Part II

Choice of Inhibitors

Chapter 15

Mechanisms of inhibitor action - passivation and self-healing

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Many inhibitors passivate the surface with a self-healing film: In this chapter, we will briefly review the systematics of corrosion inhibitors and the classical mechanisms of action of corrosion inhibitors, the latter with an emphasis on inhibitors interacting with the material surface. The different roles corrosion inhibitors have in protecting materials surfaces will

be described - with examples from applications in the oil and gas sector, but also more general. We will discuss in some detail the interaction of an imidazoline based surfactant inhibitor with mild steel and the interaction of 2-mercaptobenzothiazole (MBT) with copper and zinc. By adsorbing to surfaces, molecules in general block sites for metal dissolution. Good inhibitors furthermore react with dissolution products to form insoluble films, in analogy to the formation of conversion coatings. Furthermore, inhibitors may interfere with the kinetics of the cathodic reaction. Over decades, a challenge for the use of inhibitors has been leaching into the environment of inhibiting molecules. Modern triggered release concepts ensure that inhibitors become available only if a corrosion attack has begun. Such triggered release systems have successfully been used for the self-healing of coatings, and we will discuss one example of the interaction of a cyclodextrin with MBT to see how this works for inhibitors. Future applications in the oil and gas sector may consider the use of intelligent coatings.

15.1. Introduction

Corrosion inhibitors are substances that can significantly increase the corrosion resistance of a given material in a given environment, either by interacting with the material surface or by changing the properties of the corrosive environment that the material is being exposed to. The chosen chemical formulation needs to satisfy key requirements, such as being environmentally friendly, easy to apply, inexpensive and efficient at very low concentrations, 10-1000 parts per million (ppm) in case of the continuous injection mode and 1 to 20 vol.-% in batch treatment mode [1]. Corrosion inhibitors are used in various industrial applications, such as drinking water produc-

tion, protection of cooling systems, processing and preparation of metal surfaces prior to the coating application, protection of reinforced concrete structures, as a part of organic coatings formulation, or in the oil and gas industry [2–4].

Since most oil and gas pipelines are made of carbon steel, a corrosion mitigation program is necessary to achieve the designed operation lifetime. Furthermore, in the oil and gas industry, corrosion is being controlled to a high degree by use of corrosion inhibitors as they are considered the most cost-effective way to protect construction materials in various operational stages such as production, transportation and processing of oil and gas. Corrosion inhibitors can be used to effectively combat both uniform and localized corrosion, while the successful use of corrosion inhibitors to control environmental cracking is not recommended [5, 6].

In all these applications, the function of the inhibitor is thus to limit damages, even if the damage-inducing mechanism is present. In other words, many inhibitors (see section 15.2) "heal" damages on a material. "To heal" means "to make whole or sound in bodily condition; to free from disease or ailment, restore to health or soundness; to cure (of a disease or wound)" [7]. We shall argue below that several classes of inhibitors form "self-healing" protecting structures. "Self" in this context is "used as a prefix with reflexive meaning 'oneself', 'itself', in various relations with the second element of the compound" [7], in our case "healing". In the context of this work, the term "self-healing" will be used to indicate that a damage heals without any need for intervention from the outside.

This chapter shall in section 15.2 first summarise the fundamentals of the function and action of corrosion inhibitors. We will subsequently in section 15.3 focus on inhibitors that interact with the surface of materials, as these are the once that facilitate self-healing, and explain some important mechanistic aspects of surface active

inhibitors in more detail. Subsequently, we present three case studies conducted with involvement from some of us, discussing mechanistic aspects in more detail. Section 15.4 presents a novel delivery concept and mechanistic discussions of an inhibitor system already in use in the oil and gas industry. Section 15.5 discusses the molecular level mechanism of surface interaction for one important industrial inhibitor, showing the complexity of these interactions and highlighting several aspects that are key to making a molecule a successful corrosion inhibitor. In section 15.6, we discuss how to control and influence the release of an inhibitor system, with some aspects that may become important in future corrosion inhibition systems. Without always explicitly stating that, we will in this text often focus on on inhibitors dissolved in aqueous solutions which are highly relevant also in the oil and gas industry.

15.2. Systematics and phenomenology

An important quantity that is used in the literature to characterise a corrosion inhibitor is the inhibition efficiency, often expressed in %, and calculated as

$$\text{Inhibition efficiency} = 1 - \frac{\text{corrosion rate in the presence of the inhibitor}}{\text{corrosion rate in the absence of the inhibitor}}. \quad (15.1)$$

It is worth noting that the inhibition efficiency is not an "efficiency" in the strict sense, as (i) all corrosion rates vary with time, see e.g. the discussion in ref. [8], and (ii) this efficiency is not limited to the range between 0 and 1 (0 - 100%), and may e.g. become negative. It is to be seen as a practical measure of how much, approximately, a certain corrosion inhibitor affects the corrosion rate. Inhibitors can be classified in several ways according to different criteria (Fig. 15.1). All the corrosion inhibitors are divided
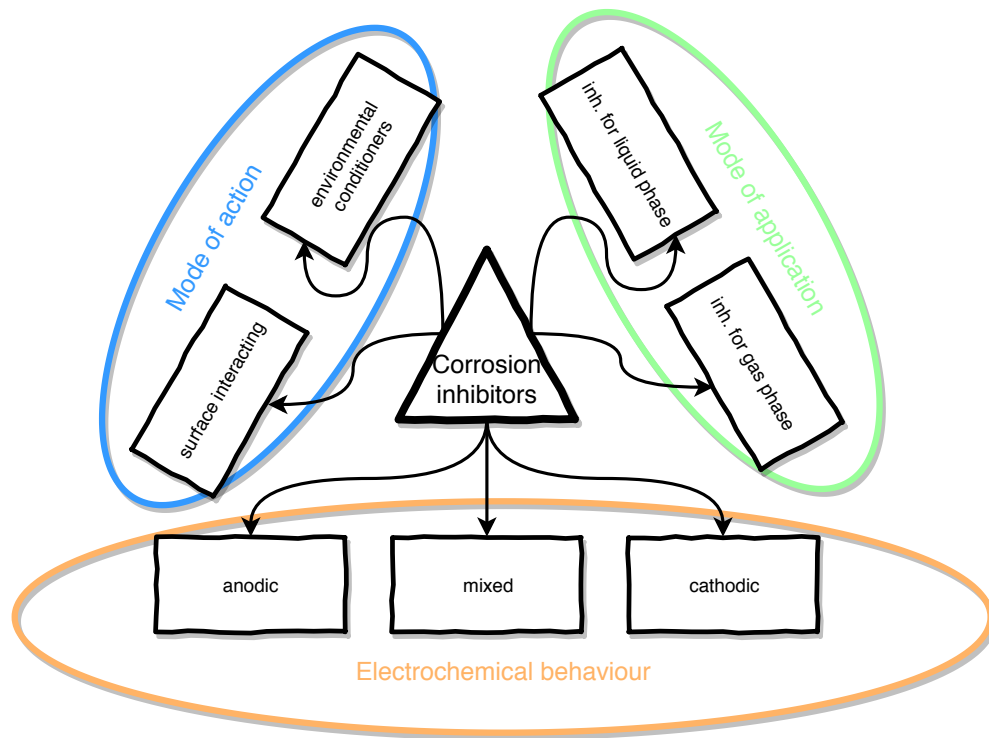
6

Figure 15.1: Overview over three different classifications of corrosion inhibitors.

in two major groups: inhibitors that interact with the metal surface (e.g. adsorption inhibitors, film-forming inhibitors) and environmental conditioners (scavengers, neutralising inhibitors). This chapter focuses on the first group. Stability and efficiency of corrosion inhibitors depends on the pH of the electrolyte, therefore making them more suitable for alkaline, acidic or neutral environments. According to the method of administration, they are divided into inhibitors for liquid and vapor phase. By the mechanism of inhibitor action on electrochemical processes on the metal surface corrosion inhibitors can be classified to anodic (passivating), cathodic or mixed corrosion inhibitors [9]. An overview over some important cases of the electrochemical effects of a corrosion inhibitor in an Evans diagram is schematically shown in Fig. 15.2. Naturally, all corrosion inhibitors should — when functioning as inhibitors — decrease the corrosion rate and thus the corrosion current density.

Anodic inhibitors affect the anodic part of the polarisation curve, thus shift the corrosion potential to higher values. To illustrate that, important cases are shown in Fig. 15.2a. A positive shift of the corrosion potential E_{corr} can be obtained in one of the following cases:

- (i) The inhibitor decreases the exchange current density $i_{\mathrm{M}}^{(0)}$ for metal dissolution.
- (ii) The inhibitor modifies the apparent Tafel slope of the metal dissolution while a Tafel-like behaviour remains.
- (iii) The inhibitor ensures polarisation into the passive region of the polarisation curve, and may induce passitivty in a material not passive by itself.
- (iv) The inhibitor decreases the passive current density, i_{pass}, of the metal.

Case (i) corresponds to a downward shift of the Tafel line for metal dissolution, and case (ii) to a change in slope of the respective Tafel line. Illustrated in Fig. 15.2a are cases (iii) and (iv). In both cases, the inhibitor ensures first of all that the metal is
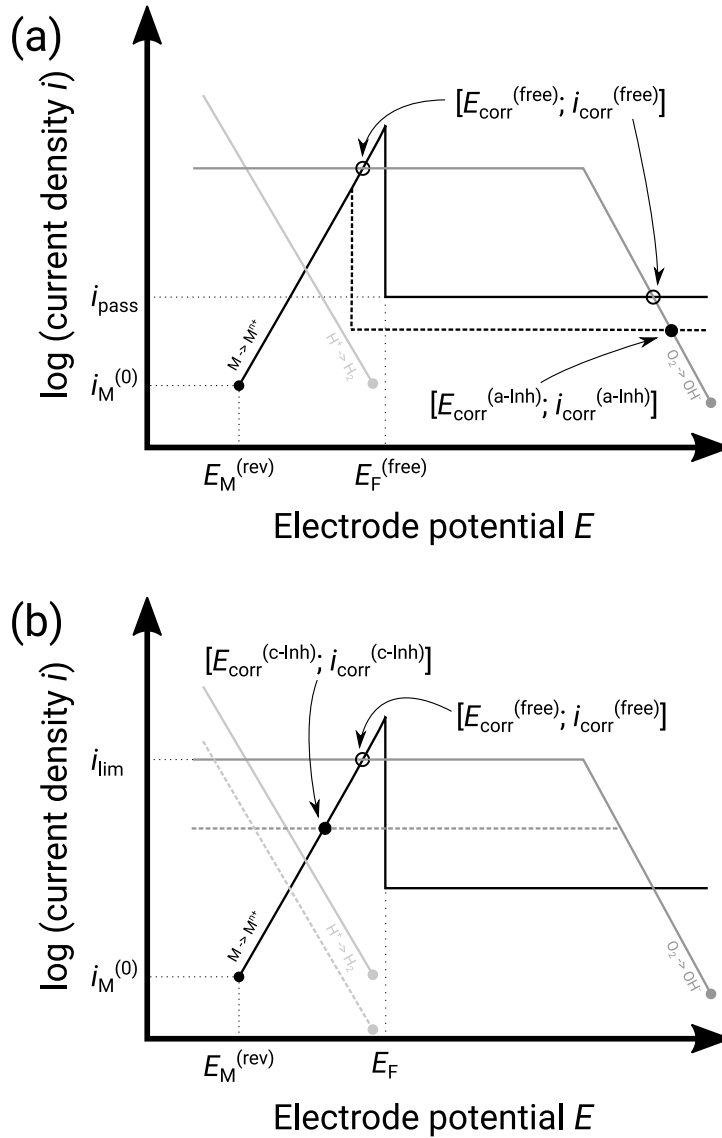
8

Figure 15.2: Scheme showing important electrochemical effects of (a) anodic and (b) cathodic corrosion inhibitors, in an Evans diagram for a passive metal. Black lines (—): Oxidation curves of the metal; dark grey lines (—): transport limited curves of the oxygen reduction, $O_2 + 4\,e^- + 2\,H_2O \longrightarrow 4\,OH^-$; light grey lines (—): curves of hydrogen evolution, $H_2O + e^- \longrightarrow \frac{1}{2}\,H_2 + OH^-$. Dashed lines indicate the situation in the presence of a respective inhibitor. $E_M^{(rev)}$ - reversible (equilibrium) potential for the metal dissolution, $M \longrightarrow M^{n+} + n\,e^-$; E_F - Flade potential; $i_M^{(0)}$ - exchange current density of the metal in the respective electrolyte; i_{pass} - current density in the passive regime; i_{lim} - transport limited current density of the oxygen reduction; E_{corr} - corrosion potential; i_{corr} - corrosion current density; (free) - in the absence of inhibitor, (a-Inh)/(c-Inh) - in the presence of anodic or cathodic inhibitors, respectively. E_{corr} and i_{corr} are found from the intersections of the metal line with the dominating cathodic process. The oxygen reduction would in many cases be dominating in the presence of oxygen; in its absence, the hydrogen evolution takes over. For an introduction into construction and interpretation of Evans diagrams see e.g. [10].

9

passive. In addition i_{pass} is decreased, so that the passive layer is more protective than than in the absence of the inhibitor. Consequently, successful anodic inhibitors are often oxidising agents. In the case of metals that exhibit passive behaviour, they act by anodically polarising the metal into the passive potential region, consequently stimulating the formation of a passive film on the surface [11]. The function of anodic inhibitors is to maintain, repair or thicken the natural oxide film already present on the surface of metals and alloys. In the case of a damage, the passive film normally reforms, possibly under assistance of the inhibitor, as expected for a self-healing system. The increased stability of the passive film formed by some passivating inhibitors is explained by additional adsorption of the inhibitor on top of passive film, followed by shift of the Flade potential E_{F} to a more negative value (see dashed line in Fig. 15.2a) [12]. Anodic corrosion inhibitors need to be present in the concentration higher than a certain critical concentration to achieve stable passivity. Below this critical value, the anodic inhibitor may actually intensify the corrosion attack [9]; such an intensification actually happens if the inhibitor concentration is not sufficient to polarise the system over E_{F} and the system thus is active at a high dissolution rate (see Fig. 15.2a). Some examples of anodic inorganic inhibitors are nitrates, nitrites, molybdates, chromates, phosphates, and silicates [13–15].

Cathodic inhibitors affect only the cathodic partial reaction. Reducing the corrosion rate using cathodic inhibitors is based on reducing the rate of cathodic reaction of the corrosion process. Cathodic inhibitors slow down the cathodic reaction by acting either on the hydrogen evolution reaction, by slowing down the recombination of hydrogen atoms on the surface or on the oxygen reduction reaction by limiting the diffusion of oxygen to the metal surface [16]. Cathodic inhibitors are often precipitation inhibitors, acting by formation of insoluble compounds precipitating on the

10

cathodic sites in the form of a barrier film. The inhibitor is deposited in the form of the compact layer on cathodic surfaces, electron transfer during the cathodic reaction. In Fig. 15.2b this is illustrated for an inhibitor decreasing the transport limited current i_{lim} of the oxygen reduction. Likewise, they can shift the hydrogen exchange current density down (dashed light gray line in Fig. 15.2b), or increase the overpotential of the hydrogen evolution. Compared with anodic inhibitors, cathodic inhibitors are significantly less efficient in equivalent concentrations. The reason becomes intuitively clear by comparing the potential impact in Fig. 15.2a and b: anodic inhibitors can change the behaviour of the system qualitatively by inducing or strengthening passivity. Some examples of cathodic inhibitors are Zn^{2+} and Mg^{2+}, that precipitate on the metal surface in the form of zinc hydroxide and magnesium hydroxide, respectively. Cathodic inhibitors in neutral and alkaline solutions are phosphates, silicates, and borates, while in acidic solutions, agar-agar, dextrin and aldehydes [17, 18].

Mixed inhibitors act on both anodic and cathodic reactions, and are mostly organic compounds that create a film on the metal surface. This film is dynamic and can reform when damaged; it is thus also self-healing. The effectiveness of mixed inhibitors in preventing corrosion depends on many factors, such as affinity to the metal surface, surface preparation, chemical composition and applied concentration of the corrosion inhibitor, pH of the electrolyte and the presence of dissolved salts [19, 20]. Important factors affecting the adsorption process are the temperature and pressure. Most of the corrosion inhibitors used in oil and gas industry are composed of heterocyclic compounds containing N, P, S and O atoms, organic compounds that contain polar functional groups, as well as unsaturated bonds that can serve as adsorption centres using e.g. a lone pair or π electrons [21–23]. In addition, the structure of these corrosion inhibitors generally includes a long-chain hydrocarbon structure (usually C14-C18).

Some examples of mixed inhibitors are aldehydes, thiourea, acetylene, nitrogen quaternary salts, sulfur compounds, thioalcohols (mercaptanes), organic sulfides, Na-salts of aromatic carboxylic acids, and salts of higher fatty acids acid [23].

The usual interpretation is that organic molecules chemisorb to the surface of the metal because of the unsaturated bonds on the heteroatoms through which they interact with the d orbital of the metal substrate. Branched hydrocarbon chains ensure orientation of some hydrophobic moieties towards the solution, and provide an additional protection by forming a non-polar layer with low permeability to water and corrosive species. Polymers are also being widely used as corrosion inhibitors because of their better film forming properties owing to increased number of adsorption centres, higher thermal stability and handling-friendly viscosity. Metal coverage with protective film largely depends on inhibitor concentration. Therefore, the right choice of concentration is the key to protection of materials against corrosion using this method [24, 25].

Two points are worth noting. First, it is rare that an inhibitor acts exclusively on only either the cathodic or the anodic partial reaction. In any case, both reactions will be affected to a certain extent. The above classification should thus be considered useful if the the inhibitor acts predominantly on one of the partial reactions and very little on the other. Second, from the presented examples it is clear that a wide range of substances act as corrosion inhibitors. Indeed, any foreign species present in solution will interact with the surface, and in most cases, e.g. because of adsorption, decrease the dissolution rate. It is thus trivial to add an organic substance with some affinity for the metal surface to the solution; such a substance will act as corrosion inhibitor. This simplicity has stimulated a large number of publications in recent years.

In the oil and gas industry, mixtures of different compounds are usually used

and referred to as inhibitor formulations. The composition of these mixtures is often protected and not publicly available. Corrosion inhibitor mixtures are most often formulated for specific conditions and contain several surfactant compounds, polar or nonpolar solvents such that the inhibitor mixture can be soluble in water, oil, volatile or well dispersible in any phase. Different types of organic compounds can be used to prevent the occurrence of corrosion by injection into the liquid phase in a pipeline [1, 26–28]. According to the classical mechanism of inhibition, the molecules of the corrosion inhibitor interact with the steel or corrosion products through the reactive polar head. The hydrophobic array attracts the hydrocarbon film so the formed layer protects the steel surface from corrosive liquid phases [26]. Known inhibitors used that form films on the surface of the steel are substituted succinic anhydride, amine imidazolines, and phosphate esters [27].

15.3. Surface active inhibitors

From section 15.2, it is clear that (i) organic molecules or molecular fragments form a very versatile toolbox for exploring corrosion inhibition, and (ii) all inhibitors other than the environmental conditioners necessarily interact with the surfaces of the corroding metal; even environmental conditioners may interact with materials surfaces. The class of surface active molecules offers thus good chances to find corrosion inhibitors.

Indeed, many successful corrosion inhibitors are surface- and interface-active amphoteric substances [29–31]. Surface active substances or in the more general sense "interface active" substances are chemical compounds that in low concentrations adsorb to the interface such as the metal(oxide)/water interface [32, 33]. At low con-

centrations, surfactant molecules are dissolved in molecularly in solution, and an equiblrium exists with molecular adsorption to all interfaces in contact with the solution. With increasing concentration, the interface coverage will increase until a saturation is reached. The surfactant concentration at which a monolayer of surfactant molecules cover the metal surface is termed the "surface aggregation concentration" (sac) [34, 35]. This concentration is critical for corrosion inhibition. As surfactant concentration increases, bilayers or multilayers may form on the metal surface. Above a "critical aggregation concentration" such as the "critical micelle concentration", amphiphilic molecules will form aggregates such as micelles in solution, and the surface coverage with these molecules is not increasing with increasing concentration. Metal and metal oxide surfaces are hydrophilic. For many amphiphilic molecules adsorbing to such surfaces, it is thus not a priori clear which adsorbate structure is obtained. There is in any case a driving force, the hydrophobic effect, for hydrophobic regions of the molecules to cluster. Hydrophobic regions of corrosion inhibitors can be saturated or unsaturated hydrocarbon chains, or systems with heterocyclic or aromatic rings. Hydrophilic regions (polar heads), dependent on the nature of the hydrophilic group, may be in the form of anions, cations, zwitterions (amphoteric) or non-ionic [32, 36]. Detailed introductions into the physical chemistry of amphiphilic molecules are available elsewhere, e.g. in ref. [37].

Water-insoluble substances, including poorly soluble corrosion inhibitors, can be "solubilised" in micellar solution (or in solution of other aggregates) of a surfactant, with a resulting thermodynamically stable isotropic solution. Since solubilization only occurs above the critical aggregation concentration, it was concluded that water-insoluble substances are actually dissolved inside micelles [38]. It has been found that the amount of solubilized substance increases with increasing concentrations of the

14

surfactant, thus increase in the number of aggregates such as micelles in the solution [39]. This mechanism illustrates the cooperative effect that several substances in the same solution may have. In commercial inhibitor formulations, the consideration of tuning the solubility of the ingredients is typically crucial.

Adsorption of a corrosion inhibitor at a metal(oxide)/solution interface naturally affects the structure of the metal(oxide)/solution interface, including the ion distribution at the interface. Inhibitor adsorption affects both the distribution of the charged species and the relative permittivity near the interface. Predicting and verifying which species will be adsorbed at different electrode potentials, especially around the corrosion potential, is important for maximising the efficiency of corrosion inhibition. The difference between the actual electrode potential and the potential of zero charge (PZC) determines the nature of the species adsorbing at the surface, if electrostatic interactions are important in the adsorption process. At more negative potentials to the PZC cations will be adsorbed preferentially at the metal/electrolyte interface, and vice versa [40]. On the other hand, the charge of the inhibitor or the partial charge of an atom depends on the electron density, e.g. via availability of lone electron pairs, delocalized π electron systems, functional groups containing elements of groups V or VI of the periodic table, or substituents on the inhibitor molecule [41–44].

Adsorption of inhibitors may occur by physisorption or by chemisorption. The tendency of an organic molecule to chemisorb to the metal surface and hence its efficiency as a corrosion inhibitor depends on its electron donating ability, molecular size, and solubility [45]. The strength of the bond depends on the nature of the metal and the presence of specific reaction centres in the inhibitor molecule. In an aqueous solution, the metal surface is covered with water molecules. In the process of the adsorption of organic molecules on the surface of the metal, a certain number of water

15

molecules need to be replaced. Therefore, adsorption of dissolved organic molecules $Org_{(aq)}$ from aqueous solutions can be represented as

$$Org_{(aq)} + nH_2O_{(ads)} \longrightarrow Org_{(ads)} + nH_2O_{(aq)}, \qquad (15.2)$$
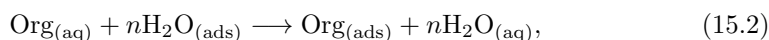
where n is the number of water molecules removed from the metal surface for each molecule of inhibitor adsorbed. In equilibrium, the chemical potentials of the species on the respective sides in eq. (15.2) is equal. A number of mathematical relations have been suggested to fit the various experimental data available, some being empirical and other theoretical [46–48]. In order to determine the type of adsorption and thermodynamic parameters, it may be useful to analyse existing models of adsorption isotherms. Some of the existing models of adsorption isotherms often used to describe adsorption of corrosion inhibitors are the Langmuir, Frumkin, Freundlich, Temkin, Flory-Huggins, Parsons, or Bockris-Devanathan-Muller isotherms [47, 49].

In the presence of adsorbing ions, e.g. halide ions, in the solution, the corrosion inhibitor competes with ions for sites on the surface of the metal. Cases exist in which the presence of certain anions increases the efficiency of the corrosion inhibitor [20]. The synergistic effect of the halide ions grows in the series $Cl^- < Br^- < I^-$, which can be explained by the increase in the size of the anion and their polarisability [50, 51].

Adsorption of organic substances, and therefore their efficiency as corrosion inhibitors, depends on the ability of the molecules to donate electrons, the size of the molecule and the substance's solubility [52, 53]. Stronger bases (higher pK_a) have a higher affinity to donate an electron pair and thus to adsorb than weaker bases [54]. Organic bases exist in acidic solutions in their own protonated form as the corresponding acid; a deprotonation during surface interaction is, however, possible. Another important factor that affects the adsorption of the organic inhibitor is the size

of the molecule and spatial placement of the substituents. An increase in size generally increases the inhibitor efficiency. However, very large molecules like polymers may suffer from steric interference between the adsorbent chains on the surface, and may hence not completely cover the surface. A third factor that significantly affects chemisorption, and therefore the inhibition efficiency, is the solubility or dispersibility of the organic molecule. Molecules that are less soluble have a larger tendency towards adsorption in comparison with higher solubility inhibitors, and compounds that are less soluble achieve a higher degree of coverage of the metal surface compared to more soluble compounds [55]. On the other hand, a certain solubility in water is needed, otherwise the compound cannot be applied if no solubilisation method exists.

Linear free energy relationships are semi-quantitative approaches often used to relate the thermodynamics of a series of reactions to kinetic parameters; they have been successfully applied to series of reactions in organic chemistry [56]. Linear free energy relationships are also suitable to correlate adsorption phenomena and corrosion inhibition [57]. This approach considers structure-adsorption relationship such as the electronic effects of substituent groups on the adsorption reaction centre of organic compounds on metals, in direct analogy to the considerations in organic chemical reaction. The reaction and substituent constants ρ and σ, respectively, are defined as known from organic chemistry for a series of reactions [56]. The magnitude of ρ indicates the relative sensitivity of the inhibition process to electronic effects, σ is a relative measure of the electron density at the reaction centre, while $\log_{10} R = -\rho\sigma$ is representing a normalised corrosion rate. Different versions of this scale exist for different classes of reactions. For details on which substituent has which effect, the reader is referred to textbooks of physical organic chemistry, e.g. [56]. For corrosion inhibitors, in a nutshell, electron withdrawing substituents reduce the electron density

17

on electron donor centres, therefore reducing the degree of corrosion protection. On the other hand, electron-donating substituents concentrate the negative charge and increase the efficiency of corrosion protection. When interacting with metal surface the corrosion inhibitor affects the metal dissolution process.

Blocking of active reaction sites on the metal surface by inhibitor molecules is a dynamic balance of adsorption and desorption of the inhibitor molecules. This dynamic balance ensures the self-healing of defects in the protecting layer. Adsorbed inhibitor molecules have some retention time on the metal surface and consequently participate in a large number of reaction steps occurring at surface.

15.4. Case study (1): Imidazoline based surfactant for mitigation of mild steel corrosion in the presence of CO_2

Imidazoline based corrosion inhibitors (see Fig. 15.3 for an example) are cationic surface active compounds widely used for protecting low-carbon steel pipelines from CO_2 corrosion in the oil and gas industry [58, 59]. Aqueous CO_2 corrosion of mild steel presents a significant problem for the oil and gas industry. The presence of hydrated CO_2 - the weak acid carbonic acid, also used as buffer system - leads to a much higher corrosion rate of carbon steel than would be found in a solution of a strong acid at

the same pH [60, 61]. (A strong acid with the pH of CO_2 saturated H_2O is, however, an extremely diluted acid on the order of a concentration of 10^{-5}M, thus not very corrosive.) Carbonic acid enables hydrogen evolution at a high rate and serves as an additional source of hydronium ions [62, 63].

In this context, another major concern for pipeline integrity is CO_2 top-of-the-line corrosion (TLC). It usually occurs in stratified or stratified-wavy flow regimes where a significant temperature gradient between the outside environment and the inner pipeline surface leads to high condensation rates [61, 64]. A thin film of condensed water forms on the sides and on the upper section of the internal pipe walls, and the presence of various corrosive species such as CO_2 and acetic acid causes a severe corrosion problem [65]. The paramount problem of TLC is the large uncertainty associated with the use of traditional corrosion mitigation techniques. Conventional mitigation methods can fall short in protecting the top of the line since the conditions do not allow the inhibitor to reach the top sections of the wall. A novel TLC mitigation method proposed consists of injecting the corrosion inhibitor within a foam matrix and delivering the corrosion inhibitor to locations where condensation occurs. This method was designed to uniformly deliver the inhibitor to the inner pipe wall. It should consequently lead to formation of strong chemical bonds that would allow the inhibitor to remain on the pipe wall for long periods of time between treatments. This method could be implemented without affecting the production conditions within a given pipeline [66, 67]. To that end, the inhibition of API X65 mild steel corrosion by a mixture in which the main inhibiting component was talloil fatty acid diethylenetriamine (TOFA/DETA) imidazoline was investigated in the presence of CO_2 for both continuous immersion and top of the line corrosion (TLC) when injected within a foam matrix (C14-16 olefin sulfonate) [59, 66–68]. Fig. 15.3 shows the main structural
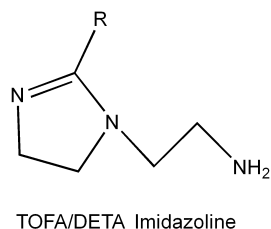
TOFA/DETA Imidazoline

Figure 15.3: Structural motif of tall oil fatty acid diethylenetriamine (TOFA/DETA) imidazoline. R is a long hydrocarbon chain.

motif of the main inhibiting compound.

TOFA/DETA imidazoline exhibited a high inhibition efficiency of mild steel corrosion in 3 wt. % NaCl solution saturated with CO_2 [59]. It is assumed that the imidazoline ring and nitrogen atom are the adsorption sites of TOFA/DETA imidazoline while the hydrocarbon chain forms a hydrophobic film and protects the metal surface from corrosive species. In the presence of 90 ppm_v or more of TOFA/DETA imidazoline in solution, the inhibition efficiency was above 90 %. Potentiodynamic sweep measurements showed that the imidazoline based compound behaves as a mixed-type corrosion inhibitor with a predominant anodic effect (see section 15.2). The values of polarisation resistance determined by linear polarisation resistance in CO_2-saturated 3 wt. % NaCl in the presence of inhibitor increased 40 times compared to the bare steel. The results of cyclic voltammetry (CV) measurements indicate inhibited electrode processes in the presence of TOFA/DETA imidazoline due to the adsorption of inhibitor molecules on a mild steel electrode. Accordingly, it was concluded that TOFA/DETA imidazoline is stable in the range of mild steel corrosion potential [59].

The adsorption of the studied imidazoline compound on steel surface followed both the Langmuir and the Temkin adsorption isotherms. The value of the molecular interaction constant calculated from the Temkin adsorption isotherm implied the existence

20

of lateral repulsion between adsorbed inhibitor molecules. Atomic force microscopy showed that TOFA/DETA imidazoline decreases the steel surface roughness and effectively protects mild steel from corrosion by formation of an inhibitor film. Quartz crystal microbalance was utilised to follow the kinetics and mechanism of adsorption on both gold coated quartz crystals as inert substrate and mild steel [58]. In addition to electrochemical measurements, weight loss measurements have confirmed the effective inhibition, with inhibition efficiency >95%, of steel corrosion due to the addition of the inhibitor.

A "proof of concept" validation of this novel TLC mitigation method was successfully conducted in a small-scale laboratory setup consisting of a foaming cell and a corrosion cell used to simulate intermittent contact between the foam and the steel surface. Electrical resistance measurements and a non-standard QCM-based measurement technique were employed to investigate the properties of corrosion inhibitor carried by the foam matrix in the gas phase [66]. Repeatable results were obtained for contact times from 15 s to 60 s between inhibitor containing foam matrix and sample, and were persistent for at least 15 h. It was shown that a foam matrix containing 1000 ppm_v corrosion inhibitor can be used to effectively apply batch inhibition at the top of the line [66]. Further validation was performed in a large scale flow loop to enable a more realistic simulation of the corrosive environments such as realistic gas temperature, gas flow rate, CO_2 partial pressure as well as condensation rate [67]. Successive injections of foam plugs containing 10 000 vol. ppm (ppm_v) of TOFA/DETA imidazoline led to approximately 90 % inhibition efficiency and the inhibition effect lasted up to 50 h. The foam matrix is a promising method to deliver a corrosion inhibitor that can control the TLC rate in wet CO_2 gas flow. The novel TLC mitigation method showed promising results in a large scale flow loop and applications in oil and gas field
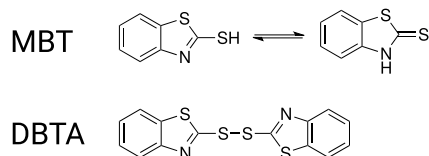
Figure 15.4: Top: Structure of 2-mercaptobenzothiazole (MBT) as tautomeric equilibrium between the thiol form (left) and the thione form (right). Bottom: Structure of 2,2'-dibenzothiazole disulfide (DBTA), a product of oxidative dimerisation of MBT.

environments could be considered [67].

15.5. Case study (2): The interaction of 2-mercaptobenzothiazole (MBT) with copper

MBT (Fig. 15.4) is known as one of the most effective organic corrosion inhibitors to copper, works also for zinc, and has thus been applied in industry for decades [69]. It is therefore instructive to look into the multiple aspects that make MBT such a successful inhibitor, which shall be done in this section. MBT is a substituted imidazoline derivative, in which one of the two nitrogen atoms in the heterocyclic ring is replaced with a sulfur atom. At room temperature, MBT exists in a tautomeric equilibrium between a thiol and a thione tautomer (Fig. 15.4).

Potentiodynamic electrochemical experiments showed that MBT acts as a mixed-type inhibitor (see section 15.2) [70, 71]. MBT was decribed as reacting with copper to form a water-insoluble CuMBT complex layer directly on the metal surface to protect

it from corrosion [69, 71]. MBT was shown to achieve a higher surface coverage and a higher inhibition efficiency compared to other common organic corrosion inhibitors [72, 73]. The concentration of MBT plays an important role in surface coverage of metal and thus corrosion inhibition. In the concentration between 0.1 mM and 2 mM, the surface coverage increased at higher concentration [72]. However, this trend is not reflected in corrosion inhibition. Arkhipushkin et al. [74] measured potentiodynamic curves to examine the corrosion behaviour of zinc and copper in different concentrations of MBT. For zinc, it was shown that the inhibition increased as concentration raised gradually from 0.05 mM to 0.5 mM. At a concentration >0.5 mM, the inhibition did not obviously increase and remained at the same level as for 0.5 mM. However, for copper, it was found that the inhibition is superior at 0.25 mM compared to 0.5 mM. Higher concentration thus does not always guarantee a better inhibition. The reason for this behaviour must be in the structure of the formed films.

There are several studies focusing on the interfacial structure of MBT at the copper/electrolyte interface [70–72, 74–80]. Several studies on the interaction of copper with MBT have used surface modification and ex situ analysis after transfer of the sample through an oxygen containing atmosphere [71, 76, 77]. Ex situ x-ray photoelectron spectroscopy (XPS) has been widely used to understand the nature of the MBT layer forming on copper. On the basis of XPS, the presence of a Cu_2O layer on the copper surface was suggested to be a requirement for the formation of a CuMBT film [74, 76, 78]. In the same studies, an increasing thickness of the forming CuMBT layer was observed with longer immersion time of copper in the MBT solution. Angle dependent XPS showed that the nitrogen and exocyclic sulfur atom of MBT are involved in the adsorption to copper [71]. Moreover, no Cu^{2+} species were detected, neither in the CuMBT complex layer, nor on the copper surface after copper was treated with

23

MBT. This observation implies that the CuMBT complex contains only Cu^+. The same result was shown in a previous study [69], were the authors prepared CuMBT by direct reaction between MBT and $Cu^{II}Cl_2$ as reactants. As products, a mixture of a Cu^+ complex and the oxidized product of MBT, DBTA (see Fig. 15.4), in a 2:1 molar ratio was obtained. This result clearly shows that Cu^{2+} is reduced to Cu^+, and oxidation of MBT to DBTA is taking place. Based on results from XPS, a probable structure of the CuMBT complex layer was proposed, in which each Cu^+ cation is surrounded by three exo-sulfur atoms and one N atom as a tetrahedron [76]. However, the forming film has likely features of a coordination polymer; it will thus contain several structural elements, and also dynamically change with time. For instance, H_2O molecules can also coordinate to the ions in the film, making the film dynamic.

Non-destructive in situ techniques have thus been used to study such systems. They can provide information during an electrochemical reaction, and thus can yield additional insight [81, 82]. In situ Surface enhanced Raman spectroscopy (SERS) was performed for copper at controlled electrode potential in solutions containing MBT at different pH values [75]. Based on in situ Raman spectra in alkaline solution (pH 9.2), MBT binds to the copper surface via the exocyclic sulfur atom. However, in acidic medium (pH 4.6), the adsorption resulted from $\pi-$bonding between the copper surface and the aromatic ring of MBT molecules. The spectra also revealed that MBT interacted with copper in the thiol form. Similar conclusions were obtained using electrochemical surface-enhanced attenuated total reflection (ATR) infrared (IR) spectroscopy in 0.1 M $NaClO_4$ with a copper-coated ATR Si crystal as working electrode [77]. It was found that at lower electrode potential (<0 V vs. saturated calomel electrode), MBT vertically adsorbed on the copper surface in the form of a thiolate bound via the exocycliy sulfur atom. At higher electrode potentials (> 0 V vs. satu-
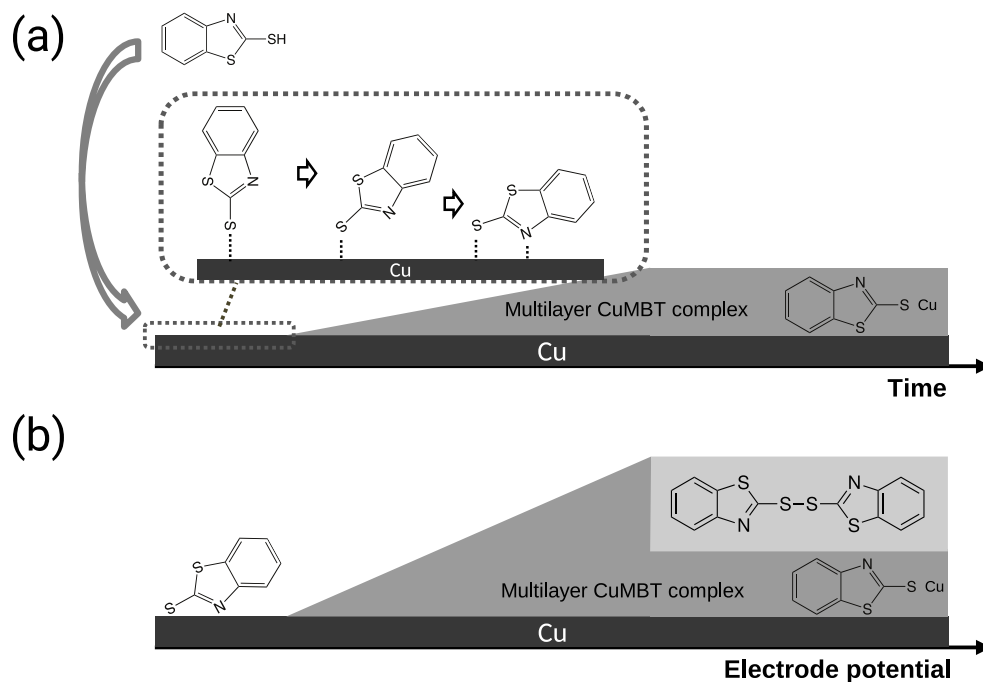
Figure 15.5: Scheme illustrating the interaction of MBT with copper (a) at a reduced surface with time and (b) during electrochemical oxidation, based on results discussed in ref. [80]

rated calomel electrode), electron transfer between copper and MBT occured, nitrogen atom and exocyclic sulfur atom coordinated to Cu^+ to form a complex polymer on the surface [77].

Our group recently investigated the copper-MBT interaction in 0.1M NaOH by using in situ ATR-IR, Raman, and ellipsometric spectroscopy, coupled to CV [80]. At negative potentials, MBT monolayers with upright molecules formed by adsorption to the oxide free metal surface via the exocyclic sulfur atom. These monolayers relaxed on a minute time scale through MBT reorientation, leading to MBT-copper binding via both the exocyclic sulfur and N-atoms. As the electrode potential increased, multilayer

films formed and effectively inhibited oxide formation. It was observed that oxide related peaks were absent in the CVs and Raman spectra. At more positive potential, instead of formation of copper oxide or copper dissolution, MBT oxidatively dimerised to DBTA, which also inhibited oxide formation. While MBT also adsorbs to oxide-covered copper surfaces, there is no evidence from our in situ experiments that the presence of an initial oxide layer is needed for adsorption of MBT; it does also adsorb to completely reduced copper. A scheme displaying some important aspects of the layer formation is shown in Fig. 15.5 [80].

These different studies show why MBT is such a successful inhibitor: it forms a self-healing film on the surface. This film has some interesting features:

- The monomeric MBT adsorbs to a bare copper surface, thus slowing down metal dissolution.
- If metal dissolution is triggered, MBT forms a complex, insoluble polymer in the presence of dissolved copper ions. This polymer deposits in multilayers on the metal surface. Under conditions of free corrosion, it functions thus like a conversion coating.
- Each individual MBT molecule has three atoms that can bind to a copper ion or the copper surface. If each copper atom is coordinated by two MBT molecules via two heteroatoms, each of the MBT molecules can further bind to more copper atoms. Defects in this structure yield cross linking, strengthening rather than weaking the film.
- If the film can be hold in equilibrium with monomeric MBT in solution, i.e if MBT remains present in solution, the film would reform in case of a mechanical damage inflicted on the surface.
- If an external effect drives the electrode potential up, the film itself will be oxi-

dised to DBTA, rather than oxidising the metal. DBTA as a dimer is still able to participate in the formation of the complex coordination polymer type of film. In this situation, the film acts as "sacrificial inhibitor", as it is oxidised instead of the metal.

15.6. Case study (3): β-cyclodextrin facilitates release of inhibitors

In the methods described so far, the main success of inhibitors, including the ability to self-heal defects in films, relies at least partly on the dynamic nature of the adsorption to a material. On the other hand, presence of an inhibitor in contact with the inhibitor film is a problem for some applications, as such a presence in an open system would lead to the leaching of inhibitors into the environment. What is needed, therefore, is a triggered release of the inhibitor in the case of the onset of corrosion from a reservoir. The solubilisation of an inhibitor in a micellar system as described in section 15.3 would already be a progress, if the micellar system could keep the inhibitor incorporated. The latter is, however, also not given. In particular, a micellar system would not normally be stable inside an aqueous phase and inside a volume phase. Instead of a micellar or other aggregate system, we would like to look briefly at the host-guest chemistry in cyclic oligosaccharides from the class of cyclodextrins (CDs).

CDs consist of 1-4 linked glucose units and are produced by enzymatic conversion of starch [83–85]. Native CDs, designated as α-, β-, and γ-CD, consist of 6, 7 or 8 glucose sub units, respectively. Because of the fact that the size of the hydrophobic "inside"
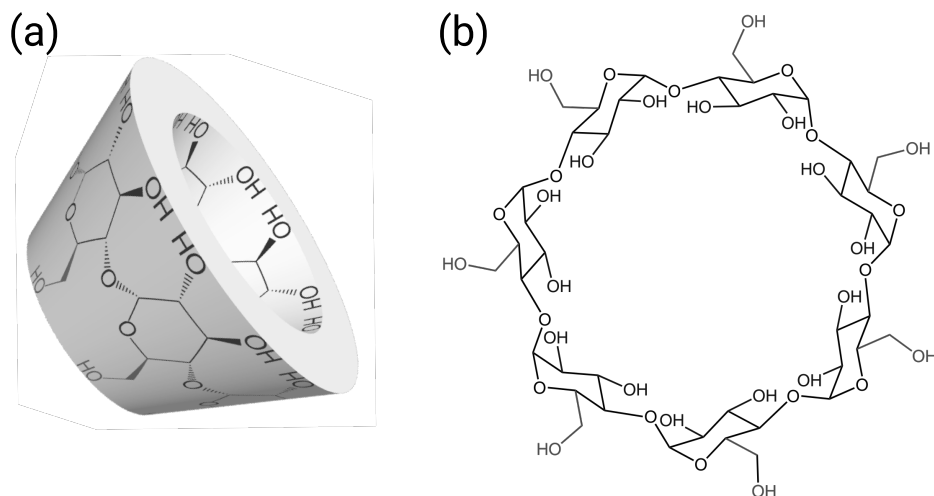
Figure 15.6: Structure of β-Cyclodextrin (β-CD); (a) 3-D cone-like spatial arrangement; (b) chemical structure.

pocket is such that MBT and similar molecules fit well, this chapter shall focus on the discussion of β-CD, which is shown in Figure 15.6. One important application of β-CD is to increase the solubility of hydrophobic, poorly soluble organic compounds, e.g. in the food of pharmaceutical industry [83, 84]. This property can also be exploited for hydrophobic corrosion inhibitors. Such inhibitors - denoted here generically as *Inh* - can be incorporated into and released from β-CD by formation of CD-inhibitor complexes,

$$\beta\text{-CD} + Inh \rightleftharpoons \beta\text{-CD}[Inh]. \tag{15.3}$$
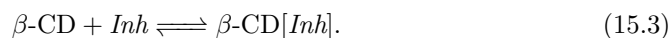
Before discussing the inclusion of corrosion inhibitors, it is interesting to look at the inhibition of corrosion by β-CD itself. Despite having a hydrophobic interior, β-CD reduces the surface tension of water only by few %, it is thus not surface active [86]. Our group has studied the effect of β-CD on corrosion of zinc, and found inhibition efficiencies of typically 80% in 0.1M KCl by using electrochemical impedance spectroscopy

28

[87]. No film formation was observed, as opposed to the situation of MBT described in section 15.5, and as opposed to the typical case of strong adsorption of amphiphiles summarised in section 15.3. Ex situ angular dependent XPS with a detailed analysis of the valence band region of ZnO combined with UV photoelectron spectroscopy of the adsorbed β-CD showed an upwards band bending of the major levels in ZnO towards the zinc oxide/inhibitor interface, and a downward band bending of the major β-CD levels at the same interface. This band structure is the result of a positive charge accumulation on the top of the zinc oxide, and a negative charge accumulation on the β-CD facing towards the ZnO. Interaction with β-CD thus leads to hole accumulation at the top of the intrinsically n-type ZnO, making it "less n-type", i.e. less rich in intrinsic defects. The reason may be that some of the OH groups of β-CD fill vacancies in ZnO. The result is a charge transfer that limits dissolution reactions through the surface [87]. This mechanism of corrosion inhibition is quite unique amongst the systems known so far. It also demonstrates in a practical example what was already said in section 15.2: Any molecule has the potential to be a corrosion inhibitor, and without clear mechanistic investigations and insight, a simple statement of inhibition may be trivial.

The release of corrosion inhibitors from β-CD[Inh] complexes with Inh = MBT or the closely related mercaptobenzoimidazole was investigated after incorporating such complexes into organosilicate-based hybrid coatings on aluminium alloy AA2024 [88]. This alloy is of limited relevance for the oil and gas industry, however, the results are likely transferable to other aluminium alloys. Healing of defects in the coating was observed by scanning vibrating electrode technique measurements [88]. The defect healing ability improved when combining the hybrid coating with an organic top coat [89]. This work inspired extensive systematic screening of several CDs with different

inhibitors, all on AA2024 [90]. Directly relevant for oil and gas may be the the application to carbon steels of chitosan modified with β-CD, which reduced the corrosion rate in hydrochloric acid compared to uncoated steel [91]. Such a reduction is, however, expected when comparing a coated and an uncoated material.

Our group studied the release of β-CD[Inh] complexes, with MBT showing very promising results, from polymer model coatings on zinc, and how this release affects the delamination of the model coating [92]. A schematic view of the release from the system is shown in Fig. 15.7. Experimentally, β-CD[MBT] was mixed with poly(vinyl butyral) [PVB]. PVB is frequently used as a weak model coating. The β-CD[MBT] containing PVB was applied on top of metallic zinc, and an artificial defect was prepared and filled with aqueous KCl. The progress of corrosion was monitored by scanning Kelvin Probe. Experiments show the beginning of cathodic delamination, as typically observed for PVB on zinc. However, in the presence of β-CD[MBT] and other inhibitor complexes, the delamination slows down with time, and with time, the potential measured in the defect by SKP moves away from the potential of corroding zinc towards the potential of passive zinc. Cathodic delamination came to a standstill [92]. Consequently, a defect that was corroding initially has been healed. The reason can only be inhibitor release in this experiment. While the self-healing is caused by the corrosion inhibitor, the β-CD increases solubility of the corrosion inhibitors in the aqueous solution, ensures thus a more even spread and accessibility of the defective, corroding surface to the inhibitor, and facilitates healing.

One can also incorporate β-CD[MBT] complexes into a pretreatment like layer on zinc [93]. To realise this, zinc has been precorroded in the presence of β-CD[MBT] in KCl for 24 h, dried and cleaned, and a coated with a PVB model coating. Again, the delamination was monitored from an artificial defect by scanning Kelvin probe. As also
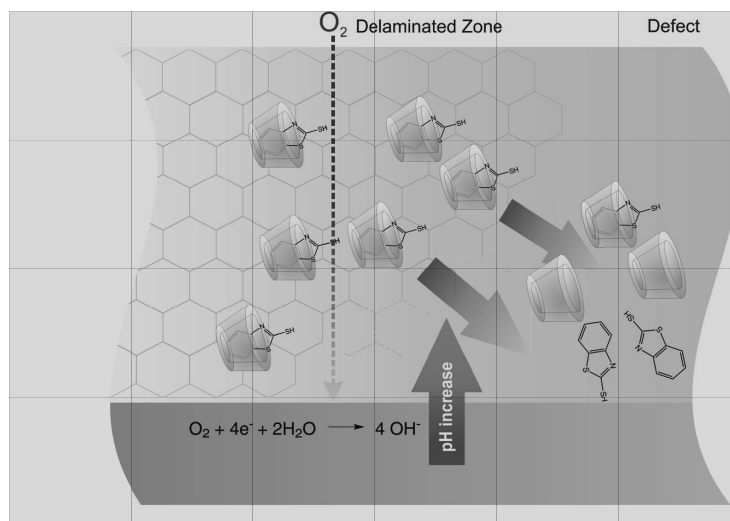
Figure 15.7: Scheme illustrating the release of a β-CD[MBT] complex from an organic polymer coating, and the subsequent release of free MBT, which inhibits progress of the corrosion process as the molecule would.

noticed in the approach when β-CD[MBT] was incorporated into a polymer coating, the defect potential went into the region of the passive zinc after several hours, i.e. the defect healed [93]. As mentioned in the previous paragraph, the healing is caused by the MBT alone, however, incorporation of MBT into the zinc oxide would not have been possible in the same way as in the form of β-CD[MBT] complexes. Likewise, β-CD increases the solubility and thus availability of MBT.

More sophisticated and complex approaches to self-healing exist, e.g. for fully autonomous corrosion protection. For instance, one component of a repair system can be incorporated into a polymer coating, while the other is incorporated into a galvanisation coating [94]. Upon initiation of corrosion, both components would be released, react with each other, and heal the defect [94].

Several of these approaches could also be realised with commercial coatings, but

a number of engineering challenges exist before they will be widely used, e.g. in the oil and gas industry. Over many decades, commercial coatings had the challenge that constant release of inhibitors could have caused problematic environmental behaviour, which may be overcome by such novel approaches.

15.7. Conclusions and Outlook

Surface interaction corrosion inhibitors facilitate self-healing. Almost all substances that may adsorb to the surface of a metal may act as corrosion inhibitors, as they can reduce the corrosion rate. Formed adsorbate layer will, in contact with a solution containing the respective substance, heal upon damage without intervention, i.e. they "self-heal". Very different structures and very different mechanisms act to make a certain inhibitor better suited for application than others.

The examples of imidazoline surfactants and of MBT showed some of the important aspects for successful corrosion inhibitors that find application in industry.

- A good corrosion inhibitor needs to interact with the respective materials surface in a robust way. Adsorption needs to happen e.g. to different crystal faces in comparable strength. Typically, substances that are good corrosion inhibitors interact with the respective materials surface through more than one atom.
- A good corrosion inhibitor needs to have some solubility in the medium in which it protects against corrosion.
- A good corrosion inhibitor interacts also with the dissolution products, and upon interaction will increase its inhibition action, e.g. by formation of a film as an "in situ conversion coating".

- Some good corrosion inhibitors which we would term "sacrificial inhibitors" can be oxidised instead of the metal, and the oxidation products would still protect the surface.

The many different aspects affecting inhibitors shows also the difficulty in optimising inhibitor actions. It is not a single quantity that needs to be optimised, but rather a good compromise between different molecular properties needs to be obtained, and the balance depends on environment and metal. The example of β-CD and MBT also shows in one particular case that the molecular interactions between substances is quite important for the actual function of inhibitors. In actual application, often complex molecular systems interact with each other to ensure a good corrosion inhibition. In recent years, molecular level simulations started to become more and more important in the field of inhibitor research, however, on the method in this field, there are also important challenges to overcome. Also environmental considerations have become more and more important in optimising inhibition systems. Consequently, there is still significant room for improvement and systematic understanding of the interaction of corrosion inhibitors. There is no "silver bullet" inhibitor or inhibitor system - and there likely never will be one.

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