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

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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 O_2 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.

Keywords: Acid inhibition; Carbon steel; Polarization; XPS; SEM

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; $C_7H_6N_2S$) 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 O_2 is

explored. Anodic and cathodic corrosion processes are characterised by means of potentiodynamic polarization (PDP) measurements. Corrosion rates are determined with linear polarisation resistance (LPR). Substrate morphology is probed with scanning electron microscopy (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 de-ionized 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 1L 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 N₂-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 x 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 Fe²⁺ and Fe³⁺ 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 1M, 0.1 M, and 0.01 M HCl are depicted in Figures 1 (a), (b), and (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 1M and 0.1 M HCl (Figures 1 (a) and (b)), a somewhat different trend is observed for 0.01 M HCl (Figure 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 undertaken in naturally aerated solutions, we hypothesise that this change in the cathodic branch may be a result of O₂ reduction becoming a significant cathodic reaction at higher MBI concentrations; O₂ reduction is a diffusion-controlled process under the current experimental conditions, and so should display a limiting cathodic current, i.e. gradient would approach infinity [35] (this behaviour is somewhat obscured in this case by the increasing current density associated with proton reduction).

To test the hypothesis that the observed change in the profile of the cathodic branch of the PDP curves acquired in 0.01 M HCl at higher MBI concentrations is indeed a result of dissolved O₂ becoming a significant cathodic reactant, additional data were recorded in deaerated solutions. Deaeration was achieved by bubbling high purity N₂ through the solution of interest prior to measuring; bubbling was discontinued once a carbon-steel sample

had been immersed. Care was taken to avoid oxygen ingress into the electrochemical cell by sealing any open ports, and employing a Drechsel-bottle to exhaust the N₂. Dissolved O₂ concentration ([O₂(aq)]) was monitored with an electrochemical sensor (Orbisphere, Hach Lange), which indicated that the deaeration procedure reduced [O₂(aq)] from ~ 7000 ppb to ~ 20 ppb.

PDP curves acquired in both naturally aerated and deaerated solutions of 1M, 0.1 M, and 0.01 M HCl, containing either 0 mM or 2 mM MBI, are compared in Figure 2. Concerning 1 M and 0.1 M HCl (Figure 2 (a) and (b)), it is evident that variation in [O₂(aq)] does not impact significantly on the PDP data. In contrast, for 0.01 M HCl (Figure 2 (c)) deaeration does lead to modification of the PDP curves. Most strikingly, the cathodic branch retains a gradient similar to that obtained in the absence of MBI. This result is consistent with O₂ reduction becoming a significant cathodic reaction at higher MBI concentrations in naturally aerated 0.01 M HCl.

It should be pointed out that the lack of any substantial change in the profiles of the cathodic branches in 1 M and 0.1 M HCl is almost certainly simply due to the increased H⁺ concentration and corresponding corrosion rates. This conclusion is derived from the following assumptions, i.e. O₂ reduction in aerated conditions is occurring at all three HCl concentrations; the oxygen concentration is approximately the same in all concentrations of HCl [36]; and the mass transport conditions are the same for all tests. Given that these three statements are valid, the corrosion rate due to O₂ reduction in all of the solutions studied here is expected to be essentially identical. Quantitatively, this corrosion rate is estimated to be approximately 0.1 mm/y. This value is obtained from the corrosion rate (corrosion current density ~ 8 x 10⁻⁶ A/cm²) exhibited in aerated *0.01 M HCl/2 mM MBI*, since the rate of hydrogen evolution is much lower in this condition, as evidenced by the far more positive OCP. 0.1 mm/y is less than the measured corrosion rates for all concentrations of MBI in 1 M and 0.1 M HCl, and so the contribution of O₂ reduction is not so evident in the PDP data. Note, however, the small increase in corrosion potential in the aerated solutions of 0.1 M

HCl/2mM MBI and 1 M HCl/2mM MBI, which may be due to the oxygen reduction reaction contributing a moderate amount to the net cathodic reaction.

Given that in 0.01 M HCl O_2 reduction becomes a significant cathodic reaction at 2 mM MBI concentration, it can be concluded that this reaction is not inhibited to the same extent as H^+ reduction; if inhibition efficiency were similar for both reactions then the cathodic branch would not change profile. This difference in behaviour is reasonable; there is a far larger driving force for the oxygen reduction reaction, so the reaction kinetics will be much faster, and the rate will remain mass-transport controlled even when the availability of active sites has been markedly reduced by inhibitor adsorption.

Corrosion rate values (determined from LPR data after 4 h immersion) of carbon-steel as a function of MBI concentration in 1 M, 0.1 M, and 0.01 M HCl are plotted (blue markers) in Figures 3 (a), (b), and (c), respectively. As expected, the corrosion rate in the absence of MBI (0 mM) decreases in line with HCl concentration, i.e. ~ 26.9 mm/y (1 M HCl), ~ 7.2 mm/y (0.1 M HCl), and ~ 2.2 mm/y (0.01 M HCl). Addition of MBI leads to significant corrosion inhibition in all three HCl solutions, with the corrosion rate decreasing asymptotically towards a limiting value with increasing MBI concentration. For a MBI concentration of 2mM (maximum studied) the corrosion rate was determined to be ~ 0.4 mm/y (1 M HCl), ~ 0.2 mm/y (0.1 M HCl), and ~ 0.1 mm/y (0.01 M HCl). In order to determine corrosion rates from the LPR data, a Stern-Geary coefficient (B) of 26 mV/decade was employed for samples exhibiting activation controlled kinetics. For substrates immersed in 0.01 M HCl containing higher concentrations of MBI, where the cathodic branch changes profile due to the increasing significance of O_2 reduction, inspection of the PDP data resulted in $B = 30$ mV/decade being used to determine the corrosion rate. It should be noted that strictly speaking [33] one criterion for determination of corrosion rates from LPR data is that there should only be one anodic reaction and one cathodic reaction. On the basis that H^+ reduction dominates O_2 reduction (as discussed above) for most of the LPR data acquired in this study, the requirement of only one cathodic reaction occurring is

essentially valid, with some errors possible for corrosion rates below 1 mm/y. Regarding the LPR data where the contribution of O_2 reduction is more substantial, there is likely to be some systematic error in the corrosion rate determination, but it is not expected to be too significant and probably less than 0.1 mm/y, the rate attributable to oxygen reduction.

Inspection of the carbon steel substrates subsequent to immersion also clearly reveals the impact of MBI. Illustrating this point, Figure 4 displays photographs of (a) polished sample, (b) sample immersed in *1 M HCl/0 mM MBI*, and (c) sample immersed in *1 M HCl/2 mM MBI*. Both the polished sample and that immersed in *1 M HCl/2 mM MBI* exhibit bright metallic-silver surfaces. In sharp contrast, the sample immersed in *1 M HCl/0 mM MBI* is black in colour. Consistent with the corrosion rate data, these observations indicate that substrate degradation is greatly reduced in the presence of 2 mM MBI. The black colour of the *1 M HCl/0 mM MBI* sample is attributed to surface accumulation of cementite (Fe_3C) and adhered corrosion products; cementite is one of the two phases that form the pearlite component of the substrate microstructure, which is not expected to undergo anodic dissolution.

Further direct evidence of significant substrate degradation is provided by SEM images. Analogous to Figure 4, Figure 5 displays SEM images (secondary electron mode), acquired following the removal of any adhered corrosion scale, from (a) polished sample, (b) sample immersed in *1 M HCl/0 mM MBI*, and (c) sample immersed in *1 M HCl/2 mM MBI*. In comparison to the rather featureless image of the polished sample, the sample immersed in *1 M HCl/0 mM MBI* exhibits considerable surface roughness, indicative of general substrate corrosion. The SEM image of the sample immersed in *1 M HCl/2 mM MBI* is not identical to that of the polished surface, i.e. some features are apparent, which are probably a consequence of the small, but finite, inhibited corrosion rate (~ 0.4 mm/y). However, in comparison to the sample immersed in 1 M HCl without MBI, this substrate appears relatively flat.

To more directly compare the performance of MBI as a function of concentration in each of the three HCl solutions, its inhibition efficiency ($\eta\%$) has been determined, which is defined as follows:

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

U (I) is the uninhibited (inhibited) corrosion rate. $\eta\%$ is plotted (red markers) in Figures 3 (a), (b), and (c); to facilitate comparison, a horizontal dashed grey line indicating an $\eta\%$ value of 95% has been appended to these graphs. From inspection, the $\eta\%$ of MBI appears to be largely independent of HCl concentration over the range studied, with only a small decrease ($\sim 5\%$) in its maximum value, i.e. from $\sim 98\%$ (1 M HCl) to $\sim 93\%$ (0.01 M HCl), and much of this difference can be attributed to the lack of inhibition of the oxygen reduction reaction. Given that there is a corresponding two orders of magnitude decrease in HCl concentration (1 M to 0.01 M), these data suggest that varying the concentration of the chloride anion does not significantly influence the inhibition performance of the MBI. This result is consistent with that reported by Popova et al. [37]. We note that for some other organic corrosion inhibitors, it has been concluded that halide anions do influence their inhibition performance (see, for example, Ref. 38 and refs. therein).

Turning to the chemical composition of the inhibited interfaces, Figures 6 (a) - (c) show overview XPS spectra ($\theta_E = 0^\circ$) acquired from carbon-steel samples subsequent to immersion in HCl ((a) 1 M, (b) 0.1 M HCl, and (c) 0.01 M) with various concentrations (0 mM - 2 mM) of MBI added. Spectra of polished samples are also displayed. Concerning these latter spectra, there are prominent peaks due to Fe (2p), O (1s), and C (1s) (as indicated by the annotation). In accord with previous work [26], Fe derives from the carbon-steel substrate, O is due to the presence of an oxidic surface film plus adsorbed species, and surface contamination is the source of C.

Immersion in any of the uninhibited HCl solutions (0 mM MBI) leads to significant changes in spectral profile. Firstly, there is a sharp decrease in the intensity of the O 1s signal, suggesting, at least, a thinning of the oxidic surface film. Peaks assigned to Cu (2p), Cl (2p), and S (2p) also appear. On the basis of energy dispersive X-ray spectroscopy (EDX) analysis (not shown), both the Cu 2p and S 2p features originate from minority substrate components, which become apparent following loss of Fe through corrosion. In contrast, the Cl 2p signal can be attributed to substrate bonding of Cl⁻ anions present in solution; this deduction is supported by the observed reduction in Cl 2p intensity as the concentration of HCl is decreased.

Addition of MBI further modifies the spectra in Figures 6 (a) - (c). Most notably, a feature assigned to the N 1s core level appears, which is consistent with MBI (C₇H₆N₂S) binding to the carbon-steel substrate. Independent of HCl concentration, this N 1s peak becomes more intense as MBI concentration in bulk solution increases, suggesting that substrate binding of MBI adheres to some type of adsorption isotherm, as is typical of organic corrosion inhibitors in acidic solution [2]. Besides giving rise to the emergence of the N 1s feature, increasing MBI concentration diminishes the Cu 2p, O 1s, and Cl 2p signals. Loss of Cu 2p intensity can most simply be attributed to the associated decrease in corrosion rate leading to less accumulation of Cu at the carbon-steel surface. The reductions in O 1s and Cl 2p intensities suggest further interfacial modification as MBI's inhibition efficiency increases.

Greater insight into the chemical nature of inhibited interfaces can be gained from higher resolution spectra of specific core levels. Such spectra are displayed in Figures 7 (a), (b), and (c) for the N 1s core level ($\theta_E = 0^\circ$). As already demonstrated in Ref. 12 for immersion in 1 M HCl solution, exposure to MBI leads to the appearance of up to three discrete N 1s peaks. Assignment of these features is undertaken on the basis that there are two tautomeric forms of MBI, thiol and thione, which contain two chemically distinct nitrogen atoms. These tautomers are depicted in Figure 8 with the chemically discrete nitrogen atoms labelled as N¹ (pyridine-like) and N² (pyrrole-like); N¹ appears only in the thiol tautomer, whereas N² is

present in both the thiol and thione forms. Applying this knowledge, along with referring to appropriate previously acquired N 1s spectra [24,39,40], the two lower BE peaks in Figure 7, labelled N^1_{thiol} and $N^2_{thiol} + N^2_{thione}$, are attributed to the two chemically distinct nitrogen atoms in the MBI tautomers. The origin of small third peak in the N 1s spectra (N_{ext} in Figure 7) is less certain, but may be due to either solution contamination or a minority substrate component [12]. It should be noted that in addition to undergoing surface adsorption, MBI could potentially exhibit further surface reactivity (e.g. dimerisation), but there is no evidence to support, or otherwise, any such phenomena in the current data.

Also displayed in Figure 7 (a) – (c) are best fits to the experimental data. These were achieved with the reasonable assumption that the two GL line shape functions (broken red lines) employed to model N 1s photoemission from the two chemically distinct nitrogen atoms in the thiol tautomer (i.e. N^1_{thiol} and N^2_{thiol}) always exhibit equal intensities. A third GL function (solid red line) was used for N^2_{thione} , along with another for N_{ext} (solid red line). As concluded in Ref. 12, these fits indicate that under the prevailing conditions MBI is typically adsorbed onto the carbon-steel substrate in both tautomeric forms. We note that at lower MBI concentrations a shift of the N^1 and N^2 features towards somewhat lower BE can be observed. One plausible reason for this phenomenon is a change in the local adsorption environment, e.g. a different substrate termination, as discussed below.

It should be noted that although MBI also contains C and S, no higher resolution XPS spectra are displayed for these elements, as their interpretation is not entirely clear due to non-MBI related signals [12]. For C, the additional signal is due to the presence of a surface layer of adventitious carbon [26,41]. As mentioned above, non-MBI S signal originates from minority substrate components, which become apparent following solution immersion.

Similar series of XPS spectra to those depicted in Figure 7 are shown in Figure 9, but for the O 1s, Fe 2p, and Cl 2p core levels. Best fits to the experimental data are also displayed. Focusing initially on the data acquired from carbon-steel immersed in 1 M HCl (Figure 9 (a))

– (c)), and reiterating previous assertions [12,26], it is proposed that the polished sample exhibits an iron oxide/hydroxide surface film. This conclusion is based upon the presence of the two lower BE O 1s features (labelled O^{2-} and OH^- in Figure 9 (a)), which can be ascribed to iron oxide (O^{2-} , BE ~ 530 eV) and hydroxide (OH^- , BE ~ 531.3 eV), as well as the $Fe^{2+/3+}$ multiplets apparent in the Fe 2p core level spectrum (Figure 9 (b)); the two higher binding energy O 1s components (labelled O^1 and O^2) are most likely due to adsorbed OH (O^1) and adventitious RC_xO_y (O^1 and O^2) species [26]. Subsequent to immersion in 1 M HCl, it is suggested that this oxidic film dissolves, being replaced at lower MBI concentrations by an iron (ferric) chloride salt film [12]. Evidence for this change is derived from the disappearance of the O^{2-} and OH^- features from the *1 M HCl/0 mM MBI* O 1s spectrum (Figure 9 (a)), together with the emergence of a significant Cl 2p signal (labelled Cl_{salt} in Figure 9 (c)) and the persistence of a Fe^{3+} multiplet (Figure 9 (b)). Finally, in the presence of sufficient MBI for effective corrosion inhibition, it is concluded that the salt film is no longer present, and the MBI binds to a film-free carbon-steel substrate. Both the loss of the majority of the Cl 2p signal, and that only a Fe^0 feature remains in the Fe 2p spectrum support this deduction. The remnant Cl 2p signal (labelled Cl_{ads} in Figure 9 (c)) is proposed to be due to surface adsorbed Cl^- rather than any chloridic salt film. This change in Cl environment is suggested by a concomitant shift in the Cl 2p BE (~ 199.2 eV to ~ 198.7 eV for the Cl $2p_{3/2}$ component ($\Delta BE \sim 0.5$ eV).

Turning to the spectra acquired from carbon-steel immersed in 0.1 M HCl (Figure 9 (d) - (f)) and 0.01 M HCl (Figure 9 (g) - (i)), similar trends to those outlined above are apparent. Most importantly, for all three HCl concentrations, MBI binds to a film-free metallic substrate on well-inhibited surfaces, i.e. adsorption is not facilitated by a surface oxide, hydroxide, or salt film. There are, however, some differences, including the persistence of a surface iron oxide/hydroxide film upon immersion in 0.01 M HCl. This conclusion is drawn from the significant O^{2-} and OH^- features in the *0.01 M HCl/0 mM MBI* and *0.01 M HCl/0.005 mM MBI* O 1s XPS spectra (Figure 9 (g)), as well as the visibility of $Fe^{3+/2+}$ multiplets in the equivalent Fe 2p spectra. Furthermore, the Cl 2p signal (Figure 9 (i)) is much reduced in

comparison to that following immersion in *1 M HCl/0 mM MBI*, suggesting that no significant iron chloride salt phase develops; the BE (~ 198.7 eV for the Cl 2p_{3/2} component) is also seemingly more consistent with Cl_{ads} rather than an iron chloride phase (see preceding paragraph).

As regards oxidic/chloridic surface phases following immersion in 0.1 M HCl, the spectra (Figure 9 (d) - (f)) suggest a behaviour that is intermediate between that exhibited for 1 M and 0.01 M HCl solutions. In line with data for 1 M HCl, any surface oxide/hydroxide is removed upon immersion in *0.1 M HCl/0 mM MBI* (i.e. there are no O²⁻ or OH⁻ features in the O 1s spectrum (Figure 9 (d))), being replaced by an iron chloride salt film, as indicated by the *0.1 M HCl/0 mM MBI* Cl 2p spectral profile (Figure 9 (f)). However, contrary to behaviour in 1 M HCl, this salt phase is seemingly not present in *0.1 M HCl/ 0.005 mM MBI*, as evidenced by the much reduced intensity of the Cl 2p signal as well as the shift in BE to that expected for Cl_{ads}. In addition, the *0.1 M HCl/ 0.005 mM MBI* Fe 2p XPS spectrum (Figure 9 (e)) shows no sign Fe^{3+/2+} features, which should be apparent if a chloridic (or oxidic) surface film was present.

Further to qualitative interpretation of the XPS spectral profiles, including peak assignments, the surface coverage of MBI molecules has been estimated from signal intensities ($\theta_E = 0^\circ$ and 50°) as a function of their concentration in bulk solution. The results for each HCl concentration are illustrated in Figure 10 ((a) – (c)), showing the total surface coverage of MBI (*Thione* + *Thiol*), along with that of each of the tautomers (*Thione* and *Thiol*). Corresponding inhibition efficiencies are also displayed. Comparing these inhibition efficiency and surface coverage plots, it is clear that both exhibit similar trends, indicating that the performance of MBI as a corrosion inhibitor is related to its surface coverage [2]. However, $\eta\%$ approaches a maximum more rapidly than MBI surface coverage, suggesting that active surface sites for corrosion are preferential locations for MBI adsorption. As regards the surface coverage of the individual tautomers, within experimental uncertainty,

there are, in our opinion, no significant differences in the uptake profiles, except that there is typically somewhat more of the thione tautomer adsorbed onto the surface.

Concerning elucidating the fraction of substrate surface covered by MBI from XPS data, it should be stressed that there are likely to be systematic errors associated with the surface coverage determinations displayed in Figure 10, e.g. no account is taken of interface roughness, and variation thereof, in the surface coverage calculations. On this basis, no significance is given to the apparently higher MBI surface coverages at lower HCl concentrations. Nevertheless, assuming that any systematic errors are not too great, it can be concluded that at 2 mM MBI concentration in bulk solution the surface coverage of MBI molecules (ranging from $1.3 \times 10^{15} \text{ cm}^{-2}$ (1 M HCl) to $1.7 \times 10^{15} \text{ cm}^{-2}$ (0.01 M HCl)) is consistent with there being close to a saturated monolayer on the substrate. This deduction is based upon a comparison of these calculated MBI coverages with an estimated density of Fe atoms at the carbon-steel surface of $\sim 2 \times 10^{15} \text{ cm}^{-2}$.

4. Conclusions

In summary, electrochemical measurements and substrate analysis, including XPS, have facilitated understanding of the functionality of MBI as a corrosion inhibitor for carbon-steel in 1 M, 0.1 M, and 0.01 M aqueous HCl solutions at room temperature. Overall, it is concluded that MBI largely behaves similarly regardless of HCl concentration over the range studied. LPR data demonstrate that upon addition of sufficient MBI inhibition efficiencies greater than 90% can be achieved in each of the HCl concentrations. PDP curves indicate that MBI performs as a mixed-type corrosion inhibitor in both 1 M, and 0.1 M HCl. Regarding 0.01 M HCl, anodic dissolution is more strongly impeded at higher MBI concentrations, which coincides with O_2 reduction becoming a significant cathodic reaction; the latter reaction is not inhibited to the same degree as H^+ reduction by MBI. Assignment of N 1s core level XPS features indicates that MBI is almost always bound to the carbon steel surface in two tautomeric forms, i.e. thione and thiol. O 1s, Fe 2p and Cl 2p core level

spectra demonstrate that substrate termination does vary as a function of both HCl and MBI concentration, with both chloridic and oxidic films being exhibited. Notably, however, once a significant degree of inhibition is achieved, there is no evidence of any surface film for any of the three HCl concentrations, i.e. MBI is adsorbed directly onto the metallic carbon-steel substrate.

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Figure Captions

- Figure 1** PDP curves acquired from carbon-steel after 4 h immersion in (a) 1 M HCl, (b) 0.1 M HCl, and (c) 0.01 M HCl solutions containing a series of MBI concentrations (0 mM, 0.005 mM, 0.05 mM, 0.5 mM, 2 mM).
- Figure 2** PDP curves acquired from carbon-steel after 4 h immersion in both naturally aerated and deaerated solutions of (a) 1 M HCl, (b) 0.1 M HCl, and (c) 0.01 M HCl, containing either 0 mM or 2 mM MBI.
- Figure 3** Corrosion rate (blue markers), determined from LPR data after 4 h immersion, of carbon-steel as a function of MBI concentration in (a) 1 M HCl, (b) 0.1 M HCl, (c) 0.01 M HCl. Also plotted are the corresponding inhibition efficiencies (red markers). Each value of corrosion rate (inhibition efficiency) is the average of two or more independent measurements at each concentration of MBI; error bars indicate the associated standard deviation. The blue and red dashed lines act as guides for the eye. The horizontal dashed grey line indicates $\eta\% = 95\%$.
- Figure 4** Photographs of carbon-steel samples: (a) polished; (b) subsequent to immersion for 4 h in 1 M HCl/0 mM MBI; (c) subsequent to immersion for 4 h in 1 M HCl/2 mM MBI.
- Figure 5** SEM images (secondary electron mode) of carbon-steel samples, acquired following the removal of any adhered corrosion scale: (a) polished; (b) subsequent to immersion for 4 h in 1 M HCl/0 mM MBI; (c) subsequent to immersion for 4 h in 1 M HCl/2 mM MBI.

Figure 6 Overview XPS spectra ($h\nu = 1486.6$ eV, $\theta_E = 0^\circ$) acquired from carbon-steel subsequent to immersion in (a) 1 M HCl, (b) 0.1 M HCl, and (c) 0.01 M HCl solutions containing various concentrations of MBI. Polished sample spectra are also shown. The spectra have been normalised to have a maximum (minimum) intensity of 1 (0).

Figure 7 N 1s core level XPS spectra ($h\nu = 1486.6$ eV, $\theta_E = 0^\circ$) acquired from carbon-steel subsequent to immersion in (a) 1 M HCl, (b) 0.1 M HCl, and (c) 0.01 M HCl solutions containing various concentrations of MBI. Polished sample spectra are also shown. Also shown are the best fits (light blue markers) to the experimental data (solid black lines), achieved with GL (solid (broken) red lines for N^2_{thione} and N_{ext} (N^1_{thiol} and N^2_{thiol}), and Shirley-type (broken grey lines) functions.

Figure 8 The thiol and thione tautomers of MBI, with the chemically distinct N atoms labelled N^1 (pyridine-like) and N^2 (pyrrole-like).

Figure 9 O 1s, Fe 2p, and Cl 2p core level XPS spectra ($h\nu = 1486.6$ eV, $\theta_E = 0^\circ$) acquired from carbon-steel subsequent to immersion in ((a) – (c)) 1 M HCl, ((d) – (f)) 0.1 M HCl, and ((g) – (i)) 0.01 M HCl solutions containing various concentrations of MBI. Polished sample spectra are also shown. Also shown are the best fits (light blue markers) to the experimental data (solid black lines), achieved with GL (red lines), LF (red lines; for Fe^0 component), and Shirley-type (broken grey lines) functions. Peak assignments, as discussed in the text, are indicated.

Figure 10 Inhibition efficiency (red markers) and MBI surface coverage (black/blue markers) as a function of MBI concentration in (a) 1 M HCl, (b) 0.1 M HCl, and (c) 0.01 M HCl. The broken lines act as guides for the eye. Both the total

MBI (*Thione* + *Thiol*) coverage, and that of each tautomer (*Thione* and *Thiol*) are plotted.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10