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Screening the anti-corrosion effect of a hybrid pigment based on zinc acetyl acetonate on the corrosion protection performance of an epoxy-ester polymeric coating

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ABSTRACT

In this study an epoxy-ester coating was filled with zinc acetyl acetonate (ZnAA). The active corrosion inhibition properties of the ZnAA pigment were studied by electrochemical noise (EN), electrochemical impedance spectroscopy (EIS) and polarization techniques. Also, the surface morphology and composition of the steel panels were examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The electrochemical measurements revealed the effective corrosion inhibition properties of the ZnAA pigment in the solution phase. Polarization test results revealed that in the presence of ZnAA both cathodic and anodic current densities decreased. In fact, the Zn²⁺ cations and acetyl acetonate anions formed inhibitive films based on Fe²⁺-acetyl acetonate and zinc oxide/hydroxide complexes on the anodic and cathodic regions. Results of theoretical ab initio quantum mechanics and molecular dynamics simulations evidenced that the inhibitors strongly adsorbed to iron surface through donor-acceptor interactions. The EIS results showed that the epoxy-ester coating protection performance was significantly enhanced by addition of ZnAA hybrid pigment. The ZnAA pigment enhanced the barrier performance of the coating and provided active inhibition properties.

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1. Introduction

Carbon steel has been widely used in different industries owing good mechanical property. However, its performance can be negatively influenced by corrosion attack in exposure with corrosive environments. Different methods have been utilized for protecting the metals from corrosion, among them organic coatings have been used as an effective method for corrosion protection of metals [1–7]. The main protection function of a polymeric coating is barrier against diffusion of corrosive agents. However, by the time the corrosive electrolyte penetrates into the coating matrix through porosities or defects and reaches the coating/metal interface. Not only the coating structure but also the coating/metal interfacial adhesion bonds can be deteriorated, leading to significant decrease in the coating barrier and protection performance [8,9].

Attempts have been done to provide organic coatings with longer service life and higher corrosion resistance through addition of various additives, fillers, pigments [10–13], nanoparticles [14–

18] and corrosion inhibitors [19–21]. There are three mechanisms of corrosion inhibition including inhibitive, barrier and sacrificial [22–26].

There are well-known anticorrosion pigments with high active inhibitive properties that can be added to the coatings for enhancement of corrosion resistance. Chromates are the most important and popular kinds of inhibitive pigments which have slight solubility in water, releasing inhibitive agents in the electrolyte and forming protective film on the active anodic and cathodic sites [27,28]. Nowadays, despite excellent inhibitive performance of this kind of pigment, its application has been strongly limited due to the carcinogenic and toxic properties of the hexavalent chromium ion [29]. Consequently, attempts have been done to find other non-toxic alternatives [30–33]. Zinc phosphates have been introduced as less toxic replacements for chromates [34,35]. Due to the poor solubility and inhibitive properties of the first generation of these pigments, a number of modifications including anionic, cationic or both, are performed on this pigment, which resulted in the formation of second and third generations of zinc phosphate *i.e.*, molybdenum zinc phosphate [36], aluminum zinc phosphate [37,38], potassium zinc phosphate [23,39], aluminum zinc polyphosphate [40], zinc pyrophosphate [41,42] and zinc triphosphosphate [41,43].

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The second and third generations show much greater water solubility and form better film on the metal surface than the conventional zinc phosphate pigment. Apart from the advantages of modification or replacement of the cationic and/or anionic parts of the pigment, loading most of the zinc phosphates into the organic coatings could not provide proper corrosion protection properties for long times. Researchers are in favor of this theory that combination of zinc phosphates with organic compound (organic-inorganic hybrid pigment) can be presented as a fourth generation with proper inhibitive performances [32,44]. In other words, a hybrid pigment can be obtained which does not have the problem of the most zinc phosphates into the organic coatings.

Therefore, in this study, the inhibition performance of zinc acetyl acetate (ZnAA) as an organic-inorganic hybrid pigment was investigated in both solution and coating phases. In the solution phase, the ZnAA extract was prepared in the 3.5% NaCl solution. Afterward, the mild steel specimens were dipped in the solution including ZnAA extract. Electrochemical impedance spectroscopy (EIS), electrochemical noise (EN) and polarization techniques were employed to assess the corrosion inhibition effects of ZnAA. The surface morphology and chemical composition of the film deposited on the steel specimens were examined by scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS). In the second part, the effect of ZnAA pigment on the epoxy-ester coating protection performance was studied by EIS.

Besides experimental investigations, theoretical approaches of ab initio quantum mechanics and molecular dynamics simulations were employed to get a deeper insight into the ZnAA inhibitor adsorptions. The first-principles QM chemical methods were used to explore the electronic features of inhibitors influencing their surface binding level.

2. Experimental

2.1. Raw material and sample preparation

Mild steel panels with dimension of 7 cm × 8 cm × 0.2 cm and chemical composition (wt.%) of 0.04 wt. % Al, 0.05 wt. % P, .05 wt. % S, 0.19 wt. % C, 0.32 wt. % Mn, 0.34 wt. % Si and 99.01 wt. % Fe were purchased from Foolad Mobarakeh Co. (Iran). Zinc acetyl acetate, $Zn(C_5H_7O_2)_2 \cdot xH_2O$ was prepared from Aldrich Co. The epoxy-ester resin based on EE-430CS (60% solid content and 5 mgKOH/g) was prepared from Resitan Co. Cobalt (60%, 0.1% metal content), Lead ((73%, 0.32% metal content) and Calcium (40%, 0.5% metal content) were prepared from Iran Color producer Co. and used as dryers for the epoxy-ester coating.

The epoxy-ester coating was prepared by addition of 1 wt. % ZnAA pigment [2]. The pigment was mixed with epoxy-ester resin by a high shear mechanical mixer for 2 h. Then, 0.2 wt. % cobalt, 0.5 wt. % lead and 1.2 wt. % calcium were added to the epoxy-ester resin, mixed for 30 min and finally the coatings without and with ZnAA were applied on the pre-cleaned steel sheets using a film applicator. Before coating application, all samples were abraded by emery papers of 600, 800 and 1200 grits, followed by acetone degreasing. To complete the curing process, the coatings applied on the steel panels were left at room temperature for a month and then cured in an oven at temperature of 70 °C for 2 h [45]. The dry thickness of about $50 \pm 5 \mu\text{m}$ was measured by a DeFelsko model instrument.

2.2. Characterization

2.2.1. Solubility of pigment

The extract of ZnAA was prepared in the 3.5 wt. % NaCl solution through addition of 1 g ZnAA pigment to 1 L of 3.5% NaCl solution, stirring for 48 h and then filtration. The extract prepared together

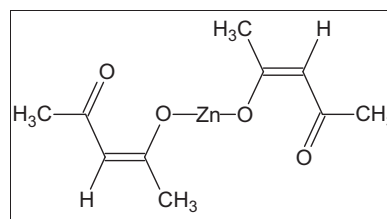


Fig. 1. Molecular structures of zinc acetylacetonate (ZnAA).

with a 3.5% NaCl solution without pigment extract was used for electrochemical studies. The type and concentration of the ions released from ZnAA pigment in 3.5% NaCl solution were evaluated by inductively coupled plasma (ICP) model Vista (Varian).

2.2.2. Surface analysis

Steel panels were dipped in the solutions without and with ZnAA pigment extract (1 g/L) for 48 h, rinsed with distilled water and finally dried. The surface morphology and composition of the films precipitated on the samples were investigated by Phenom ProX model SEM/EDS and Philips X-ray spectrometer.

2.2.3. Electrochemical studies

Steel panels were dipped in the chloride solutions without and with ZnAA pigment extract for different immersion times and studied by EIS, EN and polarization tests. Ivium Compactstat was employed to perform the EIS, EN and polarization measurements. The experiments were conducted in a three electrode cell including graphite (auxiliary electrode), Ag/AgCl (reference electrode) and mild steel panels (working electrode). The sweep rate of 1 mV/s in the range of ± 100 mV from OCP was utilized in the polarization test. Also, the EIS was performed at open circuit potential (OCP) in a frequency range of 10 kHz to 10 mHz and ± 10 mV perturbation. In the case of steel sample coated with epoxy-ester coating the experiment was done in two ways. First, an artificial defect (10 mm in length) was produced on the coating by a sharp surgery knife and then they were immersed in the chloride solutions for various times. In the second method the EIS was performed on the intact coating (1 cm²) without any defect at different immersion times. The EN measurements were conducted in a conventional three electrode cell consisting of two nominally identical mild steel as working electrodes and Ag/AgCl (3M KCl) as reference electrode. The working electrodes (1 cm²) were placed at a distance of about 2 cm. The electrochemical cell was implanted in a Faraday cage to avoid the interferences with external electromagnetic fields and stray currents. The sampling frequency for the electrochemical noise data was 20 Hz. A low pass filter of 10 Hz was used during data recording to avoid aliasing. All of the measurements in solution phase were done after 72 h immersion and the measurement duration was 800 s. EN data were analyzed with a multi-resolution wavelet technique using the orthogonal Daubechies wavelets of the fourth order (db4). The necessary calculations were performed using Matlab software.

2.3. Theoretical methods

2.3.1. DFT calculations

Before MD simulations, the structure of ZnAA pigment was optimized by means of quantum mechanics (QM) calculations based on density functional theory (DFT) methods. Fig. 1 displays the molecular structure of ZnAA. It is shown that in ZnAA pigment, two acetylacetonate ligands bonded to Zn atoms, respectively. The DFT calculations were done by the use of Dmol³ code implemented in Materials Studio software (version 7) [46].

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