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Three novel bolaamphiphiles as corrosion inhibitors for carbon steel in hydrochloric acid: Experimental and computational studies

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ABSTRACT

Three novel bolaamphiphiles were synthesized and investigated as corrosion inhibitors for carbon steel in 1 M HCl using chemical and electrochemical techniques. The results revealed that the synthesized bolaamphiphiles have good inhibitive effect. The adsorption of bolaamphiphiles on the carbon steel surface in 1 M HCl was found to obey Langmuir isotherm. Polarization results showed that these inhibitors act as mixed-type inhibitors. The inhibition efficiency of the investigated bolaamphiphiles against the corrosion of carbon steel surface was studied by means of semi empirical molecular orbital AM1 calculations. The calculations showed a good correlation between the calculated quantum chemical parameters and the experimental data.

1. Introduction

The study of corrosion processes and their inhibitions is a very active field of research. Several classes of organic compounds are widely used for protection of metals from corrosion in acid environments [1–2]. Experimental means are useful in explaining the inhibition mechanism, but they are often expensive and time-consuming. Ongoing hardware and software advances have opened the door for powerful use of theoretical chemistry in corrosion inhibition research. So, several quantum chemical methods and molecular modeling techniques have been performed in order to correlate the inhibition efficiency with the molecular properties of compounds [3–5]. The use of theoretical parameters showed two main advantages: firstly; the compounds with various fragments and substituents could be directly characterized on the basis of their molecular structures only; and secondly; the proposed mechanism of interaction could be directly accounted for the chemical reactivity of the compounds [6]. However, little work appears to have been done on the inhibiting of carbon steel in acidic media using bolaamphiphiles. This generation of bolaamphiphiles shows very interesting properties. Chebabe et al. [7] reported that 1,*n*-bis(1,2,4-triazolyl)decane and 1,*n*-bis(1,2,4-triazolyl)dodecane were suitable corrosion inhibitors for carbon steel in 1 M HCl, and the inhibition efficiency values of the tested bolaamphiphiles were 83% and 93% at 25 °C, respectively. Some studies showed that the inhibition of the corrosion process is mainly described by the formation of donor–acceptor surface complexes between free or π-electrons of an organic inhibitor, mostly containing nitrogen, sulfur or oxygen atoms, and a vacant d-orbital of a metal [8–10]. Surfactants, which are important compounds in many fields, have been reported as corrosion inhibitors for steel [11].

The task of this paper is to correlate the quantum chemical parameters with the observed inhibition efficiency of the investigated novel three bolaamphiphiles as corrosion inhibitor and explain the mechanism of their adsorptions on metal surface. The calculated quantum chemical parameters correlated to the inhibition efficiency are, the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), the separation energy (ΔE), the dipole moment (D), the softness (σ), the total negative charge (TNC), the molecular volume (MV), chemical potential (μ) and electronegativity (χ).

2. Materials and experimental techniques

2.1. Synthesis of bolaamphiphiles

Three novel bolaamphiphiles in this study were synthesized via quaternization reaction [12], of one mol 4,4′-bis(chloromethyl)-1,1′-biphenyl with two moles of triethylamine, 2-(dimethylamino)ethanol and 2,2′,2″-nitrilotriethanolin ethanol at 70 °C for 24 h to produce *N*,*N*′-([1,1′-biphenyl]-4,4′-diylbis(methylene))bis(*N*,*N*-diethylethanaminium) chloride (compound I), *N*,*N*′-([1,1′-biphenyl]-4,4′-diylbis(methylene))

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bis(2-hydroxy-*N*,*N*-dimethylethanaminium) chloride (compound II) and *N*,*N*′-([1,1′-biphenyl]-4,4′-diylbis(methylene))bis(2-hydroxy-*N*,*N*-bis(2-hydroxyethyl)ethanaminium) chloride (compound III), respectively. The mixture was allowed to cool-down; the obtained product was further purified by diethyl ether and then recrystallized from ethanol [13].

Chemical structures of the synthesized inhibitors (Fig. 1) were confirmed by ^{1}HNMR and Mass spectroscopy in addition to elemental analysis.

2.2. Steel specimen

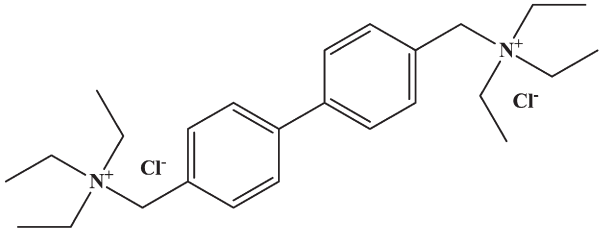
Tests were performed on a carbon steel of the following chemical composition (wt.%): 0.28 C, 0.06 Ti, 1.40 Mn, 0.03 P, 0.03 S and the remainder is Fe.

2.3. Weight loss measurements

The carbon steel pipeline sheets of 6 cm × 3 cm × 0.4 cm were abraded with a series of emery paper (grade 320–400–600–800–1000–1200),then cleaned successively with distilled water, ethanol, and acetone, and finally dried in a dry air. A&D analytical balance, (Model: HR 200, readability: 0.1 mg and standard deviation: ±0.2 mg), was used for the gravimetric analysis. After accurately weighting, the samples were immersed in 100 ml of 1 M HCl solution with and without the addition of different concentrations of the synthesized bolaamphiphiles at various temperatures. The temperature for weight loss measurements was controlled by a water bath provided with thermostat control ±0.5 °C. The carbon steel specimens were taken out after 24 h, then rinsed with distilled water twice and degreased with acetone. Finally, it was dried in a dry air and accurately weighted. The experiments were carried out in triplicates in order to give a good reproducibility and the average weight loss of three parallel carbon steel pipeline sheets was obtained. All tests in this paper were done under aerated conditions.

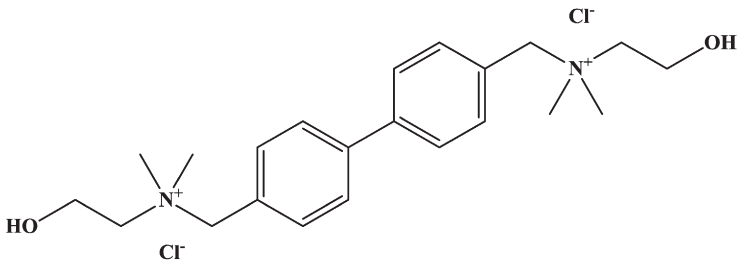
2.4. Electrochemical measurements

The electrochemical experiments were carried out in a conventional three-electrode cell with a platinum counter electrode (CE) and a



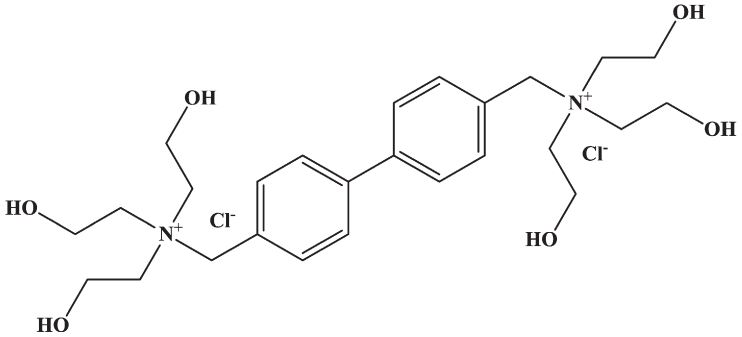
N,N'-([1,1'-biphenyl]-4,4'-diylbis(methylene))bis(N,N-diethylethanaminium) chloride

Compound (I)



N,N'-([1,1'-biphenyl]-4,4'-diylbis(methylene))bis(2-hydroxy-N,N-dimethylethanaminium) chloride

Compound (II)



***N*,*N*'-([1,1'-biphenyl]-4,4'-diylbis(methylene))bis(2-hydroxy-*N*,*N*-bis(2-hydroxyethyl)ethanaminium) chloride**

Compound (III)

Fig. 1. The chemical structure of the synthesized novel bolaamphiphiles.