



Corrosion inhibition of carbon-steel with 2-mercaptobenzimidazole in hydrochloric acid



P. Morales-Gil^{a,1}, M.S. Walczak^a, C. Ruiz Camargo^a, R.A. Cottis^a, J.M. Romero^b, R. Lindsay^{a,*}

^a Corrosion and Protection Centre, School of Materials, The University of Manchester, Sackville Street, Manchester M13 9PL, UK

^b Coordinación Tecnológica de Ingeniería de Corrosión y Producción, Dirección de Exploración y Producción, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, CP 07730 DF, Mexico

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ABSTRACT

Electrochemical measurements and substrate analysis have been employed to probe the corrosion inhibition performance of 2-mercaptobenzimidazole (MBI) for carbon-steel in 1 M, 0.1 M, and 0.01 M HCl. Data demonstrate that the inhibition efficiency of MBI is essentially independent of HCl concentration. Moreover, it is concluded that the presence of MBI impedes the cathodic reduction of dissolved O₂ to a lesser extent than H⁺. X-ray photoelectron spectra indicate that substrate termination varies as a function of both HCl and MBI concentration, with the interface consisting of MBI bound to film-free carbon-steel on highly inhibited substrates.

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1. Introduction

The use of organic compounds to inhibit corrosion in acidic solutions is of immense technical value in a number of industrial sectors, including oil production and chemical processing [1–4]. Given this importance, significant effort continues to be directed towards improving the inhibition exhibited by such species, ranging from searching for new active molecules [5–8] to studies targeting mechanistic elucidation [9–12]. Despite the latter effort, however, there is still much uncertainty as regards organic corrosion inhibitor performance at the molecular scale, restricting knowledge-based advancement. Here, we contribute to progress in this area through detailed characterisation of the functionality of 2-mercaptobenzimidazole (MBI; C₇H₆N₂S) as a corrosion inhibitor for carbon-steel in hydrochloric acid (HCl) solution.

A number of studies concerned with the corrosion inhibition properties of MBI have already been undertaken [12–24]. Results

emerging from these efforts demonstrate that MBI can act as an effective corrosion inhibitor, including significantly retarding the corrosion of carbon-steel in 1 M HCl [12,14,17,19–21]. Electrochemical measurements performed in this medium indicate that MBI behaves as a mixed inhibitor [14,17,19–21]. Furthermore, recent X-ray photoelectron spectroscopy (XPS) data provide insight into the nature of the MBI/carbon-steel interface [12], which is a key component of rigorous mechanistic understanding. Most notably, these data indicate that once significant corrosion inhibition is achieved in 1 M HCl, MBI is adsorbed onto a film-free metallic carbon-steel substrate, i.e. a surface oxide, hydroxide or salt film does not facilitate MBI binding.

In this study, we significantly extend the work carried out to date on the inhibition of carbon-steel with MBI in 1 M HCl [12,14,17,19–21]. Specifically, corrosion inhibition is explored as a function of HCl concentration across three decades (1 M–0.01 M) to assess the impact of this parameter on inhibition performance and interfacial chemistry; we note that the three concentrations of HCl employed here are lower than those typically employed in industrial applications [4]. Furthermore, the significance of the concentration of dissolved O₂ is explored. Anodic and cathodic corrosion processes are characterised by means of potentiodynamic polarisation (PDP) measurements. Corrosion rates are determined with linear polarisation resistance (LPR). Substrate morphology is probed with scanning electron microscopy

* Corresponding author. Fax: +44 161 306 4865.

E-mail address: robert.lindsay@manchester.ac.uk (R. Lindsay).

¹ Coordinación Tecnológica de Ingeniería de Corrosión y Producción, Dirección de Exploración y Producción, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, CP 07730 DF, Mexico.

(SEM), and XPS is employed to ascertain interfacial chemical composition.

2. Materials and methods

Cylindrical carbon steel rod (10 mm diameter), possessing a nominal (weight%) composition of C (0.08–0.13), Mn (0.30–0.50), P (0.04), S (0.05), and Fe (balance), was employed as the substrate throughout this study. Electron microscopy images demonstrated that this substrate consisted of a ferrite/pearlite microstructure, with a grain size of the order of 10 μm . Prior to the electrochemical measurements (PDP and LPR), samples were mounted in epoxy resin (exposed area of 0.79 cm^2), ground with a series of SiC papers (250 grit, 400 grit, 600 grit, 800 grit), washed with ethanol and deionized water, and dried. 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. They were then washed with acetone and deionised water, and dried. HCl solutions were prepared by diluting 10.2 M HCl (analytical grade, Fisher Scientific) with deionised water, and appropriate quantities of MBI (98% purity, Acros Organics) were added; a maximum concentration of 2 mM MBI was employed, which was found to be just below this compound's solubility limit in the solutions of interest. Unless explicitly stated otherwise, data presented below were acquired from substrates subsequent to 4 h of solution immersion at room temperature in naturally aerated conditions.

PDP and LPR measurements were carried out in a 1 L glass cell using a conventional three-electrode setup comprising a 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 for the electrochemical experiments. To acquire PDP (LPR) data, a scan rate of 120 mV/min (10 mV/min) was employed over the range -250 mV to $+250$ mV (-10 mV to 10 mV) with respect to open circuit potential (OCP); outside of these measurements samples were allowed to remain at OCP during immersion. It should be noted that all PDP curves are presented without compensating for the so-called IR-drop, which is essentially a result of finite solution resistance [25].

For samples subjected to LPR measurements only, substrate morphology was assessed post immersion with SEM (Phillips XL30); such data were not recorded from samples that had undergone PDP scans due to the increased possibility of polarisation-induced substrate modification. Images were recorded from samples after the removal of any adhered corrosion product, which was achieved through gentle scrubbing and washing with deionised water and acetone, followed by drying in a flow of air.

XPS measurements were 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 then inserted directly into the XPS instrument. This approach avoids exposure to the ambient laboratory atmosphere, minimising the likelihood of post immersion substrate oxidation [12]. 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 K α 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). Data were acquired at

an analyser pass energy of 80 eV for wide energy scan overview spectra, and 20 eV for short higher energy resolution spectra of single core levels. 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). Binding energies (BEs) were calibrated by assigning a BE value of 285 eV to the C 1s hydrocarbon component of adsorbed adventitious carbon [26].

Fitting of XPS profiles was undertaken with CasaXPS software [27]. 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 (LF) line shape with tail damping was used. In accord with previous work [26], only the Fe 2p $_{3/2}$ component of the Fe 2p spectra was fitted. 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 [26,28]. One or more spin-orbit split doublets (Cl 2p $_{1/2}$ and Cl 2p $_{3/2}$) were used to fit the Cl 2p core level spectra, with the BE difference and intensity ratio being fixed at expected values [29,30]. Inelastically scattered background electrons were described with a Shirley-type function [31]. MBI surface coverage was estimated from XPS peak intensities acquired at $\theta_E = 0^\circ$ and 50° through the application of expressions derived from standard equations [32]. For this determination, it was assumed that the surface region consists of a topmost layer of adventitious carbon, a 2D layer of MBI (i.e. one molecule thick), and the carbon-steel substrate.

3. Results and discussion

PDP curves for a series of MBI concentrations (0 mM to 2 mM) in 1 M, 0.1 M, and 0.01 M HCl are depicted in Fig. 1(a)–(c), respectively. It can be observed that addition of MBI to all three HCl solutions inhibits corrosion, as indicated by the systematic displacement of the curves towards lower current densities with increasing MBI concentration. Additionally, almost all of the curves exhibit profiles typical for corrosion of carbon-steel in strong acid, where kinetics are activation controlled, i.e. both the anodic and cathodic branches show Tafel-like regions [33].

Focusing on the PDP data acquired in 1 M and 0.1 M HCl, there is no significant change in the open circuit potential (OCP) with MBI concentration. Consistent with previous work [14,17,19–21], this result is indicative of MBI acting as a mixed-type corrosion inhibitor, i.e. the cathodic and anodic reactions are both impeded to a similar extent [2]. Furthermore, the gradients of both the anodic and cathodic branches do not vary significantly with MBI concentration, suggesting that inhibition is achieved largely through simply blocking active anodic/cathodic sites [34].

In contrast to the similar behaviour of the PDP curves for 1 M and 0.1 M HCl (Fig. 1(a) and (b)), a somewhat different trend is observed for 0.01 M HCl (Fig. 1(c)). Firstly, the OCP shifts towards more positive values at higher MBI concentrations. This change is accompanied by a reduction in the effect of MBI on the cathodic reaction, suggesting that in these environments (i.e. higher MBI and lower HCl concentrations), MBI inhibits anodic dissolution more than the dominant cathodic reaction, implying that the cathodic reaction may be changing. In addition, there is a clear change in the profile of the cathodic branch at 2 mM MBI concentration, i.e. the gradient becomes significantly steeper. As all measurements were

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