



Inhibition effect and mechanism of sodium oleate on passivation and pitting corrosion of steel in simulated concrete pore solution

Yishan Wang, Yu Zuo*, Yuming Tang*

Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, China

HIGHLIGHTS

- SO effectively promotes passivation and inhibits pitting corrosion of steel in SCP solution.
- SO adsorbs competitively on the surface and decreases the adsorption of Cl^- .
- Carboxyl group in adsorbed $\text{C}_{17}\text{H}_{33}\text{COO}^-$ anion may promote oxidation of Fe on the surface.
- A homogeneous SO adsorption film forms on steel surface.
- Adsorbed SO molecular film retards diffusion and approach of aggressive species.

ARTICLE INFO

Article history:

Received 30 May 2017

Received in revised form 27 December 2017

Accepted 28 January 2018

Keywords:

Carbon steel

Inhibition

Sodium oleate

Corrosion

Pitting

Concrete environments

ABSTRACT

The inhibition effect and mechanism of sodium oleate (SO) on pitting corrosion of carbon steel in simulated concrete pore solution were studied by using methods of potentiodynamic polarization, electrochemical impedance spectroscopy, scanning electronic microscopy and X-rays photoelectron spectroscopy. In simulated concrete pore solution (pH 12.5), carbon steel showed pitting corrosion behavior during the early immersion period, and SO effectively increased the pitting breakdown potential. After 10 h immersion in SCP solution, passivation was achieved and the pitting potential increased obviously. The inhibition efficiency was over 98% with 0.0008 mol/L SO addition, and after 720 h immersion the corrosion current density with SO was still one order of magnitude lower than that without SO. The results confirm that SO may inhibit the corrosion process in three ways: First, SO competitively adsorbs on the surface, decreasing the adsorption of aggressive Cl^- . Then, the carboxyl group in adsorbed $\text{C}_{17}\text{H}_{33}\text{COO}^-$ anion may promote oxidation of Fe atoms on the surface, strengthening passivation. Thirdly, the adsorbed SO forms a compact inhibition film, which would further retard diffusion and approach of water, oxygen and aggressive species to the surface.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Reinforced concrete structures are applied extensively. Usually the concrete environments show alkaline and carbon steel may be passivated. However, in engineering structures steel bars are frequently corroded due to the environmental changes such as ingress of aggressive ions, stress application or acidization and carbonization of the pore solutions [1]. Inhibitors are one of the main methods to control corrosion of metals. The frequently used inhibitors for steel bars in concrete environments are mainly inorganic inhibitors such as nitrites, chromates, molybdates and polyphosphates. These inhibitors may promote oxidation of steel surface

and resist water and chloride ions to the surface. However, during the performance of concrete structures, the inorganic inhibitor ions would be consumed continually which is irreversible. Once the concentration of the inorganic ions decreases below the critical value for passivation at local areas on the surface, corrosion may be promoted due to the oxidizing effect of the ions. In addition, it has been widely accepted that inhibitors should be non-poisonous, not harmful to human health and biodegradable. However, some inorganic salts such as chromates and nitrites are detrimental to the environments and the applications are prohibited in many fields.

Martinez et al. [2] reported corrosion inhibition behavior of selected organic anions on low-carbon steel in saturated $\text{Ca}(\text{OH})_2$ solution containing chlorides. The compounds studied include eight amino acids, two carboxylic acids, ascorbic acid and a mimosa tannin extract. All the inhibitors suppressed the reduction

* Corresponding authors.

E-mail addresses: zuoy@mail.buct.edu.cn (Y. Zuo), tangym@mail.buct.edu.cn (Y. Tang).

of O₂. The proposed mechanism of inhibition involves formation of surface chelates which tends to stabilize iron in Fe(III) state and increase the Tafel slope of the actual potential dependence of the [Fe(II)] surface centers. Sodium oleate (SO) is a common anionic surfactant [3]. Masahiko et al. [4] studied the inhibition of oleic acid on pure iron in borate buffer solution containing chloride ions and the results showed that oleic acid can increase the pitting potential of iron and inhibit pitting corrosion. Luo et al. [5] reported the inhibition behavior of SO on mild steels in acidic 0.24 mol/L Na₂SO₄ solution (pH 1–3). In the acidic solution SO showed inhibition to some extent for both the anodic and cathodic processes of mild steel, and the inhibition efficiency increased with increase of the pH value. Mohammed et al. [6] studied the inhibition effect of SO on Al and Al–Cu alloy in 1.0 mol/L H₃PO₄ solution. It was found that SO showed better inhibition for Al–Cu alloy. The inhibition efficiency increased with increased Cu content in the alloy. Li et al. [3,7] reported the effect of compounded SO and cerium ions. The compounded SO and cerium showed obviously increased inhibition for cold rolled steel in 1 mol/L H₂SO₄ and 3 mol/L H₃PO₄ solutions, in which the inhibition efficiency reached 98.6% and 93.2% when the compounded ratio was 250 mg/L:250 mg/L and 2.0 mmol/L:2.0 mmol/L respectively. When SO was compounded with sodium vanadate at the ratio of 1:2, the inhibitors showed good synergistic inhibition effect for corrosion of aluminum in 3.5% NaCl solution [8]. Shubba et al. [9] synthesized a self-assembly monolayer SO film on carbon steel. The film may impede the aggressive species to the surface and control corrosion of steel in 3.5% NaCl solution. The above studies show that SO as may inhibit corrosion process of carbon steels and aluminum alloys in sulfuric acid, phosphate acid and chloride solutions to certain extents. However, up to now there is no report on inhibition of SO for steel in reinforced concrete environments.

In this paper, the inhibition effect of SO on corrosion and passivation of carbon steel in simulated concrete pore solution is studied. The simulated concrete pore (SCP) solution was a saturated Ca(OH)₂ solution containing 0.1 mol/L NaCl. The inhibition mechanism of SO for steel in the solution was discussed.

2. Experimental methods

The studied material was Q235 carbon steel with the size of 10 × 8 × 8 mm. The chemical composition of the steel was as follows (wt%): 0.11% C, 0.13% Si, 0.74% Mn, 0.0028% S, 0.012% P, 0.010% O, 0.0040% N and Fe. The samples were abraded with 240#, 600# and 1000# abrasive papers in turn, rinsed with acetone and alcohol, and dried in an oven. Then the samples were covered by epoxy resin with an exposed area of 0.04 cm² as the working electrode. The small specimen area usually contains fewer defects, and the measured pitting potential are more positive with less data dispersity [10].

The SCP solution was saturated Ca(OH)₂ solution with 0.1 mol/L NaCl (pH 12.5) at room temperature. The inhibitors used in this study was sodium oleate (SO, C₁₇H₃₃CO₂Na), with the molecular structure shown in Fig. 1. The addition of the small amount of inhibitor did not change the pH value of the solution. The purity of SO was approximately 98%. In SO the main polar group is –RCOO[–], and the main non-polar group is long carbon chains containing double bonds. Fig. 2 shows the infrared spectrum of the SO powders. The wide peak around 3433.33 cm^{–1} is the absorption peak of –OH, and the weak peak at 3001.71 cm^{–1} is the absorption peak of =CH [11]. The peaks at 2922.73 cm^{–1} and 2852.59 cm^{–1} are respectively due to the stretching vibration peaks of –CH₃ and –CH₂ [12], and the peak at 1706.84 cm^{–1} is due to –C=O group [13]. The peak at 1562.43 cm^{–1} is the characteristic of –

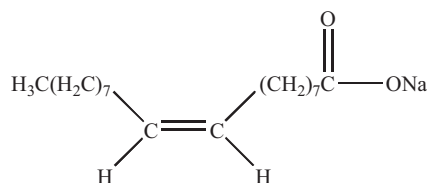


Fig. 1. The molecular structure of SO.

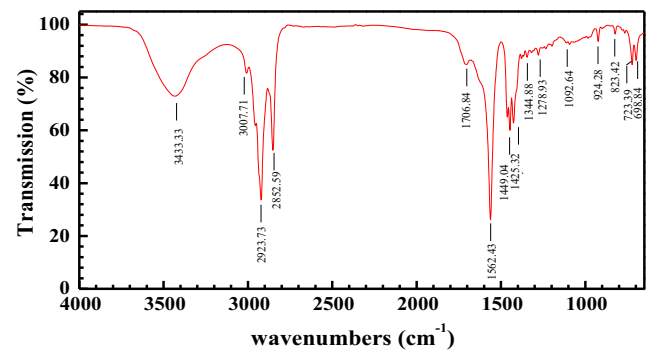


Fig. 2. FT-IR spectra of SO.

RCOO–Na [14], the peaks at 1449.04 cm^{–1} and 1425.32 cm^{–1} are the characteristics of long carbon chains [11], and the peak at 1314.88 cm^{–1} is due to the stretching vibration of –C–O bond [15]. The peaks at 1278.93 cm^{–1} and 698.84 cm^{–1} are because of the deformation vibration of =CH [11], the peak at 1092.64 cm^{–1} is due to the deformation vibration of –C=C– [11], the peaks at 924.28 cm^{–1} and 823.34 cm^{–1} are due to –CH₃ [11], and the peak at 723.39 cm^{–1} is attributed to the deformation vibration of –CH₂. The above results confirm the structure of the SO inhibitor applied.

Potentiodynamic polarization curves were measured with a CS350 electrochemical station (Costa Co. Wuhan). A three electrode system was used with a carbon steel sample as the working electrode, a Pt foil as the auxiliary electrode and a Ag/AgCl (saturated KCl solution) electrode as the reference electrode. Before polarization test the sample was immersed in solution for 1 h to obtain stable open circuit potential (OCP). The polarization potential range was from –300 mV_{SSC} to 1500 mV_{SSC}, with a scanning rate of 0.3 mV/s. For each condition five parallel tests were measured. Tafel fitting was performed for the obtained curves using a C-View software.

Potential of zero charge measurement (PZC) was measured with an electrochemical impedance instrument (Princeton 2273) with applied potential. The measured frequency range was 10 mHz–100 kHz. After the OCP got stable, the measurements were carried out respectively at the potentials ±50 mV, ±100 mV and ±150 mV relative to the OCP. The measured spectra were fitted by the equivalent circuits reported in literature [16,17]. The obtained double layer capacity (C_{dl}) values were plotted with the potential and the potential corresponding to the minimum value on each curve is the zero charge measurement (PZC).

Scanning electronic microscope plus energy dispersive spectroscopy (SEM/EDS) was used to analyze the surface morphology and composition (HITACHI S4700 (Japan)/Genesis 60). The samples were immersed in SCP solutions with 0.001 mol/L SO or without SO for 10 h, then were remove from the solutions, washed and dried before SEM analysis. The sample surface was also analyzed with X-rays photoelectronic spectroscopy (XPS) (ESCALAB 250). The measured binding energy values were calibrated by the value of C1s (285 eV).

Microscopic infrared imaging (M–IR) method was used to analyze the adsorption of the inhibitors on surface. The M–IR system used was a Spotlight 400 FT-IR imaging system (Perkin-Elmer). The data were collected at a spatial (pixel) resolution of 6.25 μm and a spectroscopic resolution of 16 cm^{–1}. The observation of the samples was taken after 10 h immersion in SCP solution with or without SO addition. The samples were carefully rinsed by distilled water and dried at the room temperature after immersion.

3. Results and discussion

3.1. Potentiodynamic polarization measurement

Fig. 3 shows the polarization curves of Q235 steel samples in SCP solution with different concentrations of SO after 30 min immersion. Table 1 shows the electrochemical parameters obtained by Tafel fitting on the polarization curves in Fig. 3. It is seen that in the SCP solution steel showed the behavior of spontaneous passivation then pitting corrosion. The pitting corrosion potential E_b is lower than 0.1 V_{SSC}. With SO added, both the cathodic and anodic current densities decreased to some extent, showing the inhibitive effect of SO, possibly because of the formation of inhibition film on the surface [18,19]. The data in Table 1 confirm that the corrosion current density shows a decreasing tendency with the increase of the SO concentration.

Download English Version:

<https://daneshyari.com/en/article/6714985>

Download Persian Version:

<https://daneshyari.com/article/6714985>

[Daneshyari.com](https://daneshyari.com)