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Full Length Article

A combined electrochemical, molecular dynamics, quantum mechanics and XPS analysis of the mild steel surface protected by a complex film composed of neodymium (III) and benzimidazole

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ABSTRACT

A mixture of Neodymium (III) nitrate (Nd) and Benzimidazole (Bi) was used for effective mild steel corrosion rate reduction in the sodium chloride solution. Results of electrochemical investigations revealed that the mixture of Bi and Nd significantly decreased both iron dissolution and oxygen reduction reactions rates and exhibited a mixed-type inhibition behavior and the best inhibition performance (about 98%) was achieved using 500 ppm Bi + 500 ppm Nd. Results of X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR) and contact angle test confirmed that the chelation between the organic and inorganic inhibitors resulted in the protective film deposition on the steel substrate. The mechanism of organic and inorganic inhibitors adsorption over the steel surface was examined by Molecular Dynamic (MD) simulation and Quantum Mechanics (QM) calculation.

1. Introduction

Mild steel is the most famous metal in the word owing to promising physical properties and high tensile strength [1–5]. However, corrosion is the fundamental process which results in the loss of appearance and physical properties of the materials, leading to the operational problems and economical loss [6]. Therefore, the protection of materials against corrosion has become a serious issue in recent studies. There are various basic techniques for prevention and/or mitigation of corrosion, such as the materials selection, the design of structures, environmental changes, cathodic protection, protective coating, and corrosion inhibitor [7,8]. Corrosion inhibitors are commonly used for controlling the corrosion rate of metals. Corrosion inhibitors are the most cost-effective chemicals that can be added to the aggressive environments in a small portion to reduce the iron dissolution rate [1,9]. The inhibitor molecules interaction with the surface of metal occurs through physical bonds and/or strong interactions based on the chemical bonds, leading to the creation of an impervious thin layer which would be compact enough to increase the metal surface resistance against the corrosion species attack like chloride ions, oxygen, and water molecules. These inhibitors can be divided into barrier (interface) and environmental conditioners inhibitors [10,11]. One important challenge in the selection of an inhibitor is that the corrosion inhibitors should not be toxic and harmful to the ecosystem. Though the most of organic and inorganic compounds, such as chromate, nitrite, and alkynol are effective inhibitors for iron, they are not environmentally safe and are harmful for human health. Therefore, extensive efforts have been taken on finding more eco-friendly alternatives. Recently, many eco-friendly inhibitors have been introduced for replacement of toxic ones. Among these inhibitors the rare earth based elements have become the forerunner and effective for corrosion prevention and mitigation of metals [2,4,12]. Yanhua et al. [5] combined three kinds of rare earth elements based on cerium nitrate, lanthanum nitrate and praseodymium nitrate with sodium molybdate to achieve effective synergic inhibition effects. They evaluated the X70 steel corrosion rate in the electrolytes protected by these compounds through electrochemical methods. The best inhibition performance (98.21%) was seen for the CeN-M sample.

Benzimidazole, benzotriazole, imidazole and pyrazole are some common effective organic inhibitors that have been frequently used for metals and alloys protection. Though the organic molecules including

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Table 1
The different solutions that used in this study.

Full name of the solution	Abbreviated name for the solution
3.5% (wt.%) NaCl	Blank
1 g/l Benzimidazole + 3.5% (wt.%) NaCl	1000 ppm Bi
1 g/l Neodymium(III) nitrate hexahydrate + 3.5% (wt.%) NaCl	1000 ppm Nd
0.5 g/l Benzimidazole + 0.5 g/l Neodymium (III) nitrate hexahydrate + 3.5% (wt.%) NaCl	500:500 ppm (Bi:Nd)
0.75 g/l Benzimidazole + 0.25 g/l Neodymium (III) nitrate hexahydrate + 3.5% (wt.%) NaCl	750:250 ppm (Bi:Nd)
0.25 g/l Benzimidazole + 0.75 g/l Neodymium (III) nitrate hexahydrate + 3.5% (wt.%) NaCl	250:750 ppm (Bi:Nd)

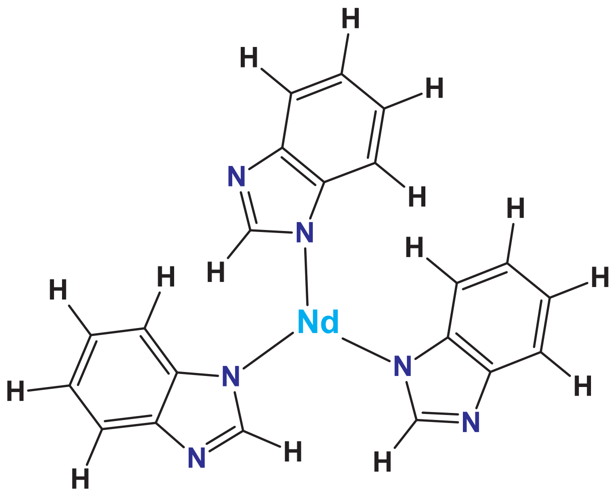

Fig. 1. Chemical structure of organic-inorganic neodymium-benzimidazole complex.

heteroatoms such as phosphor, sulphur, oxygen, and nitrogen show good corrosion inhibition activity, most of them are used in the acidic media and a few studies can be found on the studying of their corrosion inhibition activity in neutral media. Recently, the strategy of using the combination of organic/inorganic inhibitors is considered to reach the synergistic inhibition effects and solve the challenges of poor or moderate inhibition actions of the organic inhibitors in neutral media. Bahlakeh et al. [13] studied the synergic effect between zinc cations and the extract of nettle leaves on steel specimen in chloride solution. Results of EIS test revealed that the combination of green corrosion inhibitor and zinc salt effectively reduced the carbon steel dissolution rate through a mixed inhibition mechanism. Xianghongli et al. [14] studied the steel corrosion prevention in the cerium (IV) ion and 3,4-dihydroxybenzaldhyel (DHBA) H_2SO_4 containing solution. Bokati et al. [15] studied the 1H-benzotriazol (BTA) corrosion inhibition effect alone and in the presence of $Na_2MoO_4{\cdot}2H_2O$ and $Na_3PO{\cdot}12H_2O$ in the artificial sea water at different immersion times by EIS and polarization tests. They found that the combination of inhibitors resulted in greater inhibition efficiency on the surface of copper and mild steel specimens than the BTA alone. Li et al. studied the cold rolled steel corrosion in 1 M HCl solution protected by cerium (IV) ion and vanillin containing [16]. Catabig et al. investigated the synergic effect of the cerium and praseodymium mercaptoactate mixtures on the corrosion of AA2024-T3. Among the organic corrosion inhibitors studied, benzimidazole, which includes N-containing groups, has showed the most effective inhibition action in the acidic media [17,18]. However, it shows poor inhibition effect in the saline media. Therefore, in the present work the rare earth element based on neodymium (III) nitrate hexahydrate (an eco-friendly inhibitor) was used in mixture with benzimidazole. To this end, the steel panels were exposed to the chloride solutions including corrosion inhibitors with different ratios. The inhibitors inhibition actions were studied through electrochemical (EIS and polarization tests) surface analysis (FE-SEM, EDS, and FT-IR), and contact angle test methods. The inhibitors molecules attraction mechanism on the carbon steel surface was studied by molecular dynamics and quantum mechanics methods.

2. Experimental

2.1. Raw materials

Neodymium (III) nitrate hexahydrate ($Nd(NO_3)_3{\cdot}6H_2O$) and Benzimidazole (Bi) ($C_7H_6N_2$) were purchased from Sigma-Aldrich, and Merck Co., respectively. The mild steel panels with the following composition (wt.%); 93.9% Fe, 1.2% P, 1.1% Mn, 1.0% Si, 0.7% Cr and 1.7% Ni, were obtained from Foolad Mobarakeh Co. The surface of the steel samples was abraded by SiC papers (220, 400, 800 and 1200 grit). By a commercial acetone solvent the organic impurities were removed from the steel specimens' surface. The degreased samples were further cleaned by distilled water. Finally, the air dried samples were used for the electrochemical measurements. Table 1 presents the formulation of different solutions prepared and used in this study.

2.2. Electrochemical measurements

The EIS measurement was conducted by an Autolab potantiostat instrument during 2, 4, 6, 24, and 48 h of immersion in various test solutions (Table 1). The test was carried out in a common electrochemical cell. The reference electrode used was saturated calomel electrode (SCE). Platinum was employed as auxiliary electrode and the working electrode was the mild steel sheet. The EIS was done at the open circuit potential (OCP) with perturbation of ± 10 mV and in the range of 0.01 Hz to 10^3 Hz. The impedance data was analyzed by Z-view software. The polarization test was done in the same electrochemical system, −200 mV to +200 mV around OCP and the rate of potential scan was 1 mV/s. The NOVA 1.11 software was used for analyzing the polarization plots results and for obtaining various electrochemical parameters. Also the inhibition efficiency (η) values were obtained using Eq. (1):

$$\eta(\%) = \left(1 - \frac{i_i}{i_0}\right) \times 100 \tag{1}$$

where i_i and i_0 are attributed to the corrosion current densities for the unprotected and protected sodium chloride solution by Nd and Bi inhibitors, respectively. Electrochemical tests were repeated three times to examine the errors of all parameters. Also the OCP measurement was carried out on the samples immersed in the Blank, 1000 ppm Nd, and