

Kinetics of the zinc anodic dissolution reaction in near neutral EDTA solutions

SLAVKA STANKOVIĆ, BRANIMIR GRGUR[#], NEDELJKO KRSTAJIĆ[#] and MILAN VOJNOVIĆ[#]

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia and Montenegro

(Received 8 October, revised 11 November 2002)

Abstract: Polarization curves of the anodic dissolution reaction of zinc were determined in EDTA solutions of different total molar concentrations (0.05, 0.10, 0.15 and 0.20 mol dm⁻³), the pH values of which were systematically varied (pH 3.0 – 10.0). The Tafel slopes of the anodic polarization curves are close to 40 mV dec⁻¹ at lower current densities (10⁻⁵ – 5×10⁻⁴ A cm⁻²), while at higher current densities (5×10⁻⁴ – 10⁻² A cm⁻²) the slopes are in the range of 60 – 120 mV dec⁻¹. The order of the anodic reaction determined from the anodic polarization curves at lower current densities are: $z_+(H^+) \approx -1/2$ for pH < 8 and $z_+(H^+) \approx 1$ for pH > 8, while $z_+(H_4Y) \approx 1$ for all pH values of the examined EDTA solutions. On the basis of these results, two mechanisms of the zinc anodic dissolution reaction are proposed: at pH < 8 and at pH > 8. In both cases the relevant EDTA species directly participate as reactants in the anodic reaction. The dependences of the corrosion potential on pH and on total molar EDTA concentration indicate that the relevant EDTA species take part as reactants in both the cathodic (hydrogen evolution) and anodic (zinc dissolution) reactions of the zinc corrosion process.

Keywords: zinc, EDTA, anodic dissolution, kinetics, mechanisms.

INTRODUCTION

Ethylenediaminetetraacetic acid (EDTA or H₄Y in the forthcoming text) like tetrabasic polycarbonic acid exists in different forms and can be presented by general formula H_nY⁽⁴⁻ⁿ⁾⁻ (unprotonized acid residue represented as the anion Y⁴⁻, n = 0 – 4). Depending on the pH of the EDTA solution, more protonized species exist (n = 1 – 4) and unprotonized anion (n = 0). In several papers,^{1–5} it was shown that EDTA over a relatively wide pH range has interesting effects on the electrochemical behaviour of some non-noble metals. These effects include: (i) effectively prevents or removes an oxide (hydroxide) layer formed on the metal surface and (ii) participates in the hydrogen evolution reaction in such a way that the protonized EDTA anions and acid itself behave as electroactive species, *i.e.*, directly take part as reactants in the electrode reaction. The last point was con-

[#] Serbian Chemical Society active member.

firmed by kinetics examination of the hydrogen evolution reaction on silver⁶ and zinc⁷ in EDTA solutions.

As a corrosion unstable electrode material with a tendency to spontaneously form an oxide (hydroxide) surface layer, zinc in near neutral solutions should be a convenient substrate to express the EDTA effects mentioned above. Taking into account this point, kinetic examination of the zinc anodic dissolution reaction in near neutral EDTA solutions ($c_M(\text{H}_4\text{Y}) = 0.05 - 0.20 \text{ mol dm}^{-3}$, pH 3.0 – 10.0) was performed in this work as a further study of the zinc corrosion process.⁷

EXPERIMENTAL

Electrochemical cell. A conventional all glassy three-compartment cell was used. The working zinc electrode (WE) compartment was separated by fritted glass discs from the other two compartments and was provided with an inert gas inlet. Purified nitrogen was passed through the solution in WE compartment before and during each experiment.

Chemicals and solutions. All solutions examined were prepared using p.a. chemicals and deionized water. Four sets of solutions were prepared with different total molar EDTA concentrations (0.05, 0.10, 0.15 and 0.20 mol dm⁻³), the pH values of which were systematically varied in the range pH 3.0 – 10.0, adjusted by adding either a H₂SO₄ or NaOH solution. In all the examined solutions, the supporting electrolyte was 0.25 mol dm⁻³ Na₂SO₄.

Electrodes. Polycrystalline zinc wire (diam. 1 mm, purity 99.99 %, ESPI) of 1 cm² exposed surface area was used as the WE. The counter electrode was a platinum sheet of 5 cm² geometric area. The reference electrode was a saturated calomel electrode (SCE), which was kept at 25 ± 2 °C, as was the WE. However, all WE potential measured are referred to the standard hydrogen electrode (SHE) scale and those data are presented throughout this work.

Before each experiment, the WE was polished with alumina powder, degreased in hexane and rinsed with deionized water and the solution to be examined. After immersing into the to be examined solution, the WE was kept at the open circuit potential for 15 min and then the anodic polarization curves were recorded without any electrochemical pretreatment.

Measurements. Anodic Tafel lines were recorded using galvanostatic steady-state voltammetry, point by point in 60 s intervals, in the current density (cd) range from 10⁻⁶ – 10⁻² A cm⁻² (from the open circuit potential to around – 0.60 V) using a PAR 273 potentiostat-galvanostat. Anodic polarization curves were always recorded from the open circuit potential until the limited anodic potential had been reached. Before repeating the measurement, the WE was cleaned up again in the same way as presented above. The reproducibility of the measurements was good under these experimental conditions.

RESULTS

Open circuit potential. The open circuit potential values of the zinc electrode, which correspond to the corrosion potential, E_{corr} , were determined in the four sets of EDTA solutions, the compositions of which are given above. The values of the corrosion potential as a function of pH are shown in Fig. 1.

From Fig. 1 it can be seen that the corrosion potential is approximately independent of the total molar EDTA concentration. In this case, the pH-dependence of the corrosion potential using the corresponding mean values can be presented as $\langle E_{\text{corr}} \rangle - \text{pH}$. The slope of the linear dependence $\langle E_{\text{corr}} \rangle - \text{pH}$ is different at the lower and higher pH values (the change of slope arises at pH ≈ 8). The dependencies of the mean corrosion potential on pH can be presented as:

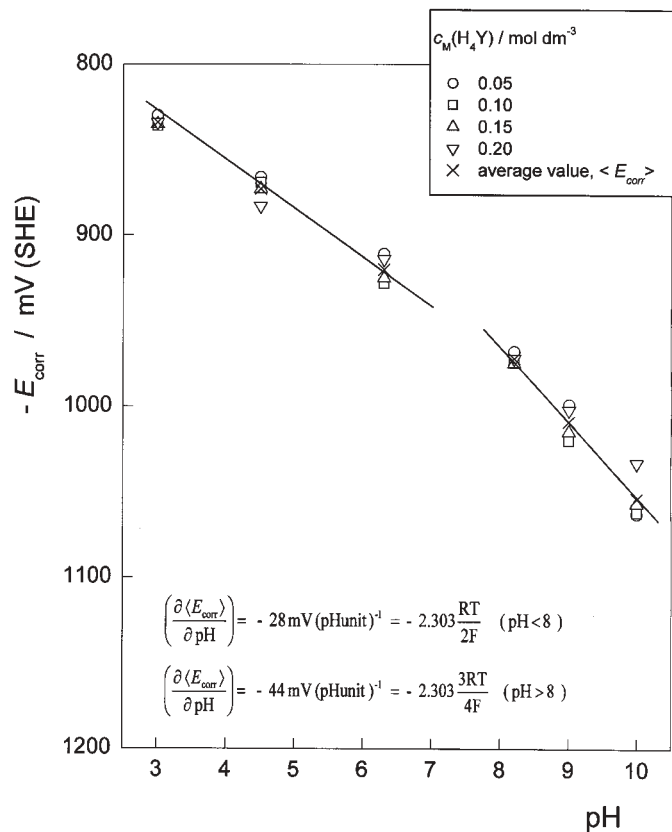


Fig. 1. The dependencies of zinc corrosion potential on pH for different constant total molar EDTA concentrations ($0.05 - 0.20 \text{ mol dm}^{-3} \text{ H}_4\text{Y} + 0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, $\text{pH} = 3.0 - 10.0$).

$$\langle E_{\text{corr}} \rangle = E_{\text{corr}(1)}^0 - 0.028 \text{ pH} \approx E_{\text{corr}(1)}^0 - 2.303 \frac{RT}{2F} \text{ pH} \quad (\text{pH} < 8) \quad (1)$$

$$\langle E_{\text{corr}} \rangle = E_{\text{corr}(2)}^0 - 0.044 \text{ pH} \approx E_{\text{corr}(2)}^0 - 2.303 \frac{3RT}{4F} \text{ pH} \quad (\text{pH} > 8) \quad (2)$$

where the $E_{\text{corr}(1)}^0$ and $E_{\text{corr}(2)}^0$ are constants.

Anodic polarization curves. Steady-state polarization curves of the anodic dissolution reaction of zinc were determined for all sets of EDTA solutions mentioned. In all cases the zinc electrode has the same type of anodic polarization behaviour. As an example, for one of the sets of solutions ($0.20 \text{ mol dm}^{-3} \text{ H}_4\text{Y} + 0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, $\text{pH} 3.0 - 10.0$), the series of anodic Tafel lines is shown in Fig. 2.

Generally, the $E - \log j_+$ dependencies show two different ranges of anodic polarization behaviour of the zinc electrode, depending on the cds (Fig. 2). At the lower cds (approximately $10^{-5} - 5 \times 10^{-4} \text{ A cm}^{-2}$), the linear parts of the polarization curves have Tafel slopes near to a nominal value of $b_+ = 40 \text{ mV dec}^{-1}$. The linear parts of anodic polarization curves in this cd region are well expressed, but become less expressed (shorter) especially

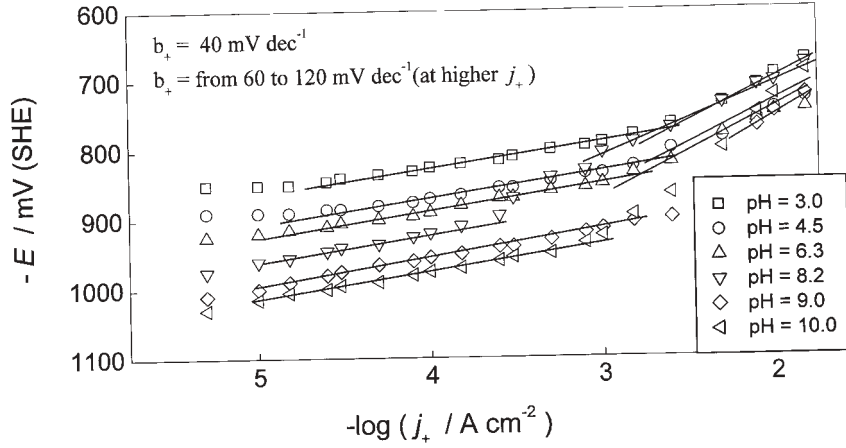


Fig. 2. Tafel plots $E - \log j_+$ of the zinc electrode in $0.20 \text{ mol dm}^{-3} \text{ H}_4\text{Y} + 0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, in the pH range 3.0 – 10.0.

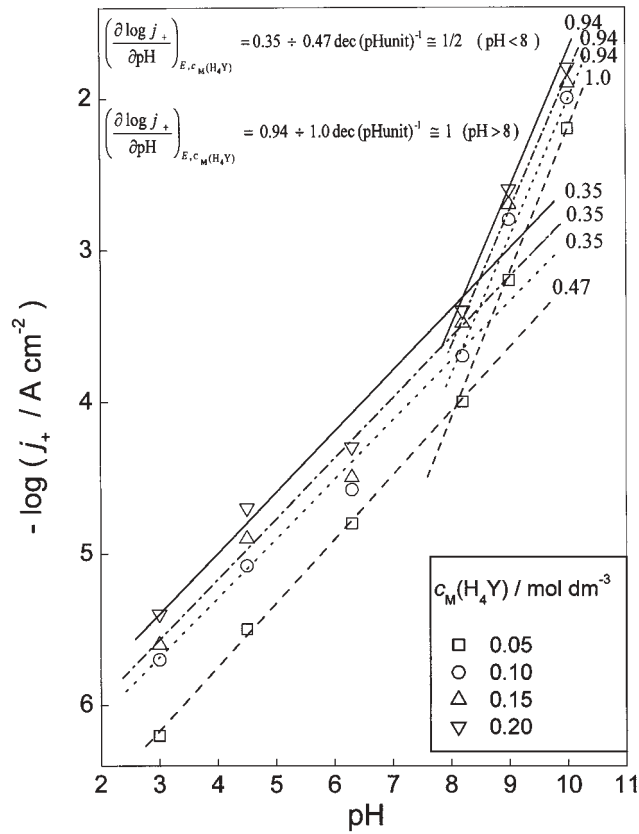


Fig. 3. The dependencies $\log j_+ - \text{pH}$ at constant potential ($E = -900 \text{ mV}$) for different constant total molar concentrations of EDTA.

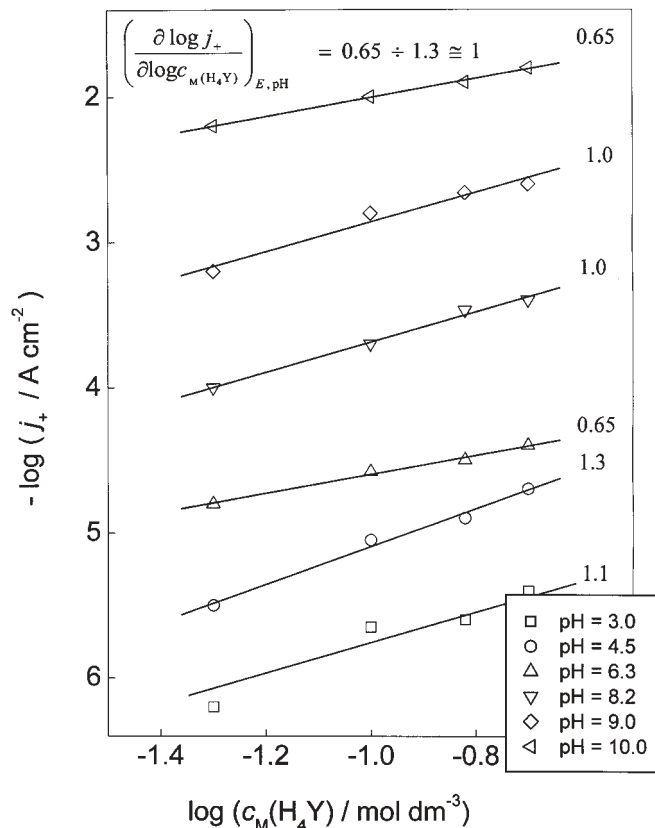


Fig. 4. The dependencies $\log j_+ - \log c_M(\text{H}_4\text{Y})$ at constant potential ($E = -900$ mV) for different constant pH values.

at $\text{pH} \approx 8$. Such a distinct anodic polarization behaviour of the zinc electrode at $\text{pH} \approx 8$ corresponds with the $E_{\text{corr}} - \text{pH}$ dependence and both indicate a changing of mechanism of the anodic dissolution reaction of zinc on passing over from the acid to alkaline region.

If all the recorded anodic polarization curves are compared in the lower cd region, the shifting of the linear parts of anodic polarization curves to more positive values of anodic potentials with increasing pH (at $c_M(\text{H}_4\text{Y}) = \text{const.}$) and total molar EDTA concentration (at $\text{pH} = \text{const.}$) is evident. This trend in the anodic polarization behaviour corresponds to an increasing of the rate of the anodic dissolution of zinc.

At the higher cds, the linear parts of the anodic polarization curves are mostly less expressed (in some cases the limiting current precedes) and the Tafel slope values are considerably higher ($b_+ = 60 - 120$ mV dec^{-1}), indicating a change in the reaction mechanism.

Kinetics parameters. In Figs. 3 and 4 $\log j_+ - \text{pH}$ and $\log j_+ - \log c_M(\text{H}_4\text{Y})$ dependencies at the constant potential ($E = -900$ mV) are shown, respectively.

The slopes of linear $\log j_+ - \text{pH}$ ($c_M(\text{H}_4\text{Y}) = \text{const.}$ in the range $0.05 - 0.20$ mol dm^{-3}) dependencies are: (i) $0.35 - 0.47$, which correspond with anodic reaction order according

to H^+ ions $z_+(H^+) \approx -1/2$ (for $pH < 8$) and (ii) $0.94 - 1.0$, *i.e.*, $z_+(H^+) \approx -1$ (for $pH > 8$). The slopes of linear $\log j_+ - \log c_M(H_4Y)$ ($pH = const.$ in the range $3.0 - 10.0$) dependencies are $0.6 - 1.0$ (mostly close to 1.0), over the entire pH region, *i.e.*, $z_+(H_4Y) \approx 1$. These data confirm the change of mechanism of the anodic reaction at $pH \approx 8$ as mentioned in the preceding section. From the kinetic parameters obtained, the expressions for the anodic reaction rates are:

$$j_+ = 2Fk_{+1} \alpha^{-1/2}(H^+) c_M(H_4Y) \exp(3FE/2RT) \quad (pH < 8) \quad (3)$$

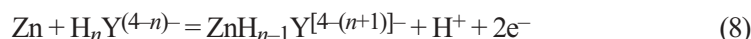
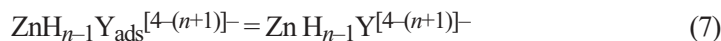
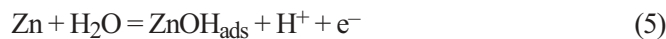
and

$$j_+ = 2Fk_{+2} \alpha^{-1}(H^+) c_M(H_4Y) \exp(3FE/2RT) \quad (pH > 8) \quad (4)$$

DISCUSSION

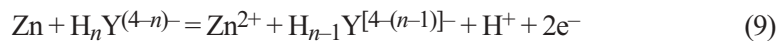
The experimental data and kinetic parameters of the anodic dissolution reaction of zinc obtained and especially the unusual fractional reaction order according to H^+ ions, indicate the direct participation of protonized EDTA species as reactants at $pH < 8$.

Bearing this in mind, one can take into consideration the following mechanism of the anodic dissolution reaction of zinc, which corresponds to: (i) $pH = 3 - 8$, (ii) the lower anodic cd range and (iii) the Tafel slope of the anodic polarization curves close to the nominal value of $b_+ = 40 \text{ mV dec}^{-1}$:

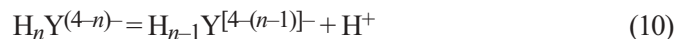


where Eq. (6) is the rate-determining step (rds).

If the total dissociation of mixed (protonized) zinc-EDTA complexes is considered, the above overall reaction can be written in the form:



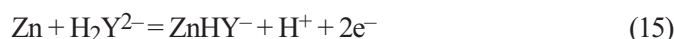
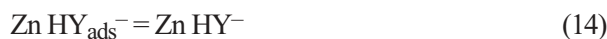
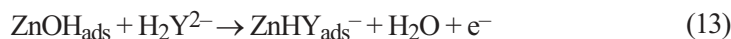
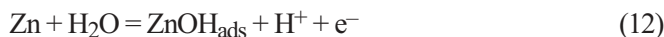
and because of the starting of the dissociation of the protonized EDTA species



from Eq. (8) the simple overall reaction is obtained

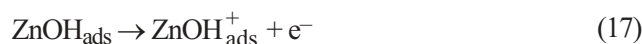
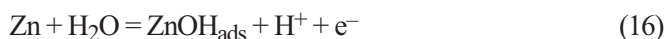


The protonized anion H_2Y^{2-} ($n = 2$, $pK_{d,2} = 6.9 \times 10^{-7} \text{ mol dm}^{-3}$)⁹ can be taken as an example of the mechanism (5) – (8) if it dominates as the reactant in the rds:



It should be noted that the products of the anodic dissolution reaction of zinc in EDTA solutions, depending on pH, can be complexes ZnH_2Y (with a cumulative stability constant $\beta_2 = 23.0$), ZnHY^- ($\beta_1 = 20.9$), ZnY^{2-} ($\beta_0 = 16.5$) and ZnOHY^{3-} ($\beta_{\text{h}} = 19.5$), known from the literature.⁹

If Eqs. (5) – (15) are compared with the analogous mechanism of the anodic dissolution reaction of zinc in the absence of complexing agents or surface active anions (otherwise often used as an interpretation of the anodic dissolution kinetics for some non-noble metals):



it can be concluded that the effect of EDTA on the kinetics of the anodic dissolution reaction of zinc is a form of acid catalysis, because the protonized EDTA species, $\text{H}_n\text{Y}^{(4-n)-}$, taking part in the rds (6) can decrease the activation barrier in comparison to the simple rds (17).

From the mechanism (5) – (8), the anodic reaction rate for the $\theta(\text{ZnOH}) \ll 1$ can be written as:

$$\begin{aligned} j_{+,n} &= 2Fk_{+,n} a^{-1}(\text{H}^+) [\text{H}_n\text{Y}^{(4-n)-}] \exp(3FE/2RT) = \\ &= 2Fk_{+,n} a^{-1}(\text{H}^+) \alpha(\text{H}_n\text{Y}^{(4-n)-}) c_{\text{M}}(\text{H}_4\text{Y}) \exp(3FE/2RT) \end{aligned} \quad (20)$$

where: $j_{+,n} / \text{cm s}^{-1}$ is rate constant; $[\text{H}_n\text{Y}^{(4-n)-}] / \text{mol cm}^{-3}$ is the actual molar concentration and $\alpha(\text{H}_n\text{Y}^{(4-n)-}) = [\text{H}_n\text{Y}^{(4-n)-}] / c_{\text{H}}(\text{H}_4\text{Y})$ is the fractional molar coefficient ($0 < \alpha(\text{H}_n\text{Y}^{(4-n)-}) < 1$) of the protonized EDTA species.

The fractional molar coefficient of the EDTA species can be calculated on the basis of the known values of the dissociation constants, the actual molar concentration of hydrogen ions (*i.e.*, pH) and the total molar EDTA concentration.^{8,10} The functions $\alpha(\text{H}_n\text{Y}^{(4-n)-}) = \phi_n(\text{pH})$, have a rather sharp maximum in a narrow pH interval (*e.g.*, see summary diagram of the functions $\alpha(\text{H}_n\text{Y}^{(4-n)-}) - \text{pH}^{10}$). Therefore the modification of the pH – dependence of zinc anodic dissolution rate (Eq. (20)) originates from presence of the EDTA in the solu-

tion. It is reasonable to suppose that all of the protonized EDTA species take part in the anodic reaction because of the shape of the $\alpha(\text{H}_n\text{Y}^{(4-n)-}) - \text{pH}$ dependencies. In the other case, the monotonous function of the reaction rate of the anodic dissolution of zinc on pH would not exist over a wider pH range. However, the experimental data at pH 3.0 – 8.0 do show a monotonous dependence of the anodic reaction rate on pH (Fig. 3). Therefore, the overall anodic cd can be given as sum of the partial anodic cds from Eq. (20):

$$\begin{aligned} j_+ &= \sum_{n=1}^{n=4} j_{+,n} = 2Fa^{-1} (\text{H}^+) c_{\text{M}}(\text{H}_4\text{Y}) \sum_{n=1}^{n=4} k_{+,n} \alpha(\text{H}_n\text{Y}^{(4-n)-}) \exp\left(\frac{3FT}{2RT}\right) = \\ &= 2Fa^{-1} (\text{H}^+) c_{\text{M}}(\text{H}_4\text{Y}) \sum_{n=1}^{n=4} k_{+,n} \phi_n(\text{pH}) \exp\left(\frac{3FE}{2RT}\right) = \\ &= 2Fa^{-1} (\text{H}^+) c_{\text{M}}(\text{H}_4\text{Y}) \phi \exp\left(\frac{3FE}{2RT}\right) \end{aligned} \quad (21)$$

where ϕ [cm s^{-1}], ($= \sum_{n=1}^{n=4} k_{+,n} \phi_n(\text{pH})$) is the sum of the partial pH – functions with appropriate rate constants as coefficients.

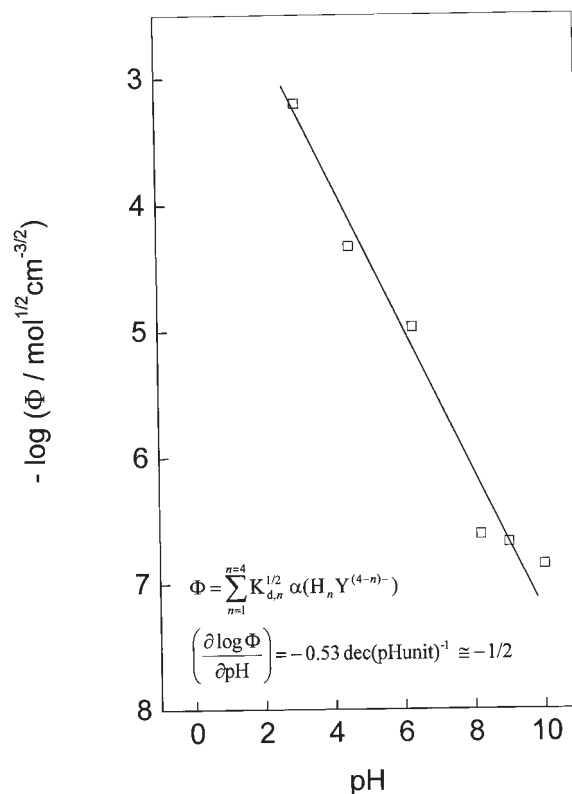
When the experimental (Eq. (3)) and theoretical (Eq. (21)) expressions are compared (at $c_{\text{M}}(\text{H}_4\text{Y}) = \text{const.}$ and $E = \text{const.}$), complete agreement is necessary if the proportionality $\phi \approx a^{1/2}(\text{H}^+)$ to this effect is valid. However, it is not possible to calculate the ϕ - function because the constant function coefficients, *i.e.*, partial rate constants, $k_{+,n}$, are unknown.

From the proposed mechanism (5) – (8), the overall anodic reaction rate is determined by rds (6), which in essence represents the reaction of proton transfer from the protonized EDTA species to the substrate (electrode surface layer – ZnOH_{ads}). In a recent work⁶ it was pointed out that the partial rate constants of the reaction of proton transfer from protonized EDTA species to the electrode surface can be estimated by using the Brønsted relation. As is well known, the Brønsted relation correlates the effectivity of acid and base catalysts in proton transfer reactions with their acid or base strength.¹¹ In the case of acid catalysis, this relation is:

$$k_{\text{H}} = \chi K_{\text{d}}^{\alpha} \quad (22)$$

where k_{H} [cm s^{-1}] is the rate constant of the proton transfer reaction; K_{d} [mol cm^{-3}] is the dissociation constant of the proton donor as a catalyst (the protonized EDTA anions and acid itself in this consideration), α is the Brønsted exponent or proton transfer coefficient reflecting the structure of transition state of the reaction ($0 < \alpha < 1$ with $\alpha = 1/2$ in the case of complete activation barrier symmetry) and χ [$\text{cm}^{5/2} \text{mol}^{-1/2} \text{s}^{-1}$] ($\alpha = 1/2$) is the proportionality coefficient.

The relation (22) is widely used in homogeneous acid catalysis. Using it in the electrode reaction is justified if the overall reaction rate is determined by the proton transfer reaction as the rds and the rate constant defined by the chemical part of the Gibbs activation energy for that reaction.

Fig. 5. The function $\log \Phi - \text{pH}$.

The usefulness of the Brønsted relation for estimating the partial rate constants in the hydrogen evolution reaction from EDTA solutions on silver⁶ and zinc⁷ electrode has been confirmed.

Therefore, if the rds of the anodic dissolution reaction of zinc (Eq. (6)) is treated as a proton transfer reaction and by using the relation (22), then $k_{\text{H}} \approx k_{+,n} = \chi K_{d,n}^{1/2}$, where the $K_{d,n}$ s correspond to the dissociation constants of the protonized EDTA species. Hence

$$\phi = \sum_{n=1}^{n=4} k_{+,n} \phi_n(\text{pH}) = \chi' \sum_{n=1}^{n=4} K_{d,n}^{1/2} \phi_n(\text{pH}) = \chi' \Phi \quad (23)$$

where Φ [$\text{mol}^{1/2} \text{cm}^{-3/2}$] is the pH dependent function ($=\chi' \sum_{n=1}^{n=4} K_{d,n}^{1/2} \alpha(H_n Y^{(4-n)-})$) and χ' [$\text{cm}^{5/2} \text{mol}^{-1/2} \text{s}^{-1}$] the proportionality coefficient.

On the basis of the known $K_{d,n}$ values⁸ and $\alpha(H_n Y^{(4-n)-})$ calculated for the EDTA solution examined in the pH range of 3.0–10.0, the Φ functions were determined and are given in Table I. From Table I, the dependence $\log \Phi - \text{pH}$ is shown in Fig. 5. A linear dependence is obtained

with the slope $\partial \log \Phi / \partial \text{pH} = -0.53 \approx -1/2$.

TABLE I. Parameters for the Φ function (pH = 3.0 – 10.0)

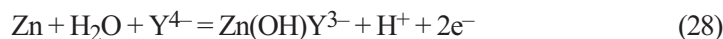
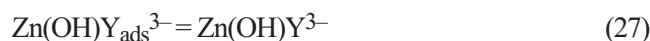
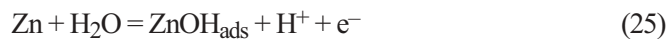
Parameters	$\text{H}_4\text{Y}^{(4-n)-}$				$\Phi / \text{mol}^{1/2} \text{cm}^{-3/2} - \log \Phi$	
	$n = 4$	$n = 3$	$n = 2$	$n = 1$		
$K_{d,n} / \text{mol cm}^{-3}$	1.0×10^{-5}	2.13×10^{-6}	6.9×10^{-10}	5.47×10^{-14}		
pH	$\alpha(\text{H}_4\text{Y})$	$\alpha(\text{H}_3\text{Y}^-)$	$\alpha(\text{H}_2\text{Y}^{2-})$	$\alpha(\text{HY}^{3-})$		
3.0	5.0×10^{-2}	3.1×10^{-1}	6.3×10^{-1}	6.3×10^{-2}	6.27×10^{-4}	3.20
4.5	4.6×10^{-5}	1.43×10^{-2}	9.6×10^{-1}	2.1×10^{-2}	4.62×10^{-5}	4.33
6.3	4.9×10^{-8}	1.40×10^{-4}	4.0×10^{-1}	5.6×10^{-1}	1.07×10^{-5}	4.97
8.2	1.0×10^{-14}	1.0×10^{-8}	3.16×10^{-4}	9.9×10^{-1}	8.16×10^{-8}	6.61
9.0	1.0×10^{-17}	1.0×10^{-9}	1.0×10^{-4}	9.1×10^{-1}	6.98×10^{-8}	6.67
10.0	1.0×10^{-19}	1.0×10^{-10}	1.0×10^{-7}	6.0×10^{-1}	4.43×10^{-8}	6.85

Therefore, the Brønsted relation gives the proportionality $\phi (\approx \Phi) \approx a^{1/2}(\text{H}^+)$ or $\log \phi (\approx \log \Phi) \approx (\text{pH})^{-1/2}$. From the first proportionality expression $\phi = k_{+,1}^2 a^{1/2}(\text{H}^+)$ can be written, where the proportionality constant $k_{+,1}^2 [\text{cm s}^{-1}]$ corresponds to the summary rate constant. Then from Eq. (21) the anodic reaction rate follows:

$$j_+ = 2Fk_{+,1}^2 a^{-1/2}(\text{H}^+) c_M(\text{H}_4\text{Y}) \exp(3FE/2RT) \quad (24)$$

which is in good agreement with the experimental data, *i.e.*, with Eq. (3).

The anodic reaction order according to H^+ ions changes at $\text{pH} > 8$ from $z_+(\text{H}^+) = -1/2$ to $z_+(\text{H}^+) = -1$, while the anodic reaction order according EDTA, $z_+(\text{H}_4\text{Y}) \approx 1$, remains unchanged over the entire pH-range of the examined solutions (pH = 3–10). Obviously, at the higher pH values, the protonized EDTA species are not kinetically significant in the anodic dissolution reaction of zinc, but unprotonized anions, Y^{4-} , prevail. Alongside this conclusion, the actual molar concentration of EDTA species must be taken into account because, according to the distribution of the $\alpha(\text{H}_n\text{Y}^{(4-n)-}) - \text{pH}$ curves over the entire pH range,¹⁰ the actual molar concentration of Y^{4-} anions dominates at the higher pH values mentioned. Therefore, it is reasonable to suggest a reaction mechanism where the Y^{4-} anions take part as reactants in the anodic dissolution reaction of zinc at $\text{pH} > 8$:



Furthermore, the overall reaction given above can be written in the form:



taking into account the equilibrium



The rate of anodic dissolution reaction of zinc according to the mechanism given above can be written as

$$\begin{aligned} j_+ &= 2Fk'_{+2} a^{-1}(\text{H}^+) [\text{Y}^{4-}] \exp(3FE/2RT) = \\ &= 2Fk'_{+2} a^{-1}(\text{H}^+) c_{\text{M}}(\text{H}_4\text{Y}) \exp(3FE/2RT) \end{aligned} \quad (31)$$

where the approximation $[\text{Y}^{4-}] \approx c_{\text{M}}(\text{H}_4\text{Y})$ is taken. On comparing Eqs. (4) and (31), it can be concluded that good agreement exists between the experimental and theoretical kinetic parameters.

The anodic polarization behaviour of the zinc electrode at higher cds (approximately in the cd range $5 \times 10^{-4} - 10^{-2} \text{ A cm}^{-2}$) where the higher Tafel slopes appear can be explained by an increase of the adsorbed intermediate coverage ($\theta(\text{ZnOH}_{\text{ads}})$) in the range of high anodic potentials. In such cases, depending on the anodic potential and the pH values, the coverage by ZnOH_{ads} increases and reaches the level where the Temkin's conditions of adsorption ($0.2 < \theta(\text{ZnOH}) < 0.8$) prevail, causing an increase of the Tafel slopes of the anodic polarization curves ($b_+ = 60 - 90 \text{ mV dec}^{-1}$). Finally, when coverage by the intermediate is complete (Langmuir's conditions of adsorption prevail and $\theta(\text{ZnOH}) \approx 1$), the rds in both mechanisms (5) – (8) and (25) – (28) is transferred from the second rds to the first one (in such case $b_+ = 120 \text{ mV dec}^{-1}$).

The functions $E_{\text{corr}} - \text{pH}$ and $E_{\text{corr}} - \log c_{\text{M}}(\text{H}_4\text{Y})$ (Eqs. (1) and (2)) obtained from the experimental data indicate that the rates of both the anodic (zinc dissolution) and the cathodic (hydrogen evolution) reactions in the zinc corrosion process depend on the relevant EDTA species. More detailed examination of the zinc corrosion process in near neutral EDTA solutions is in progress.

ИЗВОД

КИНЕТИКА АНОДНОГ РАСТВОРАЊА ЦИНКА У БЛИСКО НЕУТРАЛНИМ РАСТВОРИМА ЕДТА

СЛАВКА СТАНКОВИЋ, БРАНИМИР ГРГУР, НЕДЕЉКО КРСТАЈИЋ и МИЛАН ВОЈНОВИЋ

Технолошко-металуршки факултет, Универзитет у Београду, Карнегијева 4, 11000 Београд

Одређене су поларизационе криве анодног растварања цинка у растворима различитих укупних моларних концентрација ЕДТА (0,05, 0,10, 0,15 и 0,20 mol dm⁻³) у којима су систематски вариране рН вредности (рН = 3,0 – 10,0). Тафелови нагиби анодних поларизационих кривих имају вредности блиске 40 mV dek⁻¹ при мањим густинама струје (приближно 10⁻⁵ – 5 × 10⁻⁴ А cm⁻²) и 60 – 120 mV dek⁻¹ при већим густинама струје (приближно 5 × 10⁻⁴ – 10⁻² А cm⁻²). Редови

анодне реакције одређени из поларизационих кривих при мањим густинама струје су: $z_+(H^+) \approx -1/2$ за $pH < 8$ и $z_+(H^+) \approx 1$ за $pH > 8$, док је $z_+(H_4Y) \approx 1$ за све pH вредности испитиваних раствора. На основу ових резултата предложена су два механизма анодног растварања цинка – за $pH < 8$ и за $pH > 8$. У оба случаја релевантне врсте EDTA учествују као реактанти. Одређене вредности потенцијала корозије у функцији pH и укупне моларне концентрације EDTA индицирају да релевантне врсте EDTA учествују као ректанти како у анодној (растварање цинка) тако и катодној (издвајање водоника) реакцији процеса корозије цинка.

(Примљено 8. октобра, ревидирано 11. новембра 2002)

REFERENCES

1. P. R. Rowland, *Nature* **218** (1968) 945
2. P. R. Rowland, *J. Electroanal. Chem.* **32** (1971) 109
3. C. M. Lacnevac, M. M. Jakšić, *J. Res. Inst. Catalysis Hokkaido Univ.* **31** (1983) 7
4. R. Tunold, J. Brun, B. Johansen, M. M. Jakšić, *Russ. J. Electrochem.* **31** (1995) 638
5. M. M. Jakšić, J. Brun, B. Johansen, R. Tunold, *Russ. J. Electrochem.* **31** (1995) 1187
6. V. Marinović, A. Despić, *Russ. J. Electrochem.* **33** (1997) 965
7. S. Stanković, B. Grgur, N. Krstajić, M. Vojnović, *J. Electroanal. Chem.*, in press.
8. G. Schwarzenbach, R. Gut, G. Anderegg, *Helv. Chim. Acta* **37** (1954) 937
9. J. Incedi, *Primenenie kompleksov v analiticheskoj khimii*, Mir, Moscow, 1979, p. 330
10. H. A. Laitinen, W. E. Harris, *Chemical Analysis*, McGraw-Hill, N. Y., 1975, p. 189
11. A. J. Kresge, "The Brønsted Relation: Significance of the Exponent", in *Proton-Transfer Reaction*, E. F. Caldin and V. Gold, Eds., Chapman and Hall, London, 1975, p. 179–199.