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Assessment of the inhibition efficiency of 3,4-diaminobenzonitrile against the corrosion of steel

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ABSTRACT

The inhibition efficiency of 3,4-diaminobenzonitrile was studied against steel corrosion, using electrochemical impedance spectroscopy, potentiodynamic measurements and solution assay analysis. The corrosion rate was determined with different routes; apparent Stern–Geary coefficient (*B*) derived from solution assay analysis and compared with coefficient value obtained from Tafel slopes. For blank solution, *B* and corrosion current values were quite different, comparing results from Tafel slopes and AAS. In presence of inhibitor, the difference becomes negligible. Once anodic dissolution kinetics is governed by strongly adsorbed inhibitor, resistance against charge transfer process becomes more important and corrosion rate results obtained from different routes come closer.

1. Introduction

The organics with certain functional groups are widely studied as potential corrosion inhibitors against steel corrosion in acid solutions that are generally utilized for cleaning, pickling etc. [1–10]. For other practical applications like cooling water, oil/water systems etc., corrosion control could be succeeded with mixture formulas including corrosion inhibitor, descaling agents, dispersant additives. The organic corrosion inhibitors cannot be used alone, for corrosion protection in industrial applications. The co-additives prevent scale formation on the surface, and then the steel surface remains clean and organic corrosion inhibitor exhibits efficiency. As the major part of corrosion protective mixture formulations, there is necessity for development of effective, low cost, green organic corrosion inhibitor compounds. The inhibition efficiency is strictly related with its molecular structure and electronic properties, which govern the adsorptive interaction strength with the metal surface. Besides, inhibition efficiency is highly influenced by the surface conditions and nature of corroding system, as well as the corrosive environment [11–13].

Nitrile, azole and thiol compounds are frequently studied as potential corrosion inhibitors, since the molecules are functionalized with electronegative groups and aromatic ring. These molecules are strongly adhered to metal surface and block the active centers, generally forming a protective film. Therefore, most of the inhibitor compounds are designed in order to have these kinds of functional groups and additional substituents for tailoring the surface properties of protective film [14–18]. Amine substituted benzonitrile compounds are also generally pronounced as good inhibitor for steel and its alloys [19]. Since, they could establish film like adsorption layer on various metals, especially on copper. Moreover, nitrile group containing compounds and its derivates have been extensively used as inhibitor against steel corrosion due to their strong adsorptive interaction with metal [20–23]. Moreover, many kind of nitrogen-containing compounds (as hetero-atoms and/or amine group) have been investigated in variety corrosive environment such as; 3.5% chloride solution [24,25], CO_2 saturated chloride solution [26–28], alkaline chloride solution [29,30] and cooling water system [31] as an effective corrosion inhibitors. Besides, there are many studies in literature showed that these compounds are effective inhibitors in different kind of acid solutions [32–34].

In present study, we objected to investigate the inhibition efficiency of benzonitrile compound; acidic chloride solution has been utilized testing environment. Assessment of corrosion rate has been realized with evaluating Tafel regions and solution assay analysis. The obtained results were compared and the interaction between the surface and inhibitor molecules has been interpreted.

2. Experimental

2.1. Preparation of electrodes

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),

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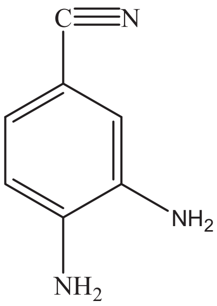

Fig. 1. The chemical structure of 34AB.

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.

2.2. *Test solutions*

The inhibitor molecule and other chemicals used without further purification. The corrosive test solution was prepared by dilution of analytical grade 37% HCl with distilled water. The concentration range of employed inhibitors 3,4-diaminobenzonitrile (34AB) was in the range from 0.5 mM to 10.0 mM in 0.5 M HCl solution. The chemical structure of inhibitor is given in Fig. 1. The electrochemical measurements were realized under air atmosphere without stirring. The temperature of the solutions was controlled thermostatically.

2.3. *Electrochemical measurements*

The electrochemical measurements were realized by using CHI 660C electrochemical analyzer. 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 open circuit potential (E_{ocp}) to −1.00 V) and anodic (from open circuit potential (E_{ocp}) to −0.10 V) with a scan rate of 2 mV/s. The stability of inhibitor on the steel surface was tested in 0.5 M HCl solution and containing 10 mM 34AB by chronoamperometry under anodic (−0.418 V) and cathodic (−0.644 V) potentials for 1 h.

2.4. *Atomic absorption spectroscopy measurements*

For the evaluation of corrosion rate, solution assay analysis was carried out with atomic absorption spectroscopy (AAS) measurement. For this aim, steel samples were immersed in 0.5 M HCl solution without and with inhibitor. These experiments were repeated for a set of temperature, between 25–55 °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.

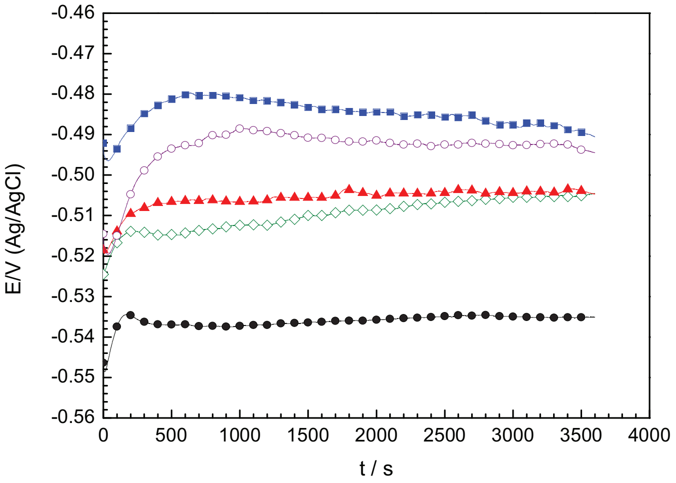

Fig. 2. The change of open circuit potential as a function of exposure time in 0.5 M HCl solution (●) and containing 0.5 (◊), 1.0 (▲), 5.0 (○), 10.0 mM (■) 34AB.

2.5. *Scanning electron microscopy studies*

The surface morphology of mild steel samples was investigated by scanning electron microscopy (SEM) after 6 days immersion in 0.5 M HCl solution and containing 10 mM inhibitor. The SEM measurements were realized employing 20 kV and given results are 250× magnitudes.

3. Results and discussion

3.1. *Open circuit potential variation with immersion time*

It is important to provide steady state conditions on the electrode surface, before recording the potentiodynamic polarization and electrochemical impedance spectroscopy measurements. The variation of open circuit potential (vs. Ag/AgCl reference electrode) as a function of immersion time is given in Fig. 2, in the absence and presence of various inhibitor concentrations. In the absence of inhibitor, the initial open circuit potential was −0.546 V (vs. Ag/AgCl) and this value becomes almost constant value after 2500 s. In presence of inhibitor solutions, open circuit potential value shifts toward more positive potentials during the immersion period. This case could be attributed to the adsorption of inhibitor molecules on the metal surface. When the inhibitor molecules adsorb on the surface via their negatively charged functional groups, the metal surface become positively charged. Therefore, the potential shift toward positive region is meaningful. For reaching a steady state, the required immersion period was slightly different for various inhibitor concentrations, therefore 1 h was utilized for all conditions, in order to equalize pre-treatment conditions. The potentiodynamic polarization and electrochemical impedance spectroscopy measurements were recorded after the achievement of the steady state condition.

3.2. *Potentiodynamic polarization measurements*

The potentiodynamic measurements which give information to learn more about corrosion inhibition mechanism were carried out. PD measurement results of mild steel recorded in 0.5 M HCl solution in absence and presence of different inhibitor concentration at 25 °C is shown in Fig 3. Both anodic and cathodic current values decreased gradually with increasing inhibitor concentration. In the case of 5.0 mM and 10.0 mM inhibitor concentrations, the anodic current value tended to remain significantly lower in a wide poten-