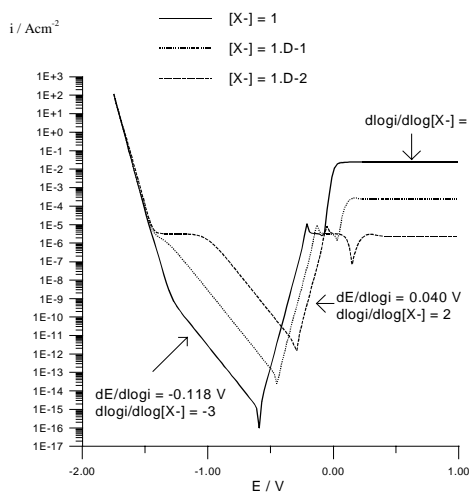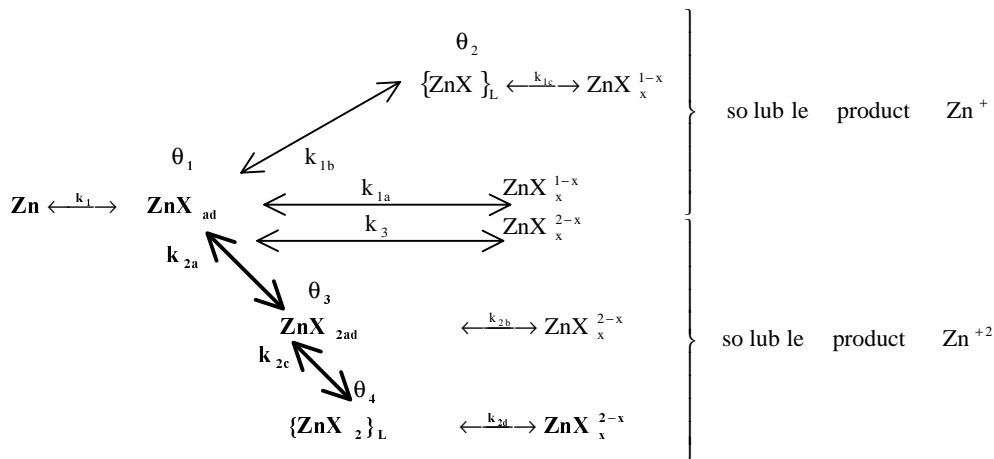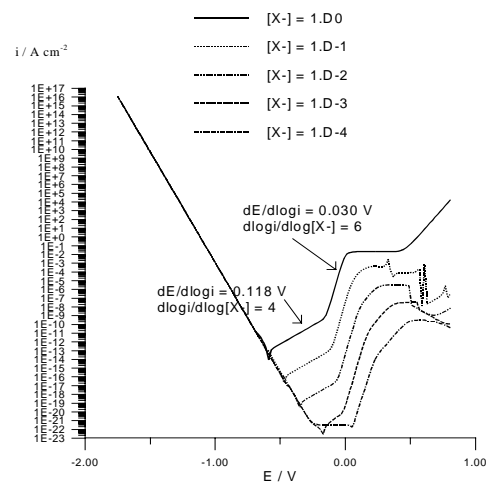

Fig.1 Simulation of the influence of anion concentration $[X^-]$ on the stationary polarisation curves of zinc. Data used in the simulation: $\alpha = 0,5$, T= 298 K, c = 21 V^{-1}, $k_1^{0\pm} = 10^{-1}$, $k_{1a}^{0\pm} = 10^{-30}$ $k_{1b}^{0\pm} = 10^{-30}$, $k_{1c}^{0\pm} = 10^{-3}$, $k_{2a}^{0\pm} = 10^{-5}$, $k_{2b}^{\pm} = 10^{-30}$, $k_{2c}^{0\pm} = 10^{-3}$, $k_{2d}^{\pm} = 10^{-6}$, $k_3^{0\pm} = 10^{-30}$ mol/cm²sec, $[Zn^{*0}] = 10^{-13}$ mol/cm², $[ZnX_x^{x-1}] = [ZnX_x^{2-x}] = 10^{-20}$ mol/dcm³.

Fig.2 Simulation of the influence of anion concentration $[X^-]$ on the stationary polarisation curves of zinc. Data used in the simulation: $\alpha = 0.5$, T= 298 K, c = 21 V^{-1}, $k_1^{0\pm} = 10^{-1}$, $k_{1a}^{0\pm} = 10^{-30}$ $k_{1b}^{0\pm} = 10^{-30}$, $k_{1c}^{0\pm} = 10^{-3}$, $k_{2a}^{0\pm} = 10^{-5}$, $k_{2b}^{\pm} = 10^{-30}$, $k_{2c}^{0\pm} = 10^{-3}$, $k_{2d}^{\pm} = 10^{-6}$, $k_3^{0\pm} = 10^{-3}$ mol/cm²sec, $[Zn^{*0}] = 10^{-7}$ mol/cm², $[ZnX_x^{x-1}] = [ZnX_x^{2-x}] = 10^{-20}$ mol/dcm³.

We assume that the reaction i_{2a} (oxidation of ZnX_{ad}) and i_{2d} (dissolution of 3D layer of ZnX_2) are the rate determining steps (rds) of the overall electrochemical process. Fig.1 presents the simulation of stationary polarisation curves (i = f(E)) for the system. The polarisation curves show two Tafel slopes +0.120 V (+2.303RT/0.5F) and +0.040V (+2.303RT/1.5F) for cathodic and anodic reaction respectively what is confirmed by the experimental results (Gaiser and Heusler, 1970; Heusler and Knoedler, 1973; Banaś et al., 1986). The reaction order vs. concentration of anion is equal 3 for the cathodic and 2 for the anodic brunch what is coincident with the number of anions X participating in the rds reactions. The change of rds step occurs at high overvoltage. The Tafel slope of -0.040 V (-2.303RT/1.5F) at high cathodic overvoltage is connected with the increase of the role of the reaction i_3. The reaction i_3 proceeds on the active places of metal surface Zn* (structural imperfection). At high anodic overvoltage the limiting current corresponding to the reaction 4d can be observed. The reaction order of this reaction dlogi/dlog[X$^-$] equal 2 is connected with the number of anion X participating in the reaction i_{2d}.

5. SIMULATION OF THE CONSECUTIVE - PARALLEL MECHANISM
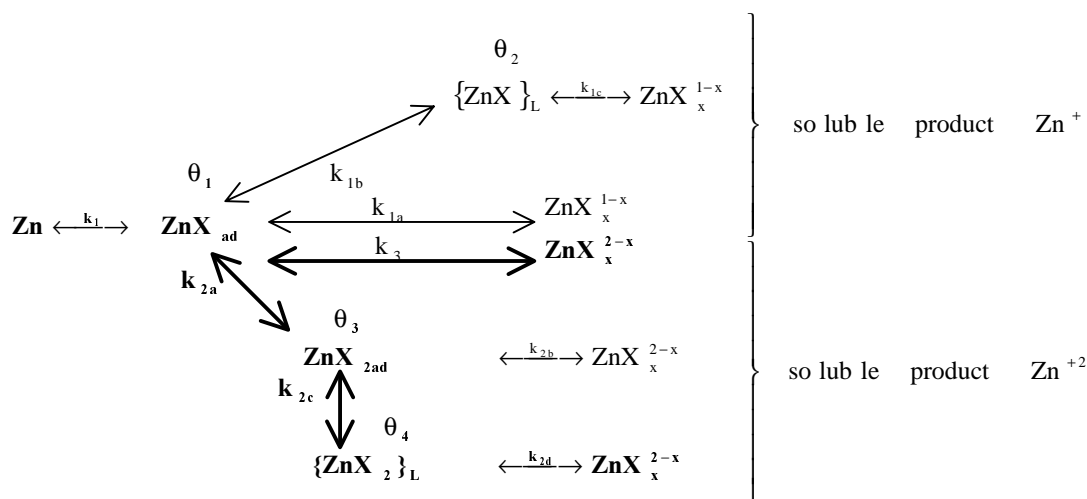
In this process besides the consecutive mechanism the path k_3 plays very important role:
The reaction i_3, which proceeds on active places of the metal surface, dominates the metal dissolution especially at low anodic overvoltage. Fig.2 presents the simulation of stationary polarisation curves of the system. The polarisation curves show the characteristic "S" shape with two Tafel slopes 0.120V (2.303RT/0.5F) and 0.030V (2.303RT/2F). The slopes correspond to the reactions i_3 and i_2. Increase of anion concentration increases anodic current. The reaction order in the region of Tafel slope 0.120V is equal 4 while four anion molecule participate in the path k_1 - k_3. For the Tafel slope 0.030V the reaction order is equal 6 what corresponds to the six anion molecules participating in the path k_1 - k_{2a} - k_{2c} - k_{2d}. At low concentration of complexing agent (anion concentration $[X^-] < 10^{-2}$ m/l) the 3D dimensional ZnX_2 layer is growing on the metal surface and decrease of the anodic current is observed.
Simulated polarisation curves for zinc dissolution according to the coupled consecutive - parallel mechanism explain the shape of experimental polarisation measurements performed in organic solvents. Fig.3 presents the anodic polarisation curve for zinc in acetonitrile - 0.1mLiClO$_4$ solutions. The "S" shape of i - E curve shows two Tafel slopes of 0.120V and 0.030V. Similar results have been obtained in methanolic solutions (Fig.4).
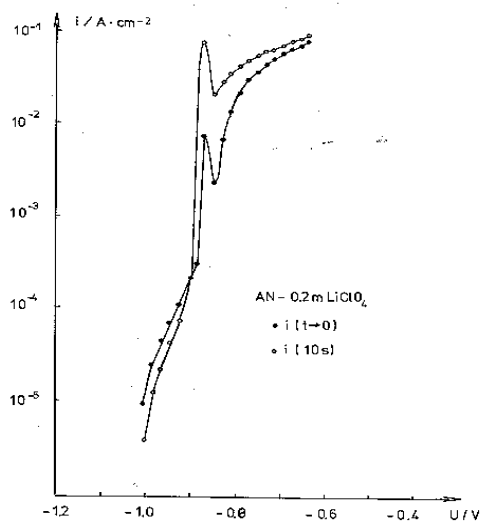
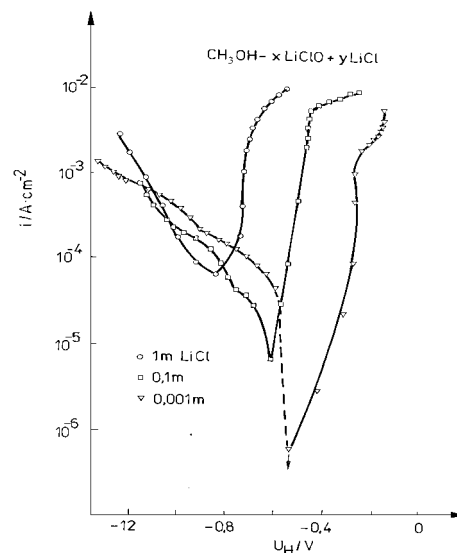Fig.3 Stationary polarisation curves of zinc in the solution CH_3CN - 0,2m $LiClO_4$.

Fig.4 Stationary polarisation curves of zinc in the solution CH_3OH - $xLiClO_4$ - $yLiCl$ (x+y = 0,1m).

6. CONCLUSIONS

Numerical simulation enables to explain the complicate dissolution mechanism of metals in organic solvents. In this media the presence of low soluble surface species influences strongly the electrochemical reaction. The simulation shows both the distribution of partial currents connected with the partial electrochemical reaction and the distribution of surface compounds on the metal surface during electrochemical polarisation.

Presented model is able to reproduce laboratory results for stationary polarisation measurements of zinc in organic solvents, therefore predicting results on experiments on complicated systems. The numerical algorithm is robust and will be used for nonstationary predictions.

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