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THE ROLE OF COMPLEXATION IN THE ANODIC DISSOLUTION OF METALS

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The influence of the sodium salts of dicarbonic, nitrilotriacetic (NTA) and etilendiamintetraacetic (EDTA) asids on the peculiarities of the anodic dissolution of cobalt has been studied.

The measumrents have been carried out by means of a potenthyodinamic method. The anodic polarization curves have been taken from the polycrystalline cobait in the naturally aeratied perchlorate solutions in the pH interval 1.7-9.5 at the concentration of the anion 0.1 M. The concentration of the salts of the acids enumerated above has been changed from $5 \cdot 10^{-5}$ to $5 \cdot 10^{-2}$ M. All potentials have been referred to the normal hydrogen scale.

Cobalt hasn't been in the passive state in the investigation of pH interval. This has been conditioned by the strong active effect of CIO₄⁻ ions (Fig.1). The critical current has been reached at $E_a \ge 0.15$ B and this value doesn't depend on pH solution. The anodic dissolution of cobalt is considered in two pH intervals 1.7-6.0 and 6.0-9.5. Cobalt dissolves with the formation of Co²⁺ ions in

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the first pH interval. In the second pH interval the metal as well as its oxides and hydroxides can dissolve.

The order of the anodic reaction on OH⁻ ions (m_{oH}) depends on the pH value and interval of potentials. In acid solution m m_{oH} ⁻ has the value 1.1±0.05. The change of the sign m m_{oH} ⁻ has been observed at pH 3.0. In feebly acid and alkaline solutions m m_{oH} ⁻ has the values -0.30±0.05 and -0.40±0.05 accordingly.

In virtue of the experimental data the schemes of the anodic dissolution of cobalt in the active region of the perchlorate solutions have been suggested. It has been assumed that the adsorption of the intermediate products is described with Langmuir adsorption isotherm. For instance, at pH 2.0-8.0 the mechanism described with scheme acts:

$Co + H_2O \leftrightarrow [CoOH]_{ads} + H^+ + e_{,}$	(1.1)
$[CoOH]_{ads} \rightarrow CoOH^+ + e,$	(1.2)
$CoOH^{+} + H^{+} \leftrightarrow Co^{2+} + H_2O,$ $[CoOH]_{ads} + CIO_4 \leftrightarrow [Co(OH)CIO_4]_{ads} + e,$	(1.3) (1.4)

The anodic polarization curves with the application of non-linear regressive analysis have been calculated. Between the calculative and experimental curves the good conformity has been observed.

Conformity to natural laws of the anodic dissolution of cobalt has been considered accoding to the formation of the cobalt (II) complexes in the solution with the dicarbonic acids, NTA and EDTA. The addition of sodium salts of the succinic, glutaric, adipic acids, NTA, EDTA promots the slowing-down of the rate of the cobalt dissolution in the acid solution (pH 2.0). Cobalt (II) doesn't form the complexes with the succinic, glutaric, adlpic acids and NTA in the solution at pH 2.0, at the same time Co²⁺ ions form the complex CoHY⁻ with EDTA. Thus, the slowing-down

of the process of the cobalt dissolution has been observed in pH interval of solutions, where the protonated complexes exist or the complexes with these anions are not formed. In case of the deprotonated complexes the rate of the dissolution is being increased. It's necessary to note that the higher is the constant of the complex stability the higher is rate of the dissolution. The acceleration of the process is characterized by the lesser values of the current density (i'_a) at C_{add} > 10⁻³ M as compared with i'_a at $C_{add} < 10^{-3}$ M. For example, the complexes of cobalt (II) with NTA (CoL, logarithm of the constant stability is $lg\beta=10.05$) and EDTA (CoY²⁻, Ig β =16.64) are present been in solution at pH 6.0. The complex of cobalt (II) with EDTA is more stable than that with NTA. The addition of NTA and EDTA in solutions with pH 6.0 has promoted the acceleration of the process of cobalt dissolution (Fig.2). The rate of the metal dissolution is higher at the addition of EDTA, but this effect is observed at Cadd<10⁻³ M. The small decrease of i'_{a} has occured in C_{EDTA}>10⁻³ M.

Schemes, which describe the mechanism of the anodic dissolution of cobalt in presence NTA, EDTA have been suggested. The schemes include parallel proceeding rate determining stages with the participation of the complexones particles.

So, in the process of changing from the acid perchlorate solutions to alkaline the mechanism of the cobalt dissolution has changed. This has been conditioned by different composition of the intermediate surface compounds. The influence of the sodium salts of the dicarbonic acids, NTA and EDTA is observed in pH interval of cobalt (II) complex existence with the dicarbonic acids, complexons in solution. The character of the influence is connected with the complex stability, their composition and form.



Fig.1. Anodic polarization curves of cobalt in 0.1 M NaClO₄ at pH: 1-1.7, 2-2.0, 3-3.0, 4-4.0, 5-6.0, 6-9.5.



Fig.2. Anodic polarization curves of cobait in 0.1 M NaClO₄ at pH 6.0 and $C_{NTA}=C_{EDTA}=5\cdot10^{-4}$ M: 1-background, 2-NTA, 3-EDTA.

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