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Simultaneous impedance and volumetric studies and additionally potentiodynamic polarization measurements of molasses as a carbon steel corrosion inhibitor in 1M hydrochloric acid solution

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HIGHLIGHTS

- We have identified corrosion of carbon steel in hydrochloric acid with Molasses extract.
- We found that inhibition efficiency of 6000ppm molasses concentration is around 90%.
- The relation of two simultaneous techniques: DEIS and volumetric, was described.

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ABSTRACT

The inhibition effect of molasses on the corrosion of low carbon steel in 1M hydrochloric acid solution was investigated by volumetric and electrochemical measurements. Potentiodynamic polarization and dynamic electrochemical impedance spectroscopy (DEIS) results were obtained and compared with to those, obtained with the hydrogen evolution technique. All results indicate that molasses functioned as a good inhibitor in 1M hydrochloric solution and inhibition efficiency increased with molasses concentration. The advantage of DEIS as a tool for investigation of molasses influence was discussed.

1. Introduction

Carbon steel is still one of the most common and popular construction material. Carbon steel, is counted for approximately 94% of the annual steel production in United States. Relatively limited corrosion resistance of carbon steel do not change the fact that it is used in marine applications, pipelines, mining, chemical processing, nuclear power plants, fossil fuel power plants, transportation, petroleum production and refining, construction and metal-processing equipment and many more [1].

Costs of corrosion degradation of carbon steel materials are estimated to be hundreds of millions dollars each year [2]. Corrosion of carbon steel is a problem of enormous practical importance, because this material represents the largest single class of alloys in use, alike in terms of total cost and tonnage. This is the reason why providing corrosion protective systems is so important and the existence of the entire industry devoted to corrosion protection techniques is necessary. The carbon steel is the most widely used engineering material, accounts for approximately 85%, of the annual steel production worldwide [3] and the worldwide consumption of finished steel products in million tones is expected to reach 1463 million tones in 2014 [4]. Short calculation gives 124 million tones of carbon steel in 2014.

The extending life time of carbon steel is of major importance. To achieve this goal, corrosion protection methods like galvanizing, coating and plating are used. Coatings provide a simple barrier of protection. The coating should provide protection by inhibiting contact of metal with aggressive environment [5–9]. Paintings are a commonly used barrier coatings; the sample preparation before applying layer is extremely important, its success in resisting corrosion depends on the cleanliness of the surface prior to application [10–13].

This step comprises etching of the steel surface. It allows to remove effectively non-metallic substances (i.e. rust, scale and other corrosion products) formed during rolling and annealing components and natural oxides layer. The most popular method of etching bath is in hydrochloric acid [14].

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The etching process have also risk sides, it can weaken the surface of the steel, enhancing corrosion possibility. Inhibitors are also often added to protect the metal surface from attack during the etching process [15,16]. Also other steel processing steps undergo in acid solutions, like widely used in industrial acid cleaning, acid descaling, acid pickling, and oil well acidizing. This requires the use of corrosion inhibitors in order to hold down corrosion attack on the metallic materials [17].

For the reason of increasing environmental protection importance, green inhibitors became very popular. Over the years, many scientist tried to find suitable green corrosion inhibitors in various corrosive media [18–21]. Green organic corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Inhibition of the corrosion of carbon steel with naturally occurring substances in acidic and alkaline environments were reported by many research groups. Succinic acid inhibit the corrosion in hydrochloric acid solutions [22], mimosa tannin was studied as corrosion inhibitor in the sulfuric acid [23], 12-aminododecanoic acid proved to be in CO_2-saturated hydrochloric acid [24].

Beet molasses, an economic by-product of refined sugar, was not yet evaluated in order to inhibit corrosion processes. Nowadays molasses is mostly used as a cattle feed [25]. Molasses was investigated as a potential corrosion inhibitor because of economical and environmental reasons like: management of wastes obtained during production of sugar, ecological purposes, good physico-chemical properties, which are solubility and stability in acidic media. In this work authors present the influence of organic green molasses on the carbon steel etching process in hydrochloric acid. Presented research were carried out using Dynamic Electrochemical Impedance Spectroscopy (DEIS), potentiodynamic polarization and volumetric techniques.

2. Experimental study

The carbon steel wire was used as a working electrode (1.8 mm in diameter, area of 4.4 cm^2) Its chemical composition is presented in Table 1. The working electrode surface was polished with a series of abrasive papers of 400, 800, 1500 grades and cleaned with acetone before each measurement.

The reference electrode was silver/silver chloride (Ag/AgCl), platinum mesh was used as counter electrode. All electrodes were placed in the bottom part of 50 cm^3 thermostatic flask, where all experiments were carried out. The upper part of the experimental set (Fig. 1) was a burette allowing measurement of amount of released hydrogen. The lower part contain outputs which allow connection to the electrochemical device.

Measurements were carried out in the environment of 1 M hydrochloric acid with addition of 0 ppm, 500 ppm, 1500 ppm and 6000 ppm of molasses. Before each experiment the solution was treated with ultrasounds in order to remove gas, the solution was also saturated with hydrogen and brought to working temperature of 35 °C. Time of electrodes exposition, volumetric and impedance research took about 6 h.

Tafel plots were obtained using Gamry 600. The impedance measurements were carried out with the corrosion potential. For this reason, galvanostatic conditions with direct current component $I_{dc} = 0$ was used. AC perturbation signal was a package composed of sinusoids in the frequency range from 4.5 kHz to 0.7 Hz. The package was chosen in a way to prevent maximum response peak-to-peak amplitude from exceeding 30 mV.

Generation of the current perturbation was performed with a PXI 4462 National Instruments digital-analog card. That card was also used to measure the current and the voltage signals. Fast home-build galvanostat was used to provide galvanostatic conditions and the current-voltage conversion. The system control and analysis of results were done using short time Fourier transformation (STFT) with an application created in LabView environment. The analysis of impedance spectra and fitting of experimental results to equivalent circuits were performed using ZsimpWin 3.1 software.

Table 1
Composition of working electrode.

C	Si	Mn	P	S	Cu	Cr	Ni	Fe
<0.22	0.1–0.35	<1.1	<0.05	<0.05	<0.3	<0.3	<0.3	Balance

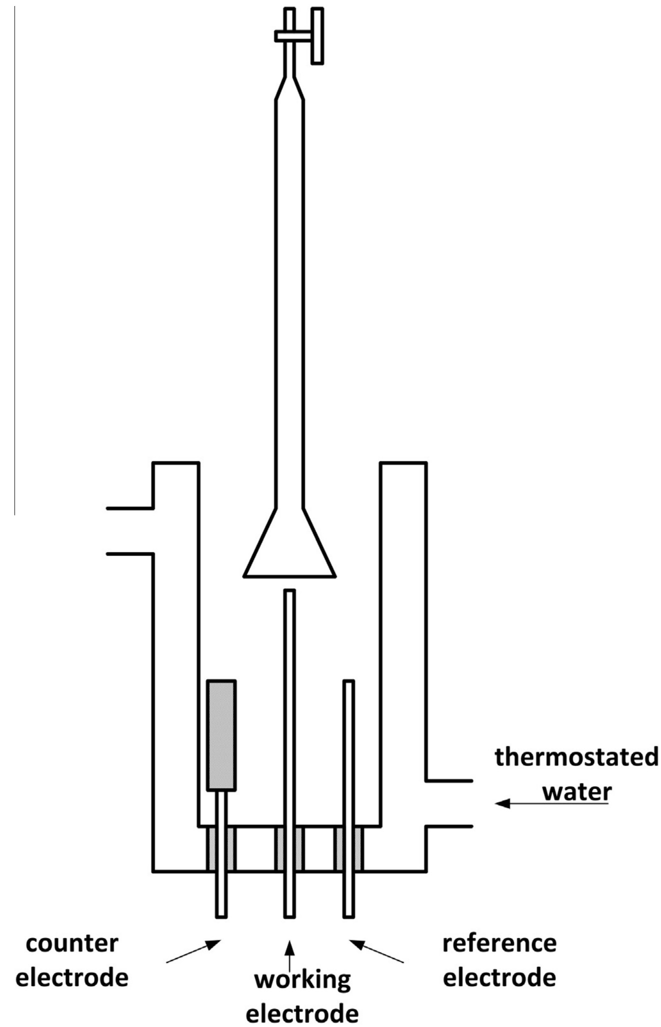

Fig. 1. Scheme of investigated system.

Detailed information regarding principles of DEIS measurement in galvanostatic mode was presented by Slepski et al. [26].

3. Results and discussion

Impedance results, obtained during exposition of the carbon steel in the hydrochloric acid solution with the addition of molasses in amounts from 0-6000 ppm, are presented on Fig. 2a–d.

The acquired impedance spectra demonstrate a flattened circular shape. Slow decrease of the impedance during the measurement can be observed. The size of impedance semicircles increases as the molasses concentration in the solution increases.

In order to obtain more qualitative information of inhibition mechanism the impedance data were analyzed with the use of the electrical equivalent circuit (Fig. 3).

The equivalent circuit consists of the resistor, representing the solution between working and the reference electrodes R_s, in series to a parallel combination of the resistor, R_{ct}, playing the role of the charge transfer (corrosion) resistance and constant phase element CPE. Its impedance, Q is used instead of capacitor due to presence of depressed semicircles in the spectra.

This is the typical equivalent circuit representing simple electrode reaction under activation control. The value of charge transfer resistance is of high importance and decides about the dynamic of the corrosion process. Changes of R_{ct} obtained from impedance spectra are presented on Fig. 4.