Journal of Molecular Liquids 255 (2018) 185–198

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Glycyrrhiza glabra leaves extract as a green corrosion inhibitor for mild steel in 1 M hydrochloric acid solution: Experimental, molecular dynamics, Monte Carlo and quantum mechanics study

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ARTICLE INFO

Article history:
Received 14 December 2017
Received in revised form 23 January 2018
Accepted 24 January 2018
Available online xxxx

Keywords:
Green corrosion inhibitor
Mild steel
Potentiodynamic polarization
EIS
AFM
Molecular dynamics
Monte Carlo
Quantum mechanics

ABSTRACT

The objective of this study is to investigate the inhibition of *Glycyrrhiza glabra* extract, commonly known as licorice, as a green source of corrosion inhibitor against mild steel corrosion in 1 M HCl solution. The extract of *Glycyrrhiza glabra* has been used for mild steel inhibition in 1 M HCl solution. By means of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) the corrosion inhibition performance and by atomic force microscopy (AFM) and contact angle test the surface characteristics were evaluated. The results of polarization test revealed that the *Glycyrrhiza glabra* leaves extract acted as mixed type inhibitor and retarded both anodic and cathodic reactions rates. Results revealed that by addition of *Glycyrrhiza glabra* leaves extract the corrosion current density of mild steel significantly decreased from 260 μA/cm^2 for the sample without inhibitor to 40.2 μA/cm^2 for the sample containing 800 ppm inhibitor. In addition, it was found that in the presence of *Glycyrrhiza glabra* leaves extract the hydrogen evolution mechanism did not change but the anodic dissolution mechanism of iron was affected in the presence of inhibitors. The EIS results showed that the increase of *Glycyrrhiza glabra* leaves extract concentration and immersion time resulted in the increase of corrosion inhibition efficiency. The maximum corrosion inhibition efficiency (about 88%) and surface coverage (about 72%) were obtained in the presence of 800 ppm *Glycyrrhiza glabra* leaves extract after 24 h immersion. Atomic force microscopy test results showed lower mild steel surface degradation in the HCl solution with 800 ppm *Glycyrrhiza glabra* leaves extract. Also, the decrease in surface hydrophilicity in the presence of *Glycyrrhiza glabra* leaves extract confirmed the adsorption of organic molecules of the inhibitors, such as Glycyrrhizin (GL), 18β-Glycyrrhetinic acid (GA), Liquiritigenin (LTG), Licochalcone A (LCA), Licochalcone E (LCE), and Glabridin (GLD), on the active sites of mild steel. In addition, the modeling studies based on classical molecular dynamics (MD), Monte Carlo (MC) and quantum mechanics (QM) techniques evidenced that all corrosion inhibiting materials exist in *Glycyrrhiza glabra* adsorbed to steel surface, and thereby form a corrosion-protective film over the steel surface.

1. Introduction

HCl based acidic solutions have been frequently used in various industries for chemical cleaning and pickling. However, the rapid corrosion of metals due to the aggressiveness of acidic solutions has become the main concern for industries [1–3]. Therefore, finding methods for controlling the rate of corrosion has become the topic of current research [4,5]. Among various methods the employment of organic inhibitors is one of the most effective methods for metals protection against corrosion. Although most of the synthetic corrosion inhibitors are highly efficient in acidic environments but they are expensive and provide health and ecological risks [6–16]. Therefore, due to the hazardous environmental effects of synthetic inhibitors the researchers' attention has been drawn towards finding cheaper and non-toxic inhibitors. In this regard, the highly effective environmental friendly corrosion inhibitors obtained from natural products such as, different parts of plants like root, seeds, leaves, stem, flower and fruits are recently attracted the high consideration of the researchers [17–25]. Most of the organic compounds existed in the extracts of natural products include many π bonds and heteroatoms like N, S and O with

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https://doi.org/10.1016/j.molliq.2018.01.144

high capability of electrostatic and/or covalent bonds formation with the atoms of metal surface. Different parameters including the chemical structure of the inhibitor and surface nature of metallic substrate. The inhibitors adsorption on the metal surface takes place through the interaction of the electron pair and/or the π-electron cloud of the donor atoms and the metal surface [20–24]. The corrosion inhibition effects of green corrosion inhibitors come from the adsorption of organic molecules on the metal surface and the capability of the heteroatoms for sharing lone pair of electrons with empty orbitals of metal cations like Fe^{2+} [13,24,26–29].

In our recent studies the corrosion inhibition effects of green corrosion inhibitors have been studied in acidic and chloride solutions. The effects of Aloe plant extract on the corrosion inhibition of stainless steel in 1 M H_2SO_4 were studied [30]. The effectiveness of the *Urtica dioica* leaves extract on the corrosion inhibition of mild steel in chloride solution has been previously studied. Results revealed that combination of *Urtica dioica* and zinc acetate resulted in the high corrosion inhibition efficiency [31]. The corrosion inhibition effect of *Cichorium intybus* L leaves extract in chloride solution on mild steel has been shown in our previous study [32]. Mourya et al. [33] reported the corrosion inhibition of mild steel in acidic solution by *Tagetes erecta* (TEE). They found that TEE acted as a mixed type inhibitor and the inhibitor molecules adsorption on the mild steel followed the Langmuir adsorption isotherm. The high inhibition efficiency of about 98% was obtained at maximum inhibitor concentration of 1 g/L. Ji et al. [34] revealed the effectiveness of Musa Paradisica Peel extract as green corrosion inhibitor for mild steel in HCl solution. They showed that the maximum corrosion inhibition of about 90% was obtained using 300 mg/L raw banana peel extracts and the minimum inhibition efficiency of 78% was obtained by using 300 mg/L ripe banana peel extract.

In this study the *Glycyrrhiza glabra*, commonly known as licorice, is used as a green source of corrosion inhibitors for mild steel inhibition from corrosion in acidic solution. For many years the *Glycyrrhiza glabra*, which is an herbaceous perennial, has been used in foods and medicinal remedies. Glycyrrhizin, glycyrrhetinic acid, flavonoids, isoflavonoids, and chalcones are some of the active components existed in the *Glycyrrhiza glabra* composition. Glycyrrhizin (GL), 18β-Glycyrrhetinic acid (GA), Liquritigenin (LTG), Licochalcone A (LCA), Licochalcone E (LCE), and Glabridin (GLD) have been considered as the main active components and potent inhibitors due to their steroid-like structures [5,35,36]. According to literature the *Glycyrrhiza glabra* has been used as candies or sweeteners in some European and Middle Eastern countries. The extract of *Glycyrrhiza glabra* has been also used in herbalism and traditional medicine. The United States Food and Drug Administration believes that *Glycyrrhiza glabra* and its derivatives are safe and nontoxic [37,38]. To the best of our knowledge the *Glycyrrhiza glabra* leaves extract against mild steel corrosion in 1 M HCl solution has not been studied previously.

2. Experimental

2.1. Raw materials and sample preparation

The composition (wt%) of mild steel samples used in this study was as follows: (93.9% Fe, 1.2% P, 1.1% Mn, 1.0% Si, 0.7% Cr and 1.7% Ni). *Glycyrrhiza glabra* leaves were bought from the local market. According to literature, Glycyrrhizin (GL), 18β-Glycyrrhetinic acid (GA), Liquritigenin (LTG), Licochalcone A (LCA), Licochalcone E (LCE), and Glabridin (GLD) are some of the most important ingredients of *Glycyrrhiza glabra* leaves extract [33,34]. The chemical structures of the mentioned compounds are shown in Fig. 1. Hydrochloric acid (37%) was purchased from Merck Co. The steel coupons with dimension of 5 cm × 3 cm × 0.2 cm were prepared from Foolad Mobarakeh Co. (Iran). Before the experiments the steel samples were abraded by SiC papers of 600, 800 and 1200 grits, degreased by acetone, washed with double distilled water and dried in air. The 1 M HCl solution was prepared by dilution of analytical grade HCl with distilled water. Then, the HCl solutions containing 200, 400, 600 and 800 ppm *Glycyrrhiza glabra* leaves extract were then prepared.

2.2. Characterization

2.2.1. Electrochemical measurements

Mild steel panels were dipped in 1 M HCl solutions without and with different concentrations of *Glycyrrhiza glabra* leaves extract. The corrosion inhibition properties of the inhibitors were studied by EIS and potentiodynamic polarization tests at room temperature (25 °C). The EIS measurements were conducted in a conventional three electrode cell including saturated calomel electrode (SCE), Platinum and mild steel as reference, counter and working electrodes, respectively. By an Ivium Compactstat model EIS instrument the EIS measurements were performed in the frequency range of 10 kHz to 10 mHz, peak to zero amplitude sinusoidal voltage of 10 mV at open circuit potential (OCP). The potentiodynamic polarization test was done in the potential range and scan rate of −250 to +250 mV versus OCP and 1 mV/s, respectively.

2.2.2. Surface characterization

The effects of HCl solution on the mild steel surface degradation and the influence of the inhibitors adsorption on the morphology surface morphology and chemistry were evaluated by AFM model Dualscope DS 95-200, DME, Denmark and static contact angle measuring system based on an OCA 15 plus type system.

3. Details of modeling studies

3.1. Quantum mechanics optimization of inhibitors

In order to get detailed electronic-level insights into the interactions and adhesion behavior of corrosion inhibitors the electronic-structure quantum mechanics (QM) calculations were applied. The molecular structures of some of the inhibiting agents exist in green *Glycyrrhiza glabra* corrosion inhibitors are demonstrated in Fig. 1. As our experiments were done in acidic pH conditions, within computational studies the protonated forms of these inhibiting materials were used. For inhibitors protonation, two protons (i.e., H^+) were covalently bonded to two oxygen atoms in hydroxyl or carbonyl functionalities of inhibitors, as shown in Fig. 1.

The molecular structures of these protonated species were subjected to geometry optimization to find their corresponding stabilized configurations. To this purpose, the inhibitors structures were initially equilibrated using Hartree-Fock theory together with 6-31G** basis function [39]. The HF-optimized geometries of inhibitors were then subjected to further optimization executed through density functional theory (DFT) [40,41] using hybrid B3LYP functional in connection with the same 6-31G** basis function, which was followed by a larger basis set based on 6-311G** [42–44], as successfully applied in our recent works [45,46]. All these HF and DFT based QM calculations were conducted in the presence of water solvent molecules, which was taken into consideration employing the theory of self-consistent reaction field (SCRF) based on Tomasi's PCM model [47]. These successive ab initio QM computations were carried out using Gaussian 09 package [48]. The inhibitor molecules with the minimum energy structures extracted from the last step of QM calculations (i.e., DFT/B3LYP/6-311G** level) were adopted for the analyses of electronic-structure properties of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO), eigenvalues or energies of these frontier orbitals (i.e., E_{HOMO}, E_{LUMO}), LUMO-HOMO energy gap (i.e., $E_{LUMO} - E_{HOMO} = \Delta E_{L\text{-}H}$) and partial charges distributed on the inhibitors atoms. To compute the partial atomic charges the electrostatic potential based method of ChelpG was utilized [49]. In addition, the chemical reactivity of chosen green inhibitors was evaluated in terms of the global molecular properties including electronegativity (χ), hardness (η), and