Cyclodextrins as Carriers for Organic Corrosion Inhibitors in Organic Coatings

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Coatings are widely applied on metal surfaces for protection against corrosion. Once a coating is damaged and a defect is filled by aqueous solutions, delamination of the coating initiates further materials degradation. Cathodic delamination can be suppressed by adding active additives to the coating matrix. In this study, the impact was investigated of β-cyclodextrin inhibitor complex (β-CD[*Inh*]) additives in polyvinylbutyral model coatings on the cathodic delamination of coatings on zinc, using the scanning Kelvin probe (SKP). With the presence of the β-CD[*Inh*] in the coating, a decrease was observed of the delamination rate to 1/4 of that in the reference system without β-CD[*Inh*]. Release experiments using UV-Vis spectroscopy showed that in the presence of cyclodextrins, the released concentration of the inhibitor 2-mercaptobenzothiazole from the coating increased. The increase was most pronounced under alkaline conditions, where the released concentration within 24 h increased by a factor of 6 compared to a reference system without β-CD. The delamination experiments performed with 0.1 M KOH in the defect showed a quick stop of the delamination. When 1 M KCl was used as electrolyte, the defect potential rose after 16 h to the passive potential of zinc, if a sufficient amount of β-CD[*Inh*] was present in the polymer model coating.

Zinc and its alloys are industrial products for cathodic corrosion protection of steel components. They are hence used in a variety of applications, e.g. in metallic coatings.[1] On the other hand, zinc may corrode itself actively, which is why a protection of the metal is needed. A straightforward way to protect non-noble metals such as zinc against corrosion is the application of organic coatings.[2–4] The coating functions as a barrier against water and dissolved ionic species, which are crucial for initiation of corrosion processes.[5,6] The protection against corrosion simply by providing a physical barrier works as long as the coating is not damaged. If the coating is damaged down to the underlying metal, aqueous solutions can access the metal surface, and corrosion of the base material begins.[7] (On the other hand, the presence of water and electrolytes is not sufficient for fast coating failure.[8]) A further consequence is that the coating may start to delaminate, exposing more free metal surface.[9] The fastest mechanism of coating delamination initiated from a defect is cathodic delamination.[5] It is assumed that reactive intermediates formed as product of the oxygen reduction reaction are the cause for the debonding of the coating from the metal.[6,10–12] The scanning Kelvin probe (SKP) can be used to determine the kinetics of this process.[4,6,13,14] The progress of cathodic delamination depends on different factors, including type and concentration of the cation,[15,16] oxygen partial pressure,[17] and surface roughness.[18,19] A critical point is the bonding between the metal and the polymer, which can significantly reduce the delamination rate.[12,20,21]

An approach for further suppression of cathodic delamination is the addition of active components into the organic coating.[22,23] The most effective inhibitors are based on Cr^{VI}. These are banned in many countries because of toxicity.[24,25] Organic corrosion inhibitors promise good protection of several metals.[26,27] However, these are often aromatic heterocyclic compounds which are hydrophobic, making the release in sufficient amounts into aqueous solutions a challenge. More recent approaches use inhibitor release systems with complex chemical composition which are released as soon as the potential change or pH change associated with the onset of corrosion is detected.[28–30] Recent overviews about "smart" coating systems, where release of inhibitors is initiated by a certain trigger, compiled the state of the art

in this field.[31–33] This work looked at a possibility to solubilize the hydrophobic corrosion inhibitors on a molecular level, which requires significantly less chemical complexity.

An interesting molecular carrier system for small organic molecules are cyclodextrins (CDs). CDs are cyclic oligosaccharides produced from starch by means of enzymatic conversion.[34] They have α-1-4 linked glucosepyranose subunits. Natural CDs consist of six (α-), seven (β-), or eight (γ-CD) glycosyl units. The structure of β-CD, which was subject of investigation in this work, is shown in Figure 1. Due to the geometric arrangement, CD can be used as a host for organic guest molecules, mostly in its hydrophobic "inside" pocket. Applications of such host-guest complexes have been described, amongst others, in pharmaceutical, biomedical and food applications.[35,36] The
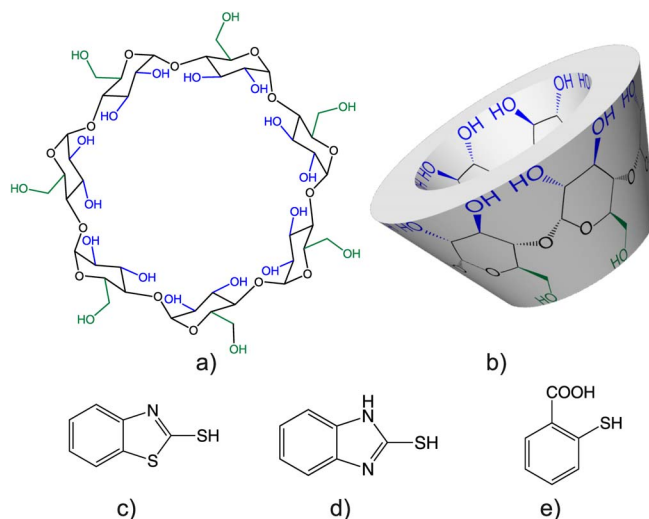

Figure 1. Structure of β-cyclodextrin (β-CD), (a) chemical structure, and (b) structure illustrating the cone-like spatial arrangement. Chemical structure of the organic corrosion inhibitors used in this work; (c) 2-mercaptobenzothiazole (MBT), (d) 2-mercaptobenzoimidazole (MBI), and (e) thiosalicylic acid (TSA).

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propensity of CD to host organic guest molecules depends, e.g., on the size of the guest molecule. If the guest has the wrong size, it will not fit into the CD cavity. Misfit contributes to the thermodynamics of the interaction between CD, guest and solvent.[34,37] β-CD will preferentially form complexes with aromatic and heterocyclic compounds,[37] making it ideal for complexing poorly water soluble corrosion inhibitors such as 2-mercaptobenzothiazole (MBT; Figure 1). The size of MBT is such that it fits into the hydrophobic pocket of β-CD. The formation constants of β-CD inhibitor complexes, CD[*Inh*], according to

$$\beta\text{-CD} + Inh \rightleftharpoons \beta\text{-CD}[Inh] \qquad [1]$$
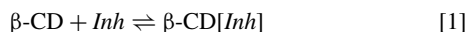
for inhibitors *Inh* MBT and 2-mercaptobenzoimidazole (MBI) were reported to be on the order of 10^2 L mol^{-1}.[38] This order of magnitude indicates that although complexes are formed in water, these are still facilitating release of the complexed inhibitor in relevant concentrations. The dissociation of the β-CD guest complexes in general is a rapid process,[36] faster than the time scales relevant in corrosion research.

So far, there are only few application of cyclodextrins in corrosion science. The effect was shown of complexes of β-CD with corrosion inhibitors on the repassivation of AA2024-T3.[38,39] The natural polymer chitosan was modified with β-CD, and applied as a corrosion inhibitor for carbon steel in hydrochloric acid, achieving an inhibition efficiency of over 90%.[40] Physisorption of the β-CD on the steel surface was proposed as explanation for this observation.[40] So far, there is no study on the use of β-CD as a carrier for corrosion inhibitors in coatings, and their effect on cathodic delamination. In this work, β-CD was used as a carrier for selected organic corrosion inhibitors, as shown in Figure 1c–d. The release of the inhibitors complexed with β-CD from organic model coatings was investigated by UV-Vis spectroscopy, and the corrosion-driven cathodic delamination of model coatings from zinc was investigated by SKP.

Experimental

Materials.—Zinc sheets with a thickness of 1.5 mm (99.95%) were purchased from Goodfellow and cropped for the delamination experiments to a size of 15 mm · 20 mm. The specimens were ground with 1000P SiC paper to ensure constant roughness throughout all experiments. All surfaces were cleaned before the experiments with ultrapure water and ethanol, and subsequently dried under a nitrogen stream. The chemicals KCl, β-CD (purity 97%; without chemical modification of the oligosaccharide), MBT, MBI, thiosalicylic acid (TSA), and poly(vinyl butyral) [PVB; M_w = 50000-80000 g mol^{-1}] were purchased from Sigma-Aldrich, and used as received. All aqueous electrolytes were prepared using water from a USF ELGA water purification system with a conductivity of less than 0.055 μS cm^{-1}.

Preparation of β-CD inhibitor complexes, β-CD[Inh].—Preparation of the β-CD inhibitor complexes proceeded in suspension, which a common method for large scale preparations.[41] In a 200 mL beaker, 2 g of β-CD were added to 100 mL ultra pure water. During fast stirring, an equimolar amount of the respective corrosion inhibitor was slowly added to enable formation of a 1:1 β-CD-inhbitor complex.[c] The corrosion inhibitors used in this study were MBT, MBI, and TSA, shown in Figure 1. The solution was stirred for at least 24 h.[41] To obtain the complex as powder, the solution was subsequently centrifuged. The resulting slightly yellow powder was dried at 50°C for 24 h in vacuum.

Within this work, the β-CD inhibitor complexes will be denoted as β-CD[*Inh*], where *Inh* stands for the abbreviation of the respective inhibitor.

Preparation of model coatings for delamination experiments.—The β-CD[*Inh*] powder was added in the desired quantity to a 10 wt% PVB solution in ethanol. Zinc samples were subsequently spin-coated with this solution at 2500 rpm for 20 s. The β-CD[*Inh*] PVB solution was spin-coated twice, followed by a single step of coating pure PVB without the complex to simulate a top-coat. The coatings were dried for 30 min at 70°C. The coated zinc sheets were placed for at least 1 h in the SKP chamber at 95% relative humidity prior to delamination studies to avoid charging effects. For initiation of the cathodic delamination, the coatings were subsequently scratched with a scalpel. Scratches were ≈2 mm in length and 200 μm in width. The defect was covered with 7.5 μL of 1 M KCl and immediately transferred to the SKP chamber. Selected experiments were carried out with 0.1 M KOH, instead of KCl, in the defect.

The delamination experiments were executed using a SKP system from KM Soft Control with a 100 μm NiCr tip.[14] Calibration of the SKP tip was done with Cu/CuSO$_4$ (saturated). All potentials given here are referenced to the standard hydrogen electrode. For determining the corrosion potential in the defect with time, the SKP tip was placed over the electrolyte drop. The delamintion experiments were conducted and analyzed as reported previously.[6] Delamination rates were extracted by performing a linear fit in plots of position x_{del} as function of time over the full time range of the experiment.

Release of MBT.—To investigate the release of organic corrosion inhibitors from β-CD using UV-Vis spectroscopy, the complex with MBT was chosen. Inhibitor release at different pHs (4.3, 6.3, 11.1) in phosphate buffer was quantified using a UV-Vis spectrometer Perkin Elmer Lambda 800 at 320 nm. The same amount of inhibitor was added either with or without β-CD to the PVB solution. The resulting solution was then spin-coated onto a glass sheet. After drying for 30 min at 70°C, the coated glass sheet was placed in a beaker filled with the buffer solution. At defined times, 1 mL of the solution was transferred to the UV-Vis spectrometer. The concentrations were calculated by a calibration curve for the different pHs,[29] using absorption coefficients of (25.08 ± 0.04) L mmol^{-1} cm^{-1} (pH 4.3; wavelength 320 nm), (25 ± 1) L mmol^{-1} cm^{-1} (pH 6.3; wavelength 320 nm), and (20.0 ± 0.2) L mmol^{-1} cm^{-1} (pH 11.1; wavelength 233 nm).

The release of MBT in environments with different pH was evaluated in the presence and absence of β-CD by UV-Vis spectroscopy. For this purpose, solutions of MBT and of the β-CD-MBT complex in phosphate buffer at different pH (4.3, 6.3, 11.1) were prepared by stirring the respective powder in the respective buffer for 1 h at room temperature. After filtration, UV-Vis spectra were recorded, and the MBT concentration was determined as described above.

Electrochemical impedance spectroscopy (EIS).—The prepared model coatings were investigated by EIS in 1 M KCl. EIS investigations were conducted using a CompactStat (Ivium Technologies, Eindhoven, The Netherlands) in a three electrode setup. A commercial Ag/AgCl (3 M KCl) electrode (Metrohm, Filderstadt, Germany), connected with a luggin capillary, was used as a reference electrode. A platinum foil was set as a counter electrode, while the coated zinc sample was utilized as working electrode. The measurements were executed in a frequency range of 10^5 to 10^{-1} Hz with 10 mV amplitude of the sinusoidal voltage modulation around the initial open circuit potential. The spectra shown here were recorded after 7 h of immersion.

Results and Discussion

EIS experiments were performed, comparing the impedance of β-CD[MBT] to the preparations containing the individual components (Figure 2). No fitting was conducted, rather shall we limit the discussion to the low-frequency impedance modulus. This value increased by almost 4 orders of magnitude through addition of β-CD[MBT] to PVB. Consequently, there was a strong effect of β-CD[MBT] on the interfacial electrochemical processes. Addition of CD and MBT alone

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[c]This synthesis approach replaced an earlier approach working below the solubility limit of β-CD. In that route, a solution of inhibitor was added to an equimolar amount of dissolved rather than suspended β-CD. The β-CD inhibitor complex then precipitated. This synthesis route gave significantly lower yields than the suspension route, and was hence discontinued.
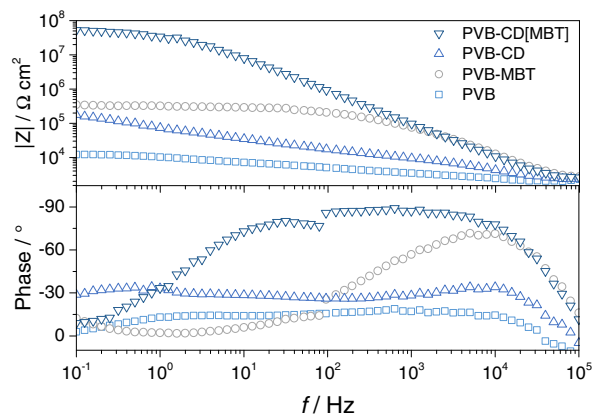
Figure 2. EIS results for Zn coated with 15 wt% β-CD[MBT] in PVB after 7 h exposure to 1 M KCl, together with control experiments for Zn coated with pure PVB, 5 wt% MBT in PVB and 10 wt% β-CD in PVB, respectively.

led only to an increase in charge transfer resistance of about one order of magnitude.

As the main topic of this work, the effect of β-CD inhibitor complexes on cathodic delamination on zinc was investigated. Figure 3 shows SKP potential profiles acquired during the delamination of PVB and composite coatings containing β-CD[*Inh*]. The SKP potential profiles followed in all cases the typical progress for delamination of coatings from zinc.[42] The low potential region initially located in the defect propagated with time under the coating. The region with high potential, in which the potential was 200–300 mV higher than the defect potential is the region where the metal/polymer interface is still intact.

The respective progress of the delamination front of the different applied coatings is shown in Figure 4. A double logarithmic plot, in the style shown elsewhere,[8,12] confirmed that the progress of the delamination front scaled linearly with time t after an initiation phase where delamination progress scaled with an exponent > 1. (The fast initial delamination may be caused by the preparation method of the artificial defect used here.) Delamination rates were determined from the slopes of linear fits to the data shown in Figure 4. The delamination
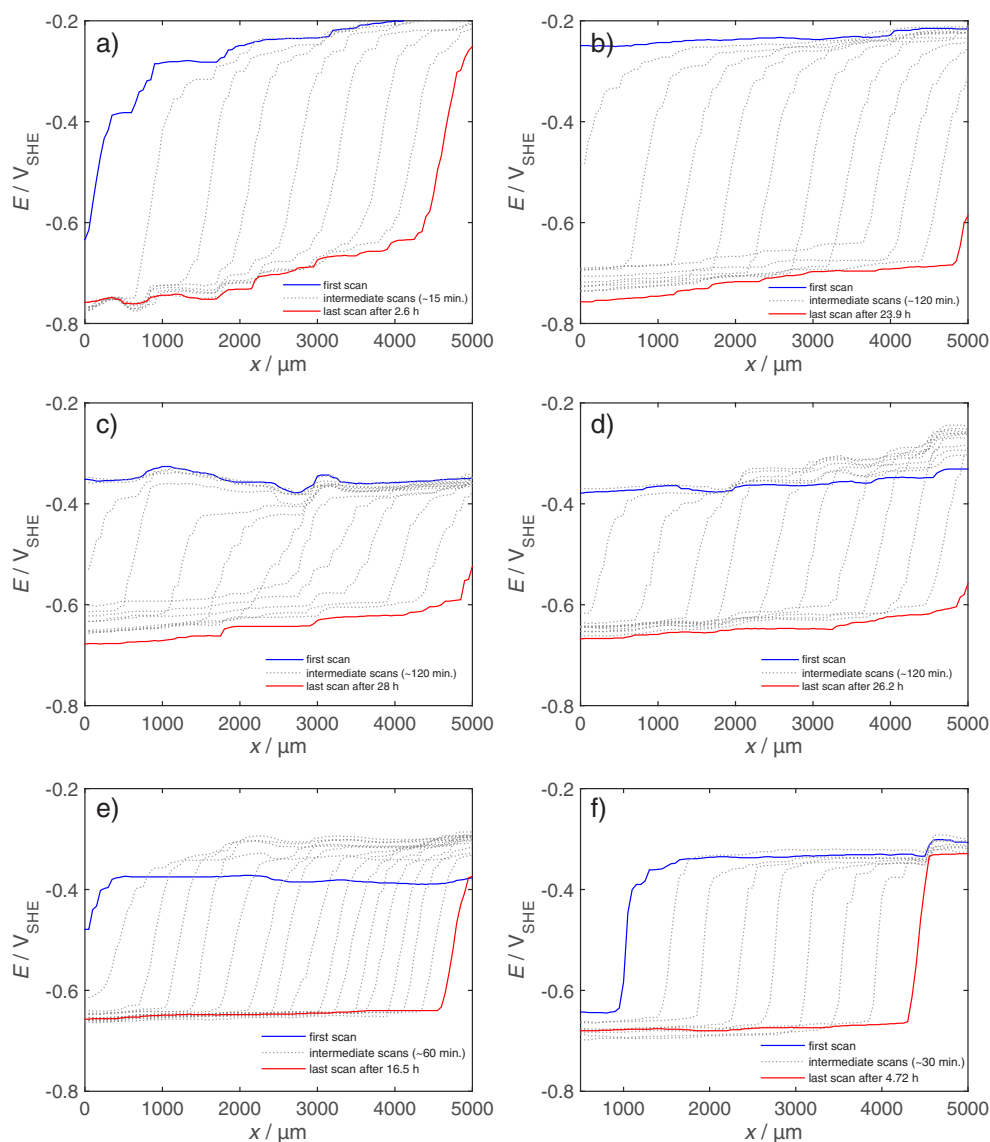

Figure 3. SKP delamination profiles of Zn coated with the different model coatings investigated, showing electrode potential E as function of position x after certain times t; (a) pure PVB coating, (b) PVB + 15 wt% β-CD[MBT], (c) PVB + β-CD[MBI], (d) PVB + β-CD[TSA], (e) PVB + 10 wt% β-CD, (f) PVB + 5 wt% MBT. The progress of the position of the delamination front was evaluated in Figure 4.
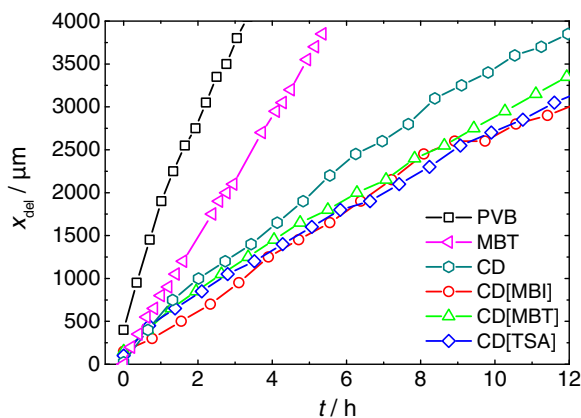
Figure 4. Position x_{del} of the delamination front with time for PVB with different β-CD[*Inh*], and different control experiments. Data was extracted from SKP potential profiles such as those shown in Figure 3. The resulting delamination rates are summarized in Table 1. Time $t = t_x - t_0$, where t_0 is the time of initiation of cathodic delmination, and t_x the time at which delamination has progressed to distance x_{del}.

rates extracted from this plot are compiled in Table I. The delamination rates were reduced to ≈1/4 with the addition of the β-CD[*Inh*] into the PVB. The delamination rates for the composite coatings with the different β-CD[*Inh*] agreed within the triple standard deviation, which is also easily visible in the curves in Figure 4. This good agreement between delamination rates with structurally very different corrosion inhibitors can be taken as a hint that β-CD facilitated the release of the corrosion inhibitors from the polymer coating. β-CD alone also decreased the delamination rate of PVB significantly, which might have been caused by enhanced barrier properties. It is, however, more likely that β-CD alone also acts as corrosion inhibitor. This interpretation is consistent with the EIS data in Figure 2, where CD also reduced the charge transfer resistance. The exact mechanism of interaction of β-CD alone with the metal surface is currently unclear, and requires further investigation. There may simply be adsorption on the surface, limiting the amount of active sites for dissolution. On the other hand, there is clearly an additional effect of the well-known inhibitors complexed to β-CD, so that the action of β-CD alone cannot be the explanation for the observed decrease in delamination rate.

Consequently, the effect of β-CD on the release of corrosion inhibitors from a polymer coating was investigated. To this end, MBT was chosen as the inhibitor. PVB coatings containing β-CD[MBT] and MBT on glass were prepared, exposed to aqueous buffers at different pH, and the concentration in the buffer of MBT was monitored with time by UV-Vis spectroscopy. The selected pH range was chosen to simulate the different zones which occur during cathodic delamination. The pH of 4.3 simulated the initially slightly acidic environment in the defect. The alkaline pH of 11.1 simulated the delamintion front where the oxygen reduction is taking place.[43] The near neutral pH 6.3 is an intermediate pH between the defect and the delamination front,
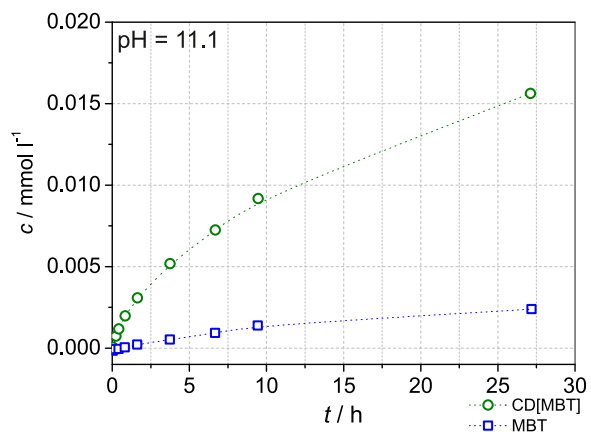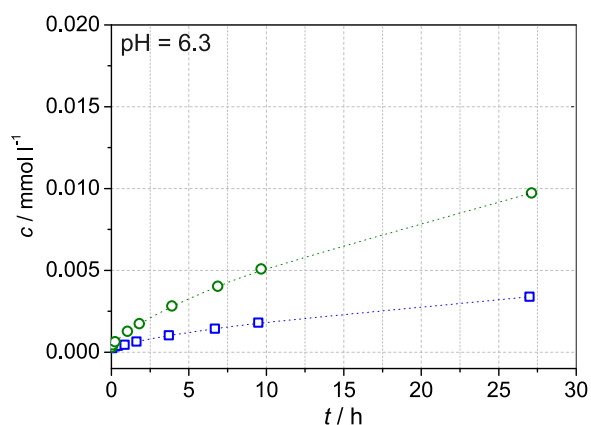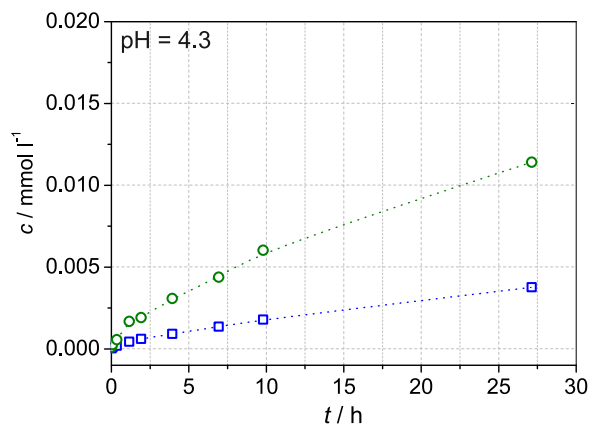

Figure 5. Release of pure MBT and β-CD[MBT] from PVB coating at different pH as function of time. (a) pH = 4.3; (b) pH = 6.3; (c) pH = 11.1. Concentration of MBT in the coating was in all cases 2.5 wt%.

which occurs in the aftermath of the passing front. Resulting release curves are shown in Figure 5.

At all the three investigated pHs, the presence of β-CD increased the amount of MBT released from the coating. The difference between β-CD[MBT] and pure MBT was largest at pH 11.1. In the first 5 h of the experiment, the complexing with β-CD increased the released amount of MBT to 5 times the amount observed in the absence of β-CD. A possible reason may be the poor solubility of pure MBT. MBT is more soluble under alkaline conditions, compared to acidic or neutral conditions. Solubility may have increased by incorporating MBT into the hydrophobic pocket of the otherwise hydrophilic β-CD.

Therefore, the concentration of MBT was determined in the same buffers as used for the release experiments after 1 h exposure (Table II). In the presence of β-CD, concentration of MBT tripled at

Table I. Overview of the delamination rates for different model coatings on Zn in contact with 1 M KCl in the defect. The second column shows the number of moles of CD, *Inh*, or CD[*Inh*] added per unit of mass PVB.

Coating	Added moles mmol / g PVB	Delamination rate μm h^{-1}
PVB	0	990 ± 20
PVB + MBT 5 wt%	0.3	704 ± 4
PVB + β-CD 10 wt%	0.09	276 ± 2
PVB + β-CD[MBT] 15 wt%	0.12	226 ± 2
PVB + β-CD[MBI] 15 wt%	0.12	223 ± 3
PVB + β-CD[TSA] 15 wt%	0.12	216 ± 2

Table II. Concentration of dissolved MBT and β-CD[MBT], in mmol L^{-1}, at different pHs.

|	pH 4.3	pH 6.3	pH 11.1
MBT	0.63 ± 0.02	0.48 ± 0.02	2.03 ± 0.03
β-CD[MBT]	1.53 ± 0.02	1.57 ± 0.07	4.45 ± 0.06

the lower pHs, and more than doubled at pH 11.1. Increase of concentration was hence lowest at the highest pH, while the increase in release (Figure 5) was largest at the highest pH. Therefore, the observed increase in release by incorporating MBT into β-CD cannot be explained purely on the basis of an improved solubility. The transport out of the hydrophobic coating must also have been affected.

Inspired by the previous results, the effect of β-CD on the delamination under alkaline conditions was investigated. For this purpose, delamination experiments were conducted with 0.1 M KOH. The corresponding delamination potential profiles measured by SKP are shown in Figure 6. In the early stages of delamination, the rates were in the same range. After ≈4 h, a slowing down in delamination was observed in the coating containing β-CD[MBT] (Figure 6). Afterwards, an increase in the defect potential was observed, which reached the passive potential of zinc.[42] A complete passivation was monitored after ≈14 h. A double logarithmic plot of the data shown in Figure 6c also confirmed that the time dependence had a lower exponent than $1/2$ in the final phase of the delamination. The β-CD therefore facilitated release of MBT from the coating to an extent which led to passivation, i.e. a significant slow down in corrosion and in this case, a stop in delamination.
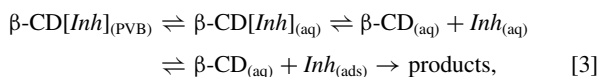
In a final set of experiments, the effect of β-CD[MBT] at neutral pH in chloride containing electrolyte was investigated. For this purpose, the potential in the defect was monitored with time for coatings containing MBT and β-CD[MBT] (Figure 7). After adding a sufficient amount of the β-CD[MBT] powder, self-passivation was observed in neutral chloride containing electrolyte also. In contrast, no self-passivation was observed for PVB containing the same amount MBT which was not complexed by β-CD, and for pure PVB. An increase of the defect potential within 24 h was only observed with at least 3 wt% of MBT incorporated into the PVB, which corresponds to 25wt-% of β-CD[MBT].

The concentration dependence of the delamination rate from a KCl-filled defect (Figure 8) shows that increased content of β-CD[MBT] led to a slow down of delamination even in the initial phase of delamination, when a linear time dependence of the progress of the delamination front was observed.

The results show that β-CD[*Inh*] slowed down delamination, and in the case of β-CD[MBT], even a stop and a repassivation of the defect was observed. This is a clear indication that β-CD[*Inh*] participate in the electrochemical processes at the interface. While it is possible that presence of β-CD[*Inh*] enhanced the barrier properties of the coatings, and inhibited oxygen diffusion to the interface, the observation of self-passivation of a defect cannot be explained simply by improved barrier properties. The β-CD takes the role of increasing the availability of the inhibitors in the aqueous phase. In the absence of CD, the involvement of the inhibitor from inside the coating to the actually corroding surface proceeds according to

$$Inh_{(PVB)} \rightleftharpoons Inh_{(aq)} \rightleftharpoons Inh_{(ads)} \rightarrow products. \qquad [2]$$
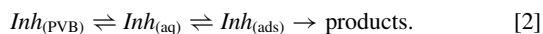
If the β-CD[*Inh*] were added to the polymer, the inhibitor got into its active state as

$$\beta\text{-CD}[Inh]_{(PVB)} \rightleftharpoons \beta\text{-CD}[Inh]_{(aq)} \rightleftharpoons \beta\text{-CD}_{(aq)} + Inh_{(aq)}$$

$$\rightleftharpoons \beta\text{-CD}_{(aq)} + Inh_{(ads)} \rightarrow products, \qquad [3]$$

where β-CD adsorption is a further possible route contributing to surface protection. However, the accessible inhibitor is the the sum of freely dissolved and complexed inhibitor. Its total concentration is expected to be higher when the complexing agent β-CD is present.
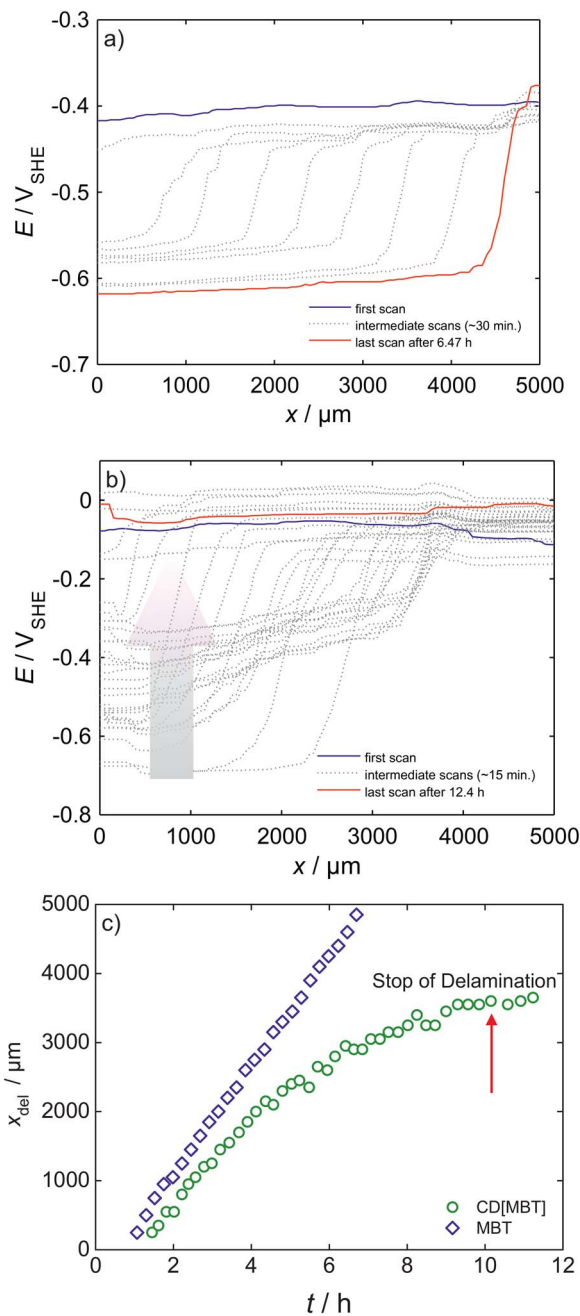

Figure 6. Delamination experiments of PVB with 0.1 M KOH in the defect. SKP potential profiles recorded with (a) MBT and (b) β-CD[MBT] in the PVB. (c) Position x_{del} of the delamination front with time t.

Results here share some features with results reported for AA-2024.[38] By the the presence of the β-CD, a sustained release of MBT over a wide pH range was detected, which led to self-passivation of a defect. The highest release was observed at alkaline pH. On the other hand, the previous study on AA-2024 was conducted under immersion in solution, and delamination of coatings was not investigated.[38] Stop of delamination and increase of the defect potential to the passive potential of zinc as reported here was so far only observed with an electrode potential triggered, capsule based release system.[29] Suppression of the cathodic delamination with PVB-β-CD[*Inh*] composite coatings in this work was comparable with Cr^{VI} based pigments in PVB,[23] although a quantitative comparison of data, which is of stochastic nature as, e.g., the time to self-passivation of a defect in a model system, is not a suitable performance indicator.
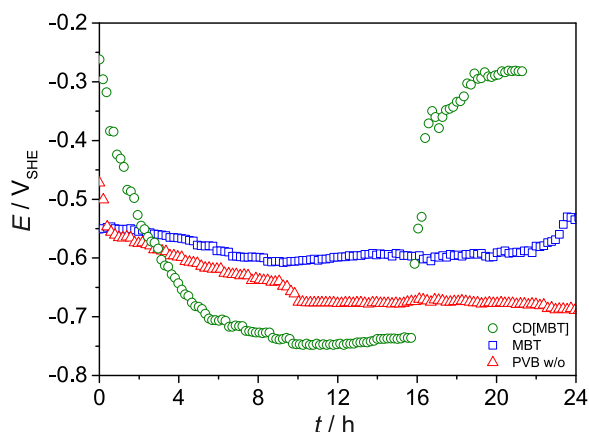
Figure 7. Development of the corrosion potential in a defect covered with 1 M KCl with time for different coatings, as measured by SKP. The different curves show PVB without inhibitor, PVB containing 3 wt% MBT with and without β-CD.

Overall, organic corrosion inhibitors, such as MBT, show good inhibition efficiencies.[27] However, many of these corrosion inhibitors are poorly soluble in aqueous solution. As a sufficient concentration is needed for the inhibitors to act, their incorporation as a guest in host-guest complexes in CDs, as shown here, may be a general route toward increasing protection over a large pH range. At this stage, the amounts that need to be added for self-passivation to occur are rather large, however, a systematic investigation in the interaction of organic inhibitors with β-CDs and similar substances may help to bring down the needed concentration. Likewise, the exact mechanism of the self-passivation remains yet to be investigated.

Conclusions

Increased release of organic corrosion inhibitors was observed from organic model coatings in a wide pH range after the corrosion inh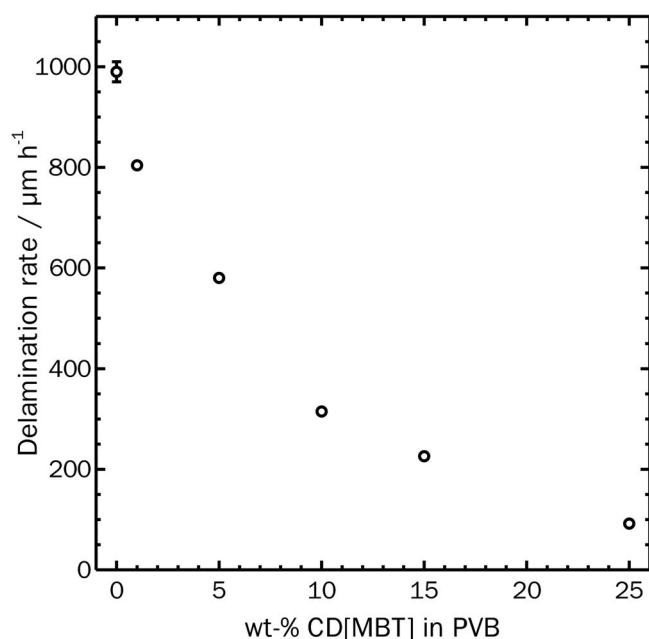ibitors were complexed with β-CD. The effect is particularly pronounced at high pH. The solubility of the corrosion inhibitors in aqueous solutions was also increased by complexing them with β-CD. The cathodic delamination rate of PVB as a weak model coating was significantly reduced by adding β-CD[*Inh*] to the coating. For the three investigated inhibitors, the observed delamination rates agree well within the experimental uncertainty. Under alkaline conditions, a stop of delamination was observed in the presence of β-CD[MBT], as well as the self-passivation of the defect. At neutral pH, passivation of a defect was also observed when β-CD[MBT] was released from the coating. Inclusion β-CD[MBT] also increased the observed low frequency impedance modulus of the weak model coating PVB by 4 orders of magnitude.

Acknowledgment

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Figure 8. Delamination rate for different concentrations of β-CD[MBT] in PVB in contact with 1 M KCl in a regime in which the progress of the delamination from scales approximately linearly with time. Uncertainty estimates are typically lower than the size of the symbol.

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