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Corrosion inhibitor binding in an acidic medium: Interaction of 2-mercaptobenizmidazole with carbon-steel in hydrochloric acid

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ABSTRACT

Mechanistic understanding of the functionality of organic corrosion inhibitors in acidic media is essential to knowledge-based performance optimization. In this study, we address a key issue hindering progress in this area, namely the chemical nature of the corrosion inhibitor/substrate interface. X-ray photoelectron spectroscopy (XPS) is employed to reveal the surface termination of carbon-steel, following immersion in 1 M hydrochloric acid inhibited with 2-mercaptobenzimidazole (MBI). Core level spectra indicate that the termination varies as a function of MBI concentration, with the interface consisting of MBI bound to film-free carbon-steel on highly inhibited substrates.

1. Introduction

For more than a century, corrosion inhibitors have been added to aggressive environments to protect metallic materials [1]. Nevertheless, there are still considerable gaps in fundamental knowledge of corrosion inhibitor (CI) functionality, severely restricting rational development [2–7]. One outstanding issue is the precise nature of the interfaces formed by inhibitive organic species in corrosive acidic solutions, which are widely encountered in engineering applications, e.g. chemical processing and oil production. It is generally accepted that inhibition in this environment is normally achieved by formation of an adsorbed 2D layer [2], but rudimentary details key to mechanistic understanding remain speculative, including the nature of the organic-CI/substrate interface. Recent experimental evidence suggests that a surface oxide, hydroxide or salt film may facilitate corrosion inhibitor binding [8–10], although direct attachment to the metallic substrate is implicitly assumed in other contemporary work [3,6,7]. Here, we employ X-ray photoelectron spectroscopy (XPS) to provide direct experimental evidence of the latter scenario, i.e. organic species can inhibit corrosion through binding to film-free substrate.

A variety of factors determine the functionality of organic compounds as corrosion inhibitors, with one of the most important being the strength of substrate binding [1,2]. Stronger interfacial bonding largely equates to increased inhibition efficiency, and is therefore a desirable goal of corrosion inhibitor optimisation. On this basis, significant effort is directed towards predicting this interaction through theoretical modeling [5–7,11–15]. To date, however, the vast majority of such work has been concerned solely with calculating supposedly relevant organic-CI characteristics, with no consideration of the substrate (see, for example, [11] and references therein, and [12,13]). In terms of predictive power, such an approach has at best limited value, and is potentially simply misleading. Attempting to overcome this shortcoming, some theoretical studies have explicitly incorporated organic-CI/substrate bonding into their modelling e.g. [5–7,14,15]. Such studies are much more likely to deliver valid predictions, although a lack of reliable experimental input data (e.g. nature of the organic-CI/substrate interface) hinders their applicability.

In this study, XPS is employed to reveal the interface formed between an organic-CI, 2-mercaptobenzimidazole (MBI), and carbon-steel in 1 M hydrochloric acid; complementary electrochemical measurements are undertaken to evaluate the performance of MBI as a corrosion inhibitor under the prevailing conditions. Motivation for selecting this specific system is that the effectiveness of MBI as a corrosion inhibitor for carbon-steel in acidic environments has already been proven by means of both gravimetric and electrochemical studies [16–22]. Most pertinently, it has been determined that MBI significantly inhibits the corrosion of carbon steel in 1 M HCl [16,18,20–22]. In this medium, it is concluded that MBI acts by binding to the carbon-steel substrate, and thermodynamic parameters governing this process (e.g. free energy of adsorption) have been estimated. Furthermore, it is reported that

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MBI behaves as a mixed inhibitor, i.e. both the rate of the anodic (Fe^0 oxidation) and cathodic (H^+ reduction) reactions are reduced. These previous studies [16,18,20–22], however, do not provide any insight into the chemical nature of the MBI/carbon-steel interface, which is the goal of this study.

2. Materials and methods

Cylindrical carbon-steel rod (10 mm diameter), possessing a nominal weight% composition (as specified by the supplier, RS Components) of C (0.08–0.13), Mn (0.30–0.50), P (0.04), S (0.05), and Fe (balance), was employed for both electrochemical and XPS studies. For the former measurements, samples were mounted in epoxy resin (exposed area 0.79 cm^2), ground with a series of SiC papers (250 grit, 400 grit, 600 grit, 800 grit) washed with ethanol and de-ionized water, and dried in a flow of air. As regards XPS, samples again underwent grinding with SiC papers (600 grit, 800 grit, 1200 grit, 2400 grit, 4000 grit), and were then polished with either alumina powder or diamond paste (3 μm, and 1 μm) until a mirror finish was obtained. Subsequently, they were washed with acetone and de-ionized water, and dried. 1 M HCl, prepared by diluting 10.2 M HCl with deonised water, served as the corrosive medium, with appropriate quantities of MBI (98% purity, Arcos Organics) added to achieve the required series of concentrations up to 2 mM.

Corrosion rates, and hence inhibition efficiencies (see below for definition), were determined by means of linear polarisation resistance (LPR) measurements [23]. These data were acquired in a 1 L glass cell, using a typical three-electrode arrangement comprising the working electrode (carbon steel), platinum counter electrode, and saturated calomel electrode (SCE) as reference electrode; the latter was located in a separate vessel connected to the primary cell by means of a Luggin probe. A computer-controlled potentiostat (ACM Gill AC 930) was used to acquire the LPR data, employing a sweep rate of 10 mV/min.

XPS was performed in a Kratos Axis Ultra facility (base pressure $\sim 2 \times 10^{-9}$ mbar), equipped with a glove box/load lock system for sample introduction. Samples for XPS analysis were immersed in solution inside the N_2-purged glove box, and subsequently removed and inserted directly into the XPS instrument. This approach circumvents exposure to the ambient laboratory atmosphere, avoiding likely post immersion substrate oxidation. It should be noted that upon removal of a sample from solution, it was blown-dry with a stream of nitrogen to prevent evaporation and subsequent physical deposition of solution components onto the sample surface. For acquisition of XPS data, monochromated Al Kα X-rays ($h\nu = 1486.6$ eV, $\Delta h\nu \sim 0.6$ eV) were employed as the photon source. Emitted photoelectrons were collected using a 165 mm hemispherical energy analyser incorporating a delay line detection system (analysis area ~ 3 mm $\times$ 2 mm, using electrostatic lens mode). Data were acquired at an analyser pass energy of 20 eV. Two photoelectron emission angles (θ_E), namely 0° (emission along the surface normal) and 50°, were utilised during the measurements. The angle subtended by the X-ray beam and the entrance lens of the analyser was 60°, and the sample holder's rotation axis was perpendicular to the plane containing these two elements. To prevent any vertical differential charging due to the presence of oxide surface films, samples were mounted using vacuum compatible double-sided adhesive tape. Charge accumulation during data collection was compensated by exposing samples to a flood of low energy electrons (⩽3 eV). BEs were calibrated by assigning a BE value of 285 eV to the C 1s hydrocarbon component of adsorbed adventitious carbon [24].

Fitting of XPS profiles was undertaken with CasaXPS software [25]. Gaussian–Lorentzian (GL) line shape functions (30% Lorentzian) were employed to model all of the photoelectron peaks except for the Fe 2p level of metallic iron, where a Lorentzian asymmetric line shape with tail damping (LF) was used. In accord with previous work, only the Fe $2p_{3/2}$ component of the Fe 2p spectra was fitted [24]. For fitting of Fe^{2+} and Fe^{3+} states, multiplet envelopes consisting of 3 and 4 GL functions, respectively, and two broader GL functions for satellite peaks have been employed [24,26]. Inelastically scattered background electrons were described with a Shirley-type function [27].

3. Results and discussion

To demonstrate the functionality of MBI under the conditions prevailing in this study, the corrosion inhibition efficiency (η%) of this species for carbon-steel in 1 M HCl (4 h of immersion) is plotted as a function of its concentration in bulk solution in Fig. 1. η% is defined as:

$$\eta\% = \frac{(U - I)}{U} \times 100; \quad (1)$$

U (I) is the uninhibited (inhibited) corrosion rate. As is typical for such systems [2], the corrosion inhibition efficiency of MBI increases asymptotically with its concentration in bulk solution. Moreover, in agreement with previous studies of the corrosion inhibition performance of MBI in acidic solution [16–22], these data indicate that it is a very effective corrosion inhibitor; corrosion rate is reduced from $\sim$ 27 mm/year to $\sim$0.4 mm/year (IE $\sim$ 99%) for the largest MBI concentration (2 mM) studied.

Concerning the chemical composition of the inhibited interfaces, Fig. 2 depicts XPS spectra of the N 1s, O 1s, Fe 2p, and Cl 2p core levels acquired from carbon-steel samples subsequent to immersion in 1 M HCl with various concentrations of MBI added (0–2 mM). Spectra from a polished sample are also shown. Focusing on the N 1s spectra (Fig. 2(a)), it is clear that significant intensity is obtained only once the carbon-steel has been exposed to MBI, which then increases with MBI concentration. Fitting of these data reveals three peaks, labeled N^1, N^2, and N^3. Most simply, the two most intense peaks, N^1 and N^2, located at binding energies (BE) of $\sim$399.0 eV and $\sim$400.6 eV can be assigned, respectively, to the two chemically distinct nitrogen atoms (i.e. pyridine-like and

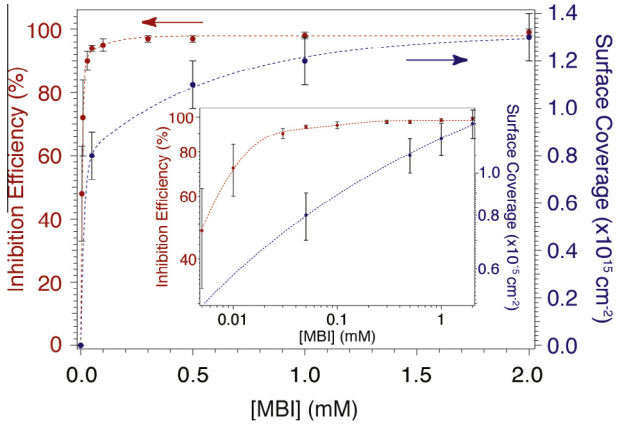

Fig. 1. Inhibition efficiency (red markers) and MBI surface coverage (blue markers) as a function of MBI concentration in bulk solution for carbon-steel after 4 h of immersion in 1 M HCl. Each value of inhibition efficiency has been calculated on the basis of two or more corrosion rate determinations (different samples) at each concentration of MBI (0–2 mM); error bars indicate the associated standard deviation. Displayed errors in MBI surface coverage have been derived from the uncertainty in the intensity of core level peaks. Inset shows the same data but on a log–log plot. Dashed lines act as guides for the eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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