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Electroanalytical, quantum and surface characterization studies on imidazole derivatives as corrosion inhibitors for aluminum in acidic media

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ABSTRACT

In this study, the effect of imidazole derivatives on the inhibition of aluminum corrosion in 0.5 M HCl has been studied using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) measurements. The results show that all imidazole derivatives are good inhibitors, and inhibition efficiency follows the order: B > A. Polarization curves demonstrated that the imidazole derivatives were of mixed-type inhibitors. The adsorption of each inhibitor on aluminum surface obeys Frumkin adsorption isotherm. Surface morphology studies were done using scanning electron microscopy (SEM) to characterize the film formed on aluminum surface. Quantum chemical calculations show that imidazole derivatives can adsorb on the aluminum surface through the nitrogen atoms as well as π-electrons in the imidazole ring.

1. Introduction

Aluminum is commercially an important metal and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries because of their advantages. Many authors were devoted to study the corrosion of aluminum in different aqueous solutions. Hydrochloric acid solutions are used for pickling of aluminum for its chemical or electrochemical etching. It is very important to add a corrosion inhibitor to decrease the rate of aluminum dissolution in such solutions [1–3]. So, numerous researches used organic compounds containing heteroatom such as O, N, and S as a corrosion inhibitors of aluminum in acidic solutions [4–10]. In the present work, the corrosion inhibition of aluminum in 0.5 M HCl solution was investigated by imidazole derivatives using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) methods. Scanning electron microscopy (SEM) was studied to investigate the film formed on the metal surface. In addition, *DMol*^{3} numerical DFT were carried out to support the adsorption mechanism with the molecular structure of imidazole derivatives [11–17].

2. Experimental

2.1. Material preparation

The pure aluminum (99.99%) used for this study as a working electrode was obtained from Sigma-Aldrich. Imidazole derivatives used for inhibition of aluminum from corrosion were obtained from Sigma-Aldrich Company. Fig. 1 shows the molecular structure of imidazole derivatives. Stock solutions (10^{-2} M) of inhibitors were prepared by dissolving an accurately weighed quantity of each inhibitor in (100 mL) absolute ethanol, and then the required concentrations of inhibitors (3×10^{-5}–18×10^{-5} M) were prepared by dilution with distilled water. The aggressive solution of 0.5 M HCl was prepared by dilution of analytical grade 37% HCl with distilled water.

2.2. Electrochemical measurements

The electrochemical measurements were performed in a conventional three-electrode cell with a platinum counter electrode (CE), a saturated calomel electrode (SCE) as the reference electrode and the aluminum as working electrode (WE) which was in a cylindrical form welded with Cu-wire for electrical connection embedded in a glass tube of appropriate diameter using epoxy resin to offer an active flat disc shaped surface of (0.5 cm^2) geometric area, to contact the test solution. Before each experiment, the WE surface area was abraded

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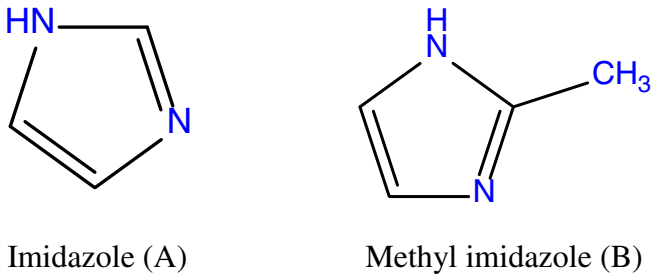

Fig. 1. Chemical molecular structure of imidazole derivatives.

with emery paper (grades 320–500–800) on test face, rinsed with distilled water, degreased with acetone, and dried with a cold air stream. Before measurement the electrode was immersed in test solution at open circuit potential (OCP) for 30 min at 30 °C to attain a stable state. All electrochemical measurements were carried out using a Gamry PCI4G750 Potentiostat/Galvanostat/ZRA analyzer, with a Gamry framework system based on ESA400 connected to a personal computer. Gamry applications include dc105 for dc corrosion measurements, EIS300 for EIS measurements and EFM140 for EFM measurements along with a computer for collecting data. Echem Analyst 5.5 software was used for plotting, graphing and fitting data. Each run was carried out in aerated solutions at the required temperature, using a water thermostat. The potential of potentiodynamic polarization curves was done from a potential of −250 mV vs. OCP, to 250 mV vs. OCP at a sweep rate of 0.5 mV s^{-1}. Inhibition efficiency (IE_p%) and the surface coverages (θ) are defined as [18]:

$$IE_p\% = \theta \times 100 = \left(\frac{I_{corr} - I_{inh}}{I_{corr}}\right) \times 100 \quad (1)$$

where I_{corr} and I_{inh} represent corrosion current density values without and with inhibitor, respectively. Electrochemical impedance spectroscopy (EIS) was carried out at OCP in the frequency range of 10 mHz–100 kHz using a 10 mV peak-to-peak voltage excitation. Inhibition efficiency (IE_{EIS}%) and the surface coverages (θ) are calculated on the basis of the equation [19]:

$$IE_{EIS}\% = \theta \times 100 = \left(\frac{R_{ct} - R^{\circ}_{ct}}{R_{ct}}\right) \times 100 \quad (2)$$

where R°_{ct} and R_{ct} are the charge transfer resistance values without and with inhibitor, respectively. EFM carried out using two frequencies 2.0 and 5.0 Hz. The base frequency was 1.0 Hz. We use a perturbation signal with amplitude of 10 mV for both perturbation frequencies of 2.0 and 5.0 Hz [18]. Inhibition efficiency (IE_{EFM}%) and the surface coverages (θ) were calculated using the following the equation:

$$IE_{EFM}\% = \theta \times 100 = \left(\frac{I^{\circ}_{corr} - I_{corr}}{I^{\circ}_{corr}}\right) \times 100 \quad (3)$$

2.3. Morphology of surface examination

The scanning electron microscope (SEM) analysis is used for the examination of surface of Al specimens, and it is carried out with SEM, JOEL, JSM-T20, Japan. Prior to analysis, the Al specimens were immersed in 0.5 M HCl solutions without and with addition of 18×10^{-5} M of inhibitors at 30 °C for 24 h. After that, the specimens were rinsed with distilled water, dried with a cold air steam, and then examined.

3. Quantum chemical calculations

The quantum chemical calculation was performed using Materials Studio 5.0 program [20]. *DMol*^{3} numerical DFT method was employed to obtain the optimized geometry of investigated inhibitors. Then the molecule's frontier orbital was expressed as relative density distribution figures. *DMol*^{3} contains certain COSMO controls which allow for the solvation effects treatment. Hence, the quantum chemical calculations for investigated imidazole derivatives were performed in liquid phase. *DMol*^{3} numerical DFT theory used in this study has been reported by other authors and was shown to give good results [13].

4. Results and discussion

4.1. Potentiodynamic polarization measurement

Potentiodynamic polarization curves for aluminum in 0.5 M HCl containing various concentrations of inhibitor (B) at 30 °C are shown in Fig. 2. A similar polarization curve (not shown) was obtained for inhibitor (A). It can be observed that from Fig. 2, both the cathodic and anodic reactions were suppressed with the addition of inhibitor, which suggested that the imidazole derivatives reduced anodic dissolution and also retarded the hydrogen evolution reaction [21]. The intersection of Tafel regions of cathodic and anodic branches gives the corrosion current density (I_{corr}) and the corrosion potential (E_{corr}). The values of cathodic (β_c) and anodic (β_a) Tafel constants were calculated from slopes of the linear region of the polarization curves. The values of electrochemical kinetic parameters of imidazole derivatives obtained from analysis Tafel slopes, as well as the inhibition effeminacy (IE_p%) are listed in Table 1. It can be seen from this table that no definite trend was observed in the shift of E_{corr} values, which suggested that the imidazole derivatives act as mixed-type corrosion inhibitors for aluminum in 0.5 M HCl solution [22]. The anodic and cathodic Tafel slopes slightly changed in the presence of the imidazole derivatives, which suggesting that the inhibitors were first adsorbed onto the Surface of metal and impeded by merely blocking the reaction sites of the metal surface without affecting the anodic and cathodic reaction mechanism [23]. For imidazole derivatives, the common ground was that the corrosion current density (I_{corr}) decreased and the inhibition efficiency increased with increasing inhibitors concentration, and the order of the imidazole derivatives according to their inhibition efficiencies are in the following sequence: B > A.

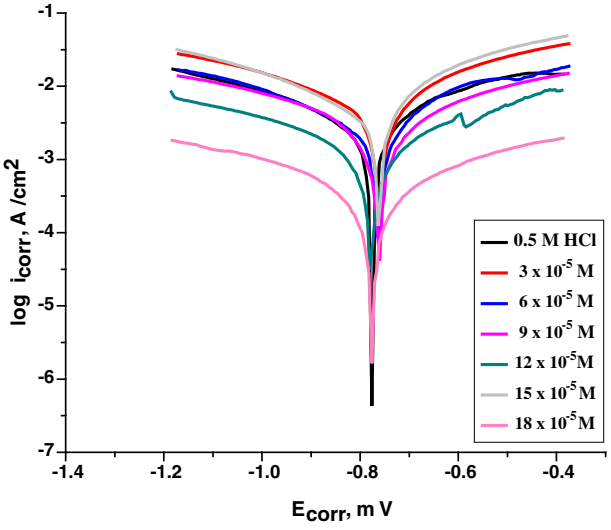

Fig. 2. Potentiodynamic polarization curves for the corrosion of aluminum in 0.5 M HCl in absence and presence of different concentrations of inhibitor (B) at 30 °C.