

**ELECTROCHEMICAL BEHAVIOUR OF LOW CARBON STEEL
IN OXALATE AND BIPHTHALATE SOLUTIONS**

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ABSTRACT

The corrosion behaviour of carbon steel in different concentrations of oxalate and biphthalate solutions ranging from (0.01M – 0.1M) was studied by potentiodynamic polarization. The results showed that the peak current density increases with increasing of concentration of organic acid salt. The results indicate that low carbon steel displays typical active passive transition behavior in the absence of halide ions. The effect of concentration, scan rate, temperature and halide ions on the behaviour of carbon steel in oxalate and biphthalate solutions was studied. The corrosion rate of carbon steel in oxalate solutions was higher than in biphthalate solutions.

1. INTRODUCTION

Steel is a very important alloy that finds wide applications in industry, metallurgy and construction fields. Low carbon steel is a very important electrode material for a lot of applications. However, high corrosion rates in most cases, especially at low pH values limit its applications. The study of corrosion behaviour of steel in different environments is very important to achieve the most suitable passivators and inhibitors to increase the life period of steel equipments.

The continued manifestation of corrosion and corrosion products on steel structures is still causing a lot of concern to corrosion scientists

and engineers. Investigation into the mechanism of corrosion inhibition by certain organic compounds has continued to reveal interesting results [Singh, et al., (1995), Hansen, et al., (1995), Vasudevan, et al., (1995), Jayaperumal et al., (1995) Quraishi, et al, (1995), Gomma and Wahdan, (1995),Singh, et al., (1995),Jianguo, et al., (1995) Monticelli, et al., (1993)].

The inhibition effect of benzoic acid and salicylic acid in sulfuric acid medium on the steel with known composition has been investigated [Bilgiç, (2002)]. It has been determined that the corrosion rates decrease and that percentage inhibition efficiencies and the degree surface coverage increase with increasing acid concentration in all cases. However, benzoic acid acts as a better inhibitor compared to salicylic acid under identical conditions. It has been determined that the adsorption for both organic acids on the steel complies with the Langmuir isotherm.

The inhibition effect of succinic acid on the corrosion resistance of mild steel in sulfuric acid solutions was investigated [Giacomelli, et al., (2004)] by potentiodynamic polarization, electrochemical impedance spectroscopy, weight loss and optical microscopic analysis. The results suggest that succinic acid acts as mixed type inhibitor. Inhibition efficiencies up to 80% were recorded at pH = 2 and 3 solutions, whereas no effect was perceived for pH > 4 solutions.

The corrosion behaviour of steel containing various carbon contents in 0.05 M solutions of (acetic acid, oxalic acid and citric acid in the absence of Fe²⁺ ions at pH 2.8 was studied [Abd Aal, et al., (1995)]. The extent to which corrosion is promoted depends on the carbon content, the concentration of Fe²⁺ ion and the dissociation constant, K_a, of the of the corresponding acids. Gomma., (1998) studied the effect of 0.05 M tartaric and malic acids on the corrosion behavior of 0.5 C% carbon steel in the absence and in the presence of Fe⁺⁺ at pH 2.8 by measuring the corrosion potential and the corrosion rates using galvanostatic polarization technique. The extent to which corrosion is promoted depends on the concentration of Fe⁺⁺ ion. Tartaric acid has a more pronounced effect on the corrosion rate. The activation energy of hydrogen evolution was found to be 5.46 and 4.55 Kcal mol⁻¹ for tartaric and malic acid respectively. The activation energies for the overall corrosion process was found to be 5.6 and 5 Kcal mol⁻¹ for tartaric and malic acid respectively. These values are characteristic of a diffusion controlled process.

The electrochemical behaviour of low carbon steel in various concentrations of tartarate and gluconate solutions was investigated [Abd El-Maksoud, et al., (2005)] in our laboratory. In the present study, the electrochemical behaviour of low carbon steel in various concentrations of oxalate and biphthalate solutions using potentiodynamic and open circuit measurements was investigated. Also, the effect of scan rate and the contents of chloride ions on the electrochemical behaviour was studied.

2. EXPERIMENTAL

The investigation of the behaviour of carbon steel in oxalate and biphthalate solutions solutions was performed by electrochemical methods using potentiodynamic measurements, and. The working electrode was made from low carbon steel with the chemical composition depending on weight percentages (0.4% C, 0.2% Si, 0.26% Mn, 0.015% S, 0.014 P, 0.081% Al, 0.14% Ni). The electrode investigated was cut as cylindrical rods, welded with Cu wire for electrical connection and mounted into glass tubes of appropriate diameter using Araldite, to offer an active flat disc shaped surface of 0.78 cm² geometric area. Prior to each experiment, the surface pretreatment of the working electrode was performed by mechanical polishing of the electrode surface with successive grades of emery paper down to 1200 grit, to a mirror finish. The electrode was then rinsed with acetone, distilled water and finally dried with filter paper. The electrode was immediately immersed in the tested solution. The electrode was allowed to corrode freely, then the potentiodynamic run started from the cathodic to the anodic direction.

The experiments were performed in a 50 cm³ volume Pyrex glass cell using Pt wire and a saturated calomel electrode (SCE) as auxiliary and reference electrodes, respectively. The experiments were carried out in either sodium oxalate or potassium biphthalate solutions of various concentrations varying from 0.01M to 0.1M. All solutions were freshly prepared from analytical grade chemical reagents using doubly distilled water and were used without further purification. For each run, a freshly prepared solution as well as a clean electrode was used. Experiments were carried out at constant temperature 298 K using ultrathermostatic bath. Instruments used in this study were described previously [Abd El-Maksoud (2004)]. The potentiodynamic current/potential curves were recorded by changing the electrode potential, from -1 up to 2 V (SCE).

Potentiodynamic measurements were carried out by sweeping the potential linearly from the starting potential into the positive direction at a given scan rate till reaching the required potential.

3. RESULTS AND DISCUSSION

Potentiodynamic experiments

Figure 1 illustrates the potentiodynamic $E-i$ anodic polarization curves for carbon steel in 0.1 M oxalate or biphthalate solutions, recorded between -1 and 2 V vs. SCE with a scan rate $v = 25$ mVs⁻¹ at 25°C. The anodic responses for both solutions are characterized by the occurrence of an active/passive transition state prior to an oxygen evolution reaction. The active region involves an anodic peak prior to the passive region. The anodic current peak due to the dissolution is characterized by its peak current density i_p and the peak potential E_p . Thereafter the current decreases to a limiting value, after that there is an oxygen evolution.

The barrier layer is a Fe³⁺ oxide in the passive potential region and contain a small percentage of Fe²⁺, while the deposit layer is a hydrated Fe³⁺ oxide or oxyhydroxide [Sato, et al., (1975) and Seo., et al., (1977)]. The formation of Fe³⁺ species may take place either by direct oxidation of Fe metal or by conversion of Fe²⁺ to Fe³⁺ species. Previous studies proved that both Fe²⁺ and Fe³⁺ formed a soluble complexes with gluconate ions [Singh, et al., (1994), Refaey, et al., (1996) and ahodny-SarcO.(1988) 537]. Foley, et al., (1967) identified by electron diffraction the passive film as γ -Fe₂O₃ and detected Fe₃O₄ in the active and transpassive regions. The decrease of the passive current could be explained on the basis that dehydration of the hydroxides could occur on the electrode surface during the potential sweep in the noble direction.

The anodic dissolution current density in the case of oxalate solutions is higher than that of biphthalate and a clear peak current was observed, and then drops to a very small value, i_{pass} , indicating the onset of passivation. The value of i_{pass} is limited by the chemical dissolution of the film; the chemical film dissolution is counterbalanced by film formation. The rates of these two processes are nearly the same at the steady-state of polarization so as to keep the thickness of the passive film nearly constant.

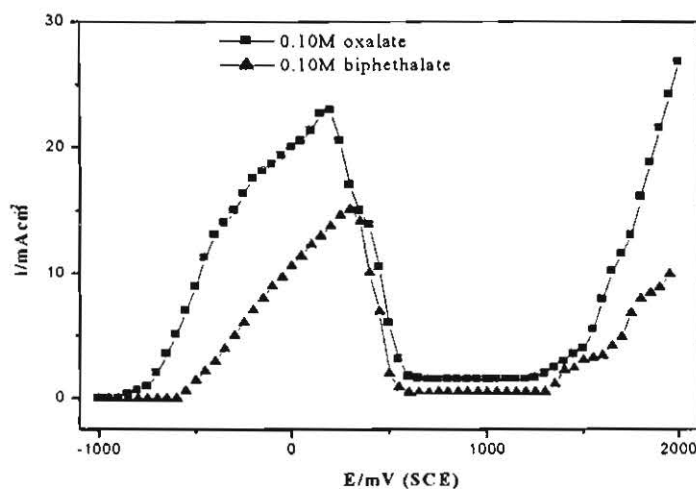


Fig.1

Fig.(1): Anodic potentiodynamic curves for carbon steel in different concentrations from oxalate and biphthalate at 25 mVs^{-1} .

Effect of concentration

The peak current density (i_p) is influenced by both concentrations of oxalate and biphthalate solutions. Fig.2 shows the effect of concentrations of both oxalate and biphthalate solutions on the peak current density (i_p), increases with increasing concentration, the peak current in oxalate solution is higher than biphthalate solution at the same concentrations. Fig.3 shows the effect of concentration on the peak potential, it is clear that the peak potential (E_p) is shifted to more negative value with the increasing of concentrations of both the case of oxalate and biphthalate.

Effect of scan rate

Potentiodynamic anodic polarization curves of a carbon steel electrode in 0.1 M oxalate and 0.1 M biphthalate solutions at different scan rate ranging from $10 - 100 \text{ mVs}^{-1}$ were carried out. The results show that the increase of the scan rate increases the general corrosion of carbon steel. The peak current density (i_p) increases with increasing of scan rate. Figs.4 shows the relationship between the peak current density as a function of the square root of the potential scan rate ($v^{1/2}$). The peak current (i_p) was found to increases linearly with $v^{1/2}$, which suggests the

participation of a diffusion process [Wiecckowski, et al., (1985), Slvarezza, et al., (1987) and Azambuja, et al., (1999)]. The plots do not cross the origin, which may indicate that the reaction is under mixed kinetic and diffusion control. For a diffusion controlled process under potentiodynamic conditions, the slopes of the i_p vs $v^{1/2}$ plots are proportional to the concentration of the diffusing species and to the square root of their diffusion coefficients according to the Delahay equation [Delahay P. (1954)]:

$$i_p = \frac{1}{4} abz^{1/2} cD^{1/2} v^{1/2} \quad (1)$$

a and b are constants, z is the number of exchanged electrons, c is the concentration and D is the diffusion coefficient of the diffusing species and v is the scan rate.

Fig.5 shows the relation between the peak potential (E_p) of carbon steel in 0.1 M oxalate and 0.1M biphthalate solutions and the square root of the potential scan rate ($v^{1/2}$). E_p shifts to more positive potential with the increasing of scan rate.

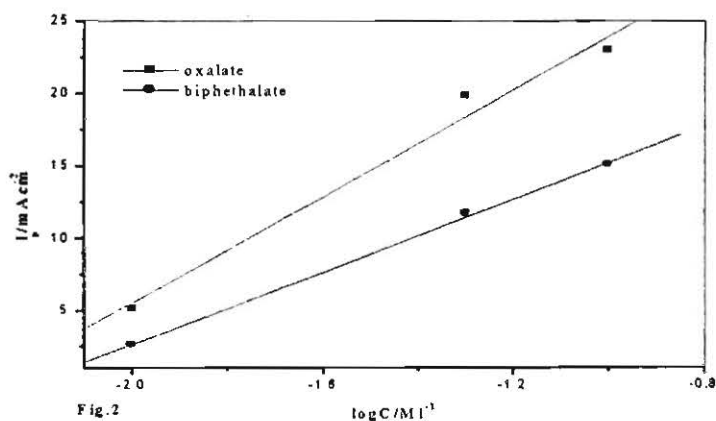


Fig.(2): Peak current density (i_p) as a function of oxalate and biphthalate concentrations.

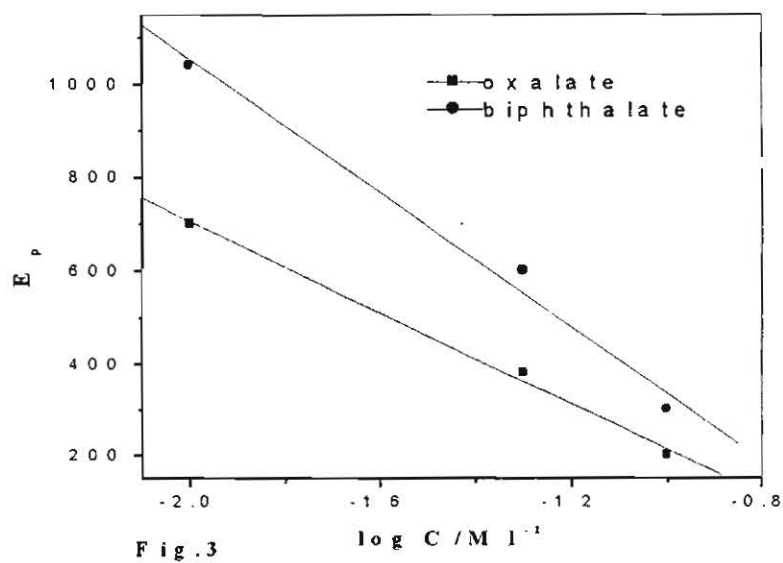


Fig. 3

Fig.(3): Peak potential (E_p) as a function of oxalate and biphthalate concentrations.

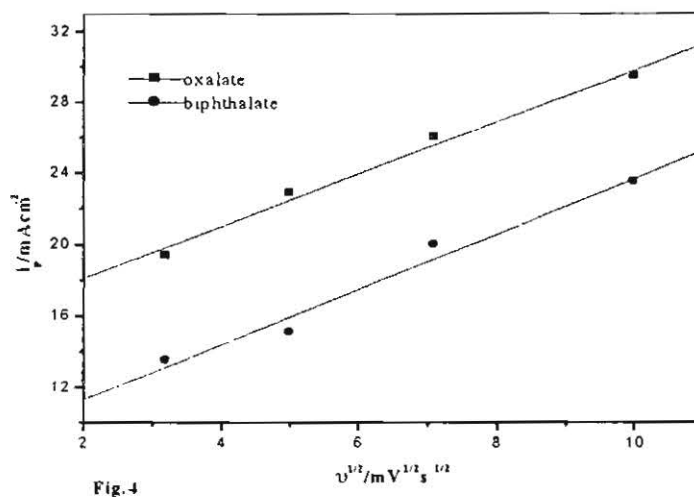


Fig. 4

Fig.(4): Dependence of the peak current density (i_p) for carbon steel in 0.1 M oxalate and 0.1 M biphthalate on the square root of the potential scan rate ($v^{1/2}$).

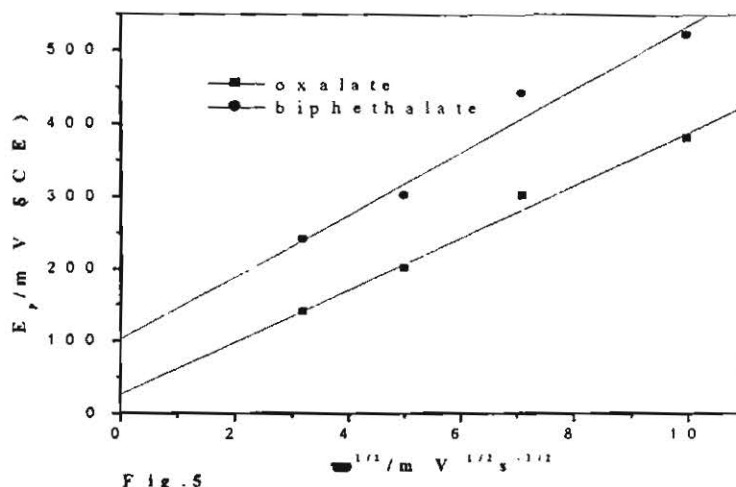


Fig.(5): Dependence of peak potential (Ep) for carbon steel in 0.1 M oxalate and 0.1 M biphthalate on the square root of the potential scan rate (v^{1/2}).

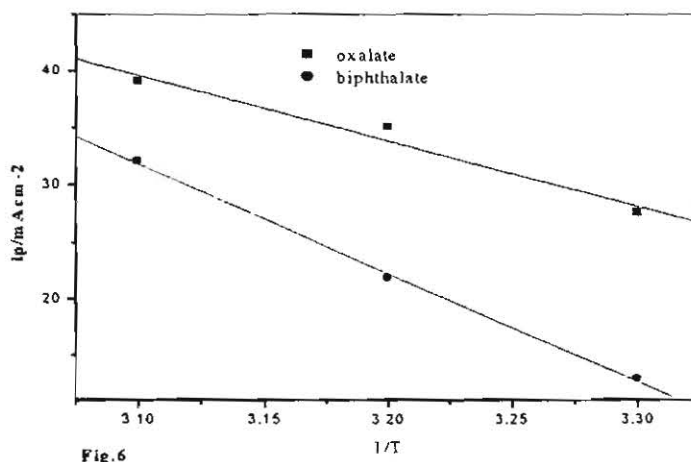


Fig.(6): Dependence of the peak current density (ip) on the temperature for carbon steel in 0.1 M oxalate and 0.1 M biphthalate solutions.

Effect of temperature

The effect of temperature on the feature of the voltammogram was studied in the rang 30 — 60°C for carbon steel in the 0.1M of both oxalate and biphthalate solutions. Fig.6 shows the relation of peak current (i_p) and temperature, it is clear that, the i_p increases with the increasing of temperature values, this indicates that with increasing temperature the corrosion rate increases. Also the peak current values in the case of oxalate solutions are higher than that of biphthalate at all temperatures.

Effect of the addition of halide ions

The effect of the addition of halide ions on the potentiodynamic anodic polarization curves for carbon steel in 0.05M oxalate and 0.05 M biphthalate solutions was studied. Figs. 7 and 8 show the effect of addition of 5×10^{-3} M halide ions at 25°C and with a scan rate of 25 mVs^{-1} . The data reveal that the presence of halide ions results in an increase of current density. The increase in the halide concentrations decreases the pitting corrosion resistance. The decreases of the current density values was in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$, this is in agreement with the ability of pitting of the passive film.

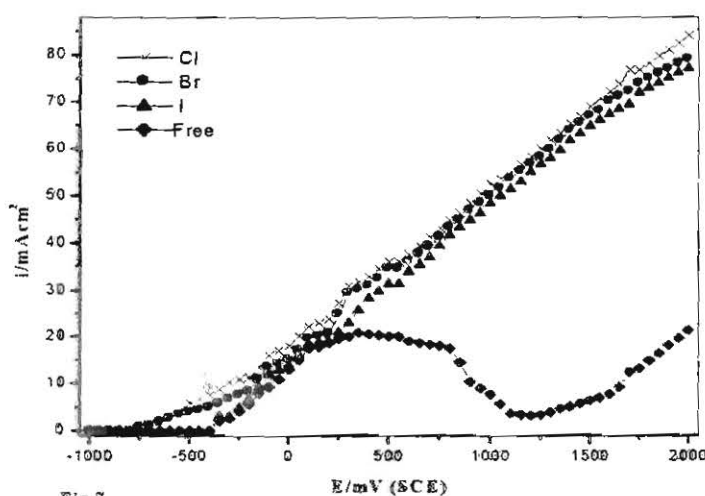


Fig. 7

Fig.(7): Anodic potentiodynamic curves for carbon steel in 0.05 M oxalate solution containing 5×10^{-3} M halide ions at 25 mVs^{-1} .

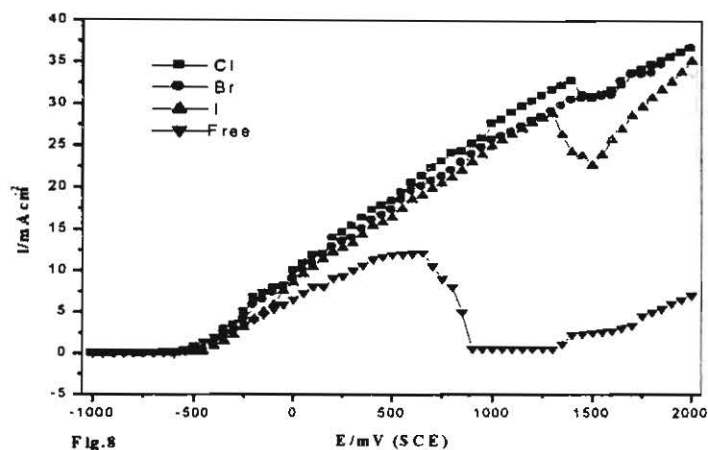


Fig.(8): Anodic potentiodynamic curves for carbon steel in 0.05 M biphthalate solution containing 5×10^{-3} M halide ions at 25mVs^{-1} .

From the above experiments, one can conclude that the corrosivity of carbon steel in oxalate solutions is higher than in the case of biphthalate solutions, this may be attributed to, the high possibility of formation of soluble complex in the case of oxalate solutions by electron donation via the coordination bonds between the two oxygen in the carboxylic groups and Fe^{2+} (Fig. 9a). In the case of biphthalate solutions there is a benzene ring attached to the two carboxylic groups, the delocalization of the π -orbitals in benzene ring makes the negative charge on the oxygen of the carboxylic groups lesser than that in the case of oxalate solutions. Thus the possibility of the formation of soluble complex of biphthalate solutions with Fe^{2+} (Fig.9b) is lesser than in the case of oxalate solutions. So the corrosivity of carbon steel is higher in the case of oxalate solutions.

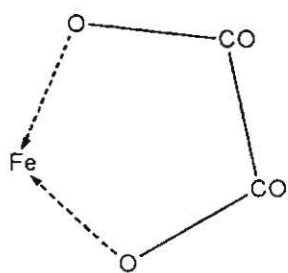


Fig. 9a

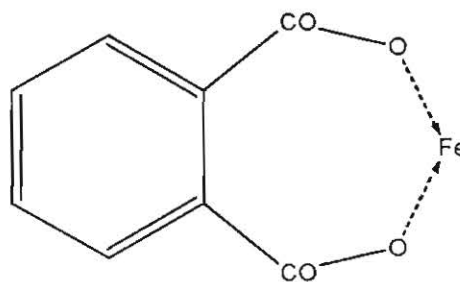


Fig. 9b

4. CONCLUSIONS

- 1- The results indicate that low carbon steel displays typical active to passive transition behaviour in the absence of chloride ions.
- 2- The anodic dissolution of carbon steel electrode in oxalate and tartarate solutions increases with increasing of concentrations, scan rate and temperature.
- 3- The presence of halide ions leads to the occurrence of pitting corrosion, leading to the increase of peak current density; i_p .
- 4- The corrosivity of carbon steel in oxalate was higher than in biphthalate solutions.

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السلوك الكهروكيميائي للصلب الكربوني في محاليل الأكسالات والبايفثالات

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تمت دراسة السلوك الكهروكيميائي للصلب الكربوني في محاليل مختلفة التركيزات تتراوح من (0.1 - 0.01) مولارى من كل من الأوكسالات والبايفثالات. وقد تم استخدام الطرق الجهدية الديناميكية في تلك الدراسة. ولقد أوضحت الدراسات أن كثافة تيار القمة تزداد بزيادة تركيزات أملاح الأحماض العضوية المستخدمة. وأوضحت الدراسة أن للصلب الكربوني منطقة نشاط ومنطقة خمول مميزة لنوع الملح العضوى المستخدم فى غياب أيونات الهاليدات. ولقد تم دراسة تأثيى كل من معدلات المسح الجهدى، تأثير درجة الحرارة وتأثير وجود أيونات الهاليدات على السلوك الكهروكيميائى للصلب الكربونى فى محاليل الأوكسالات والبايفثالات. ووجد أن معدلات التآكل فى محاليل الأوكسالات أكثر من معدلاتها فى محاليل البايثالات.