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MECHANISM OF THE ANODIC DISSOLUTION OF THE ARMCO IRON IN
HClO$_4$ SOLUTIONS IN MIXED WATER-ALCOHOL SOLVENTS. II

ARMCO iron anodic dissolution in HClO$_4$ solutions in
mixed water-alcohol solvents has been investigated. On
the basis of Frumkin's isotherm the adsorptive effects
of the particles involved in the electrode reaction de-
termining step has been discussed.

In the proposals of the iron electrochemical corrosion me-
chanism in aqueous acidic electrolyte solutions, without spe-
cifically adsorbing ions or molecules, hydroxyl ions play an
important role. According to the metal surface properties the
catalyzed or noncatalyzed mechanisms of the anodic dissolu-
tion of the iron in H$_2$SO$_4$ or HClO$_4$ solutions have been descri-
bed [1-7].

Discrepancies in literature data concern the application
of the electrodes with different pre-treatments of the working
surface for the use of the method of iron zero charge potenti-
al values $(_{Fe}E_{\delta=0})$[6] and capacitance curves determination
[4,8-10].

On the basis of the measurements of iron RDE impedance in
H$_2$SO$_4$ solutions E p e l b o i n et a l. [11-17] the influ-
ence of the hydrogen adsorption and of the active complexes
FeOH$^+$ on the mixed mechanism of the anodic reaction in the
range of the polarization potentials characterized by so-cal-
led "negative impedance have been defined. The investigation
of a physical model confirms the influence of Warburg's impeda-
nce on the process under discussion, but the electrochemical
layer impedance cannot be included as a constant capacitance
in a parallel connection with faradaic impedance.

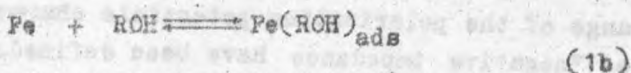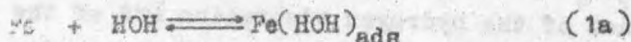The author's experiments have been described in [18].

Discussion

The investigation of the iron corrosion in acidid solutio-
ns in mixed aqueous - nonaqueous solvents encounters additio-
nal difficulties for the following reasons:

1° adsorption of the nonaqueous solvent molecules on the
electrode surface. If the solvent is not involved in creating
active complexes, then its participation is described by means
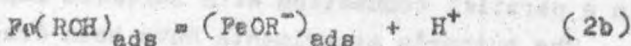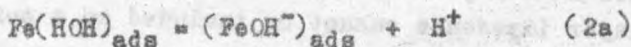of various models used in inhibited reactions descriptions;

2° an appearance of the solvent molecules on the electrode
surface leads to the $_{Fe}E_{\delta=0}$ shift and to the influence of the
polycrystalline metal surface energetic heterogeneity on the
potential shift. Theorefore the charge "anisotropy" determines
the adsorption anisotropy which limits the inhibitor action.
The proposals of the formal equations taking into account the
total sum of the adsorption, kinetic, chemical and electroche-
mical effects, and the mechanical interlocking are reported in
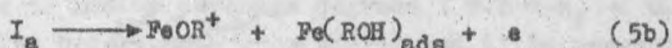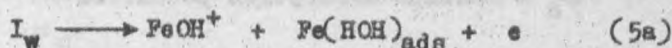the works of Antropov's and Parsons'schools;

3° the nonaqueous solvents molecules are involved in crea-
ting of the active complexes. So far the reaction mechanism of
few solvents, especially of the mixtures H_2O - DMSO [19,20]
H_2O - DMF [?1], H_2O - MeOH [21] and H_2O - EtOH [18,22] has
been put forward.

The mechanism of the anodic dissolution reaction suggested
by other authors [22], is based on the participation of the
active complexes of $FeOR^+$ type in the rate determining step
(RDS). Using these proposals we have:

$$Fe + HOH \rightleftharpoons Fe(HOH)_{ads} \qquad (1a)$$

$$Fe + ROH \rightleftharpoons Fe(ROH)_{ads} \qquad (1b)$$

$$(ROH = MeOH; EtOH; 1-PrOH; 2-PrOH)$$

$$Fe(HOH)_{ads} = (FeOH^-)_{ads} + H^+ \qquad (2a)$$

$$Fe(ROH)_{ads} = (FeOR^-)_{ads} + H^+ \qquad (2b)$$

$$(FeOH^{-})_{ads} = (FeOH)_{ads} + e \qquad (3a)$$

$$(FeOR^{-})_{ads} = (FeOR)_{ads} + e \qquad (3b)$$

$$(FeOH)_{ads} + Fe(HOH)_{ads} = [(FeOH) \cdot Fe(HOH)]_{ads} \equiv I_w \qquad (4a)$$

$$(FeOH)_{ads} + Fe(ROH)_{ads} = [(FeOR) \cdot Fe(ROH)]_{ads} \equiv I_a \qquad (4b)$$

$$I_w \longrightarrow FeOH^{+} + Fe(HOH)_{ads} + e \qquad (5a)$$

$$I_a \longrightarrow FeOR^{+} + Fe(ROH)_{ads} + e \qquad (5b)$$
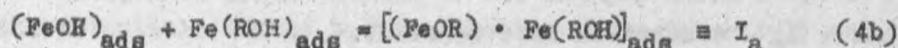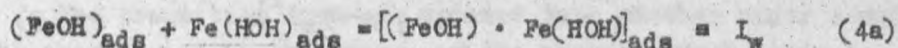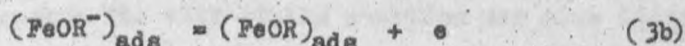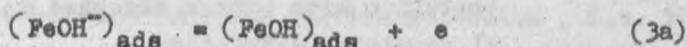
The electrode reaction rate determining step in mixed water-alcohol solvents has the form of the following equation according to [22]:
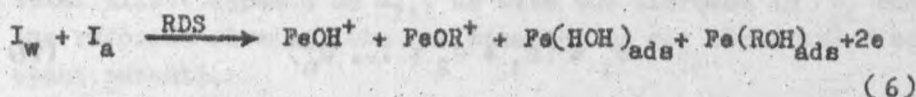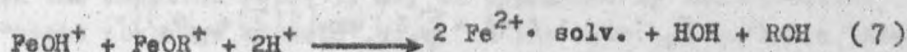
$$I_w + I_a \xrightarrow{\text{RDS}} FeOH^{+} + FeOR^{+} + Fe(HOH)_{ads} + Fe(ROH)_{ads} + 2e$$
$$(6)$$

and finally:

$$FeOH^{+} + FeOR^{+} + 2H^{+} \longrightarrow 2 Fe^{2+} \cdot solv. + HOH + ROH \qquad (7)$$

The reaction mechanism of the iron anodic dissolution does not solely depend on the solvent dipoles adsorption but also on the sum of interactions of adsorbed active complexes with the electrode and between the neighbouring solvent molecules.

The phenomenon of the self-acting adsorption of the mixture of reacting and electrode inactive substances is described by general Frumkin's isotherm [24]:

$$B_1 \cdot c_1 \cdot f_1 = \frac{\theta_1}{1 - \sum_1 \theta_1} \exp\left(-2 \sum_1 a_{11}\theta_i\right) \qquad (8)$$

where: f_1 - the reacting substance activity officient defined by Debye - Hückel theory,

a_{11} - characteristic constant of reacting substance interaction with others adsorbed molecules (lateral repulsive attraction)

and

$$B_1 = B_m \cdot \exp\left[-\gamma(\varphi - \varphi_m)^2\right] \qquad (9)$$

where: B_m - adsorption rate constant
φ_m - maximum adsorption potential

$$\gamma = \frac{K_{\theta=0} - K_{\theta i}}{2RT\Gamma_\infty} \qquad (10)$$

and where: $K_{\theta=0}$, $K_{\theta i}$ - integral capacitances for given coverage degrees respectively,
Γ_m - max. Gibbs' surface excess

$$\theta_i = (\theta_1 + \theta_2 + \dots \theta_n) \qquad (11)$$

When we substitute [9] into [8], we obtain:

$$\theta_1 = B_m \cdot c_1 \cdot f_1 \left(1 - \sum_i \theta_i\right) \exp\left[2\left(\sum_i a_{11}\theta_i\right)\right] \cdot$$

$$\cdot \exp\left[(1-\alpha)\frac{F}{RT}(\varphi - \varphi_1) - \right. \qquad ((12)$$

$$\left. - \frac{K_{\theta=0} - K_{\theta i}}{2RT\Gamma_\infty}(\varphi - \varphi_m)^2\right]$$

Independently of eq [12] we get the reaction current equation:

$$i = KB_m \cdot c_1 \cdot f_1 \cdot \left(1 - \sum_i \theta_i\right) \exp\left(2\sum_i a_{11}\theta_i\right) \cdot$$

$$\cdot \exp\left[(1-\alpha)\frac{F}{RT}(\varphi - \varphi_1) - \right. \qquad (13)$$

$$\left. - \frac{K_{\theta=0} - K_{\theta i}}{2RT\Gamma_\infty} \cdot (\varphi - \varphi_m)^2\right]$$

The so-called "salting out" takes place as the result of the interaction between ions and solvent molecules , i.e. the activity of organic substances in the solution is increased and as a consequence the rate of the reaction may also increase [19].

The transition from one solvent into another under const is accompanied by the change of the charge, which leads to the potentials change ψ_1 (the reaction plane potential) and to the rate change. The same situation takes place for the quantities Γ_∞ and φ_m.

In the range of medium coverage degrees ($0.2 < \theta_1 < 0.8$) the reaction rules become more complicated and it is necessary to take into consideration the terms $(1 - \sum_i \theta_i)$ and $\exp(2\sum a_{ii}\theta_i)$.

The increase in θ_i should bring about the decrease in the reaction rate together with the decrease in $(1 - \sum_i \theta_i)$. Simultaneously, the $\exp(2\sum_i a_{ii}\theta_i)$ value increases. The total effect depends on a_{ii}, so with the increase in θ_i both the reaction slowing down and speading up may occur under constant potential.

The increase in the amount of adsorbed molecules which cover the electrode surface leads to the considerable decrease in the reaction rate. It may be explained by the so-called "great coverage effects", i.e. in the adsorbed molecule takes up more place on the surface than in the equilibrium conditions. This is closely connected with the increase in molecule preorientation energy and with reorganization of the adsorptive layer what in consequence leads to the descrease in the rate of the reaction under coverage degrees $\theta \approx 1$.

For the discussion about the mechanism of the iron anodic dissolution reaction let us designate:

A. for solution in water:

coverage degrees: $\theta_{11} = \theta_{FeOH^+}$; $\theta_{12} = \theta_{Fe(HOH)_{ads}}$

lateral repulsive attraction constans:

$$a_{11} - \text{of FeOH}^+ \text{ complex}$$
$$a_{12} - \text{of Fe(HOH)}_{ads}$$

and w_{a_1} - FeOH$^+$ complex activity in water.

B. for solutions in water - alcohol solvents:

coverage degrees: $\theta_{21} \equiv \theta_{FeOH^+}$; $\theta_{22} \equiv \theta_{Fe(HOH)_{ads}}$

$\theta_{23} \equiv \theta_{FeOR^+}$; $\theta_{24} \equiv \theta_{Fe(ROH)_{ads}}$

taleral repulsive attraction constans:

a_{11} - of $FeOH^+$ complex ; a_{22} - Fe HOH $_{ads}$

a_{23} - of $FeOR^+$ complex ; a_{24} - Fe ROH $_{ads}$

activities:

s_{a_1} - of $FeOH^+$ complex;

s_{a_3} - $FeOR^+$ complex;

Let us write anodic reaction current equation expressed by equation (5a) applying formula (13):

$$w_{1_+} = w_k \cdot w_{B_m} \cdot w_{a_1}[1 - (\theta_{11} + \theta_{12})]\exp[2 \cdot (a_{11}\theta_{11} + a_{12}\theta_{12})] \cdot$$

$$\cdot \exp\left[(1 - \alpha_{5a})\frac{F}{RT}(^w\varphi_{corr} - ^w\psi_1) - \right. \qquad (14)$$

$$\left. \frac{^wK_{\theta=0} - ^wK_{\theta i}}{2RT \; ^w\Gamma_\infty}(^w\varphi_{corr} - ^w\varphi_m)^2\right]$$

and analagously for equation (5b):

$$s_{1_+} = s_k \cdot s_{B_m} \cdot s_{a_1} \cdot s_{a_3}\left\{[1 - (\theta_{21} + \theta_{22} + \theta_{23} + \theta_{24})]\right\} \cdot$$

$$\cdot \exp[2(a_{21} \cdot \theta_{21} + a_{22}\theta_{22} + a_{23}\theta_{23} + a_{24}\theta_{24})] \cdot$$

$$\cdot \exp\left[(1 - \alpha_{5b})\frac{F}{RT}(^s\varphi_{corr} - ^s\psi_1) - \right. \qquad (15)$$

$$\left. \frac{^sK_{\theta=0} - ^sK_{\theta i}}{2RT \cdot s\Gamma_\infty}(^s\varphi_{corr} - ^s\varphi_m)^2\right]$$

In RDS we get $\varphi_{corr} = \varphi_m$, which allows us to the neglect last terms ion equations (14) and(15).

Experimentally determined values of coefficient b_+ [18,22] satisfy the relationship:

$$(1 - \alpha_{5a}) = (1 - \alpha_{5b}) = (1 - \alpha) \qquad (16)$$

which allows us to divide equation (14) by eq. (15). So we get:

$$\frac{s_{i_{corr}}}{w_{i_{corr}}} = \frac{s_k \cdot s_{B_m} \cdot s_{a_1} \cdot s_{a_3}}{w_k \cdot w_{B_m} \cdot w_{a_1}} \cdot \frac{[1 - (\theta_{21} + \theta_{22} + \theta_{23} + \theta_{24})]}{[1 - (\theta_{11} + \theta_{12})]} \cdot$$

$$(17)$$

$$\cdot \exp\left\{2\left[(a_{21} \cdot \theta_{21} + a_{22}\theta_{22} + a_{23}\theta_{23} + a_{24}\theta_{24}) - \right.\right.$$

$$\left.\left. - (a_{11}\theta_{11} + a_{12}\theta_{12})\right]\right\} \cdot \exp\left[\frac{(1 - \alpha)F}{RT}(\Delta_w^s \varphi_{corr} - \Delta_w^s\psi_1)\right]$$

Among the terms of eq. (17) we can obtain experimentally the values: $s_{i_{corr}} / w_{i_{corr}}$, $(1 - \alpha)$ and $\Delta_w^s \varphi_{corr}$ and to calculate $\Delta_w^s \psi_1$.

The remaining quantities of equation (17) cannot be directly measured and the influence of the adsorption of particular molecules involved in the reaction (6) on the corrosion currents values may be disscused, for particular instances, only after introducing appropriate assumptions:

Conclusions

1° - let us assume that for small(< 1 mol %) concentration of alcohol in water:

$$\theta_{11} \cong \theta_{21} \quad \text{and} \quad \theta_{12} \cong \theta_{22} \qquad (18)$$

$$a_{11} \cong a_{21} \quad \text{and} \quad a_{12} \cong a_{22} \qquad (19)$$

$$s_{a_1} \cong w_{a_1} \qquad (20)$$

Then, the equation (17) takes the form:

$$\frac{{}^s i_{corr}}{{}^w i_{corr}} = \frac{{}^s k \cdot {}^s B_m \cdot {}^s a_3}{{}^w k \cdot {}^w B_m} \cdot \frac{[1 - (\theta_{11} + \theta_{12} + \theta_{23} + \theta_{24})]}{[1 - (\theta_{11} + \theta_{12})]} \cdot$$

$$\cdot \exp[2(a_{23} \cdot \theta_{23} + a_{24}\,\theta_{24})] \cdot \qquad (21)$$

$$\cdot \exp\left[\frac{(1-\alpha)F}{RT}(\Delta_w^s \varphi_{corr} - \Delta_w^s \psi_1)\right]$$

At the same time, θ_{23} and θ_{24} in the second term of eq. (21) are very small enough to neglect them. And we obtain:

$$\frac{{}^s i_{corr}}{{}^w i_{corr}} = \frac{{}^s k \cdot {}^s B_m \cdot {}^s a_3}{{}^w k \cdot {}^w B_m} \cdot \exp[2\,a_{23}\theta_{23} + a_{24}\theta_{24}] \cdot$$

$$(22)$$

$$\cdot \exp\left[\frac{(1-\alpha)F}{RT}(\Delta_w^s \varphi_{corr} - \Delta_w^s \psi_1)\right]$$

As it can be seen from above equation the reaction determining step depends on the adsorptive interaction between $FeOR^+$ and $Fe(ROH)_{ads}$ and on the activity of the complex $FeOR^+$.

2^0 - let us assume, for small water (< 1 mol %) concentration in alcohol, that:

$$\theta_{24} \gg \theta_{22} \quad ; \quad \theta_{23} \gg \theta_{21} \qquad (23)$$

and

$$a_{21} \cong a_{23} \qquad (24)$$

$$a_{24} \cong a_{22} \qquad (25)$$

$${}^s a_1 \cong 1 \qquad (26)$$

Then, equation (17) will take the form:

$$\frac{{}^s i_{corr}}{{}^w i_{corr}} = \frac{{}^s k \cdot {}^s B_m \cdot {}^s a_3}{{}^w k \cdot {}^w B_m \cdot {}^w a_1} \cdot \frac{[1 - (\theta_{23} + \theta_{24})]}{[1 - (\theta_{11} + \theta_{12})]} \cdot$$

$$(27)$$

$$\cdot \exp\{2[2(a_{23}\theta_{23} + a_{24}\theta_{24}) - (a_{11}\theta_{11} + a_{12}\theta_{12})]\} \cdot$$

$$\cdot \exp\left[\frac{(1-\alpha)F}{RT}(\Delta_w^s \varphi_{corr} - \Delta_w^s \psi_1)\right]$$

Contrary to the conclusion in point 1°, there is no explicite to the question whether water molecules in alcohol inhibit the electrode reaction. Equation (27) contains the sums of factors which describe the characteristic adsorptive interactions in water and in water- alcohol mixtures. The literature data are quoted the inhibition of this type in the case of the anodic reaction of steel [25] or titanium [26] in H_2SO_4 solutions in the same mixed solvents.

However, one should accept the results of corrosion investigations in anhydrous alcohol since it is probable that esters may form as the additional components of the solution.

Simultaneously, strong water inhibition in aprotic solvents has been also observed [27].

3° The adsorptive conditions at the interface become fixed in a wide range of concentrations of the water - alcohol mixtures (1 - 99 mol, % of alcohol). The difficulty in interpretation of the process has previously been explained by discussion of the uselulness of eq.(13) for the coverage degress $0.2 < \Theta < 0.8$.

The assumptions made in points 1° and 2° cannot be made in this case. However, solvation processes have a considerable effects on the reaction which constitutes the final stage of the iron anodic dissolution (eq. (7)).

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MECHANIZM REAKCJI ANODOWEGO ROZTWARZANIA ŻELAZA ARMCO
W ROZTWORACH HClO$_4$ W MIESZANYCH ROZPUSZCZALNIKACH
WODNO-ALKOHOLOWYCH. II.

Przedyskutowano propozycje mechanizmu reakcji anodowego
roztwarzania żelaza ARMCO w kwaśnych roztworach w mieszanych
rozpuszczalnikach woda-alkohol. W oparciu o izoterme Frumkina
przedyskutowano adsorpcyjne efekty cząstek biorących udział w
decydującym stadium reakcji elektrodowej.