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Egyptian Journal of Petroleum

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Experimental and theoretical studies on the corrosion inhibition of vitamins – Thiamine hydrochloride or biotin in corrosion of mild steel in aqueous chloride environment

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ARTICLE INFO

Article history:

Received 22 February 2017

Revised 23 May 2017

Accepted 18 June 2017

Available online xxxxx

Keywords:

Green corrosion inhibitor

Vitamin

Thiamine hydrochloride

Biotin

Mild steel

240 ppm chloride medium

ABSTRACT

The corrosion inhibition of thiamine hydrochloride (vitamin B1) or biotin (vitamin B7) on corrosion of mild steel in 240 ppm chloride ions solution was studied using weight loss method, potentiodynamic polarization curves and electrochemical impedance spectroscopy. UV–Vis, FTIR and surface analysis using SEM and EDS characterization were carried out to understand the corrosion inhibition property of these inhibitors in 240 ppm aqueous chloride medium. Experimental results show that both thiamine hydrochloride and biotin act as a good corrosion inhibitors. Quantum chemical parameters obtained from density functional theory (DFT) calculations were discussed with experimental results.

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1. Introduction

Cooling water is needed for most industrial production processes for efficient and proper operation. The operation of cooling water circulation systems is faced with several challenges; one of the most significant is corrosion of the metal equipment. Various dissolved substances in cooling water may have different influences on the corrosion of metals. For water-cooled systems, commonly corrosion is of an electrochemical nature and there are several major types of corrosion [1]. The corrosion of iron in corrosive environments, especially in cooling water containing chloride, limits its uses. The mechanisms of pitting and crevice corrosion are similar and they most commonly occur in chloride environments [2–4]. But crevice corrosion occurs more readily because it is helped by the existence of a physical crevice, whereas pitting has to initiate on a flat surface. Chloride and sulfate ions adversely

affect the corrosion resistance of most metals and the presence of 100 ppm chloride ions in the water causes pitting corrosion of steel [5]. The chloride ions cause the passive film to break down at certain weak spots on the metal surface and assist corrosion.

Organic compounds like natural products, drugs act as corrosion inhibitors in different environment for various metals [6–8]. Extensive research on organic compounds reveals that compounds containing hetero atoms such as sulphur, phosphorous, nitrogen or oxygen and compounds containing double bonds and triple bonds inhibit corrosion of metal by surface adsorption [9–18]. Corrosion inhibitors for cooling water systems are several types and are studied in detail [19]. Vitamins are used as green inhibitors [20] on corrosion of metals and their inhibition efficiency of vitamins on corrosion of metals in chloride [21] and acid [22–27] medium were studied in detail. Among vitamins, B vitamins are a class of eight water-soluble chemically distinct vitamins but their use as corrosion inhibitors are not much studied in aqueous chloride environment.

Thiamine hydrochloride (vitamin B1) and Biotin (vitamin B7 or vitamin H), are members of the water soluble B vitamins family needed in our health system. The structure of thiamine hydrochloride, Fig. 1(a) consists of two rings, an amino pyrimidine and a

Peer review under responsibility of Egyptian Petroleum Research Institute.

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<http://dx.doi.org/10.1016/j.ejpe.2017.06.003>

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Please cite this article in press as: A. Aloysius et al., Experimental and theoretical studies on the corrosion inhibition of vitamins – Thiamine hydrochloride or biotin in corrosion of mild steel in aqueous chloride environment, Egypt. J. Petrol. (2017), <http://dx.doi.org/10.1016/j.ejpe.2017.06.003>

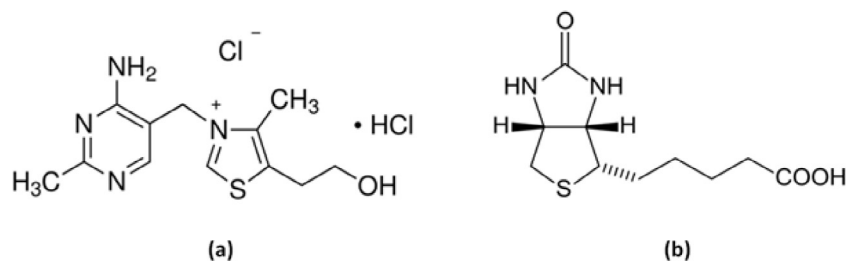


Fig. 1. Structure of (a) thiamine hydrochloride and (b) biotin.

thiazole ring linked by a methylene bridge. On the contrary, the structure of biotin, Fig. 1(b) also consists of two rings, an ureido and a thiophene ring but fused together through one of its sides. Thiamine is naturally present in cereal grains, sun flower seed and eggs and biotin is also naturally present in peanuts and leafy green vegetables. In this research, corrosion inhibition effect of thiamine hydrochloride and biotin on corrosion of mild steel in 240 ppm chloride ions solution was studied using weight loss method, potentiodynamic polarization curves, electrochemical impedance, UV–Vis and FT-IR spectroscopy.

2. Experimental

2.1. Material and specimens

The test material was mild steel with a chemical composition (mass%) of 0.10 C, 0.06 P, 0.40 Mn, 0.026 S, and the balance of Fe. Specimens with a size of $1 \times 4 \times 0.2 \text{ cm}^3$ were cut and their surfaces were abraded using 150–600 grit emery papers. Prior to testing, the specimens were degreased with acetone and rinsed with de-ionized pure water. Thiamine hydrochloride and biotin were purchased from Loba Chemie, India. FeSO_4 and NaCl were purchased from Merck, India and used as such without further purification. Double-distilled water was used to prepare solution of chloride ions concentration of 240 ppm and various concentrations of ferrous ions, thiamine hydrochloride and biotin inhibitors solution. Corrosion medium was an aqueous solution having a fixed concentration of 240 ppm of chloride ions in water. The corrosion tests were carried out with inhibitors concentration of 25, 50, 100, 150 and 200 ppm in the corrosion medium.

2.2. Weight loss method

For weight loss measurements, each run was carried out in a glass vessel containing 100 mL of 240 ppm chloride ion solution. The experiments were carried out at an ambient temperature of 30 °C by immersing the mild steel specimen using glass hooks in 100 mL of the blank solutions or solution with respective inhibitor. After 24 h immersion, the specimens were taken out from solution, rinsed with double distilled water, dried thoroughly and weighed.

The weight loss (ΔW) was used to calculate the corrosion rate denoted as CR, ($\text{mg} \cdot \text{dm}^{-2} \cdot \text{day}^{-1}$) and the inhibition efficiency as IE, (%):

$$\text{CR}(\text{mg} \cdot \text{dm}^{-2} \cdot \text{day}^{-1}) = M_1 - M_2 / SP$$

where, M_1 and M_2 is the mass of the specimen before and after the corrosion respectively, S is the surface area of the specimen in dm^2 and P is the period of immersion in days. The IE was calculated by using the following equation:

$$\text{IE}(\%) = (W_0 - W_i) / W_0 \times 100$$

Here $\Delta W = (W_0 - W_i)$, where W_0 and W_i are the corrosion rate of mild steel in the absence and presence of inhibitor respectively,

In this study, the CR value is calculated using the formula,

$$\text{CR}(\text{mg} \cdot \text{dm}^{-2} \cdot \text{day}^{-1}) = \Delta W(\text{mg}) / [0.096(\text{dm}^2) \times 1 \text{day}]$$

where, the surface area S takes the value of 0.096 dm^2 .

2.3. Potentiodynamic polarization studies

Electrochemical experiments were carried out using conventional three electrode cell assembly. The working electrode was a mild steel specimen with an exposed surface area of 1 cm^2 was fitted to a holder and the rest of the area was covered with epoxy coating. Saturated calomel electrode and platinum wire were used as reference and counter electrode. The working electrode was vertically immersed in the test solution and open circuit potential was recorded by using Princeton Applied Research (2 channels) analyzer. The samples were immersed in the test solution for 30 min for stabilization of open circuit potential and then potentiodynamic polarization tests were performed. The open circuit potential test was conducted for 30 min for every sample and with respect to open circuit potential value, the Tafel polarization studies were carried out at a scan rate of 0.5 mV/s . The reason for choosing slow scan rate (0.5 mV/s) was to reduce the disturbance of the charging current to avoid distortion of potentiodynamic polarization curves. This will extend the polarization time and the polarization potential will cause some irreversible changes to the interfacial structure especially in the anodic region. Corrosion current (I_{corr}) and corrosion potential (E_{corr}) were obtained by extrapolating the anodic and cathodic curves of Tafel plot. Inhibition efficiency was calculated by using respective I_{corr} values. Electrochemical impedance analyses were performed in the frequency range from 1 Hz to 1 MHz with amplitude of 10 mV peak-to-peak using AC signal at E_{corr} . The mild steel specimens used for this study have a surface area of 1 cm^2 , which were exposed to the corrosive solution. All these measurements were done at the atmospheric conditions without any stirring. The experiments were conducted in the absence and presence of inhibitor with different concentration in the 240 ppm chloride ion medium.

2.4. Characterization of surface morphology

Surface morphologies of the films were mainly observed under scanning electron microscopy, SEM (TESCAN Vega 3) using electron acceleration between 5 and 10 kV.

2.5. Fourier transforms infrared (FT-IR) spectroscopy

FT-IR spectra were recorded in Perkin Elmer Spectrum RX I with a spectral range of 4000 cm^{-1} to 400 cm^{-1} and a spectral resolution of 4 cm^{-1} . The mild steel specimens were immersed for 24 h in 100 mL of 240 ppm of aqueous chloride ion medium containing various concentrations of vitamins. After 24 h, the specimens were taken out and dried. Finally, the specimens were rubbed with a

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