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Corrosion inhibition and adsorption behavior of methionine on mild steel in sulfuric acid and synergistic effect of iodide ion

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Abstract

The corrosion inhibition of mild steel in sulfuric acid by methionine (MTI) was investigated using electrochemical techniques. The effect of KI additives on corrosion inhibition efficiency was also studied. The results reveal that MTI inhibited the corrosion reaction by adsorption onto the metal/solution interface. Inhibition efficiency increased with MTI concentration and synergistically increased in the presence of KI, with an optimum [KI]/[MTI] ratio of 5/5, due to stabilization of adsorbed MTI cations as revealed by AFM surface morphological images. Potentiodynamic polarization data suggest that the compound functioned via a mixed-inhibition mechanism. This observation was further corroborated by the fit of the experimental adsorption data to the Temkin and Langmuir isotherms. The inhibition mechanism has been discussed vis-à-vis the presence of both nitrogen and sulfur atoms in the MTI molecule.

Keywords: Mild steel; Corrosion inhibition; Adsorption; Amino acid; Iodide ion; Synergism

1. Introduction

Excessive corrosion attack is known to occur on mild steel surfaces deployed in service in aqueous acidic environments. In efforts to mitigate electrochemical corrosion, the primary strategy is to isolate the metal from corrosive agents. A useful method for achieving in this is addition of species to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate. Owing to increasing ecological awareness and strict environmental regulations and the need to develop environmentally friendly processes, attention is now focused on the development of substitute nontoxic alternatives to inorganic inhibitors applied earlier. Natural products extracted from plant sources [1–5], as well as some nontoxic organic compounds, which contain polar functions with nitrogen, oxygen, and/or sulfur in conjugated systems in their molecules [6–12], have been effectively used as inhibitors in many corrosion systems. The inhibiting action of such compounds is attributed as a first stage to the adsorption of the additives to the metal/solution interface. Inhibitor adsorption on mild steel in acid solutions usually leads to a structural modification in the double layer with subsequent reduction in the rates of the electrochemical half-cell reactions—the anodic metal dissolution and the cathodic reduction of hydrogen ions. To further upgrade the performance of organic inhibitors, extensive studies have been undertaken to identify synergistic effects of other additives. Interestingly, addition of halide ions to sulfuric acid solutions containing some organic compound has been reported to yield the required enhancement [9–14].

The roles of the individual functional groups in the inhibition mechanism of organic molecules have been widely reported, but the effect of having two different groups in one molecule, which may influence the corrosion process by different mechanisms, has not been properly documented and is an important consideration in this study. The test inhibitor for the present study is methionine [CH_3–S–CH_2–CH_2–CH(CO_2H)NH_2], an amino acid containing both the (–NH_2) and (–S–CH_3) groups in its molecule. Amino acids are attractive as corrosion inhibitors because they are relatively easy to produce with high purity at

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low cost and are soluble in aqueous media. Ashassi-Sorkhabi et al. [15] reported the successful application of methionine as a corrosion inhibitor for aluminum in mixed acid solution and pointed out the role of the S atom in increasing the interaction of the molecule with the metal surface. Morad et al. [5], in their study of the inhibiting effect of methionine on mild steel corrosion in phosphoric acid, observed that adsorption of the compound onto the metal surface obeyed the Frumkin isotherm with an adsorption free energy ($\Delta G^0_{\mathrm{ads}}$) value of 25.4 $\mathrm{kJ\,mol^{-1}}$.

The present study investigates the inhibition mechanism of methionine on mild steel corrosion in sulfuric acid solution using electrochemical techniques. In addition to providing information on the corrosion rate, electrochemical techniques are well suited for monitoring in situ any perturbation by an inhibitor with respect to electrochemical processes in the metal/corrodent interface. The influence of iodide ions on the adsorption and corrosion-inhibitive properties of methionine has also been studied in order to ascertain the specific mode (ionic or molecular) in which the compound exerts its inhibiting action. Morphological changes on the corroding steel surface have been visualized by atomic force microscopy (AFM).

2. Experimental

Tests were performed on a mild steel specimen of the percentage composition C: 0.22; Si: 0.1–0.3; Mn: 0.6; P: 0.045. This was machined into test electrodes of dimension 1 × 1 cm and fixed in polytetrafluoroethylene (PTFE) rods by epoxy resin in such a way that only one surface, of area 1 $\mathrm{cm^2}$, was left uncovered. The exposed surface was wet-polished with silicon carbide abrasive paper (from grade #200 to #1000), degreased in acetone, rinsed with distilled water, and dried in warm air. The aggressive solution was 0.5 M H_2SO_4 solution, prepared from analytical reagent grade sulfuric acid and distilled water. The test inhibitor methionine (MTI), obtained from (SCRC, China), was dissolved in 0.5 M H_2SO_4 solution to obtain the desired concentration (0.05–10 mM). Potassium iodide solutions (0.5–5.0 mM) were prepared in the blank corrodent and in 5.0 mM MTI.

Electrochemical experiments were conducted in a conventional three-electrode glass cell of capacity 400 ml, using a PARC Parstat-2273 Advanced Electrochemical System. A platinum foil was used as counterelectrode and a saturated calomel electrode (SCE) as reference electrode. The latter was connected via a Luggin's capillary. Electrochemical impedance spectroscopy (EIS) tests were performed at the end of 30 min of immersion at 30 ± 1 °C. Measurements were made at corrosion potentials (E_{corr}) over a frequency range of 100 kHz–10 MHz, with a signal amplitude perturbation of 5 mV. The data were collected using Powersine software and interpreted with Zsimpwin software, also supplied by PARC. Polarization studies were carried out after the EIS tests with Powercorr software in the potential range ±250 mV versus corrosion potential (E_{corr}) at a scan rate of 0.333 $\mathrm{mV\,s^{-1}}$. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (i_{corr}). Each test was run in triplicate to verify the reproducibility and the average values reported.

Morphological studies of the mild steel electrode surface were undertaken by atomic force microscopy, AFM (PicoPlus scanning probe microscope, Molecular Imaging Corp.). AFM images were realized in tapping mode at room temperature. Mild steel specimens of dimensions 15 × 10 × 2 mm were cleaned as previously described and immersed for 3 h in the blank solution (0.5 M H_2SO_4) and in 5.0 mM MTI and 5.0 mM MTI + 5.0 mM KI solutions at 30 ± 2 °C, and then washed with distilled water, dried in warm air, and submitted for AFM surface examination.

3. Results and discussion

3.1. Corrosion inhibition by methionine (MTI)

Measurements were undertaken to assess the impedance parameters of the mild steel/electrolyte interface in the presence of different concentrations of MTI. Representative examples of the impedance spectra are given in Fig. 1, panels a, b, and c, which exemplify, respectively, the Nyquist, Bode, and phase-angle plots obtained for mild steel in 0.5 M H_2SO_4 solution in the absence and presence of 0.05–10 mM MTI. The spectra obtained without and with inhibitor consist of one depressed capacitive loop corresponding to one time constant in the Bode plots. The high-frequency part of the impedance and phase angle describes the behavior of an inhomogeneous surface layer, whereas the low-frequency component depicts the kinetic response for the charge transfer reaction [16]. It is observed that increasing the concentration of MTI results in an increase in the size of the semicircle in Fig. 1a, in the impedance of the interface in Fig. 1b, and in the maximum phase angle in Fig. 1c, which indicate inhibition of the corrosion process. The impedance spectra for the Nyquist plots were analyzed by fitting to the equivalent circuit model shown in Fig. 2, which has been used previously to model the mild steel/acid interface [17,18]. The circuit comprises a solution resistance R_{s} shorted by a constant phase element (CPE) that is placed in parallel to the charge transfer resistance R_{ct}. The value of the charge transfer resistance is indicative of electron transfer across the interface. The use of the CPE, defined by the values Q and n, has been extensively described in the literature [19,20] and is employed in the model to compensate for the inhomogeneities in the electrode surface as depicted by the depressed nature of the Nyquist semicircle. The introduction of such a CPE is often used to interpret data for rough solid electrodes. The impedance, Z, of the CPE is [19,20]

$$Z_{\mathrm{CPE}} = Q^{-1}(j\omega)^{-n}, \tag{1}$$

where Q and n stand for the CPE constant and exponent, respectively, $j = (-1)^{1/2}$ is an imaginary number, and ω is the angular frequency in $\mathrm{rad\,s^{-1}}$ ($\omega = 2\pi f$ when f is the frequency in Hz). The values of the double-layer capacitance, C_{dl}, were obtained at the frequency at which the imaginary component of