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Synthesis, spectroscopic characterization and a comparative study of the corrosion inhibitive efficiency of an α-aminophosphonate and Schiff base derivatives: Experimental and theoretical investigations

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ABSTRACT

New α-aminophosphonate (**α-APD**) and Schiff base (**E-NDPIMA**) derivatives have been prepared and their structures ware proved by IR, UV–Vis, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. Their inhibitive capacities on the XC48 carbon steel corrosion in 0.5 mol L^{-1} H_2SO_4 solution were explored by weight loss, Tafel polarization, electrochemical impedance spectroscopy (EIS) and atomic force microscope (AFM). Experimental results illustrate that the synthesized compounds are an effectives inhibitors and the adsorption of inhibitors molecules on the carbon steel surface obeys Langmuir adsorption isotherm. In addition, quantum chemical calculations performed with density function theory (DFT) method have been used to correlate the inhibition efficiency established experimentally. Also, the molecular dynamics simulations have been utilized to simulate the interactions between the inhibitors molecules and Fe (100) surface in aqueous solution.

1. Introduction

Corrosion of steel is a major problem in our daily lives and in various industrial plants. In this context, many techniques and methods have been developed and used to protect steel against corrosion. However, in practice, the most employed technique is the use of organic inhibitors and it has a great importance and applications in the protection of metals and alloys. Many studies have been conducted to determine the inhibition activity in aqueous solutions of several synthesized organic compounds [1–6].

α-aminophosphonate and Schiff bases derivatives have been attracting an outstanding attention during the last decade as a promising class of viable compounds in the corrosion inhibition field. The aromatic α-aminophosphonates and Schiff bases containing nitrogen, oxygen and sulfur atoms in their structure are also very attractive inhibition agents [7–10]. In the literature, many α-aminophosphonate and Schiff bases have announced as powerful corrosion inhibitors for various metals and alloys in acidic mediums [11–14]. Many synthetic methods for the synthesis of this type of compounds have been developed during the past years [15–19]. Of these methods, the Kabachnik-Field's [20–23] synthesis of α-aminophosphonates, promoted by acidic or basic catalysts, is the most appropriate.

Many reviews have been recently reported considering the employ of quantum chemical methods and molecular dynamic simulations techniques in corrosion inhibitor studies [24–26]. A number of investigators inform that the protecting activity of an inhibitor generally relies on several physicochemical and electronic properties of the protective molecules, especially, its organic functional groups, steric properties, electronic density of contributor atoms, and orbital characteristic of sharing electrons [27,28]. The great importance of the molecular dynamic simulations is the understanding of the fixation manner of inhibitor molecules on metal surface at molecular level and permits determining the adsorption energy value [29,30].

In the present study, we detail the preparation and characterization of two new α-aminophosphonate **α-APD** and Schiff base **E-**

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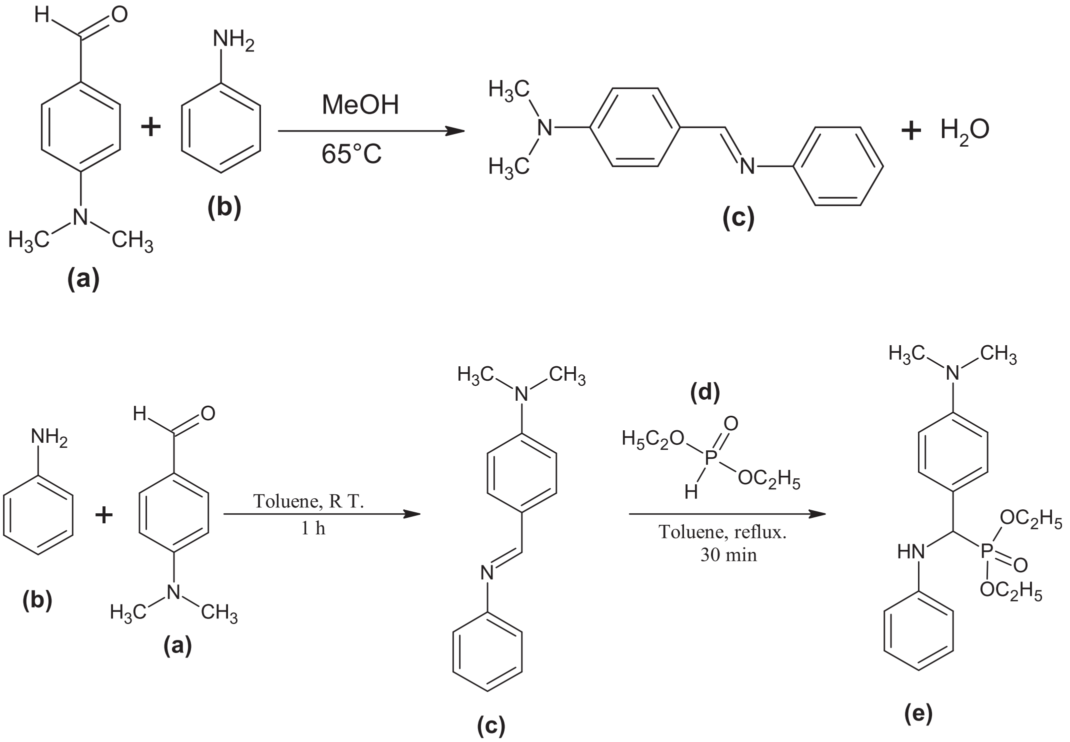

Fig. 1. Synthesis route of the studied compounds:**(a)** 4-(dimethylamino)benzaldehyd **(b)** Aniline **(c)** (E)-N, N-dimethyl-4-((phenylimino) methyl) aniline (**E-NDPIMA**) **(d)** diethylphosphite **(e)** diethyl ((4-(dimethylamino)phenyl)(phenylamino)methyl)phosphonate (**α-APD**).

NDPIMA derivatives. We also report a discussion of carbon steel XC48 corrosion in sulfuric acid medium by means of gravimetric tests, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). The adsorption isotherm of the inhibitors molecules on carbon steel surface and the thermodynamics parameters were obtained. On the other hand, the surface state of the carbon steel specimens was observed by employing atomic force microscopy (AFM). Besides, quantum chemical computations were applied to correlate experimental results. Finally, molecular dynamic simulations studies were performed to determinate the fixation forms and energies of the studied inhibitors on the iron face.

2. Experimental and theoretical layouts

2.1. Material, steel specimens, electrodes and solutions

All essays were realized on XC48 carbon steel of the corresponding chemical composition: ($C = 0.418\%$, $Mn = 0.730\%$, $Mo = 0.012\%$, $P = .016\%$, $S = 0.019\%$, $Si = 0.245\%$, $Ni = 0.079\%$, $F = 0.777\%$ and $Fe = 98.09873\%$). The carbon steel samples applied in weight loss measurements are sectioned to cylindrical samples of 9.42 cm^2 area. The working electrode employed in electrochemical measurements has a cylindrical form of 1.131 cm^2 frontal area prepared from rod XC48 carbon steel and soldered in the opposite area with Copper cable for an electrical connection. In the other hand, the side surface of the working electrode is installed on a plastic support to present only one active plane face displayed to the corrosive medium. The all metallic samples were mechanically polished on SiC papers of grades (600, 800, 1000, 1200, 1800 and 2500) and rinsed with distilled water. The analytical grade of 98% H_2SO_4 is used to obtain the 0.5 mol L^{-1} H_2SO_4 solutions by dilution with distilled water and varying amounts of the investigated derivatives were dissolved in 0.5 mol L^{-1} H_2SO_4 to prepare various concentrations of inhibitors solutions.

2.2. Preparation of the studied inhibitors

2.2.1. Preparation of the Schiff base derivative

The studied Schiff base derivative; namely (E)-N,N-dimethyl-4-((phenylimino)methyl)aniline (**E-NDPIMA**), was synthesized by condensation of 1.0 mmol of aniline with 1.0 mmol of 4-(dimethylamino)benzaldehyde in methanol at 65 °C. After a few hours a yellow mixture was obtained which was concentrated under vacuum to remove the solvent and the residue was filtered, washed with diethylether and dried in air (Fig. 1).

Yield: 82% of yellow solid, m. p. 138°C. **UV–vis** (MeOH): $\lambda_{max(n)}$ (nm). $\lambda_{max(1)}$ (207), $\lambda_{max(2)}$ (237), $\lambda_{max(3)}$ (356.55). **IR** (Solid state), ν_x (cm^{-1}): $\nu_{C-H(aromatic)}$ (3086 3029), $\nu_{C-H(aliphatic)}$ (2941 2838), $\nu_{C=N}$ (1600), $\nu_{C=C(aromatic)}$ (1582 1522), $\nu_{C\ \ C=C(aromatic)}$ (1479), $\nu_{N(CH_3)_2}$ (1436 and 1359), $\nu_{C-N(aromatic)}$ (1230 1067), $\nu_{C-N(aliphatic)}$ (964), $\nu_{=C-H}$ (904), ν_{Ar-CH} (758). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm): 3.08 ppm (6H, s, $C\underline{\mathbf{H_3}}-N-C\underline{\mathbf{H_3}}$), 6.76–6.79 ppm (2H, d, $J = 9.1$ Hz, $-C\underline{\mathbf{H}}_{Ar}-$), 7.21 ppm (1H, s, $-C\underline{\mathbf{H}}_{Ar}-$),7.23–7.28 ppm (2H, m, $-C\underline{\mathbf{H}}_{Ar}-$), 7.40–7.44 ppm (2H, t, $J = 7.7$ Hz, $-C\underline{\mathbf{H}}_{Ar}-$), 7.82–7.85 ppm (2H, d, $J = 8.9$ Hz, $-C\underline{\mathbf{H}}_{Ar}-$), 8.38 ppm (1H, s, $-C\underline{\mathbf{H}}=N$-). **^{13}C NMR** (300 MHz, $CDCl_3$), δ (ppm): 40.06 ppm (2C, $\underline{\mathbf{C}}H_3-N-\underline{\mathbf{C}}H_3$), 111.63 ppm (2C, $-\underline{\mathbf{C}}H_{Ar}-$), 121.02 ppm (2C, $-\underline{\mathbf{C}}H_{Ar}-$), 124.51 and 125.03 ppm (2C, $-\underline{\mathbf{C}}H_{Ar}$), 129.09 ppm (2C, $-\underline{\mathbf{C}}H_{Ar}$), 130.5 ppm (2C, $-\underline{\mathbf{C}}H_{Ar}$), 152.56 (1C, $-\underline{\mathbf{C}}H_{Ar}-$), 153.05 (1C, $-\underline{\mathbf{C}}H_{Ar}-$), 160.29 (1C, $-\underline{\mathbf{C}}H=N$-).

2.2.2. Preparation of the α-aminophosphonate derivative

The studied α-aminophosphonate derivative, namely diethyl ((4-(dimethylamino) phenyl) (phenylamino) methyl) phosphonate (**α-APD**), was prepared by adding equimolar amount of diethylphosphite (1.0 mmol) to previous imine **E-NDPIMA** (1.0 mmol)