Inhibition effect of 2-amino-4-methylpyridine on mild steel corrosion: Experimental and theoretical investigation

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ABSTRACT

The effect of 2-amino-4-methylpyridine (AMP) on the corrosion behavior of mild steel (MS) in 0.5 M HCl is investigated with electrochemical methods and theoretical calculations. The electrochemical tests show that the polarization resistance of MS increasing the presence of AMP in acid solution. Adsorption of AMP on MS surface is a physical and obeys the Langmuir isotherm. The quantum parameters signaled adsorption occurs on amine and methyl substituents of AMP. The inhibition efficiency is related to frontier orbital's energy band gap of AMP, which are 5.357 and 6.490 eV for neutral and protonated molecules in aqueous solution, respectively.

1. Introduction

The corrosion is a main problem for steel industry, especially in acidic media. The inorganic acids are widely used in many processes such as pickling, cleaning and descaling therefore; corrosion prevention has critical importance [1–3]. In closed loop systems, organic inhibitor molecules are effectively used against corrosion. Generally, the most efficient inhibitor molecules contain nitrogen, sulfur, oxygen, multiple bonds and aromatic rings [4–12]. Due to chemical and physical properties, pyridine and its derivatives use in a variety of industrial products (food, medicinal and chemical). Lashkari and Arshadi [13] studied molecular behavior of some pyridine derivatives as corrosion inhibitors, and their results showed that pyridine molecules strongly adsorb the iron surface and protect effectively against corrosion. They suggested that, adsorption took place on vertical and parallel positions (through π electrons of aromatic ring), although the vertical is predominant. Kosari et al. [14] investigated the corrosion performance of pyridine-2-thiol (P2T) and 2-pyridyl disulfide (2PD) in HCl solution. The corrosion rate of MS decreases with increasing of P2T and 2PD concentrations. Quantum chemical calculations showed nearly similar E_{HOMO} for both compounds while 2PD has lower E_{LUMO} than P2T. They suggested that, it may be deduced that both inhibitors have an equal ability to offer electrons to the unoccupied d-orbital of the iron; however the higher ability of accepting the electron is expected for 2PD in comparison with P2T. The inhibition effect of

bis-2,6-(3,5-dimethylpyrazolyl)pyridine (DPP) on the corrosion of steel in 2 M HCl solution was studied by Ergun et al. [15], and the results shown that DPP was an efficient inhibitor. Consequently, pyridine and its derivatives could prefer as an inhibitor against corrosion.

In this study, the inhibition effect of 2-amino-4-methylpyridine (AMP) on MS corrosion was investigated in 0.5 M HCl. The thermodynamic, kinetic and quantum parameters were determined. The electrochemical impedance spectroscopy (EIS) and polarization measurements were used for clarification of corrosion and adsorption behavior. In theoretical part of this study, we aimed to find suitable quantum parameters to characterize the inhibition property and adsorption center of AMP. The correlation between inhibition efficiency and electronic properties of AMP were discussed. Therefore energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE), Mulliken and natural bonding orbital (NBO) charges on the backbone atoms, absolute electronegativity (χ), absolute hardness (η) and the fraction of electrons (ΔN) transferred from AMP and protonated AMP (p-AMP) were calculated. The theoretical part of this study was carried out using ab initio density functional theory (DFT) at the level of Beck's, three parameter were exchanged functional and the Lee–Yang–Parr non-local correlation functional (B3LYP) with 6-31G (d) and 6-311G (++ d,p) basis sets. These are most commonly used basis sets in literature, 6-311G (++ d,p) more complex than 6-31G (d) and it has higher correlation with experimental results. Other sides the main advantage of 6-31G (d) is shorter operation time. We wanted to compare these two basis sets due to offering suitable results.

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2. Experimental

The electrochemical measurements were carried out in a conventional three-electrode set up, open to the atmosphere with using a CHI 604A electrochemical analyzer (serial number 6A721A). The platinum sheet (with 2 cm^2 surface area) was the counter electrode and Ag/AgCl (3 M KCl) electrode was the reference electrode. The working electrodes (with 0.502 cm^2 surface area) were mild steel alloy with following chemical composition (wt%); 0.09645 C, 0.22423 Si, 0.41797 Mn, 0.02095 P, 0.04229 S, 0.02533 Cu, 0.03594 Ni, 0.01396 Cr, 0.00271 Mo, 0.00591 V, 0.00216 Sn and balance with Fe. While the rest of an electrode was isolated with thick polyester block and electrical conductivity was provided by a copper wire. The surface of MS electrodes was abraded using emery paper up to 1200 grades prior to each experiment. Then, it was cleaned with distilled water and dried with a filter paper. The experimental tests were performed in 50 mL, 0.5 M HCl solution in the absence and presence of various AMP concentrations. The structure of AMP and protonated AMP (p-AMP) were given in Fig. 1.

The various concentrations of the AMP were used (0.5–50.0 mM). All chemicals were purchased from Sigma–Aldrich (Adana, Turkey) products. The test solutions were prepared from analytical-grade chemical reagents in distilled water without further purification. For each experiment, a freshly prepared solution was used. The test solutions were opened to the atmosphere, and the temperature was controlled with thermostat (Nuve BS 302 serial number 03-0033). The EIS experiments were employed between 100 kHz and 0.006 Hz at open circuit potential during 168 h immersion times. The amplitude was 5 mV. The EIS parameters were calculated by fitting the experimental results to an equivalent circuit using ZView software. The linear polarization resistance (LPR) measurements were carried out by recording the electrode potential ±10 mV around open circuit potential with 0.1 mV s^{-1} scan rate. The polarization resistance (R_p) was determined from the slope of the current–potential curves obtained. The polarization curves were determined potentiodynamically in the potential range from open circuit potential (E_{ocp}) to -0.1 V (vs. Ag/AgCl) with 1 mV s^{-1} scan rate, under stirred conditions. The adsorption isotherms were obtained with various AMP concentrations (0.5–50.0 mM) after 1 h immersion time. The effect of temperature on the inhibition mechanism was investigated, and activation energy of the corrosion process was calculated. The polarization curves were obtained at different temperatures (298–318 K) in the absence and the presence of 50 mM AMP after 1 h immersion time.

2.1. Theoretical details

The theoretical study was operated with Gaussian 09 program package [16]; the geometry optimizations of the AMP and p-AMP were performed by using the DFT/B3LYP/6-31G (d) and DFT/B3LYP/6-311G (++ d,p) methods.

Some electronic properties such as Mulliken and NBO charges [17], E_{HOMO}, E_{LUMO}, ΔE, χ, η and ΔN were determined in water phase. The optimized molecular structures and HOMO, LUMO surfaces were visualized using Gauss View 5.0 [18].

3. Results and discussion

3.1. Corrosion performance

The EIS measurements of the MS were obtained in 0.5 M HCl solution in the absence and presence of various concentrations of AMP and Nyquist plots were presented in Fig. 2.

The Nyquist's plot of MS in the absence of the inhibitor contains a slightly depressed semi-circular shape and only one time constant was seen as expected from literature [19,20]. The diameter of Nyquist plot which was attributed R_p, which was determined from differences in real impedance at lower and higher frequencies, was detected as 39.0 Ω cm^2 (Fig. 2, Table 1).

In the presence of AMP, R_p increases with increasing the inhibitor concentration. The R_p presents the polarization resistance, which contains charge transfer resistance (R_{ct}), diffuse layer resistance (R_d), inhibitor film resistance (R_f) and all other accumulated kinds (R_a), ($R_p = R_{ct} + R_d + R_f + R_a$) [21–23]. The maximum R_p was determined as 635.3 Ω cm^2 in the presence of 50 mM AMP after 1 h immersion time (Fig. 2, Table 1). Kosari et al. [14] studied other pyridine derivatives, which were pyridine-2-thiol (P2T) and 2-pyridyl disulfide (2PD), against corrosion of MS in HCl medium. In their research, the R_p values of MS electrode in 200 ppm P2T and 2PD containing 0.1 M HCl solutions were 918 and 701 Ω cm^2, respectively.

As seen from Fig. 2, the Nyquist plots were not observed as perfect semicircles. Due to heterogeneity of surface, ideal capacitive behavior does not see at the metal/solution interface. Instead of fitting a capacitance behavior, it is usually preferred using a
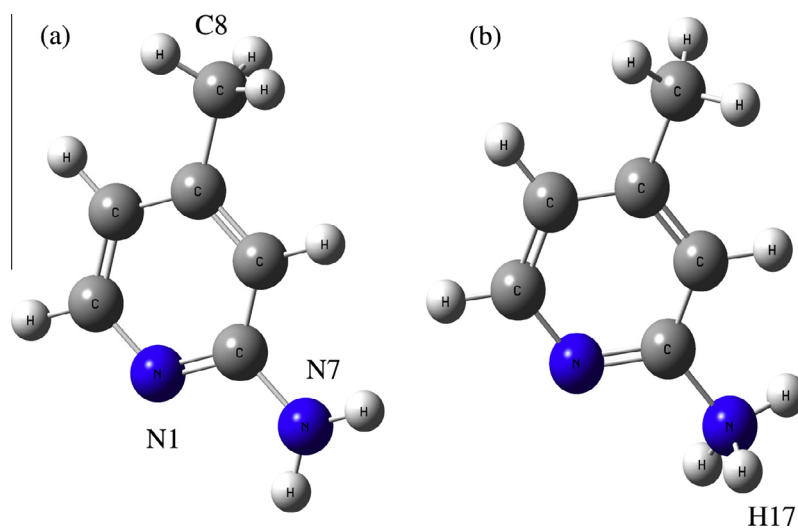

Fig. 1. Chemical structure of 2-Amino-4-methylpyridine (AMP) in neutral (a) and acidic (b) media.