

Review Article

Effect of Halides Ions and Temperature on the Electrochemical Behavior and Corrosion of Carbon Steel in Organic Acid

Deyab MA*

Egyptian Petroleum Research Institute, Egypt

*Corresponding author: Deyab MA, Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, Egypt

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Abstract

Hydrogen evolution and cyclic voltammetry techniques were used to investigate the corrosion behavior of carbon steel in formic acid solution under different experimental conditions. Results obtained reveal that the carbon steel corrodes in formic acid solutions and the corrosion rate increases with the increase in acid concentration and temperature. Cyclic voltammograms of carbon steel in formic acid exhibit active/passive transition. The data reveal that increasing formic acid concentration and temperature increases the anodic peak current density (j_{PA}) and shifts its peak potential towards more positive values. Activation parameters for the corrosion process were evaluated. Additions of Cl⁻, Br⁻ and I⁻ ions increase both the hydrogen evolution rate and the active dissolution rate of carbon steel and tend to breakdown the passive film and induce pitting attack. The aggressiveness of the halide ions towards the stability of the passive film decreases in the order Cl⁻ > Br⁻ > I⁻.

Keywords: Halides; Carbon steel; Organic acid; Corrosion

Introduction

Most research on corrosion behavior of carbon steel has been done in mineral acids [1-4]. Despite the importance of organic acids in industry, few corrosion studies involving these acids have been made [5-7]. However, at high temperatures, these acids can dissociate, forming more aggressive ions that can cause faster corrosion than might otherwise be expected. Formic acid is the most corrosive of the common organic acids. However, no systematic study of the corrosion behavior of carbon steel in formic acid solution has been found in the literatures.

The corrosion of carbon in acid environment proceeds according to the overall reaction:



This reaction includes the anodic partial reaction (2) and the cathodic partial reaction (3):



According to Faraday's law, there is a linear relationship between the metal dissolution rate at any potential (C_{RM}), and the partial anodic current density for metal dissolution j_{PA} [8].

$$C_{\text{RM}} = j_{\text{PA}} / n \times F \quad (4)$$

In this equation n is the number of electrons exchanged in the dissolution reaction, and F is the Faraday constant.

Additions of halide ions in the Fe/acid system causes destabilize the iron passive film [9]. They influence the chemical, ionic and electronic properties of the oxide. It has been proposed that halides ions interact with the oxide layer preferentially at local sites. This

interaction results in the film breakdown and initiation of pitting corrosion [10].

The work described in this paper was undertaken to apply the hydrogen evolution and cyclic voltammetry measurements to study the corrosion behavior of carbon steel in formic acid solutions. It was also the purpose of the present work is to study the effect of some halides as aggressive anions on the pitting corrosion of carbon steel in formic acid solution.

Experimental

Corrosion tests were performed on a carbon steel of the following percentage composition (in wt.%): 0.06 C; 0.06 Si; 0.7 Mn; 0.005 P; 0.001 S; 0.012 Ni; 0.015 Cr; 0.004 Mo; 0.002 V; 0.02 Cu and balance Fe. Prior to each experiment, the carbon steel electrodes were first briefly ground with different grades of emery paper (120, 400, 800, 1000 and 1200) and washed thoroughly with distilled water and degreased with acetone.

The apparatus and procedure followed for hydrogen evolution and cyclic voltammetry methods were similar to that earlier reported [11-12]. In hydrogen evolution method, 100 ml of the corroder (formic acid) was introduced into the reaction vessel and carbon steel sheets of dimensions 2 cm x 3 cm were carefully dropped into the test solution of formic acid and the reaction vessel was quickly closed to avoid any escape of hydrogen gas. The volume of hydrogen gas evolved from the corrosion reaction was monitored by the depression (in cm³) in the paraffin oil level. This depression was monitored at fixed time intervals. From the volume of hydrogen gas evolved, the hydrogen evolution rate (which can be correlated to corrosion rate) was calculated using the following expression [11]:

$$\text{CR}_{\text{H}} = (V_t - V_i) / (t_t - t_i) \quad (5)$$

where V_t and V_i are the volumes of hydrogen evolved at time t_t and t_i , respectively.

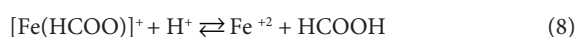
In cyclic voltammetry method, the electrochemical set-up consisted of a classical three electrode arrangement in a transparent glass cell with a Pt counter electrode and a saturated calomel reference electrode. Cyclic voltammetry experiments were performed with cylindrical rods of carbon steel with an apparent surface area of 0.358 cm². Cyclic voltammetry studies were carried out using a potentiostat type (potentiostat/Galvan stat EG&G model 273) connected with a personal computer. Cyclic voltammetry measurements were carried out by sweeping linearly the potential from the starting potential (-2.0 V vs. SCE) into the positive direction at a given scan rate till a required potential value and then reversed with the same scan rate till the starting potential to form one complete cycle.

Water used was triply distilled. All chemicals were used as received without further purification. Formic acid (Merck) of AR grade was used for preparing solutions. The temperature of the test electrolyte was controlled by immersing the cell in a water thermostat.

Results and Discussion

Hydrogen evolution measurements

Figure 1 shows the hydrogen evolution rate (i.e. corrosion rate) during the corrosion reaction of carbon steel electrode in formic acid measured as a function of acid concentration at 25°C. Inspection of the figure reveals that the hydrogen evolution rate increases with increase in formic acid concentration (from 0.2 to 1.0 M), indicating acceleration behavior for the carbon steel dissolution. The dissolution of carbon steel in formic acid solution may be considered in the following steps [13]:



The evolution of hydrogen occurs by the following mechanism [14]:

1- A primary discharge step (Volmer reaction)

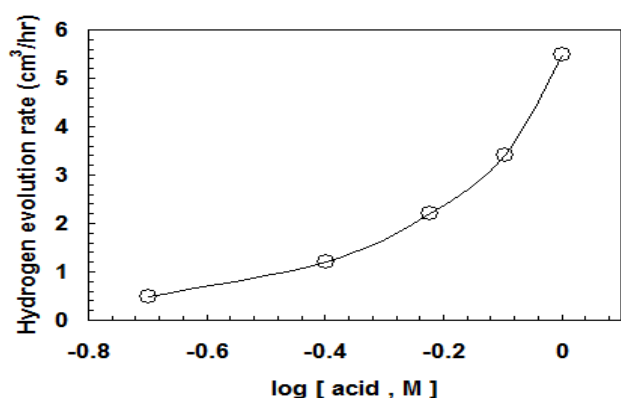
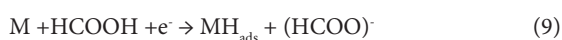


Figure 1: Relation between hydrogen evolution rate vs. log [formic acid] for carbon steel at 25°C.

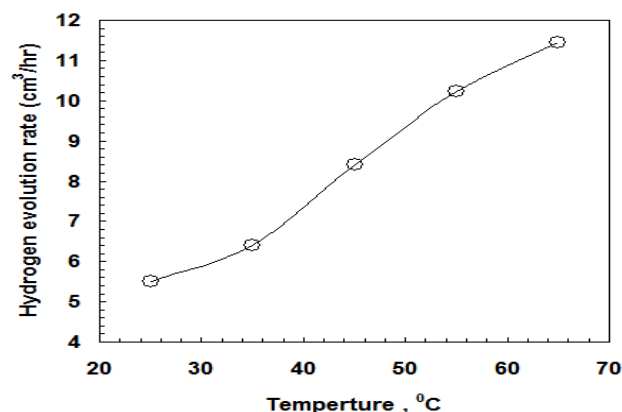
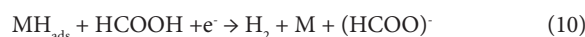


Figure 2: Relation between hydrogen evolution rate vs. temperature for carbon steel in 1.0 M formic acid solution.

2- Desorption step (Heyrowsky reaction)



3- A recombination step (Tafel reaction)



Figure 2 displays the influence of temperature (25-65°C) on the hydrogen evolution rate (i.e. corrosion rate) during the corrosion reaction of carbon steel in 1.0 M formic acid solution. It is clear from Figure 2 that the rate of hydrogen evolution and in turn the dissolution of carbon steel increases with increasing solution temperature. This indicates that higher temperatures enhance the hydrogen evolution reaction. The increase in corrosion rate with temperature is due to an increase in the extent of adsorption, assuming that the formic acid is chemisorbed on the surface of the cathode. Ultimately, this leads to an increase in the rate of hydrogen evolution reaction [15].

The apparent activation energy (E_a) for the process responsible for hydrogen generation (diffusion of both protons and uncharged hydrogen in solution) was calculated from the slope of Arrhenius plot (Figure 3). The data furnish an apparent activation energy value $E_a = 15.65 \text{ kJ mol}^{-1}$.

Figure 4 represents the hydrogen evolution rate during the corrosion reaction of carbon steel in 1.0 M formic acid solution in

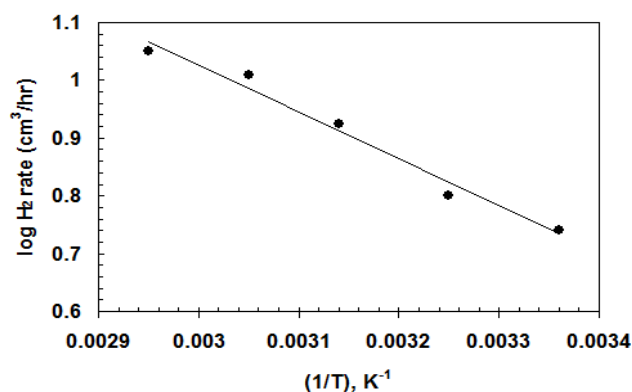


Figure 3: Arrhenius plot for hydrogen generation process.

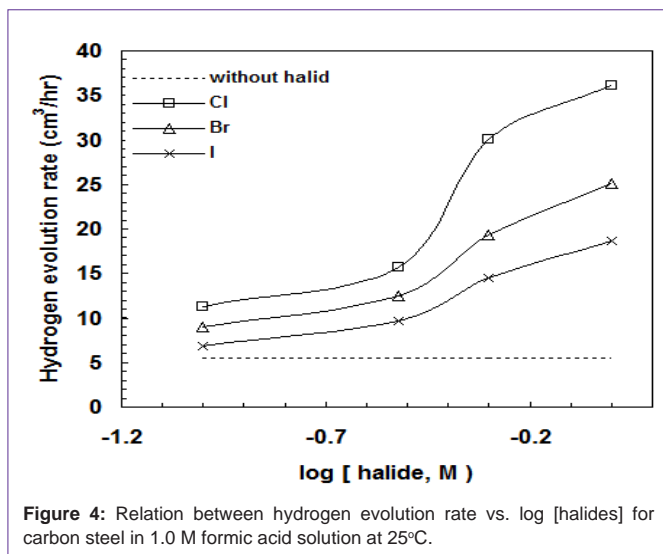


Figure 4: Relation between hydrogen evolution rate vs. log [halides] for carbon steel in 1.0 M formic acid solution at 25°C.

the absence and presence of various concentrations of halides ions at 25°C. Results shown in Figure 4 clearly indicate that the hydrogen evolution rate during the corrosion reaction of carbon steel in 1.0 M formic acid solution increase in the presence of halides ions compared to in their absence. This is an indication that halides ions accelerate the rate of hydrogen evolution and in turn the rate of carbon steel dissolution. This behavior could be ascribed to adsorption of halides ions (X) on the oxide/solution interface under the influence of electric field (at the oxide/solution interface) in competition With (HCOO)⁻. The adsorption process is followed by chemical reaction between the adsorbed halides ions and iron oxide cations on the hydrated oxide surface. These processes lead to the formation of FeX²⁻ complexes. The soluble complexes immediately separate from the oxide lattice and readily go in solution and this leads to increase the metal dissolution and enhances the rate of evolution. It is also seen that the hydrogen evolution rate increases with increase in halides ions concentration. At the temperatures studied, the hydrogen evolution rate in the presence of the halides ions was found to be in the order: Cl⁻ > Br⁻ > I⁻. These results indicate that Cl⁻ ion is the most aggressive anion, while I⁻ is the least aggressive one.

Cyclic voltammetry measurements

The effect of formic acid concentrations (0.2 to 1.0 M) on the cyclic voltammetry characteristic of carbon steel electrode was examined; the results were given in Figure 5. Inspection of the data reveals that, on positive going sweep, the cathodic current decrease continually and changes its sign at corrosion potential (E_{corr}). The anodic sweep exhibits an active-passive transition. The active region displays one anodic peak (A). Beyond the peak potential (E_{PA}) of peak A, the active dissolution current falls rapidly to a very small value due to the formation of passive film. Initially, formic acid can form soluble complexes with carbon steel and this leads to stimulate the dissolution of Fe, but later, owing to the formation of other sparingly soluble carbon steel complex compounds, cause passivation and can sequentially the drop in the dissolution current [13]. When sweeping back in the reverse direction, the cathode sweep exhibits one cathode peak (C), which is due to the reduction at the anodically formed passive film. The data reveal also that the charge during anodic sweep is much higher than the amount used during the cathodic sweep.

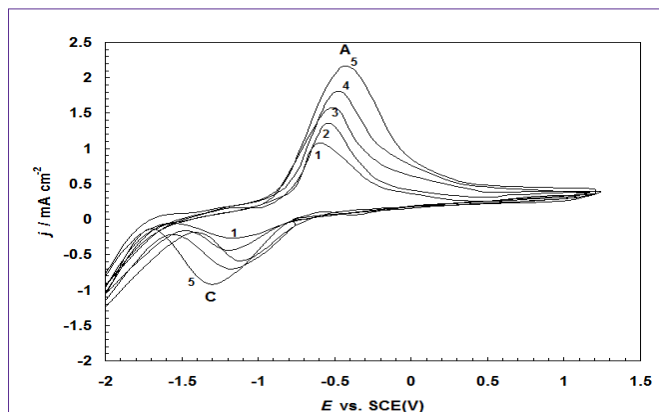


Figure 5: Cyclic voltammograms for carbon steel at 25°C with scan rate of 2.5mVs⁻¹ at various formic acid solution concentrations. (1) 0.2 M, (2) 0.4 M, (3) 0.6 M, (4) 0.8 M, (5) 1.0 M formic acid.

Figure 5 reveals that the increase in formic acid concentration (from 0.2 to 1.0 M) causes an increase in both the anodic and cathodic current peaks as well as the passive current density. Moreover, the anodic peak potential slightly shifts to more positive direction (-0.6 to -0.44 V) while the cathodic peak potential shifts to more negative values (-1.14 to -1.35 V) as formic acid solution concentrations increases.

The adsorption of acid ions at the Fe/solution interface brings about a positive shift of the electrode potential.

The linear relation between j_{PA} vs $\log C_{acid}$ is shown in Figure 6. Where this relation obeys the following equation:

$$j_{PA} = 0.75 + 0.87 \log C_{acid} \quad (12)$$

The adsorption of formate ions on the surface of carbon steel is a prerequisite for the anodic dissolution to occur; thus, the rate of corrosion should depend on the concentration of formate ion in the solution.

Figure 7 displays the influence of temperature (25-65°C) on the cyclic voltammogram curves of carbon steel in 1.0 M formic acid solution at scan rate 2.5mV s⁻¹. An increase in temperature enhances the peak current density of peak A and shifts its peak potential towards

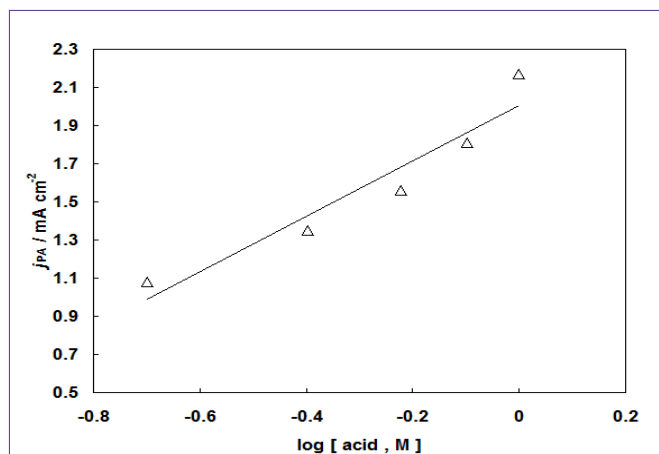
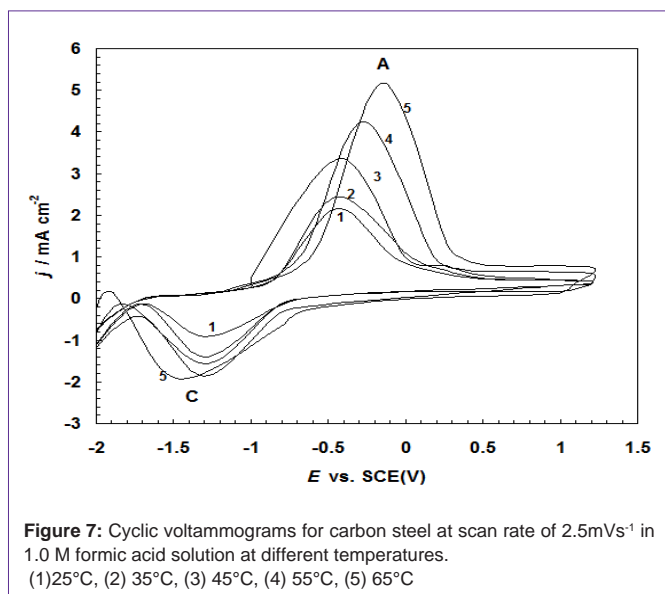


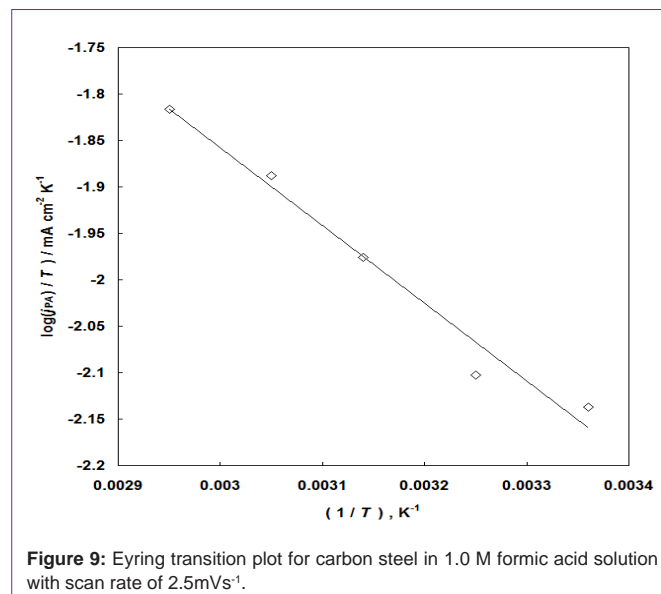
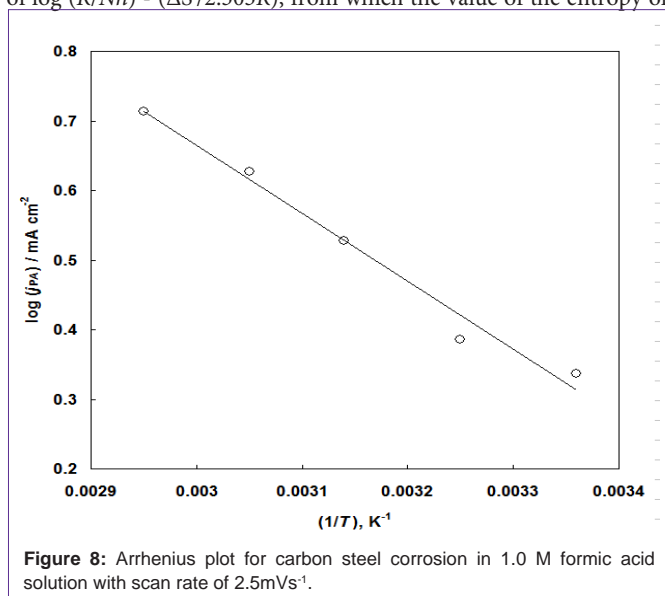
Figure 6: Relation between (j_{PA}) vs. log [formic acid] for carbon steel at 25°C with scan rate of 2.5mVs⁻¹.



more positive values. The value of $\log(j_{PA})$ for various temperatures were plotted as a function of $1/T$ is shown in Figure 8 (Arrhenius plot) [16]. The data reveal that the increase in temperature accelerates the rate of the corrosion reaction [17].

The apparent activation energy (E_a) for the corrosion of carbon steel electrode in formic acid (dissolution of carbon steel in formic acid process) was calculated from the slope of Arrhenius plot. The data furnish an apparent activation energy value $E_a = 14.53 \text{ kJ mol}^{-1}$. This means that the minimum energy that must be input to a chemical system with potential reactants to cause corrosion process should be equal $14.53 \text{ kJ mol}^{-1}$. It clearly seen that the apparent activation energy (E_a) value for the corrosion of carbon steel electrode in formic acid and for hydrogen generation process are consistent.

Plotting the relation between $\log(j_{PA}/T)$ and $(1/T)$ (Eyring transition plot) for carbon steel in formic acid solution give straight line, as shown in Figure 9 with a slope $(-\Delta H/2.303R)$ and an intercept of $\log(R/Nh) - (\Delta S/2.303R)$, from which the value of the entropy of

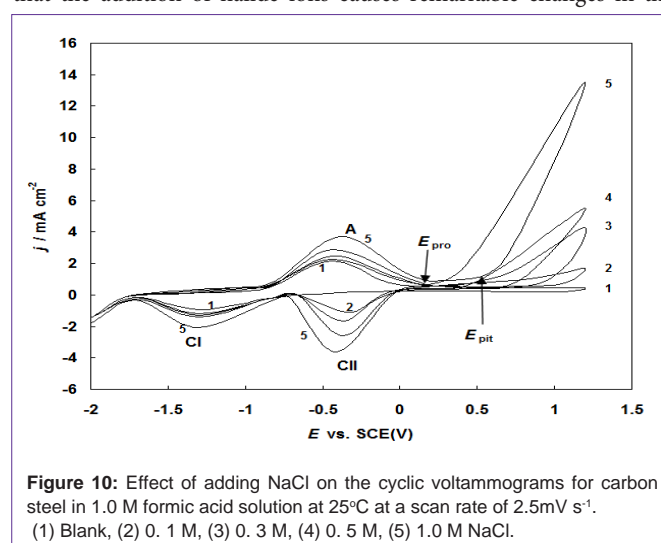


activation (ΔS) and the enthalpy of activation (ΔH) were -265.32 and $14.26 \text{ kJ mol}^{-1}$ respectively.

where R is the molar gas constant, T is the absolute temperature, h is the Planck's constant and N is the Avogadro's number.

The positive signs of the enthalpy of activation (ΔH) reflect the endothermic nature of the carbon steel dissolution process. Large and negative values of the entropy of activation (ΔS) imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex.

The effect of adding various concentrations of some halides (Cl^- , Br^- and I^-) on the cyclic voltammograms of carbon steel in 1.0 M formic acid solution was investigated at 25°C. Figure 10 represents the cyclic voltammograms of carbon steel in 1.0 M formic acid solution in the absence and presence of various concentrations of Cl^- ions. Similar results were obtained for Br^- and I^- ions. The data reveal that the addition of halide ions causes remarkable changes in the



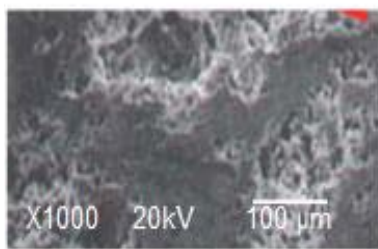


Figure 11: SEM micrographs of the carbon steel surface in formic acid solution containing 1.0 NaCl after E_{pit} .

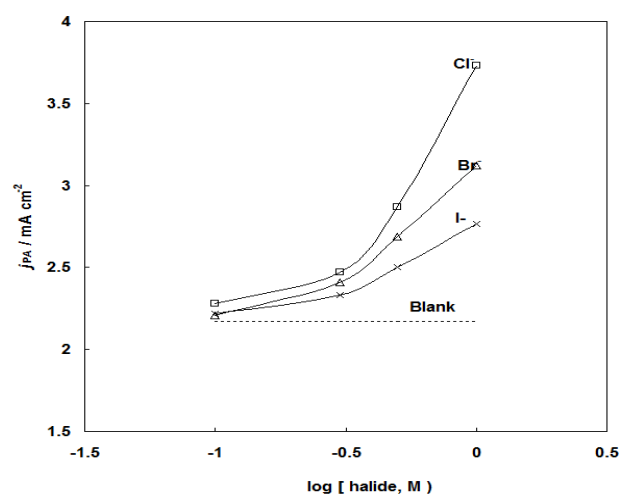


Figure 12: Relation between (j_{pA}) vs. log [halides] for carbon steel in 1.0 M formic acid solution at 25°C with scan rate of 2.5mVs⁻¹.

passive region. It is observed that at a certain critical potential (pitting potential E_{pit}), the passive current density increases steeply without any sign for oxygen evolution. The rapid rise in anodic current density at E_{pit} indicates initiation and growth of pitting attack [18-20]. During the potential sweep reversal, hysteresis loop characteristic of localized pitting corrosion phenomenon is observed. The hysteresis loop follows a certain protection (repassivation) potential (E_{pro}) where all the pits repassivate. The cathode excursion exhibits a new cathode peak (CII) at 0.355 V (SCE) before the appearance of the cathode peak (CI). The cathode peak (CII) can be assigned to the reduction of corrosion products.

Beyond E_{pit} SEM observations reveal the presence of pits on the metal surface after removing the corrosion products (see Figure 11).

The data of Figure 12 clearly show that, anodic peak current j_{pA} increase with increasing halide ions concentration. The corrosion current density (and hence the corrosion rate) decreases in the order: $Cl^- > Br^- > I^-$, indicating that, the aggressive of the halide ions decrease in the same sequence. In this case, the aggressiveness of halide ions on the dissolution of carbon steel in formic acid solution could be attributed to formation of the soluble complex species, i.e., FeX^{2-} in excess of halide ions [21]. Such complexation process leads to a further decrease in the free Fe^{2+} ion concentration at the electrode surface.

It is observed that the pitting potential E_{pit} shifts to more negative potentials as the halide ion concentration increases. Data of Figure 13 show that E_{pit} is linearly dependent on the log [halide] according to the equation:

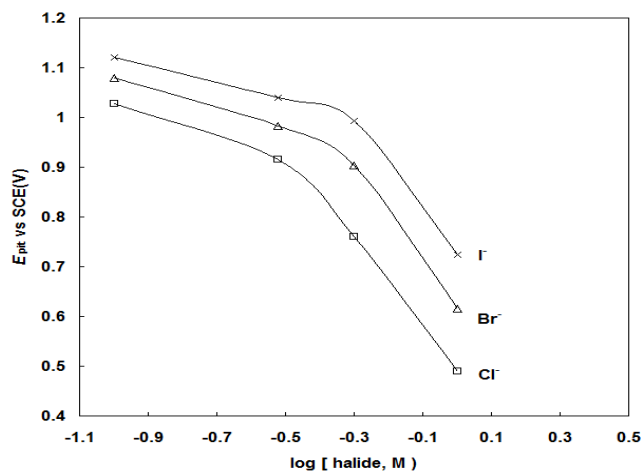


Figure 13: Relation between E_{pit} vs. log [halides] for carbon steel in 1.0 M formic acid solution at 25°C with scan rate of 2.5mVs⁻¹.

$$E_{pit} = a - b \log [\text{halide}] \quad (13)$$

where a and b are constants. Breakdown of the permanent passive layer and initiation of pitting attack can be ascribed as a competitive adsorption between halide ions and oxygenated species at adsorption sites on oxide covered layer [22]. Moreover, the adsorbed halide ions can penetrate through the passive layer especially at its point defects and flaws with the assistance of high electric field across the passive film to reach the base metal surface and initiate pitting [23]. The aggressiveness of the halide ions towards the stability of the passive film decreases in the order $Cl^- > Br^- > I^-$. In spite of the fact that Br^- and I^- are more polarizable and hence absorbable than Cl^- ion, the ionic radius of halide ions seems to be an important parameter since the ionic radii decrease in the order: $Cl^- < Br^- < I^-$. Therefore, it is reasonable to assume that the smaller the size of the aggressive ion, the higher is its ability to breakdown the passive layer [24]. On the basis of the small size of Cl^- ion as compared to Br^- and I^- , the smaller the size of the aggressive ion, the higher ability to breakdown the passive layer.

Conclusion

Hydrogen evolution and cyclic voltammetry techniques adopted to investigate the corrosion behavior of carbon steel in formic acid solution showed that hydrogen evolution rate (i.e. corrosion rate) during the corrosion reaction of carbon steel electrode in formic acid increases with increasing the formic acid concentration and solution temperature.

In absence of halide ions, the cyclic voltammogram exhibits active/passive transition. The active region displays one anodic peak corresponding to the active dissolution of carbon steel. Addition of halide ions enhance the active dissolution of carbon steel and tend to breakdown the passive film and induce pitting attack. The pitting corrosion of carbon steel increases with increasing halide ions concentrations but decreases in the order: $Cl^- > Br^- > I^-$.

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