Corrosion Science 92 (2015) 287–300

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Corrosion inhibition of C38 steel by alkaloids extract of *Geissospermum laeve* in 1 M hydrochloric acid: Electrochemical and phytochemical studies

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ARTICLE INFO

Article history:
Received 26 May 2014
Accepted 4 December 2014
Available online 18 December 2014

Keywords:
A. C38 steel
B. EIS
B. SEM
C. Acid corrosion
C. Cathodic protection
C. Anodic protection

ABSTRACT

Corrosion inhibition by alkaloids extract (AE) from *Geissospermum laeve* on C38 steel in 1 M HCl is investigated with electrochemical studies. Inhibition efficiency of 92% is reached with 100 mg/L of AE at 25 °C. Potentiodynamic polarization showed that the extract behaves as mixed-type inhibitors. The Nyquist plots showed that increasing AE concentration, charge-transfer resistance increased and double-layer capacitance decreased, involving increased inhibition efficiency. Adsorption of the inhibitor molecules corresponds to Langmuir adsorption isotherm. Immersion time and temperature effects were investigated using EIS and potentiodynamic polarization. SEM and EDX supported the adsorption conclusions. The active compound responsible for the corrosion inhibition is geissospermine.

1. Introduction

The use of chemical inhibitors is one of the most practiced methods for protecting against corrosion, especially in acid media, to prevent metal dissolution and acid consumption [1]. Various organic and non-organic compounds have been studied as inhibitors to protect metals from corrosion. Usually, organic compounds exert a significant influence on metal surface adsorption and therefore can be used as effective corrosion inhibitors. The efficiency of these organic corrosion inhibitors is related to the presence of polar functions containing S, O or N atoms which are centers for the establishment of the adsorption process [2–8].

Nevertheless, most of these synthetic organic compounds are not only expensive but also toxic for live beings. Now, the restrictive environmental regulations have made researchers to focus on the need to develop cheap, non-toxic and environmentally benign natural corrosion inhibitors. These natural organic compounds could be either synthesized or extracted from aromatic herbs, spices and medicinal plants. Plant extracts are viewed as an incredibly rich source of natural chemical compounds which can be extracted by simple and low-cost procedures and which are biodegradable in nature. The use as corrosion inhibitors of natural compounds extracted from leaves or seeds, for example, have been widely reported by several authors [9–14].

Corrosion inhibition of leaf extracts of *Occimum viridis*, *Telferia occidentalis*, *Azadirachta indica* and *Hibiscus sabdariffa* on mild steel in acidic solutions were investigated by Oguzie [15]. Gunasekaran et al. [16] studied the corrosion inhibition of *Zanthoxylum alatum* plant extracts on steel in hydrochloric acid and phosphoric acid media. Commonly, the inhibitive effect of plant extract is attributed to the adsorption of organic substances on the metal surface therefore blocking active sites or even forming a protective barrier. Among the plant extract natural products, there are alkaloids which contain one or more nitrogen atoms. For example, L-histidine [18], tryptamine [18] and caffeine [19] are used as corrosion inhibitors. Papaverine, strychnine, quinine, nicotine, atropine sulfate showed high inhibition efficiencies for zinc and mild steel in acidic solutions [20–22]. The use of peptic compounds and some amino acids, was investigated for their anticorrosion activity [23,24] and the application of bgugaine in the steel corrosion control was patented [25]. Berberine extracted from *Coptis chinensis* had high inhibition efficiency with a value up to 98% for mild steel in 1 M H_2SO_4 [26]. The acid extract of dry leaves of *Emblica officinalis* acted as a good corrosion inhibitor for mild steel in 1 N HCl medium [27]. Recently, an ethanol extract of *Mansoa alliacea* was tested as a corrosion inhibitor for zinc in NaCl 3%: the inhibition efficiency was about 92% with 300 mg/L of extract [28]. In this case, the inhibition behavior of the crude extract was due to the presence of compounds

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http://dx.doi.org/10.1016/j.corsci.2014.12.005
0010-938X/

belonging to the flavonoids family. The inhibiting effect of the *Aniba rosaeodora* alkaloidic extract on the corrosion of C38 steel in 1 M hydrochloric acid was reported [29]. This corrosion inhibitive effect can be attributed to the presence of anibine, the major alkaloid, which produces high efficiency of inhibition. XPS studies confirmed that the *A. rosaeodora* alkaloidic extract and the anibine are strongly adsorbed onto the steel surface.

A literature research reveals few studies related to the anti-corrosion properties of extracts from Amazonian trees. Yet the Amazon is well known to have the richest biodiversity in the world. In French Guiana, there are about to 170 species of trees per hectare and more than 1200 tree species in the country [30]. *Geissospermum laeve* (Vell) Baillon, belonging to Apocynaceae family, is a tree widely found throughout the Amazonian forest. Commonly, this plant is named Pao Pereira and its amorphous bark extracts have long enjoyed a reputation as a febrifuge [31] in the Brazilian folk medicine and have recently been reported to have a curare-like activity [32]. Pao Pereira barks are popularly used to treat malaria, poor digestion, constipation and dizziness [33]. Because of its properties, this plant is the subject of intensive research, since 1838 at the earliest, from both the chemical and pharmacological standpoints. The bark is rich in alkaloids and presents various actions. For example, geissospermine, the most abundant alkaloid, acted at the autonomic nervous system [34], whereas the flavopereirine and its analogues have been proposed as useful drugs to treat HIV infection [35]. However, it has never been studied for the purpose of corrosion inhibition.

The objective of the present work is to study the inhibitory action of alkaloids extract of *G. laeve* as a substance naturally acting on corrosion behavior of C38 steel in 1 M HCl solution. Polarization curves and the electrochemical impedance spectroscopy were carried out to study the mechanism of corrosion inhibition. The effect of temperature on the values of the electrochemical parameters characterizing the systems has been recorded by polarization curves. It is quite likely that geissospermine is the main active ingredient responsible for the corrosion inhibition of *G. laeve*. To show that geissospermine is responsible of the anti-corrosion effect, this molecule is isolated by Centrifugal Partition Chromatography (CPC) in the pH-zone refining mode. Then a comparative study of alkaloids extract of *G. laeve* and geissospermine alone is performed.

2. Experimental

2.1. Specimen preparation and solution

2.1.1. Corrosion tests

Corrosion tests have been carried out on electrodes cut from sheets of C38 steel. The steel strips contained 0.36 wt% C, 0.66 wt% Mn, 0.27 wt% Si, 0.02 wt% S, 0.015 wt% P, 0.21 wt% Cr, 0.02 wt% Mo, 0.22 wt% Cu, 0.06 wt% Al and the remainder in iron. The specimens were embedded in epoxy resin, leaving a working area of 0.78 cm^2. The working surface was subsequently ground with 180 and 1200 grit grinding papers, cleaned by distilled water and ethanol. The solutions (1 M HCl) were prepared by dilution of an analytical reagent grade 37% HCl with doubly distilled water.

2.1.2. Preparation of plant extract

G. laeve bark was collected in Roura (French Guiana) and dried at room temperature (30–35 °C). The typical alkaloids extractions were performed according to a previously described experimental procedure [9,10,12,13,36]. The concentration range of alkaloids plant extract from *G. laeve* employed was 10–100 mg/L in acidic media.

2.2. Electrochemical measurements

Electrochemical measurements, including potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS), were performed in a three-electrode cell. The C38 steel specimen was used as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Before each polarization and EIS experiments, the electrode was allowed to corrode freely and its open-circuit potential (OCP) was recorded as a function of time. Three hours were necessary to reach a quasi-stationary value for the open-circuit potential. This steady-state OCP corresponds to the corrosion potential (E_{corr}) of the working electrode. The polarization curves, anodic and cathodic, were recorded with a 20 mV/min constant sweep rate, from −300 mV to 300 mV around the open-circuit potential. Electrochemical impedance spectroscopy (EIS) measurements were carried out using ac signals of 5 mV of amplitude, peak to peak, at different conditions in the frequency range of 100 kHz to 10 mHz. Electrochemical measurements were performed through a VSP electrochemical measurement system (Bio-Logic). The above procedures were repeated for each concentration of the two tested inhibitors. The Tafel and EIS data were analyzed using graphing and analyzing impedance software, version EC-Lab V9.97.

2.3. Surface analysis

The surface morphology after immersion in 1 M HCl solution in the absence and presence of inhibitor was imaged using an environmental scanning electron microscope (ESEM – F.E.I Quanta 250).

2.4. Geissospermine isolation by pH-zone refining Centrifugal Partition Chromatography (CPC)

The separations were performed using a CPC Sanki Engineering (Tokyo, Japan). The column is a stacked circular partition disk rotor which contains 2136 channels with a total internal volume of around 230 mL. The column is connected to the injector. A four port valve installed on the CPC allows its operation both in ascending and descending modes. The biphasic solvent system for alkaloids separation is composed of a solution of 2-MeTHF/H_2O 1:1 (v/v). The solvent mixture was vigorously shaken and then allowed to settle until the phases became limpid. The upper organic phase was made basic with DEA (eluter) to obtain a final concentration of 100 mM and HCl (retainer) was added to lower aqueous stationary phase to obtain a same final concentration of 100 mM. The sample solution was prepared by dissolving 1 g of crude alkaloids extract in 5 mL of stationary phase solution. Keeping the rotor speed at 1000 rpm and flow-rate 5 mL/min, the column was first filled with aqueous stationary phase containing HCl in ascending mode. Then the rotor speed was increased to 1800 rpm and the basic upper organic layer containing DEA was pumped into the column as mobile phase in ascending mode with a flow rate of 1 mL/min. When equilibrium was maintained between mobile and stationary phase, the sample was injected through the sample port. After loading the sample, fractions were collected at a regular interval of 3 min.

3. Results and discussion

3.1. Polarization measurements

Potentiodynamic anodic and cathodic polarization plots for C38 steel in 1 M HCl solution, in the absence and presence of different concentrations of alkaloids extract of *G. laeve*, are shown in Fig. 1. This figure shows that the anodic and cathodic reactions are affected by the alkaloids extract. It means that the addition of