



Contents lists available at ScienceDirect

Corrosion Science

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

An experimental and theoretical approach towards understanding the inhibitive behavior of a nitrile substituted coumarin compound as an effective acidic media inhibitor

Alper Fitoz, Hasan Nazır, Mehtap Özgür (nee Yakut), Emel Emregül, Kaan C. Emregül*

Ankara University, Science Faculty, Department of Chemistry, 06100 Tandoğan, Ankara, Turkey

ARTICLE INFO

Keywords:

Coumarin

Nitrile compound

Corrosion inhibition

EIS

DFT

ABSTRACT

The inhibiting ability of 2H-chromen-2-one (Ch) or coumarin and its corresponding nitrile substituted compound 2-Oxo-2H-chromen-3-carbonitrile (ChCN), has been studied using electrochemical techniques, SEM and theoretical calculation methods. The Langmuir adsorption isotherm model best described the adsorption characteristics of the compounds under study. Scanning electron microscopy studies revealed the formation of a protective inhibitor layer on the mild steel surface. Quantum chemical parameters obtained using the density functional theory (DFT) supported the experimental results. Substitution of a –CN group was seen to increase the inhibitor efficiency up to 98%.

1. Introduction

Industrial systems like oil pipelines, gas distribution networks, boilers, are very important in this field where steel is the main material used for construction. Mild steel is widely used in various chemical industries due to its low cost, good mechanical properties and easy availability for fabrication of vessels. But unfortunately low resistance to corrosion is its main problem. Therefore, protection of this metal against corrosion is essential [1,2]. The use of corrosion inhibitors is one of the best options for preventing corrosion failures of metals in a readily built system. It is a simple and low-cost routine method in a great number of industrial fields, and in many applications has no real alternatives. A large number of organic compounds have been studied and analyzed to investigate their potential as corrosion inhibitors, revealing almost all organic molecules containing heteroatoms such as nitrogen, sulphur, phosphorus and oxygen to show significant inhibition efficiencies; some examples are aliphatic or aromatic thiourea, pyrazole, pyrimidine, amine, benzylidene, carbazone, azole, Schiff base, benzo nitrile and some coumarin compounds [3–32]. The inhibitor efficiency of these molecules depends mainly on their ability to adhere onto the metal surfaces by displacing water molecules leading to the formation of a protective surface layer [33–36]. Studies have shown that solutions containing chloride ions play an important role, due to chloride ion adsorption [37]. In industrial applications, HCl (aq) is one of the most frequently used acids for degreasing, descaling, pickling, etc. [2]. Therefore, the protection efficiency of inhibitors in acidic

media is quite important. Most organic substances used as corrosion inhibitors act through adsorption on the metal surface due to the presence of π -electrons and heteroatoms, which tend to increase the adsorption of inhibitor molecules.

Coumarin (2H-chromen-2-one) is a fragrant organic chemical compound in the benzopyrone chemical class, found in many plants; (*Dipteryx odorata*), vanilla grass (*Anthoxanthum odoratum*), sweet woodruff (*Galium odoratum*), mullein (*Verbascum* spp.), sweet grass (*Hierochloa odorata*), cassia cinnamon (*Cinnamomum cassia*) not to be confused with, sweet-clover (*Melilotus* spp.), deertongue (*Dichanthelium clandestinum*), and the leaves of many cherry blossom tree varieties (of the *Prunus* genus). Coumarin is also found naturally in many edible plants such as strawberries, black currants, apricots, and cherries [38,39]. It being an oxygen-containing heterocyclic compound with diverse biological activity, as an anticoagulant and antithrombotic that are of both natural and synthetic origin, has led to its use in many areas ranging from medical applications to the food industry [40,41].

Theoretical calculations are a very powerful tool for determining the mechanism and finding a correlation between molecular structure and inhibition efficiency in addition to validation of the experimental results [42–48]. A review published by Obot et al. (2015) summarizes the importance and relevance of theoretical applications in correlation with experimental corrosion studies [44]. In accordance, it is important to compute certain parameters, such as the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the fraction of electrons transferred (ΔN)

* Corresponding author.

E-mail address: kcemregul@yahoo.com (K.C. Emregül).

<http://dx.doi.org/10.1016/j.corsci.2017.10.004>

Received 25 April 2017; Received in revised form 10 October 2017; Accepted 13 October 2017
0010-938X/ © 2017 Elsevier Ltd. All rights reserved.



2H-chromen-2-one (Ch) 2-Oxo-2H-chromen-3-carbonitrile (ChCN)

Fig. 1. The chemical structure of 2H-chromen-2-one (Ch) and 2-Oxo-2H-chromen-3-carbonitrile (ChCN).

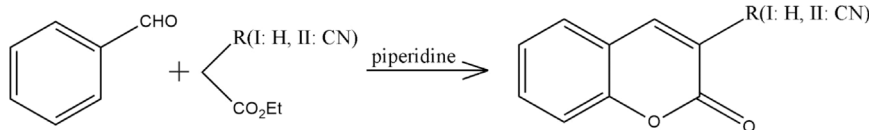
and the energies of the frontier molecular orbitals. In the present study, density functional theory (DFT) was used in determining the molecular structure of Ch and ChCN as a corrosion inhibitor in addition to validating and correlating experimental results.

The present study aims at showing the effect of structural nitrile substitution on the inhibition behavior of coumarin (Ch) in 2 M HCl using both experimental (weight loss, polarization and impedance techniques) and theoretical calculation methods. Best to our knowledge there are no studies dealing directly with compound ChCN. Fig. 1 shows the chemical structure of the inhibitor compounds used in this study.

2. Experimental

2.1. Synthesis and materials

Chromen-2-one (Ch) was used directly as the reference compound and 2-Oxo-2H-chromene-3-carbonitrile (ChCN) was synthesized according to the following scheme.



Salicylaldehyde (12.2 g, 100 mmol), the carbonyl compound (ethyl cyanoacetate, 12.44 g) and piperidine (0.2 g, 2.4 mmol) were boiled at 100 °C for 20 min in ethanol that was later removed using a rotary evaporator. After removal of ethanol, 10 ml of ethanol was again added to the remainder and left to crystallize.

Salicylaldehyde, ethyl cyanoacetate, piperidine, ethanol and coumarin (Chromen-2-one) as reference, were obtained from Aldrich and used without further purification.

Melting points were determined with a Gallenkamp apparatus without correction. The elemental analyzer was a LECO CHNS-932 instrument. IR spectra were obtained on a Mattson-1000 FTIR spectrometer using KBr pellets in the range 4000–400 cm⁻¹. Band locations were found by means of a microprocessor. ¹H NMR spectra were obtained in deuterated dimethyl sulphoxide (DMSO-*d*₆) or CDCl₃ solvent on a Bruker DPX 400 FT-NMR spectrometer with TMS as internal standard. All results are given below.

2-Oxo- 2H-chromene-3-carbonitrile (ChCN): Red-brown, water-soluble. Yield, 14.55 g (85%); m.p. 184–188 °C.

¹H NMR (DMSO-*d*₆) δ (ppm): 8.88 (s, 1H), 7.97–7.69 (m, 2H), 7.52–7.40 (m, 2H).

IR (neat, cm⁻¹): 2210 (C≡N), 1722 (lactone C=O).

C₁₀H₅NO₂ (171.16 g/mol) Calc.: C, 70.18; H, 2.94; N, 8.18; Found: C, 70.12; H, 2.88; N, 8.25%.

Mild steel specimens with the following composition (wt%) C < 0.2%; Mn 1.32%; P 0.03%; S 0.02%; Fe balance, were machined into cylindrical bars and embedded in polyester leaving a working area of 0.2 cm² in contact with the test solution. Prior to all measurements, surface pre-treatment was carried out by grinding the electrode surface using 1200 and 1000 grade abrasive paper, washing in acetone and finally ultrasonic cleaning in ethanol.

2 M HCl was prepared from analytical grade 37% HCl. The

concentration of both 2H-chromen-2-one (Ch) and its corresponding nitrile substituted compound, 2-Oxo-2H-chromen-3-carbonitrile (ChCN), were within a range of 10⁻² M to 10⁻⁵ M. All tests were performed in aerated and still solutions at 303 K.

2.2. Weight loss measurements

Weight loss measurements were carried out in glass vessels containing 50 mL 2 M HCl in the presence and absence of various concentrations of Ch and ChCN at 303 K for a 12-h immersion period. The specimens were taken out, rinsed in double distilled water, washed in ethanol, blow dried with nitrogen and weighed. Each experiment was performed at least three times to ensure reliability. Average values of the weight loss data were used in corresponding calculations.

Inhibition efficiencies ($\eta_{WL}\%$), were calculated using the relation

$$\eta_{WL}\% = \frac{w_0 - w_i}{w_0} \times 100 \quad (1)$$

where w_0 and w_i are the values of weight in uninhibited and inhibited solutions, respectively.

2.3. Electrochemical measurements

Electrochemical measurements were conducted in a 100 ml three electrode Pyrex cell placed in a constant temperature bath. Platinum foil and a saturated calomel electrode (SCE) was used as a counter and

reference electrode, respectively. All potentials within the text are referred to the SCE. Electrochemical experiments were performed on a Volta lab PGZ 301 Instrument with a Volta master 4.0 software package for experimental and data fitting applications. Tafel curves were obtained by changing the electrode potential automatically from –250 to +250 mV versus the open circuit potential (E_{ocp}) at a scan rate of 1 mVs⁻¹.

Surface coverage ratio (θ) and inhibition efficiency values ($\eta_{Pol}\%$) were calculated from the following equations:

$$\theta = \frac{i_{corr} - i'_{corr}}{i_{corr}} \quad (2)$$

$$\eta_{Pol}\% = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100 \quad (3)$$

where i_{corr} and i'_{corr} are the values of the corrosion current density of uninhibited and inhibited solutions, respectively.

Polarization resistance measurements were carried out by recording the electrode potential in the proximity (± 10 mV) of E_{ocp} at a scan rate of 0.1 mV⁻¹ using the linear sweep voltammetry technique. Before each experiment, the working electrode was immersed in the test solution for 30 min until it reached a steady state value. The measurements were repeated at least three times and the average values have been presented. The polarization resistance, R_p , values were used to calculate the inhibition efficiencies, ($\mu_{Rp}\%$), using the relation

$$\eta_{Rp}\% = \frac{R_{pi} - R_{po}}{R_{pi}} \times 100 \quad (4)$$

where R_{pi} and R_{po} are the polarization resistance values in the presence and absence of the organic additives respectively.

Electrochemical impedance spectroscopy (EIS) is a frequently applied technique in corrosion studies. EIS measurements were carried

Download English Version:

<https://daneshyari.com/en/article/7894009>

Download Persian Version:

<https://daneshyari.com/article/7894009>

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