SUMMARY AND CONCLUSION

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1- The introduction included a literature survey of the different theories of corrosion and corrosion inhibition. The electrochemical behaviour of iron and steel in aqueous solutions (acidic, alkaline and neutral) is given with particular emphasis on the effect of aggressive as well as inhibitive anions.

2-a- Potential-time curves were constructed for Fe and the steel samples I, II and III (whose composition is given in chapter I) in oxygentated solutions of H_2SO_4 of concentration ranging from 10^{-6} to 1M. In concentrated acid solutions (10^{-2}-1 M) there were an increase in the corrosion rate with increasing the acid concentration and a positive shift of the corrosion potential according to :

$$E_{st.} = a + b \log C_{H_2SO_4}$$

The corrosion process was found to be controlled by the rate of H^+ ion discharge (cathodic control). In dilute acid solutions (10^{-6} - 10^{-3}M) there were a negative shift in the corrosion potential according to :

$$E_{st.} = a - b \log C_{H_2SO_4}$$

with increasing the acid concentration, accompanied by an increase in the corrosion rate. In these solutions the reduction d- The inhibiting efficiency of the organic additives used was found to be dependent on the amount of the C-content in the steel samples, where :

i) The inhibitive efficiency of aniline for Fe and steel samples decreases in the order:

Steel I > Steel II > Steel III $\simeq$ Fe

ii) For p-nitroaniline the inhibitive efficiency decreases in the order :

Fe > Steel I > Steel II > Steel III

iii) For p-methoxyaniline the inhibitive efficiency decreases in the order :

Steel III > Steel II > Steel I $\simeq$ Fe

From the above observations, it is clear that, the inhibiting efficiency of p-nitroaniline and, to some extent, aniline decreases as the carbon content in the steel samples is increased. The reverse order is observed for p-methoxyaniline. This character may be ascribed to the surface defects and the variation of pearlite/ferrite ratio in the steel samples.

3- The anodic and cathodic Tafel lines were constructed for Fe and the steel samples in deaerated H_2SO_4 solutions. This was made to elucidate the effect of acid concentration, C-content and its para-substituted derivatives on the kinetic of oxygen to water molecules acts as a cathodic depolarizer for hydrogen evolution reaction. Therefore, the corrosion process is also cathodically controlled.

b- the presence of increasing amounts of carbon from zero (iron) to 0.4% (Steel III) shifted the steady-state potentials toward more negative values with increasing the corrosion rate at one and the same H_2SO_4 concentration. This was correlated with the ratios of pearlite and ferrite phases, since the hydrogen ovrvoltage on pearlite is lower than on ferrite.

c- Addition of aniline, p-nitroaniline, p-chloroaniline, p-aminobenzoic acid, p-methoxyaniline, p-phenylene diamine, p-toluidine and p-hydroxyaniline retards the dissolution of Fe and steel samples studied as their concentration is increased. This may probably due to their adsorption on the surface sites which are preferred for adsorption. It was deduced that these compounds affect the anodic partial process more than the cathodic partial process at high concentrations. While at low concentrations both processes are affected to, more or less, the same extent. It was found also that the efficiency of the additive amines is dependent on the C-content. This was ascribed to the surface defects and the variation of pearlite/ferrite ratio in the steel ssmples.

parameters of the dissolution of the different electrodes studied.

a- Increase of acid concentration (decrease of pH) was accompanied by :

i) An increase in the anodic dissolution current density (i_a, A/cm^2) according to :

$$i_a = K_a [OH^-]^n \exp [\alpha Z FE/RT].$$

ii) An increase of the cathodic current density (of the h.e.r.) i_c, A/cm^2 according to :

$$i_c = K_c [H^+] \exp [- \beta FE/RT]$$

iii) An increase of both corrosion potential, $E_{corr.}$, and corrosion rate, $i_{corr.}$. This was explained on the basis of competitive adsorption between OH^- and SO_4^{2-} ions at low and high acid concentration of anions in solution.

iv) An increase of the exchange current density, i_o(A/cm^2) of h.e.r.

v) Slight change of cathodic Tafel slopes, b_c, (mV, S.C.E.).

b- At one and the same acid concentration the increase of carbon caused.

i) An increase of the different kinetic parameters, namely, anodic dissolution current density (i_a), cathodic current density of h.e.r. (i_c) and corrosion current density, $i_{corr.}$.

ii) Shift of corrosion potential ($E_{corr.}$) towards more negative values.

iii) An increase of the cathodic Tafel slopes (b_c).

c- Addition of aniline, p-nitroaniline, p-chloroaniline, p-aminobenzoic acid, p-methoxyaniline, p-phenylene diamine, p-toluidine and p-hydroxyaniline affected on the kinetic parameters of the dissolution reaction of Fe and steel samples as follow:

i) Shift of the corrosion potential ($E_{corr.}$) towards positive direction.

ii) Decrease of, anodic current density, cathodic current density of h.e.r. and the corrosion rate.

From the effect of the above mentioned amines on the kinetic parameters, it was concluded that: these compounds are mixed inhibitors, i.e., interfering with both anodic and cathodic reactions to different extents, depending upon the type of the group attached to the aniline molecule.

d- The inhibition efficiency of the different amines was found to be affected by the C-content of the steel samples as follows :

i) The inhibitive efficiency of aniline p-methoxyaniline for

Fe and steel samples decreases in the order.

Steel III > Steel II > Steel I > Fe

ii) The above order is reversed for p-nitroaniline, namely,

Fe > Steel I > Steel II > Steel III.

4- Cyclic voltammogram curves constructed for Fe and steel samples in H_2SO_4 solution as a function of both electrolyte concentration and voltage scanning rate.

b- Increase of the H_2SO_4 concentration resulted in:

i) Shift of the anodic active dissolution peaks potential (peak A) of Fe and steel samples towards more negative direction.

ii) Shift of the Flade potential, E_f, (potential of complete passivation) towards more negative values. This was explained on the basis of oxidation of the insulating $FeSO_4$ film producing γ -Fe_2O_3.

iii) Shift of peaks current, "i"$_{peak}$, (for peak A) towards more positive values according to the equation :

$$\log i_{peak} = \alpha_1 + \beta_1 \log C_{H_2SO_4}$$

b- Reversing the scan to the cathodic direction was accompanied by current drop to zero value along the passive region. At the passivating potential another dissolution peak (peak B) was obtained instead of cathodic reduction peaks. This was explained on the assumption of a reductive dissolution mechanism. Peak current, "i"$_{peak}$; (for peak B) was shifted towards more positive values according to the equation.

$$\text{Log } i_{peak} = \alpha_2 + \beta_2 \log C_{H_2SO_4}$$

c- From the values of peaks potential, peaks current density and the Flade potentials of the different steel samples, it was concluded that, the increase of the C-content retards the tendency of steel samples for passivation

5- The effect of increasing concentrations of Cl^- ions on the stability of the passive film formed on Fe and steel samples was examined using cyclic voltammetry and potentiodynamic single sweep techniques.

a- The results of cyclic voltammetry technique showed that:

i) The peak potential of peak "A", "E_{peak}", and the Flade potential, E_f, were shifted towards positive values for Fe and the different steel samples as the Cl^- ion concentration was increased.

ii) The integrated charges under the CVs increased markedly with increasing the Cl^- ion concentration, due to the propagation of pitting corrosion. The variation of the charge amount Δq_a in the presence and absence of Cl^- ions was taken as a measure of the extent of pitting corrosion to take place. Δq_a varies with Cl^- ion concentration (especially at higher concentrations) according to :

$$\Delta q_a = a_2 + b_2 \log C_{Cl^-}$$

iii) At low Cl^- ion concentrations, the peaks current of peak "B" was slightly increased. Whereas at higher concentrations this peak disappeared, this was attributed to complete destruction of the oxide film and formation of visible pits.

b- The results of the potentiodynamic technique showed that:

i) An increase of the current flowing along the passive region indicating the destruction of the passivating oxide film and initiatiation and propagation of pitting.

ii) The current density change ($\Delta i = i_{Cl^-} - i_o$) was found to be varied with the Cl^- ion concentration according to:

$$\text{Log } \Delta i = a_3 + b_3 \log C_{Cl^-}$$

6- Increase of the C-content from zero to 0.4% caused :

i) Shift of the peak potential of the active dissolution peak (peak A), "E_{peak}", and Flade potential, E_f, obtained from the CVs, towards more positive values at one and the same Cl^- ion cocentration, indicating the decrease of the tendency for passivation.

ii) Increase of the integrated charge under the CVs, Δq_a, and the current density change, Δi, obtained from the potentiodynamic polarization curves, at one and the same Cl^- ion concentration.

7- Inhibition of the pitting corrosion of Fe was tried using aniline, p-nitroaniline and p-methoxyaniline in 0.1M H_2SO_4 + 0.1 NaCl solution. Also aniline, p-nitroaniline, p-chloroaniline, p-aminobenzoic acid, p-methoxyaniline, p-phenylene diamine, p-toluidine and p-hydroxyaniline were used to inhibit the pitting corrosion of steel samples I, II and III in the same solution. These compounds (especially at higher concentration) decreased the current density flowing along the passive region indicating the onset of inhibition. The variation of the current density change, i, ($\Delta i = i_{inh.} - i_{Cl^-}$), taken at a certain potential, was taken as a measure of the inhibiting efficiency of these compounds. Log Δi was found to be varied with log $C_{inh.}$ according to the equation :

$$\log \Delta i = a_4 - b_4 \log C_{inh.} \;.$$