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Inhibition efficiency of aminobenzonitrile compounds on steel surface

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ABSTRACT

The aim of this study is to investigate the inhibition efficiency of benzonitriles with functional amine groups in different positions, for mild steel corrosion in 0.5 M HCl solution. For this purpose, electrochemical impedance spectroscopy and potentiodynamic measurements were realized. Besides, these electrochemical analyses were carried out at different temperatures in order to obtain temperature dependency of inhibition efficiency. By using atomic absorption spectroscopy techniques, the amount of iron ions that released to the solution was determined, during immersion time. The surface analysis was also carried out by scanning electron microscopy technique. The results show that all these inhibitors have a good inhibition effect on mild steel in 0.5 M HCl solution, and it depends on the position of amine group.

1. Introduction

It is well known that mild steel is widely used material in a variety of industrial applications. The use of inhibitor in order to protect metal from corrosion is still in the foreground of many researchers [1–4]. Mostly used acid corrosion inhibitors are functionalized organic compounds which contain electronegative atoms (such as N, S, P, O, etc.). The effect of inhibitor depends on the molecular structure, size and the number of electron rich functional groups. Furthermore, the surface state and surface potential of used metal can play important role for the inhibition efficiency [5–7]. Many organic compounds like triazoles [8–10], imidazoles [11–13], ionic liquids [14–17] and Schiff bases [18–20] have been studied. Besides, benzonitrile compounds could be good inhibitor due to their molecular structure [21]. It is obviously known that the efficiency of these organic molecules is strictly related to their strong adsorptive interaction with the metal surface, which reduces the corrosive effect of acidic media. Also, the number and position of functional groups should be considered in aspect of their activating effect on the aromatic ring. This issue should be taken into account for discussion of benzonitrile compounds as corrosion inhibitors.

In this study, the inhibition efficiency of benzonitriles with functional amine groups in different positions have been investigated for mild steel corrosion in 0.5 M HCl solution. For this aim, electrochemical and non-electrochemical measurements were realized. The results show that all these inhibitors have a good inhibition effect on mild steel in this corrosive media.

2. Experimental

Mild steel samples (MS) were cylindrical rods measuring 0.8 cm in the radius (0.502 cm^2 exposure surface area). The chemical composition of mild steel (wt%) was C (0.173), Si (0.046), Mn (0.435), P (0.026), S (0.023) and Fe (balancing). The working surface area was abraded mechanically with SiC paper to a 1200 grit finish, then degreased with 1:1 ethanol/water mixture and washed with distilled water, finally dried at room temperature. The corrosive test solution was prepared by dilution of analytical grade 37% HCl with distilled water. The concentration range of employed inhibitors 2-aminobenzonitrile (2-AB), 3-aminobenzonitrile (3-AB) was 0.5 to 10.0 mM in 0.5 M HCl. The chemical structures of inhibitors were given in Fig. 1.

The electrochemical measurements were realized by using CHI 660 C electrochemical analyzer; open to the atmosphere and without stirring. The electrochemical cell consisted of a three electrode set up where the auxiliary electrode was a platinum sheet (2 cm^2 surface area) and Ag/AgCl (3 M KCl) electrode was used as the reference. All the potentials given in this paper are referred to this electrode. The electrochemical impedance spectroscopy (EIS) measurements were realized at corrosion potential (E_{corr}), which is the open circuit value measured after 1 h immersion period in test solution and steady state conditions are reached. The employed frequency range was 10 mHz–100 kHz and the amplitude was 7 mV. The EIS results were fitted by using Zview 2 software. The potentiodynamic (PD) measurements were carried out for cathodic (from

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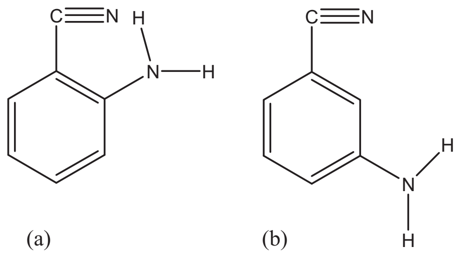

(a) (b)

Fig. 1. The chemical structures of 2-AB (a) and 3-AB (b).

open circuit potential (E_{ocp}) to −1.00V) and anodic (from open circuit potential (E_{ocp}) to −0.20V) with a scan rate of 2 mV/s. For the assessment of corrosion rate, solution assay analysis was realized with atomic absorption spectroscopy (AAS) measurement. For this purpose, mild steel samples were immersed in 0.5 M HCl solution without and with 10 mM inhibitor (2-AB, 3-AB). These experiments were repeated for a set of temperature, between 25 °C–55 °C. All solutions have the same volume (50 mL) and all electrodes were exposed to test solutions for 18 h. After, removing the immersed electrode, all solutions were mixed with HCl in order to solve all the iron species in solutions. A calibration curve was obtained with using standardized solutions prepared with analytical grade chemicals. The surface morphology of mild steel samples after 6 days immersion in HCl solution with and without inhibitor was investigated by scanning electron microscopy (SEM). The SEM measurements were realized employing 20 kV and given results are 250x magnitudes.

3. Result and discussion

The studied inhibitor compounds have the same molecular formula; an aromatic ring functionalized with a —C≡N and —NH_2 groups. The studied inhibitor compounds have the same molecular formula; an aromatic ring functionalized with —C≡N and —NH_2 groups. These polar groups also have unshared electron pairs which increase the strength of adsorptive interaction with unoccupied d-orbitals of metal. Besides, these unshared electron pairs on nitrogen atoms could be donated to aromatic ring that higher charge density is provided. Then, the molecule becomes highly advantageous for adsorption, when approaching to the steel surface. Extra π-electrons and higher charge density of —C≡N group promote the electrostatic attraction forces via this group, with respect to —NH_2 group. However, the position of amine group on the ring is different for 2-AB and 3-AB compounds. When it is attached to the ring from ortho- position (2-AB), some kind of steric effect may be expected. However, the ortho- and meta- positions are selected in order to distinguish the effect of amine group on the adsorptive interaction and resulting electrical properties of the metal/solution interface. The nitrile group has strong dipole character and considered to create strong electrostatic attraction with the surface, as well as amine group. Also, both nitrogen atoms of these functional groups are suspicious to bind a proton from highly acidic test solution.

This position of amine group is important for adsorptive interaction, thus the dielectric properties of the interface. Therefore, the interfacial capacitance (C_{dl}) values obtained from EIS data and PD measurements are evaluated together to interpret the relation between the efficiency and the position of functional groups.

3.1. Electrochemical impedance spectroscopy measurements

The corrosion behavior of mild steel in 0.5 M HCl solution without and with different inhibitor concentrations was investigated by EIS at 25 °C. In Figs. 2 and 3, the EIS results were given for studied inhibitors. The inset figure shows the Nyquist plot of bare steel. As seen from figure, Nyquist plots of mild steel is a slightly depressed semicircle and only one time constant is observed in Bode plots. This observation indicates that the corrosion of mild steel in 0.5 M HCl solution is mainly controlled by the rate of charge transfer process [22,23]. The polarization resistance value is directly obtained from Nyquist plot, which includes charge transfer resistance and diffuse layer resistance. This value increased regularly with increasing concentration of inhibitor. This could be explained with the surface coverage ratio dependency on bulk inhibitor concentration, in such physical adsorption process. The inhibition efficiencies are calculated handling these R_p values and given in Table 1. Reasonably high efficiency value (higher than 93%) is obtained with 10 mM inhibitor concentration for both compounds.

It was also clearly seen that the break point frequency shifted gradually to lower values, as the inhibitor concentration increases. The said value can be read from intersection of the frequency

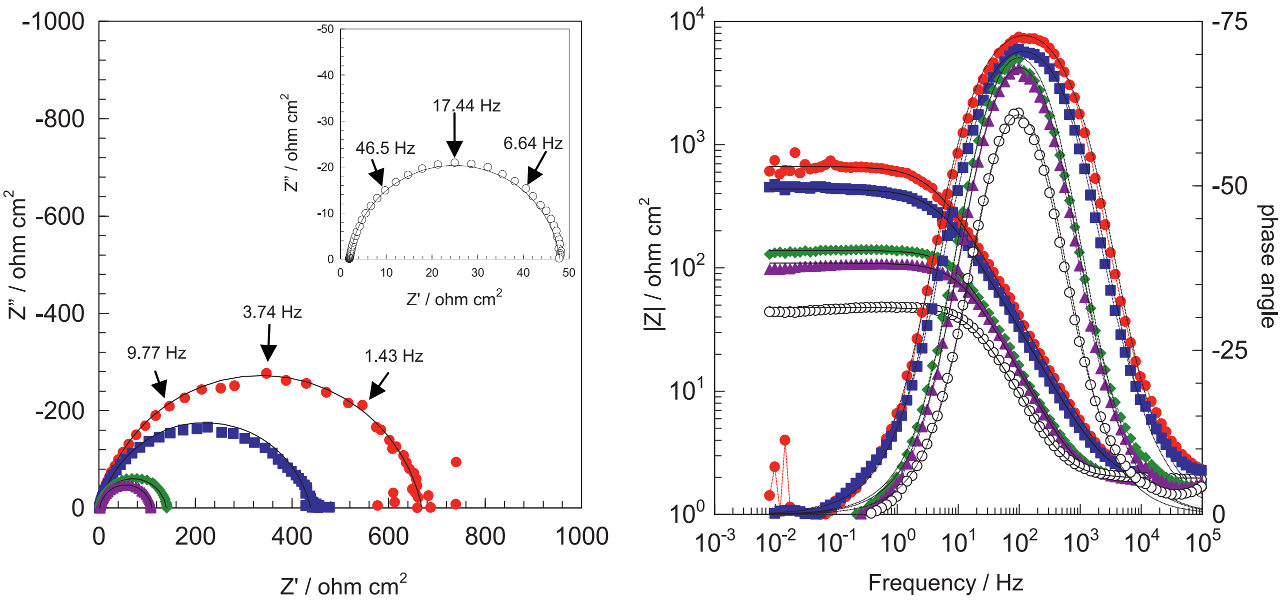

Fig. 2. The EIS results of mild steel obtained in 0.5 M HCl solution (○) (inset) and containing 0.5 (▲), 1.0 (◆), 5.0 (■), 10.0 mM (●) 2-AB. (solid lines show fitted results).