Journal of Molecular Liquids xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

A newly synthesized sulphated 8-hydroxyquinoline derivative to effectively control aluminum corrosion in perchloric acid: Electrochemical and positron annihilation studies

Mohamed Ramadan El Sayed Aly [a,b,*], H. Shokry [c], T. Sharshar [d,e], Mohammed A. Amin [a,f,*]

[a] Department of Chemistry, Faculty of Science, Taif University, 888 Hawiya, Saudi Arabia
[b] Chemistry Department, Faculty of Applied Science, Port Said University, 42522 Port Said, Egypt
[c] Chemistry Department, Faculty of Science, Kafrelsheikh University, Kafr El-Sheikh 33516, Egypt
[d] Physics Department, Faculty of Science, Taif University, P.O. Box 888, Al-Hawiah, Taif 21974, Saudi Arabia
[e] Physics Department, Faculty of Science, Kafrelsheikh University, Kafr El-Sheikh 33516, Egypt
[f] Department of Chemistry, Faculty of Science, Ain Shams University, 11566 Abbassia, Cairo, Egypt

ARTICLE INFO

Article history:
Received 29 July 2015
Received in revised form 27 November 2015
Accepted 28 November 2015
Available online xxxx

Keywords:
Aluminum
Corrosion inhibition
8-Hydroxyquinoline derivatives
Tafel extrapolation method
Linear polarization resistance
Positron annihilation spectroscopy

ABSTRACT

The corrosion of aluminum in 1.0 M $HClO_4$ was effectively controlled by a newly synthesized sulphated 8-hydroxy-quinoline derivative (8HQD), namely 2-(2-(quinolin-8-yloxy)acetamido)ethyl hydrogen sulfate. Rates of corrosion were monitored as a function of C_{8HQD} (C_{8HQD}: 10^{-4}–10^{-2} M) using Tafel extrapolation method and linear polarization resistance (LPR) measurements. The electron density and corrosion-related defects in corroded and inhibited Al samples were probed using the positron annihilation lifetime (PAL) and positron annihilation Doppler broadening (PADB) techniques. Results were compared with 8-hydroxyquinoline (8HQ) itself. Polarization studies indicated that 8HQD acted as a mixed-type inhibitor with anodic predominance. PAS measurements demonstrated that the PAL components (τ_i) and their corresponding intensities (I_i) as well as PADB line-shape parameters (S and W) can be used to assess the inhibition performance of the tested materials. Results obtained from the different corrosion evaluation techniques were in good agreement and went parallel with those of PAS measurements. 8HQD was much better than 8HQ in inhibiting Al corrosion in these solutions.

1. Introduction

Aluminum is one of the world's most commonly used metals. It has low density, attractive appearance, good corrosion resistance, and excellent thermal and electrical conductivity. The combination of these properties and characteristics makes it a preferred choice for many industrial applications such as automobiles, food handling, containers, electronic devices, building, and aviation [1–4]. Metallic aluminum (Al) is a very active metal; a strong reducing agent with a standard reduction potential $E^{\circ}_{Al^{3+}/Al} = -1.662$ V, and is prone to corrosion [1]. However, it resists corrosion due to passivation and subsequent formation of a stable, substantially inert oxide film. The oxide film can form instantly on Al surface when exposed to air and/or water. This passive film creates a physical barrier to corrosion and protects the substrate metal. This film is stable in aqueous media of pH values within the range 4.0–8.5, but dissolves substantially when the metal is exposed to highly acidic or alkaline environment [1]. As such, corrosion of aluminum has been a subject of numerous studies due to its importance in the recent civilization. Many researchers have devoted their work to study the corrosion of aluminum and aluminum alloys in different aqueous solutions [5–14], and also the research into their electrochemical behavior and corrosion control in a wide variety of aqueous solutions [15–25].

The use of inhibitors is one of the best known methods for corrosion protection, as no special equipments required, low cost, and easy operation. Corrosion inhibitors efficiently reduce the undesirable destructive effect due to corrosion and prevent metal dissolution. Therefore, the use of inhibitors to control the corrosion of metals and alloys which are in contact with aggressive environments is essential. Many organic compounds were investigated and well documented as efficient corrosion inhibitors. Most of them act by being adsorbed on the metal surface [26–28] forming a protective layer that isolates the metal from the corrosive medium [29–31]. The adsorption of inhibitors takes place through heteroatoms such as nitrogen, oxygen, phosphorus and sulfur, and conjugated systems. Unfortunately, most of these compounds are not only expensive but also toxic to the environment. Therefore, eco-friendly inhibitors are of great demand.

* Corresponding authors at: Department of Chemistry, Faculty of Science, Taif University, 888 Hawiya, Saudi Arabia.
E-mail addresses: mrea34@hotmail.com (M.R. El Sayed Aly), maaismail@yahoo.com (M.A. Amin).

http://dx.doi.org/10.1016/j.molliq.2015.11.056
0167-7322/

Positron annihilation spectroscopy (PAS) is widely used to study the structure changes and to probe the defects in a wide variety of materials [32,33]. Some studies were carried out to investigate corrosion of metals and alloys using PAS techniques [34–39]. The injected positron in solids is thermalized and diffused to a depth of a few hundred μm. This thermalized positron can annihilate as free particle or can form a positronium atom (Ps) with two bound states of an electron and a positron; a singlet state (*para*-Ps, *p*-Ps) and a triplet state (*ortho*-Ps, *o*-Ps). For positron annihilation lifetime (PAL) technique, the free positron or Ps will annihilate with an electron and will have a corresponding lifetime (τ) with a corresponding intensity (I) for each state at the annihilation site. In PAL technique, the measured parameters (τ_i and I_i) of the positron and Ps lifetimes in metals depend on their electronic and defect structures. In positron annihilation Doppler broadening (PADB) technique, the motion of the electron–positron pair causes a Doppler shift on the energy of the annihilation radiation. As a consequence, the line–shape of annihilation γ ray, S (for shape), and W (for wings), gives the distribution of the longitudinal momentum component of the annihilating pair. Since the positrons are thermalized, the Doppler broadening measurements provide information about the momentum distributions of electrons at the annihilation site.

8-Hydroxyquinoline (8HQ), one of the most popular and versatile organic compound, is an organic crystalline material that made up of two rings: a phenol ring fused with pyridine ring. 8HQ and its derivatives have found a great variety of applications ranging from pharmacological and pharmaceutical agents to electron carriers in organic light-emitting diodes (OLEDs) and fluorescent chemosensors for metal ions [40]. In medicinal field, 8HQ and its derivatives can be used as insecticides, antibacterial, fungicidal, neuroprotective, and anti-HIV agents. Also, 8HQ is of interest as an anti-cancer drug [41–43]. The applications of 8HQ and its derivatives are extended to corrosion research studies. For instance, they were successfully reported as safe-corrosion inhibitors for aluminum and aluminum alloys in a wide variety of aqueous solutions [44–49]. Recently, many researchers have also developed other organic molecules as well as other quinoline derivatives apart from 8-hydroxyquinoline as potential corrosion inhibitors for aluminum and steel [50–57].

The synthesis of a new 8HQ derivative with outstanding corrosion inhibition characteristics would be of great interest. In the present work, a new 8HQ derivative (8HQD), namely 2-(2-(quinolin-8-yloxy)acetamido)ethyl hydrogen sulfate is synthesized in our laboratory to effectively inhibit the corrosion of Al in $HClO_4$ solutions. Measurements were carried out employing various electrochemical methods, complemented with SEM/EDX, PAL and PADB studies to investigate the corrosion-inhibition characteristics of 8HQD. As a reference point, the inhibition characteristics of 8HQ itself was also studied.

2. Experimental

2.1. Electrodes and materials

The working electrode employed in this work was made of Al wire (SIGMA-ALDRICH, 1.0 mm diam., 99.999%, 266558-10.5G, 01311LB, CAS 7429-90-5; FW 26.98; MW05152). For electrochemical measurements, the pure Al wire was mounted into Teflon leaving a constant surface area of 0.00785 cm^2 to contact the solution. Al sheets (rectangular coupons measuring 1 cm × 2 cm) of 0.1 mm thickness of the same purity were used for surface analysis and positron annihilation studies. Prior to each experiment, the specimens (the coupons and wire electrode) were mechanically abraded with a series of emery papers up to 1200 grade. Then, it was rinsed in acetone and double-distilled water before immersion in the experimental solution. All chemicals used in the present work were purchased from Aldrich and used as received, and their solutions were freshly prepared using water purified by a Millipore Milli-Q system.

Melting points were determined on electrothermal apparatus and are uncorrected. TLC monitoring tests were carried out using plastic sheets precoated with silica gel 60 F_{245} (layer thickness 0.2 mm) purchased from Merck. Spots were visualized by their fluorescence under UV-lamp (λ 245 and 366 nm) or staining with iodine vapor. NMR spectra were recorded on Bruker 600 MHz spectrometer, Central Laboratory, King Abd El Aziz University, Jeddah, Saudi Arabia. IR-spectra were recorded on ATR-Alpha FT-IR spectrophotometer 400–4000 cm^{-1} at Taif University, Taif, Faculty of Science, Saudi Arabia. Mass spectra were recorded on GCMS-QP 1000Ex Shimadzu spectrometers in the Microanalysis Unit at Cairo University. Elemental analysis was recorded on Flash 2000 Elemental Analyzer from Thermo scientific at Suez Canal University, Faculty of Science, Ismailia, Egypt.

2.2. Synthesis of the new sulphated 8-hydroxyquinoline derivative

The new 8HQ derivative **4** was synthesized according to the procedure described in (Scheme 1).

Compound **2** was obtained by treatment of 8-hydroxyquinoline **1** with ethyl chloroacetate in refluxing acetone containing K_2CO_3. CaO was added to modify the reaction time and reduce it into just 4 h instead of being stirred overnight. Nucleophilic substitution of compound **2** with ethanolamine in refluxing MeOH afforded alcohol **3** in good yield. ^{1}H NMR showed the essential signals of the N–H and O–H protons at δ 8.91 and 4.79 ppm, respectively. The N–H proton was more deshielded than the O–H proton due to its acidity arising from being an amide. The C═O signal, ^{13}C NMR, was observed at δ 167.93 ppm. Treatment of alcohol **3** with SO_3–Pyr complex in DCM/THF containing Et_3N afforded sulfate **4** with very high yield. The IR spectrum of compound **4** (Fig. 1) showed separate signals for the O–H and N–H stretching vibrations at 3394 and 3267 cm^{-1}, respectively. *Amide I* and *Amide II* were also observed at 1668 and 1568 cm^{-1}, respectively. The ^{1}H NMR spectrum of compound **4** (Fig. 2) retained the N–H signal at δ 9.18 ppm, while the C═O signal, ^{13}C NMR (Fig. 3), was observed at δ 166.64 ppm for compound **4**. However, the O–H signal wasn't observed, presumably was too broad to be observed. Also, in the ^{1}H NMR spectrum of compound **4**, the three methylene groups were observed as separate signals with expected multiplicities and chemical shift values. Thus, the CO–CH_2–O protons were observed as singlet at δ 4.91 ppm. They were more deshielded than the protons arising from the ethanolamine moiety at δ 3.88 ppm for the SO–CH_2 and δ 3.38 ppm for the NCH_2. These two methylenes were observed as triplets.

All compounds showed mass peaks corresponding to their exact masses, for instance, the target sulfate **4** (Fig. 4) showed a molecular ion peak at m/z 326.15 and elemental analyses were in accordance with their empirical formulas.

2.2.1. N-(2-Hydroxyethyl)-2-(quinolin-8-yloxy)acetamide (**3**)

A mixture of compound **2** (0.5 g, 2.16 mmol), ethanolamine (0.15 ml, 2.4 mmol) in dry MeOH was heated under reflux for 4 h then it was allowed to crystallize out. The colorless needles were filtered at the pump, washed with little cold MeOH and dried well affording **3** (0.35 g, 66%). Mp 160–2 °C; R_f 0.16 (acetone-petroleum ether, 2:1); ^{1}H NMR (200 MHz, DMSO-d_6): δ 8.91 (dd, 1 H, J 1.3, 3.3 Hz, NH), 8.37 (dd, 2H, J 1.3, 6.7 Hz, H-2_{quin}), 7.63–7.50 (m, 3H, Ar), 7.25 (dd, 1H, J 1.1, 6.0 Hz, Ar), 4.79 (t, 1H, J 4.3, 8.6 Hz, OH), 4.74 (s, 2H, $-CH_2CO-$), 3.1–3.38 (m, 2H, $-CH_2OH$), 3.31–3.21 (m, 2H, $-CH_2N-$); ^{13}C NMR (150 MHz, DMSO-d_6): δ 167.93 (C═O), 153.87 (C_{hyp}), 149.41 (C–H_{Ar}), 139.87 (C_{hyp}), 136.07 (C–H_{Ar}), 129.13 (C_{hyp}), 126.81 (C–H_{Ar}), 122.04, 121.11, 112.16 (3 C–H_{Ar}), 69.18 ($-CH_2CO-$), 59.68 ($-CH_2OH$), 41.20 ($-CH_2N-$); EI-MS (m/z, %): 247 (M + 1, 13), 246 (M, 4), 245 (6), 239 (7), 225 (3), 216 (15); anal. calcd. For $C_{13}H_{14}N_2O_3$ (246.26): C 63.39, H 5.74, N 11.37. Found: C 62.79, H 5.44, N 12.13.

Please cite this article as: M.R. El Sayed Aly, et al., A newly synthesized sulphated 8-hydroxyquinoline derivative to effectively control aluminum corrosion in perchloric acid: Electroc..., J. Mol. Liq. (2015), http://dx.doi.org/10.1016/j.molliq.2015.11.056