

Quantum chemical investigation and statistical analysis of the relationship between corrosion inhibition efficiency and molecular structure of xanthene and its derivatives on mild steel in sulphuric acid

N.O. Obi-Egbedi^a, I.B. Obot^{b,*}, Mohammad I. El-Khaiary^c

^a Department of Chemistry, University of Ibadan, Ibadan, Nigeria

^b Department of Chemistry, Faculty of Science, University of Uyo, P.M.B 1017, Uyo, Akwa Ibom State, Nigeria

^c Chemical Engineering Department, Faculty of Engineering, Alexandria University, El-Hadara, Alexandria 21544, Egypt

ARTICLE INFO

Article history:

Received 31 December 2010

Received in revised form 1 July 2011

Accepted 2 July 2011

Available online 13 July 2011

Keywords:

Quantum chemistry

Statistical analysis

Mild steel

Corrosion inhibitors

Sulphuric acid

Density functional theory (DFT)

ABSTRACT

A density functional theory (DFT) study of xanthene (XEN) and two of its derivatives namely xanthone (XAN) and xanthione (XION) recently used as corrosion inhibitors for mild steel in 0.5 M H₂SO₄ was undertaken at the B3LYP/631G (d) level. Inhibition efficiency obtained experimentally followed the order: XEN < XAN < XION. It was found that when the organic molecules adsorbed on the steel surface, molecular structure influences their interaction mechanism and by extension their inhibition efficiencies. The quantum chemical properties/descriptors most relevant to their potential action as corrosion inhibitors have been calculated in the neutral and protonated forms in aqueous phase for comparison. They include: Total energy (TE), E_{HOMO} , E_{LUMO} , energy gap (ΔE), dipole moment (D), molecular area (MA), molecular volume (MV), hardness (η), softness (σ), the fractions of electrons transferred (ΔN), electrophilicity index (ω) and total energy change (ΔE_T). The quantum chemical parameters/descriptors were correlated with inhibition effect of the three inhibitors and were further used to explain the electron transfer mechanism between the inhibitors and the steel surface. Furthermore, equations were proposed using the non-linear and the multiple-linear regression analysis. The theoretical obtained results were found to be consistent with the experimental data reported.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

There has been a growing interest in the use of organic compounds as inhibitors for the aqueous corrosion of metals [1–4]. Organic compounds which can donate electrons to unoccupied d-orbitals of metal surface to form coordinate covalent bonds and can also accept free electrons from the metal surface by using their anti-bonding orbitals to form feedback bonds, constitute excellent corrosion inhibitors. Most of the efficient inhibitors are organic compounds which mainly contain oxygen, sulphur, nitrogen atoms and multiple bonds in the molecule through which they are adsorbed on metal surface. The effectiveness of the adsorption depends on the nature and surface charge of the metal, the corroding medium and the chemical structure of the inhibitor molecule such as functional groups, aromaticity, π -orbital character of the donating electron, steric factor, and electron density at the donor atoms [5].

Experimental means are useful to explain 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. Several quantum chemical methods and molecular modelling techniques have been performed to correlate the inhibition efficiency of the inhibitors with their molecular properties [6–15]. The reactive ability of the inhibitor is closely linked to their frontier molecular orbitals (MO), including highest occupied molecular orbital, HOMO, and lowest unoccupied molecular orbital, LUMO, and the other parameters such as hardness and softness. Density Functional Theory (DFT) has become an attractive theoretical method because it gives exact basic vital parameters for even huge complex molecules at low cost [16–18]. Furthermore, by using sophisticated computational tools, we can understand reactivity behaviour of hard and soft acid–base (HSAB) theory that provide a systematic way for the analysis of the inhibitor/surface interaction [19]. Thus, the DFT has become a main source of connecting some traditional empirical concepts with quantum mechanics. Therefore, DFT is a very powerful technique to probe the inhibitor/surface interaction and to analyze experimental data.

Xanthene and its derivatives are an important class of compound present in many chemical structures of great interest in a variety of biochemical and industrial field. They form structural elements of important classes of pharmaceutical drugs [20]. Recently, we have found out experimentally that xanthene (XEN)

* Corresponding author. Tel.: +234 8067476065.

E-mail address: proffoime@yahoo.com (I.B. Obot).

and its derivatives namely xanthone (XAN) and xanthione (XION) are excellent corrosion inhibitors for mild steel in 0.5 M H₂SO₄ [21–23]. However, the relationships between the structural parameters and corrosion inhibition of these compounds have not been studied yet. This present paper is designed to correlate the observed inhibition efficiency with the quantum chemical parameters of the investigated inhibitors (Fig. 1). The calculations of global reactivity indices of the inhibitors such as the localization of frontier molecular orbitals, E_{HOMO} , E_{LUMO} , energy gap (ΔE), dipole moment (D), hardness (η), softness (σ), the fractions of electrons transferred (ΔN), electrophilicity index (ω), and total energy change (ΔE_T) were used to explain the electron transfer mechanism between the inhibitor molecules and the steel surface. Furthermore, equations were proposed using the non-linear and the multiple-linear regression analysis. The molecular structures of xanthone and its derivatives used in this study are given in Fig. 1.

2. Materials and methods

2.1. Material

Test were performed on a freshly prepared sheet of mild steel of the following composition (wt.%): 0.13% C, 0.18% Si, 0.39% Mn, 0.40% P, 0.04% S, 0.025% Cu, and bal Fe. The metal specimens were prepared, degreased and cleaned as previously described [21].

2.2. Inhibitors

Xanthone (XEN), Xanthone (XAN) and Xanthione (XION) were purchased from SIGMA–ALDRICH and used as inhibitor. Stock solution was made in 10:1 water: methanol mixture to ensure

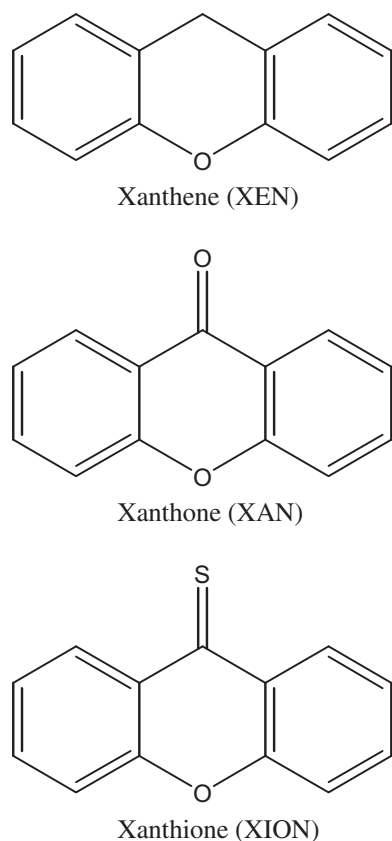


Fig. 1. Names, molecular structures and the abbreviations of the inhibitors investigated.

solubility [21–23]. This stock solution was used for all experimental purposes.

2.3. Solutions

The aggressive solutions, 0.5 M H₂SO₄ were prepared by dilution of analytical grade 98% H₂SO₄ with distilled water. The concentration range of the inhibitors prepared and used were in the range 2×10^{-6} – 10×10^{-6} M.

2.4. Gravimetric measurements

The gravimetric method (weight loss) is probably the most widely used method of inhibition assessment [2]. The simplicity and reliability of the measurement offered by the weight loss method is such that the technique forms the baseline method of measurement in many corrosion monitoring programmes [23]. Weight loss measurements were conducted under total immersion using 250 mL capacity beakers containing 200 mL test solution at 303–333 K maintained in a thermostated water bath. The mild steel coupons were weighed and suspended in the beaker with the help of rod and hook. The coupons were retrieved at 2 h interval progressively for 10 h, washed thoroughly in 20% NaOH solution containing 200 g/L of zinc dust [4] with bristle brush, rinsed severally in deionized water, cleaned, dried in acetone, and reweighed. The weight loss, in grammes, was taken as the difference in the weight of the mild steel coupons before and after immersion in different test solutions. Then the tests were repeated at different temperatures. In order to get good reproducibility, experiments were carried out in triplicate. In this present study, the standard deviation values among parallel triplicate experiments were found to be smaller than 5%, indicating good reproducibility.

The corrosion rate (ρ) in $\text{g cm}^{-2} \text{h}^{-1}$ was calculated from the following equation [22]:

$$\rho = \frac{\Delta W}{St} \quad (1)$$

where W is the average weight loss of three mild steel sheets, S the total area of one mild steel specimen, and t is the immersion time (10 h). With the calculated corrosion rate, the inhibition efficiency (%) was calculated as follows [3]:

$$\%I = \left(\frac{\rho_1 - \rho_2}{\rho_1} \right) \times 100 \quad (2)$$

where ρ_1 and ρ_2 are the corrosion rates of the mild steel coupons in the absence and presence of inhibitors, respectively.

2.5. Computational details

B3LYP, a version of the DFT method that uses Becke's three parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang and Parr (LYP) [24], was used in this paper to carry out quantum calculations. Then, full geometry optimization together with the vibrational analysis of the optimized structures of the inhibitor was carried out at the B3LYP/6-31G (d) level of theory using Spartan'06 V112 program package [25] in order to determine whether they correspond to a minimum in the potential energy curve. The quantum chemical parameters were calculated for molecules in neutral as well as in the protonated form for comparison. It is well known that the phenomenon of electrochemical corrosion occurs in liquid phase. As a result, it was necessary to include the effect of a solvent in the computational calculations. In the Spartan'06 V112 program, SCRF methods (self-consistent reaction field) were used to perform calculations in aqueous solution.

Download English Version:

<https://daneshyari.com/en/article/1410294>

Download Persian Version:

<https://daneshyari.com/article/1410294>

[Daneshyari.com](https://daneshyari.com)