Materials Chemistry and Physics 141 (2013) 240–247

Contents lists available at SciVerse ScienceDirect

Materials Chemistry and Physics

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

The use of *Euphorbia falcata* extract as eco-friendly corrosion inhibitor of carbon steel in hydrochloric acid solution

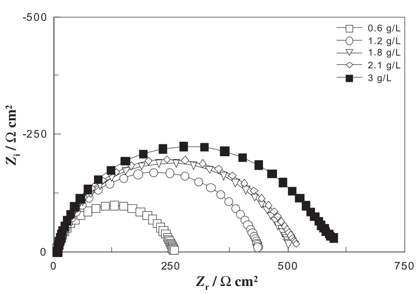
A. El Bribri [a], M. Tabyaoui [a,b,*], B. Tabyaoui [a], H. El Attari [c], F. Bentiss [c]

[a] *Laboratoire de Chimie Organique, Bioorganique et Environnement, Faculté des Sciences, Université Chouaib Doukkali, B.P. 20, M-24000 El Jadida, Morocco*
[b] *Laboratoire des Matériaux, Nanoparticules et Environnement, Université Mohamed V Agdal, Faculté des Sciences, 4 Av. Ibn Battouta, B.P. 1014 RP, M-10000 Rabat, Morocco*
[c] *Laboratoire de Catalyse et de Corrosion des Matériaux (LCCM), Faculté des Sciences, Université Chouaib Doukkali, B.P. 20, M-24000 El Jadida, Morocco*

HIGHLIGHTS

- EFE is a good eco-friendly inhibitor for the corrosion of carbon steel in 1 M HCl.
- EFE acts as mixed-type inhibitor in 1 M HCl medium.
- Weight loss, ac impedance and polarization methods are in reasonable agreement.
- The adsorption of EFE is well described by the Langmuir adsorption isotherm.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 March 2012
Received in revised form
3 April 2013
Accepted 9 May 2013

Keywords:
Organic compounds
Surfaces
Corrosion test
Adsorption

ABSTRACT

Euphorbia falcata L. extract (EFE) was investigated as eco-friendly corrosion inhibitor of carbon steel in 1 M HCl using gravimetric, ac impedance, polarization and scanning electron microscopy (SEM) techniques. The experimental results show that EFE is good corrosion inhibitor and the protection efficiency is increased with the EEF concentration. The results obtained from weight loss and ac impedance studies were in reasonable agreement. Impedance experimental data revealed a frequency distribution of the capacitance, simulated as constant phase element. Polarization curves indicated that EFE is a mixed inhibitor. The corrosion inhibition was assumed to occur via adsorption of EFE molecules on the metal surface. The adsorption of the *E. falcata* extract was well described by the Langmuir adsorption isotherm. The calculated ΔG^o_{ads} value showed that the corrosion inhibition of the carbon steel in 1 M HCl is mainly controlled by a physisorption process.

1. Introduction

Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Hydrochloric and sulphuric acids are widely used in the pickling processes of metals. Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent metal dissolution and acid consumption [1]. The use of synthetic organic compounds containing oxygen, sulphur and nitrogen to reduce corrosion attack on steel has been widely studied in some details [2–6]. The strict environmental legislations and increasing ecological awareness among scientists have led to the development of "green" alternatives to mitigate corrosion. Recently, natural compounds such as herb plants were employed as inhibitors in order to develop new cleaning chemicals for green environment

* Corresponding author. Laboratoire de Chimie Organique, Bioorganique et Environnement, Faculté des Sciences, Université Chouaib Doukkali, B.P. 20, M-24000 El Jadida, Morocco. Tel.: +212 661 749 041; fax: +212 523 342 187.
E-mail address: hamidtabyaoui@yahoo.fr (M. Tabyaoui).

0254-0584/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matchemphys.2013.05.006

[7]. Plant extracts are incredibly rich sources of naturally synthesized chemical compounds (e.g. amino and organic acids, glucosinolates, alkaloids, polyphenols, tannins) and most are known to have inhibitive action. Moreover, they can be extracted by simple procedures with low cost. The uses of the natural products as corrosion inhibitors for different metals have been reported by several authors [8–20]. Most of the natural products are nontoxic, biodegradable and readily available and renewable sources of materials. Various parts of the plants, leaves [21], fruits [22], seeds [23,24], and flowers [25,26] were extracted and used as corrosion inhibitors. The reviews of the literature on several plant extracts as corrosion inhibition of mild steel in HCl solution were recently published by Singh et al. [27]. They showed that all the reported plant extracts were found to inhibit the corrosion of mild steel in acid media. Indeed, the extract *Andrographis paniculata* has a better inhibition performance (98%) than the other leaves extract. *Strychnos nuxvomica* showed better inhibition (98%) than the other seed extracts. *Moringa oleifera* extract is reflected as a good corrosion inhibitor of mild steel in 1 M HCl with 98% inhibition efficiency among the studied fruits extract. *Bacopa monnieri* extract showed its maximum inhibition performance to be 95% at 600 ppm among the investigated stem extracts. Corrosion inhibition effect of *Justicia gendarussa* extract on mild steel in 1 M HCl medium was also studied by Satapathy et al. [28] and inhibition efficiency up to 93% was achieved with 150 mg L^{-1} of extract. Aqueous extracts of *Cordia latifolia* and *Curcumin* were investigated as corrosion inhibitors for mild steel in industrial cooling systems by Minhaj et al. [29]. The extracts showed maximum inhibition efficiency of 97.7% and 60%, respectively. Also, the inhibitive effects of aqueous extracts of *Eucalyptus* (leaves), *Hibiscus* (flower), and *Agaricus* on the corrosion of mild steel for cooling-water systems, using tap water, have been investigated by means of weight loss and polarization methods [29]. All the plant extracts were found to inhibit corrosion of mild steel following and their inhibitive efficiencies were in the order: *Agaricus* (85%), *Hibiscus* (79%), and *Eucalyptus* (74%).

Plants in the spurge family (Euphorbiaceae) are well known for the chemical diversity of their isoprenoid (sesqui-, di- and triterpenes) constituents. The genus *Euphorbia* is the largest in this family, comprising more than 2000 species, and diterpenoids are amongst their characteristic compounds. Moreover, *Euphorbia* diterpenes possess a number of interesting biological activities, such as skin irritant and tumour-promoting activities (due to their protein kinase C-activating effects), and also antiproliferative, antiviral and multidrug resistance-reversing activities [30–33]. The *Euphorbia falcata* extract was previously tested for the first time, by El Bribri et al., as corrosion inhibitor on carbon steel in 1 M HCl using only the gravimetric method [34]. The effect of temperature on the corrosion rate was also investigated. Both kinetic and standard thermodynamic parameters were calculated and discussed in detail. In a continuation of this programme, the present paper reports the detailed study of the inhibition effect of *E. falcata* extract (EFE) on the corrosion behaviour of carbon steel in normal hydrochloridric solution (1 M HCl) at 30 °C using gravimetric, ac impedance and polarization methods. Treated and untreated metallic surface are examined using scanning electron microscopy (SEM). The corrosion inhibition mechanism is discussed based on the adsorption properties of EFE on carbon steel after acid immersion.

2. Experimental details

E. falcata L. extract (EFE) was prepared according to a previously described experimental procedure [34]. The aerial part of *E. falcata* was collected in June 2008 in the region of El Jadida (Morocco). A specimen has been deposited at the Herbarium of the Faculty of Science, El Jadida (Morocco). The dried plant material is stored in the laboratory at room temperature before extraction. The plant extract is prepared by refluxing aerial parts of *E. falcata*, in absolute methanol for 4 h, then filtered, and the solvent is evaporated in vacuo to give the *E. falcata* extract (EFE). The phytochemical study of *E. falcata* extract was previously described [35]. As given in Fig. 1, four diterpenes were isolated by E. Sulyok et al. from the *E. falcata* extract by a combination of different chromatographic methods [35]. The structure elucidation was already conducted, by E. Sulyok et al., using the spectroscopic analysis, including 1D and 2D NMR ($^1H-^1H$ COSY, HSQC and HMBC) and HRESIMS experiments. The stereochemistry was studied by means of NOESY measurements [35]. The concentration range of EFE used in the corrosion tests was 0.6–3.0 g L^{-1}.

The material used in this study is a carbon steel (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370% C, 0.230% Si, 0.680% Mn, 0.016% S, 0.077% Cr, 0.011% Ti, 0.059% Ni, 0.009% Co, 0.160% Cu and the remainder iron (Fe). The steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (120, 600 and 1200); rinsed with distilled water, degreased in acetone in an ultrasonic bath immersion for 5 min, washed again with bidistilled water and then dried at room temperature before use. The acid solutions (1 M HCl) were prepared by dilution of an analytical reagent grade 37% HCl with doubly distilled water.

The gravimetric measurements were carried out at the definite time interval of 6 h at room temperature (30 ± 1 °C) using an analytical balance (precision ± 0.1 mg). The steel specimens used have a rectangular form (length = 5 cm, width = 2 cm, thickness = 0.3 cm). Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser containing 250 ml of non-de-aerated test solution. After immersion period, the steel specimens were withdrawn, carefully rinsed with bidistilled water, ultrasonic cleaning in acetone, dried at room temperature and then weighed. Duplicate experiments were performed in each case and the mean value of the weight loss is calculated.

Ac impedance tests were performed in a polymethyl methacrylate (PMMA) cell with a capacity of 1000 ml at 30 ± 1 °C, using a thermostat. A saturated calomel electrode (SCE) was used as the reference; while a platinum leaf was used as a counter electrode. All potentials are reported vs. SCE. The working electrode was prepared from a square sheet of carbon steel such that the area exposed to solution was 7.55 cm^2. The impedance spectra were

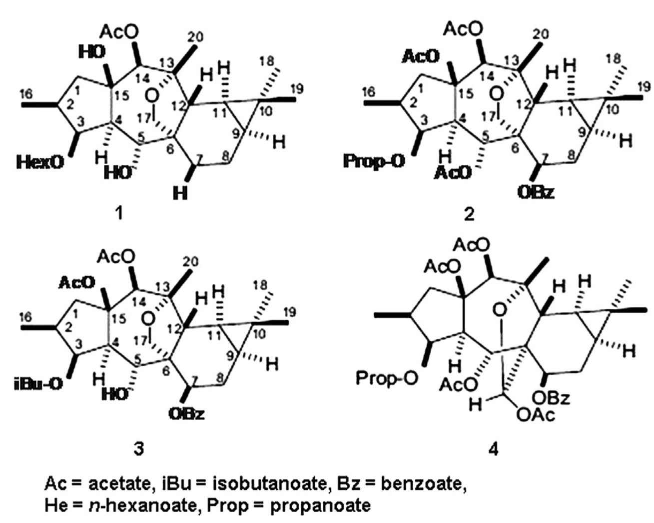


Fig. 1. Chemical structures of the four diterpenes, isolated from the *Euphorbia falcata* plant.