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# The effect of Congo red inhibitor on the corrosion of various steels in a 3.5% NaCl medium

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This study is concerned with the use of Congo red as an inhibitor for low alloyed carbon steel, petroleum steel and boron steel at 60 °C in 3.5% NaCl aqueous solution. Analysis was performed using the Tafel polarization measurements and electrochemical impedance spectroscopy. Congo red was observed to cover the surface by adsorbing upon it, and its inhibition efficiency depended on the concentration. The efficiency was the highest one in low-alloyed carbons steels, followed by petroleum and boron steels. The type of adsorption occurring on the metal surface was also determined.

Keywords: *alloy steels; corrosion testing; inhibitor; Congo red; EIS*

## 1. Introduction

One of the ways to prevent corrosion of metals and metal alloys is using inhibitors [1–3]. Inhibitors are organic or inorganic compounds which prevent the corrosion of metals and their alloys. Depending upon their structures [4], they achieve this by forming a protective film or an oxide layer, either by forming a complex with the metal after surface adsorption, or by oxidation of the metal. The surface adsorption of the inhibitors is realized by heteroatoms such as sulfur, nitrogen, oxygen or phosphorous with triple bonds, or aromatic rings present in their structures. Adsorption occurs as a result of the electrostatic interactions between the molecule and charged metal atoms or the electron pair or a π electron on the molecule and the metal surface. Thus molecules of the selected inhibitor should contain nitrogen originating from long chain aliphatic, aromatic or heterocyclic amines and their derivatives [5–8]. The inhibiting efficiency of these compounds is proportional to the number of aromatic rings and the

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number of electronegative atoms in the structure [9]. It is preferable that the inhibitor be soluble in aqueous media, since the corrosion rate is particularly high in media such as HCl, $H_2SO_4$ and NaCl.

This study is concerned with the inhibition effect of Congo red, containing N atoms and aromatic rings, on the corrosion of three different steels in 3.5% NaCl solution at 60 °C. Analyses were performed using the Tafel extrapolation, linear polarization, and electrochemical impedance spectroscopy (EIS). The chemical structure of the compound is shown in Fig. 1.

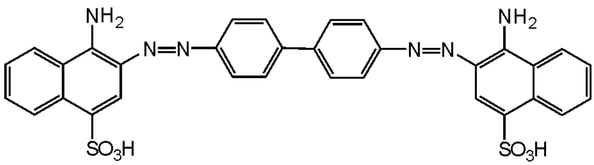


Fig. 1. Chemical structure of Congo red

## 2. Experimental

A three-compartment Pyrex glass cell was used in the experiments. The working electrodes of the compositions given in Table 1 embedded into polyester, having a 4 mm diameter surface area were placed in the middle compartment. The reference, and counter electrodes were saturated Ag/AgCl electrode and $1 cm^2$ Pt plate, respectively. The solution was purged with nitrogen purified by passing through pyrogalol, vanadium chloride, and HCl prior to each experiment in order to remove dissolved oxygen and blanketed thereafter. All solutions were prepared with triply distilled water. Before the experiments, the working electrodes were first polished with 1200 grid fine emery paper then polished with 0.5 μm alumina. The temperature of the system was kept constant within ±1 °C accuracy with a circulating water bath.

Table 1. The compositions of the steels used

| Type of steel | Content [%] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | P | Cr | Mo | Ni | B | Al | Ti | V | R |
| Petrol line steel | 0.28 | 0.44 | 1.46 | 0.01 | 1.18 | 0.07 | 1.20 | – | – | – | – | 0.1 |
| Low alloyed carbon steel | 0.30 | 0.03 | 1.35 | 0.03 | 1.0 | – | 0.40 | – | 0.050 | – | – | 0.10 |
| Boron steel | 0.2 | 0.1 | 1.70 | 0.025 | 0.80 | 0.80 | – | 0.04 | 0.03 | 0.26 | 0.60 | 0.05 |

The potentiostatic and impedance measurements were carried out with a CHI 660 electrochemical analyzer equipped with electrochemical software. The polarization curves were taken at the scan rate of 2 mV/s between 250 mV anodic and cathodic of the open circuit or the equilibrium potential.

# 3. Results and discussion

## 3.1. Polarization measurements

Figures 2–4 show the potential–current curves of three different steels in a 3.5% NaCl medium for various concentrations of the inhibitor. The corrosion potentials shifted to significantly higher anodic values and the corrosion currents showed a marked decrease upon the addition of the inhibitor. The fact that the corrosion potential

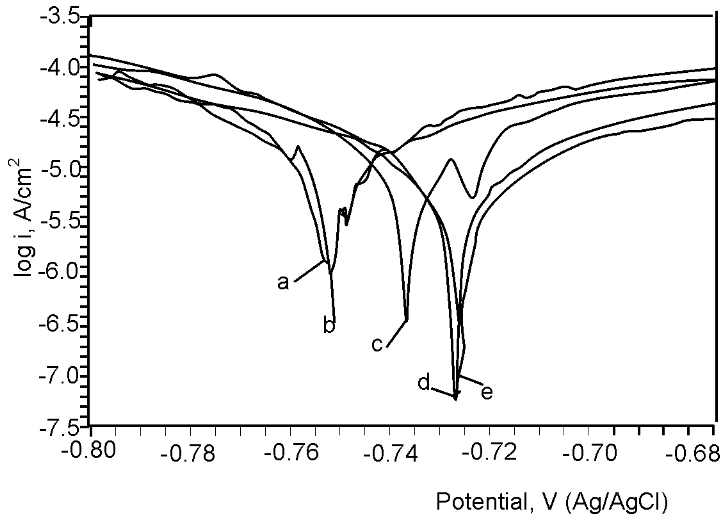


Fig. 2. The current–potential curves of low alloyed carbon steel blank (a) and with Congo red of the concentration: b) $1\times10^{-4}$ M, c) $2\times10^{-4}$ M, d) $5\times10^{-4}$ M, e) $1\times10^{-3}$ M

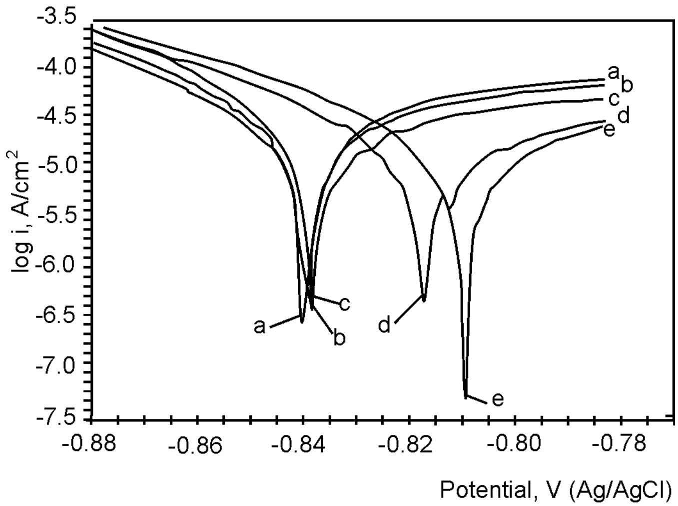


Fig. 3. The current–potential curves of petroleum steel blank (a) and with Congo red of the concentration: b) $1\times10^{-4}$ M, c) $2\times10^{-4}$ M, d) $5\times10^{-4}$ M, e) $1\times10^{-3}$ M

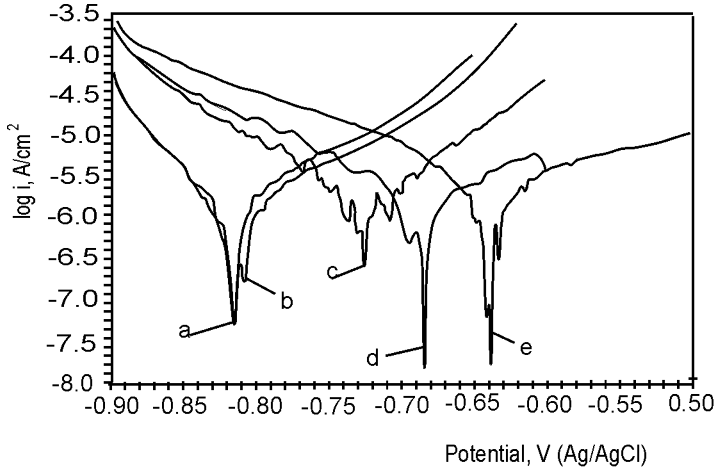


Fig. 4. The current potential curves of boron steel blank (a) and with Congo red of the concentration: b) $1\times10^{-4}$ M, c) $2\times10^{-4}$ M, d) $5\times10^{-4}$ M, e) $1\times10^{-3}$ M

displayed an anodic shift of nearly 200 mV for boron steel in the presence of Congo red indicates that it is a good anodic inhibitor. Other steels also show similar behaviour demonstrating that formation of adsorbed films on their surfaces [11]. The compound has the efficiency of 88% and acts as a good inhibitor of mixed type. Steel containing boron was found to have the corrosion resistance twenty times higher than the other steels.

### 3.2. Electrochemical impedance spectroscopy measurements

Figures 5–7 show the Nyquist diagrams obtained for the steels under investigation in a 3.5% NaCl solution for various concentrations of Congo red.

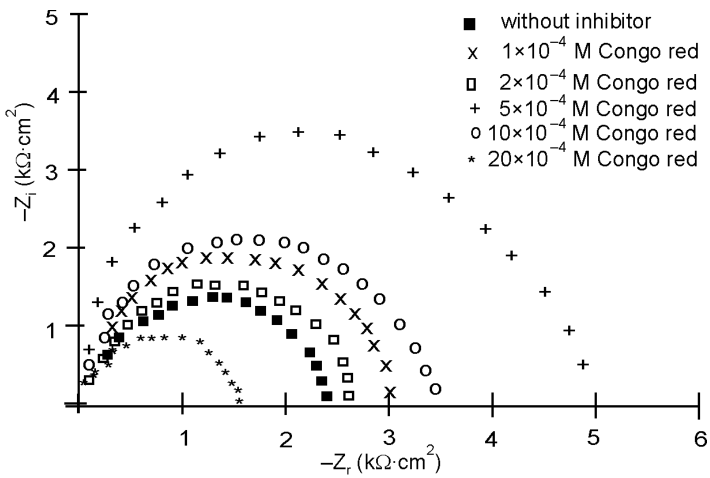


Fig. 5. The Nyquist diagrams of boron steel

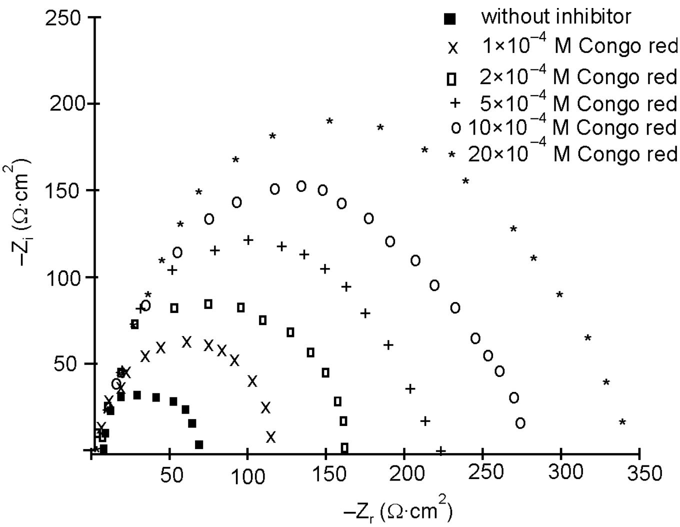


Fig. 6. The Nyquist diagrams of low alloyed carbon steel

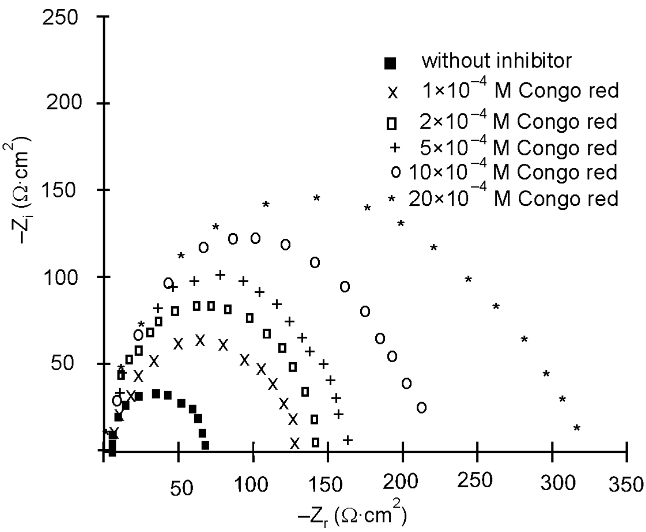


Fig. 7. The Nyquist diagrams of petroleum steel

The curves were obtained in the frequency range of $10^5$–$10^{-2}$ Hz. It is seen that the diameters of the semi circles increase as the concentration of the inhibitor increases, indicating the increase of the charge transfer resistance $R_p$ [12]. The $R_p$ values and the inhibition efficiencies $\eta_{\mathrm{eis}}$ calculated for each concentration are tabulated in Table 2. Here $\eta_{\mathrm{eis}}$ is calculated according to

$$\eta_{\mathrm{eis}} = \frac{R_{ti} - R_t}{R_{ti}} \times 100 \qquad [\%]$$

where, $R_{ti}$ and $R_t$ represent the charge transfer resistances obtained with and without the inhibitor.

### 3.3. Linear polarization method

The $R_p$ values obtained from impedance spectroscopy measurements can also be calculated by the linear polarization method. Here using the polarization curves, the $R_p$ values can be computed from the Stern–Geary equation as follows [13]:

$$i_{\mathrm{cor}} = \frac{B}{R_p}$$

where $B$ is given as

$$B = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)}$$

$R_p$ is calculated form the slope of the polarization curve. The values for the inhibition efficiency $\eta_{\mathrm{lp}}$ obtained by the linear polarization method are also given in Table 2, for comparative purposes.

Table 2. Inhibition parameters obtained by the measurements

| Steels | Concentration ($\times 10^4$ M) | $-E_{\mathrm{cor}}$ [mV] | $R_{p,\mathrm{eis}}$ [$\Omega \cdot \mathrm{cm}^2$] | $\eta_{\mathrm{eis}}$ [%] | $R_{p,\mathrm{lp}}$ [$\Omega \cdot \mathrm{cm}^2$] | $\eta_{\mathrm{lp}}$ [%] |
|---|---|---|---|---|---|---|
| Low alloyed carbon steel | blank | 775 | 62.2 | – | 68 | – |
| | 1 | 756 | 127.7 | 51.3 | 144 | 53.2 |
| | 2 | 742 | 164.1 | 62.1 | 154 | 66.2 |
| | 5 | 733 | 211.6 | 70.6 | 262 | 74.3 |
| | 10 | 735 | 286.6 | 78.3 | 357 | 81.5 |
| | 20 | 720 | 351.4 | 82.3 | 503 | 86.5 |
| Petroleum steel | blank | 840 | 67.6 | – | 73 | – |
| | 1 | 841 | 124.0 | 45.5 | 140 | 48.3 |
| | 2 | 839 | 142.6 | 52.8 | 162 | 55.6 |
| | 5 | 821 | 158.3 | 57.3 | 196 | 63.1 |
| | 10 | 816 | 218.4 | 71.3 | 331 | 78.2 |
| | 20 | 810 | 336.3 | 79.9 | 429 | 83.6 |
| Boron steel | blank | 819 | 1462.3 | – | 1510 | – |
| | 1 | 818 | 2473.7 | 40.1 | 2745 | 45.1 |
| | 2 | 727 | 2732.7 | 46.5 | 3032 | 50.2 |
| | 5 | 684 | 3064.9 | 52.3 | 3355 | 55.3 |
| | 10 | 639 | 3610.3 | 59.5 | 4070 | 63.1 |
| | 20 | 605 | 5147.8 | 71.6 | 6040 | 75.6 |

## 4. Discussion

The efficiency of an organic inhibitor of metallic corrosion is dependent not only on the size of its molecules but also on the environment, nature of the metal, experimental parameters such as the inhibitor concentration [14], molecular structure and the nature of the molecule itself [15].

The adsorption of the organic compound at metal–solution interface in aqueous solution may be illustrated by the following equation [16]

$$\mathrm{Org}_{(\mathrm{solution})} + x\mathrm{H_2O} \longleftrightarrow \mathrm{Org}_{(\mathrm{adsorbed})}) + x\mathrm{H_2O}$$

where $x$ is the number of water molecules replaced by the adsorption per mole of organic compound.

There are three major types of mathematical models describing adsorption isotherms, namely the Langmuir, Frumkin and Temkin isotherms [17–20]. All these isotherms are generally given as

$$f(\theta, x)\exp(-2a\theta) = KC$$

Here $f(\theta, x)$ is a configuration factor dependent upon the physical model employed, $\theta$ and $C$ are the surface coverage ratio and the concentration of the inhibitor, respectively; $x$ stands for the magnitude factor, being the intermolecular interaction parameter and $K$ is the adsorption parameter [21].

According to Temkin and Langmuir, isotherms are given as $\exp(-2a\theta) = KC$ and $\theta = KC(1 - \theta)$. In this study, the adsorption of the inhibitor was found to be best described by the Langmuir isotherm when boron steel was used as the adsorbent, whereas it was best described by the Temkin isotherm when other steels were used (Figs. 8, 9).

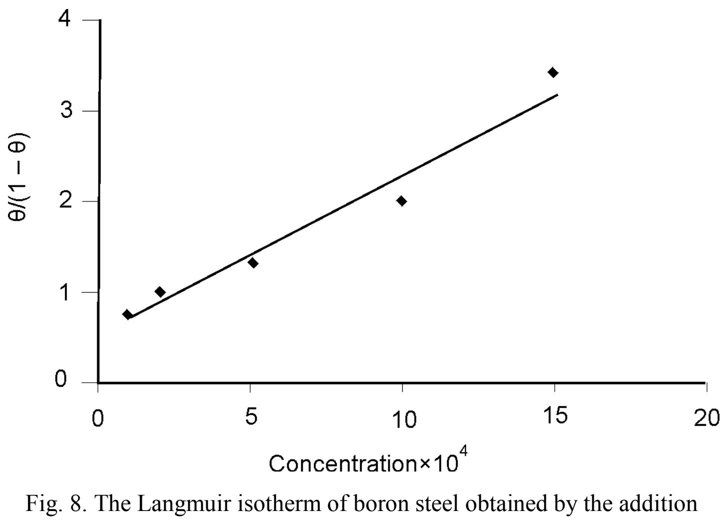


Fig. 8. The Langmuir isotherm of boron steel obtained by the addition of Congo red inhibitor at various concentrations in 3.5% NaCl medium

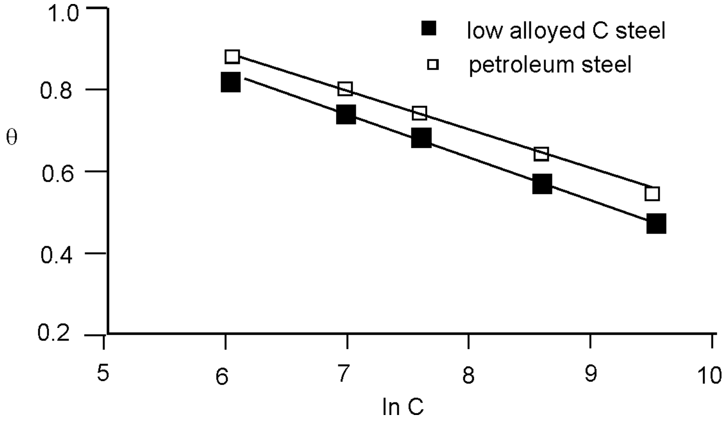


Fig. 9. The Temkin isotherms of petroleum and low alloyed carbon steel obtained by the addition of Congo red inhibitor at various concentrations in 3.5% NaCl medium

It is known that Congo red is used as an indicator in biochemical studies and precipitation of metal ions in a solution [22]. However, in this study, it was used for the first time as a corrosion inhibitor. Its inhibition efficiency was calculated by two different methods: the calculated values were found to be similar. It shows inhibition efficiency up to 80% at the inhibitor concentration of $2 \cdot 10^{-3}$ M. The corrosion potentials are shifted to more positive values compared with the equilibrium or open circuit potential. In this study, the efficiency of the inhibitor was found to be high for the low alloyed corrosion prone carbon steel and low for the corrosion resistant boron steel.

Based on the adsorption isotherms, distinction between its physical or chemical nature is ambiguous. However it is obvious that the adsorption conditions will differ depending upon the composition of the steels. The compound can easily adsorb upon the steel surface due to nitrogen atoms and π electrons of the aromatic structure. The fact that the adsorption is of Langmuir type on low alloyed carbon steel and petroleum steels, and is of Temkin type on boron steel results from various compositions of the steels.

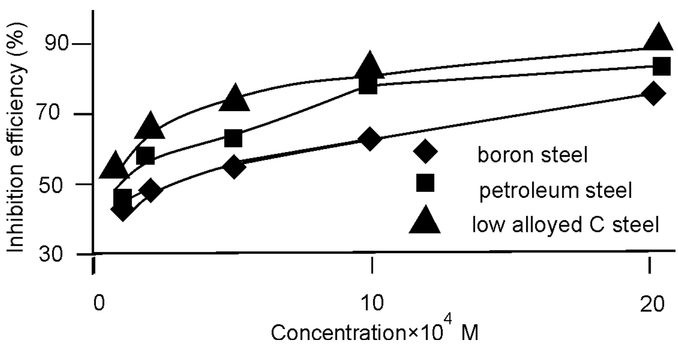


Fig. 10. Dependence of inhibition efficiency of Congo red on the concentration in 3.5% NaCl solution

In conclusion, Congo red was observed to cover the surface by adsorbing upon it and its inhibition efficiency increased with the concentration. The efficiency was highest in low alloyed carbons steels (Fig. 10)

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