



# Recent Developments in Environment-Friendly Corrosion Inhibitors for Mild Steel

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**Abstract |** In 2002, our group and collaborators began initial investigations on the use of rare-earth carboxylates as non-toxic and environment-friendly corrosion inhibitors for mild steel. This was followed by a more comprehensive study, reported in 2004 by Blin et al., in which a range of such carboxylate compounds were investigated. This study identified lanthanum 4-hydroxycinnamate, La(4-OHcin)<sub>3</sub> as a promising compound. In the review presented here our more recent investigations on mild steel corrosion inhibitors with structures closely related to La(4-OHcin)<sub>3</sub> are presented.

In another study, Lee investigated the effect on corrosion of subtle changes to the La(4-OHcin)<sub>3</sub> structure. Seter et al. found that small structural changes could have a major effect on the inhibition performance.

Nam et al. investigated cerium, lanthanum and praseodymium 4-hydroxycinnamate as corrosion inhibitors for mild steel in carbon dioxide atmospheres in sodium chloride solution. In this particular situation, Pr(4-OHcin)<sub>3</sub> led to the largest reduction in corrosion current.

A totally organic complex, imidazolium 4-hydroxycinnamate (Imn 4-OHcin) has been investigated with the aim of developing a compound that can inhibit both corrosion and microbial growth. This compound was found to inhibit mild steel corrosion across a wide pH range and was particularly effective at a pH of 2.

We have also been investigating a rare-earth compound with an alternative carboxylate structure to the cinnamate; 3-(4-methylbenzoyl) propionate(mbp). This ligand differs from 4-hydroxycinnamate by having a carbonyl group present, which may give an extra anchor point to a metal surface when forming a barrier coating. A range of rare-earth mbp complexes was investigated, with Nd(mbp)<sub>3</sub> resulting in the largest reduction in corrosion current density at a concentration of 0.125 mM.

## 1 Introduction

Due to a range of applications, mild steel structures can corrode in such uses as pipelines under a variety of conditions, such as neutral pH in air or low pH in a CO<sub>2</sub> atmosphere. It is unlikely that a single corrosion inhibitor will be ideal for each of these applications. This means particular

compounds need to be developed for each unique environment. For applications in which a range of conditions may be encountered it is envisaged that a blend of inhibitors may be the best approach to minimize corrosion and extend the lifetimes of such expensive infrastructure. In our laboratories we have been developing a range of inhibitors

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**Carboxylate compounds:**  
In this review we refer to compounds containing the carboxylate ion ( $\text{RCOO}^-$ ) as being carboxylates.

**Chromates:**  
These are a class of very effective corrosion inhibitors containing the chromate anion  $\text{CrO}_4^{2-}$ , for example strontium chromate. Due to the oxidizing power of chromium in the +6 state these compounds are all toxic and carcinogenic.

**Anodic reaction:** This is the oxidation half reaction at the anode. For steel this is typically:  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$ .

**Filiform corrosion:** A form of corrosion that occurs under a metal coating due to the local change in conditions. Typically thread like in appearance they grow from a scratch or defect to penetrate under the coating. If allowed to progress filiform corrosion leads to coating delamination.

**Cathodic reaction:** This is the reduction half reaction at the cathode. In an aqueous, aerated environment this is typically:  $2\text{H}_2\text{O} + \text{O}_2 + 4e^- \rightarrow 4\text{OH}^-$ .

based on **carboxylate compounds** that best suit particular applications.

## 2 Carboxylate Compounds

Many traditionally used corrosion inhibitors for mild steel included inorganic compounds such as **chromates** and arsenates. We are now aware of the dangers associated with many of these compounds and researchers are seeking more benign alternatives. Chromates historically have been the most widely used corrosion inhibitors, as they have proven effective at reducing both the anodic and cathodic reaction rates in a variety of applications and for a range of metal types. In the search for more environment-friendly alternatives, inorganic metal compounds, such as cerium chloride and lanthanum chloride were investigated as corrosion inhibitors for aluminum and zinc.<sup>1,2</sup> These proved to be effective at reducing the corrosion rate by inhibiting the cathodic reactions. The rare earths react with the  $\text{OH}^-$  ions produced at the cathodic sites and form a barrier coating that reduced the reaction rates at these sites.<sup>2,3</sup> Conversely, organic carboxylate compounds at relatively high concentrations had been found to inhibit corrosion by forming a barrier coating, predominantly at the anodic sites, thus reducing **anodic reaction** rates.<sup>4</sup> Various carboxylate structures investigated are shown in Figure 1. It was then proposed that, by combining rare-earth metals with carboxylates, the resulting compound may act as a corrosion inhibitor that would match the chromate inhibitors' ability of reducing both the anodic and **cathodic reaction** rates. Initial studies by Forsyth et al. on cerium combined with three carboxylates—glycolate, salicylate and anthranilate—found that not only did they exhibit mixed inhibition, but for the cerium salicylate there was a synergistic effect, with corrosion rates reduced by more than that using individual components.<sup>4,5</sup>

Blin expanded on this initial study by evaluating a range of rare-earth carboxylate compounds in an effort to identify trends in structure that would

lead to the most effective corrosion inhibition for mild steel.<sup>6</sup> In 2004, Blin et al. published some of the results from this study, with the major findings summarized in Table 1.<sup>7</sup>

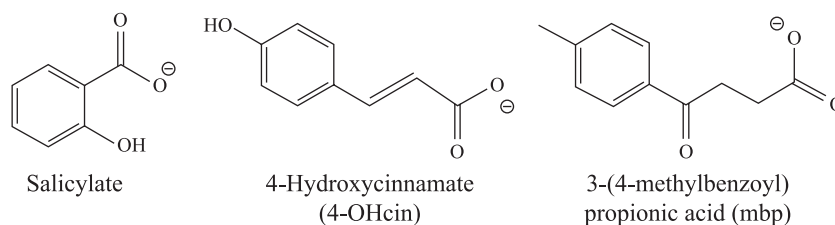
These rare-earth carboxylates reduce the anodic reaction rate after initial sample immersion, then, over time, increasingly reduce the cathodic reaction rate.<sup>4,7</sup> Lanthanum 4-hydroxycinnamate ( $\text{La}(4\text{-OHcin})_3$ ) exhibited a higher inhibition efficiency than a chromate inhibitor and at a quarter of the concentration.

Following on from the initial findings of Blin, Lee studied<sup>13</sup> the corrosion-inhibiting properties on mild steel of compounds very closely related to  $\text{La}(4\text{-OHcin})_3$ , some of which were reported by Seter et al in 2015.<sup>12</sup> As can be seen in Table 1, praseodymium 4-hydroxycinnamate,  $\text{Pr}(4\text{-OHcin})_3$ , and  $\text{La}(4\text{-OHcin})_3$ , consistently showed the highest inhibition efficiency, while lanthanum 3-hydroxycinnamate was only slightly less effective. However, cerium 4-hydroxycinnamate, lanthanum 3-hydroxycinnamate and lanthanum 2-hydroxycinnamate did not perform well.

Blin<sup>6</sup> and Lee<sup>13</sup> identified  $\text{La}(4\text{-OHcin})_3$  as a promising inhibitor and further studies were conducted on this compound. Catubig et al. incorporated 10 wt. % of the  $\text{La}(4\text{-OHcin})_3$  into a polyurethane-based coating and found that it inhibited the initiation and propagation of both coating delamination and **filiform corrosion** on mild steel.<sup>14</sup> This inhibition can clearly be seen in Figure 2, which shows corrosion filaments proceeding from the scribed surfaces of the control and 10 wt %  $\text{La}(4\text{-OHcin})_3$  samples after HCl corrosion activation and 5 days in a high humidity atmosphere. In this application, a mixed inhibitor such as  $\text{La}(4\text{-OHcin})_3$  is particularly effective, as within the head of filaments that form there is an anodic tip and a cathodic tail. A carboxylate film shuts down the anodic reaction at the tip, while a bimetallic film consisting mainly of lanthanum and iron hydroxides shuts down the cathodic areas.

In many areas in which steel pipelines are used, such as oil and gas and carbon capture

### Carboxylate Compounds



**Figure 1:** Chemical structures of various carboxylates investigated.

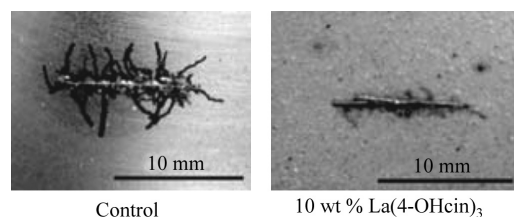
**Table 1:** Summary of results for carboxylate corrosion inhibitor compounds.

Solution	Conc. (ppm)	IE* $\eta$ (%)	Solution	Conc. (ppm)	IE* $\eta$ (%)
Blin et al. 2004 <sup>7</sup>			Seter et al. 2015 (cont)		
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	2000	87	La(4-OHcin) <sub>3</sub> pH2.5	600	76
LaCl <sub>3</sub>	217	63	Pr(4-OHcin) <sub>3</sub> pH2.5	600	52
CeCl <sub>3</sub>	200	82	Ce(4-OHcin) <sub>3</sub> pH2.5	600	-18
Na(cinnamate)	250	82	La(3-OHcin) <sub>3</sub> pH2.5	600	34
Na(4-MeOcin)	250	75	La(2-OHcin) <sub>3</sub> pH2.5	600	-27
Na(4-NO <sub>2</sub> cin)	250	83			
Na(4-OHcin)	250	83	La(4-OHcin) <sub>3</sub> pH5.5	600	71
Y(cin) <sub>3</sub>	162	83	Pr(4-OHcin) <sub>3</sub> pH5.5	600	90
La(cin) <sub>3</sub>	200	83	Ce(4-OHcin) <sub>3</sub> pH5.5	600	76
La(4-OHcin) <sub>3</sub>	500	91	La(3-OHcin) <sub>3</sub> pH5.5	600	81
La(4-MeOcin) <sub>3</sub>	191	88	La(2-OHcin) <sub>3</sub> pH5.5	600	38
La(4-NO <sub>2</sub> cin) <sub>3</sub>	190	92			
Ce(cin) <sub>3</sub>	180	77	Nam et al. 2014 <sup>8</sup>		
Ce(4-OHcin) <sub>3</sub>	200	84	Pr(4-OHcin) <sub>3</sub> CO <sub>2</sub> sat.		94
Ce(4-MeOcin) <sub>3</sub>	200	87	La(4-OHcin) <sub>3</sub> CO <sub>2</sub> sat.		92
Nd(cin) <sub>3</sub>	150	83	Ce(3-OHcin) <sub>3</sub> CO <sub>2</sub> sat.		90
Gd(cin) <sub>3</sub>	160	86			
			Chong et al. 2016 <sup>9</sup>		
Seter et al. 2012 <sup>10</sup>			2-MeHImn Sal pH7	4mM	13
La(4-OHcin) <sub>3</sub> pH8	600	98	2-MeHImn Gen pH7	4mM	49
La(4-OHcin) <sub>3</sub> pH5.5	600	71	2-MeHImn 4-OHcin pH7	4mM	84
La(4-OHcin) <sub>3</sub> pH2.5	600	68	2-MeHImn 4-OHcin pH2	4mM	72
La(4-OHcin) <sub>3</sub> pH2.5	400	31	2-MeHImn 4-OHcin pH8	4mM	86
La(4-OHcin) <sub>3</sub> pH2.5	200	17			
			Somers et al. 2016 <sup>11</sup>		
Seter et al. 2015 <sup>12</sup>			La(mbp) <sub>3</sub>	0.125mM	24
La(4-OHcin) <sub>3</sub> pH2.5	400	48	Nd(mbp) <sub>3</sub>	0.125mM	49
Pr(4-OHcin) <sub>3</sub> pH2.5	400	-6	Y(mbp) <sub>3</sub>	0.125mM	16
Ce(4-OHcin) <sub>3</sub> pH2.5	400	-8	Ce(mbp) <sub>3</sub>	0.125mM	41
La(3-OHcin) <sub>3</sub> pH2.5	400	38	Ce(mbp) <sub>3</sub>	0.250mM	62
La(2-OHcin) <sub>3</sub> pH2.5	400	-34	Ce(mbp) <sub>3</sub>	0.400mM	73
La(4-OHcin) <sub>3</sub> pH5.5	400	86			
Pr(4-OHcin) <sub>3</sub> pH5.5	400	81			
Ce(4-OHcin) <sub>3</sub> pH5.5	400	10			
La(3-OHcin) <sub>3</sub> pH5.5	400	71			
La(2-OHcin) <sub>3</sub> pH5.5	400	-5			

\*Inhibitor efficiency, IE, is defined as:

$$\eta = \frac{i_{corr}(\text{control}) - i_{corr}(\text{inhibitor})}{i_{corr}(\text{control})} \quad (1)$$

where  $i_{corr}$  is the corrosion current density quoted in each publication.



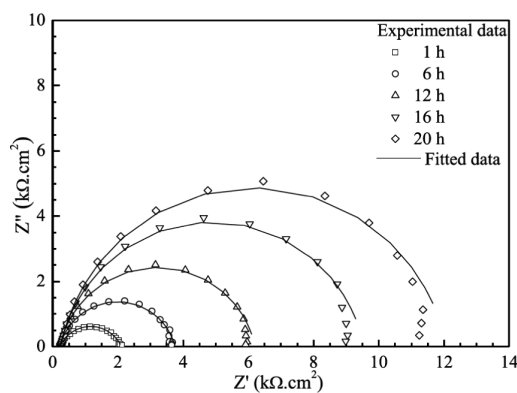
**Figure 2:** Coated and scribed steel surfaces after 5-day corrosion test. Reproduced with permission from J. Electrochem. Soc., 158, C353, (2011). Copyright 2011, The Electrochemical Society.<sup>14</sup>

applications, there is a high CO<sub>2</sub> content which, when combined with water that is often present, leads to the formation of carbonic acid.<sup>15</sup> This

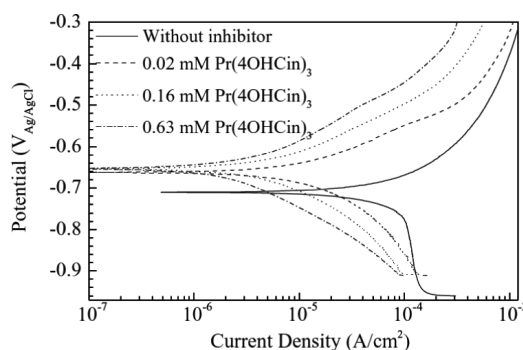
carbonic acid accelerates corrosion and can lead to rapid failure if proper precautions are not taken. For protecting steel exposed to high CO<sub>2</sub> content, Nam et al. assessed the ability of lanthanum, praseodymium and cerium 4-hydroxycinnamates to inhibit corrosion in a CO<sub>2</sub> saturated, 0.01M NaCl solution, with the Pr, La and Ce complexes showing inhibition efficiencies of 94, 92 and 90%, respectively.<sup>8</sup> Using **electrochemical impedance spectroscopy** to monitor the surface resistance with time, this study showed that this high level of inhibition was due to the growth of a protective surface film.<sup>8,16</sup> The EIS data for Pr(4-OHcin)<sub>3</sub> is shown in Figure 3. Previously, Blin et al. and Seter et al. had shown that in aerated, 0.01M

**Corrosion current density,  $i_{corr}$ :** This is the current per cm<sup>2</sup> that the metal would freely corrode at in the given solution. It is extracted experimentally from electrochemical testing.

**Electrochemical Impedance Spectroscopy (EIS):** An electrochemical test method in which an AC signal of varying frequency is used to probe the dielectric response of a material. Typically used in corrosion to model film formation and resistance on a metal surface.



**Figure 3:** Nyquist plot for mild steel in CO<sub>2</sub>-saturated 0.01 M NaCl solutions containing 0.63 mM of Pr(4-OHCin)<sub>3</sub>. Reproduced with permission from J. Electrochem. Soc., 161, C527 (2014). Copyright 2014, The Electrochemical Society.



**Figure 4:** Potentiodynamic polarization curves after 20 h for mild steel immersed in CO<sub>2</sub>-saturated 0.01 M NaCl solution at room temperature and with praseodymium 4-hydroxycinnamate compound concentrations from 0.00 to 0.63 mM. Reproduced with permission from J. Electrochem. Soc., 161, C527 (2014). Copyright 2014, The Electrochemical Society.

NaCl solutions with RE(4-OHCin)<sub>3</sub>, La and Pr have lower corrosion rates than Ce.<sup>7,12</sup> The reason for the different behavior of the RE metals is not completely understood at present although the solubility of the compound and the nature of the species in solution plays a role, as discussed below.

Additionally, the potentiodynamic polarization results after 20 hours immersion showed that, while the effect on the anodic reaction dynamics was the greatest, the three compounds also showed a significant reduction in the cathodic reaction rate. Figure 4 gives an example of the electrochemical behavior suggesting mixed inhibition by these compounds.

**Nyquist plot:** This is one way of displaying the results from an EIS experiment. It is a plot of the real and imaginary part of the impedance. Impedance is similar to resistance, but also takes into account any phase shift in the dielectric response of a material during an EIS experiment.

**Potentiodynamic polarization:** An electrochemical technique in which the potential of the electrode is varied either side of the freely corroding potential. This technique can give information on the anodic and cathodic reaction rates and the corrosion current density,  $i_{corr}$ .

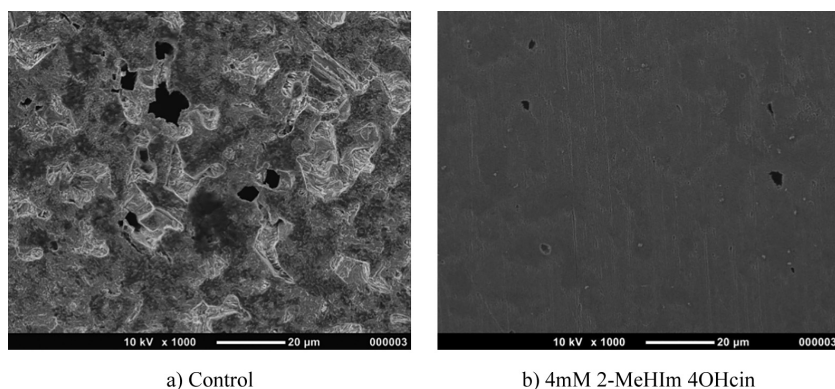
Another aspect of corrosion that can result in the rapid degradation of mild steel structures in service is microbiologically influenced corrosion (MIC). In the vast majority of operating conditions bacterial colonies will form on a metal surface, forming a biofilm under which they influence the local conditions to suit their requirements, such as acidic or anoxic. This localized change in conditions can create local anodes or cathodes and lead to aggressive corrosion. In an attempt to reduce microbial colonization on a mild steel surface a cation with antimicrobial properties, imidazolium, combined with a carboxylate anion, was proposed.<sup>17</sup> Similar to the process by which the carboxylate initially protects and brings the rare earth to the surface, the carboxylate would initially protect the surface and bring the imidazolium to the surface. Here the imidazolium could disrupt the formation of a biofilm and reduce the effects of MIC. Initially, 2-methylimidazolium (2-MeHImn) was combined with gentisate (2,5-dihydroxybenzoate) (Gen), salicylate (Sal) and 4-OHCin.<sup>18</sup> The effect of these compounds on the corrosion of mild steel was then determined (Table 1). Currently, the antimicrobial properties of 2-MeHImn 4-OHCin are being determined, however, its corrosion-inhibiting properties at a range of pH have been investigated (Table 1).

For these compounds, as with the results of Blin et al. and Seter et al., the [4-OHCin] again exhibits the best corrosion rate reduction of the carboxylates.<sup>7,12</sup> Interestingly, while the performance at neutral pH is not as good as that reported for La(4-OHCin), the 2-MeHImn 4-OHCin was able to maintain a high level of corrosion protection over a wide pH range.

The electrochemical results (Table 1) were obtained after 30 min of immersion. Over 24 h of immersion, the inhibition ability of the 2-MeHImn 4-OHCin at a pH of 2 was even greater, as can be seen from the SEM image in Figure 5, which shows the heavily corroded control sample and the largely unaffected 2-MeHImn 4-OHCin exposed sample.

The most recent investigations by our group again made some subtle changes to the 4-OHCin carboxylate and evaluated its corrosion inhibition when combined with a number of rare-earth metals.<sup>11</sup> In this research 3-(4-methylbenzoyl) propionate (mbp) (structure shown in Figure 1) was used to synthesise complexes with the rare earths, Ce, La, Nd and Y, to form RE(mbp)<sub>3</sub> compounds.<sup>19</sup> This particular ligand was chosen as modelling has suggested that the presence of the carbonyl group could result in an extra attachment point for the ligand to bond with the





**Figure 5:** SEM images of mild steel surface immersed for 24 hours at pH 2 in 0.01M NaCl: a) control, and b) 4 mM 2-MeHIm 4-OHcin. Adapted with permission from *ACS Sustainable Chem. Eng.* **2016**. Copyright 2016 American Chemical Society.

mild steel surface.<sup>20</sup> This particular ligand was commercially available from Ciba as an organic corrosion inhibitor, Irgacor 419©.

These RE(mbp)<sub>3</sub> complexes had a lower solubility than RE(4-OHcin)<sub>3</sub> complexes in the 0.01M NaCl solutions, with 0.40 mM close to their upper limit. However, even at this concentration, Ce(mbp)<sub>3</sub> exhibited good inhibition performance, with an IE value of 73% (Table 1).

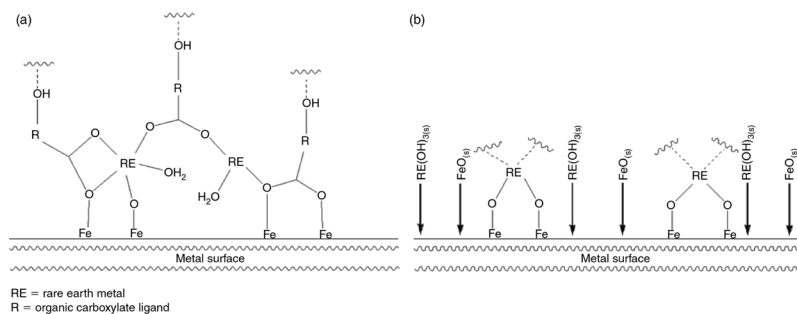
### 3 Speciation

The presence of the rare earth and the carboxylate in the one compound is important as it results in particular complexes and speciation in solution that lead to the formation of a unique protective film.<sup>3,10</sup> The mechanism proposed for the formation of this film is shown in Figure 6, where a complex, heterogeneous film forms on the steel surface. This film consists of a bimetallic compound that incorporates the Fe ions from the steel substrate and the RE bridged by the carboxylate ligand, in addition to RE hydroxide that forms at highly active cathodic sites where OH<sup>-</sup> ions are liberated from the oxygen reduction reaction. This complex surface film leads to the protection of the surface, suppressing both anodic and cathodic reactions on steel.

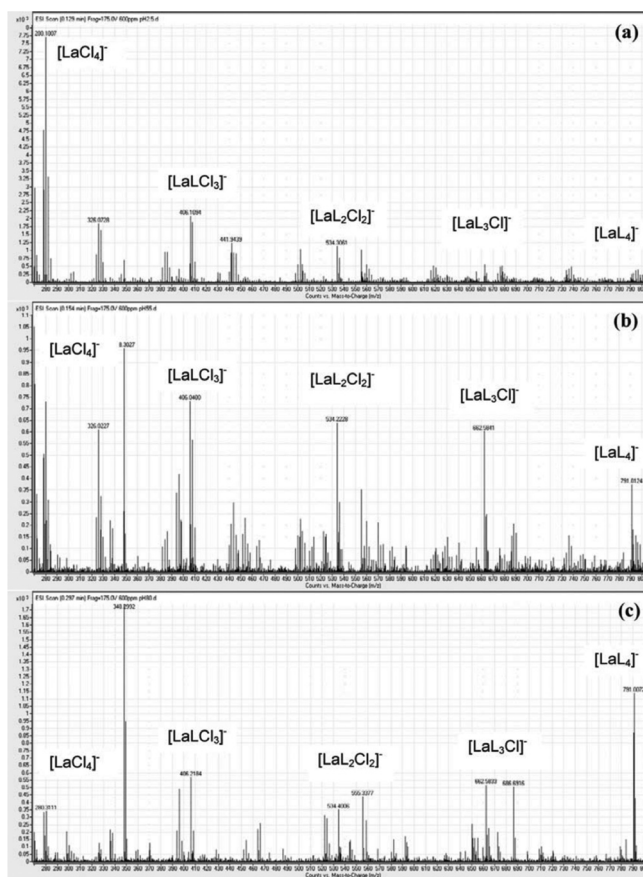
To further investigate the speciation of these compounds in solution a study was undertaken to correlate the speciation of La(4-OHcin)<sub>3</sub> with corrosion behaviour at pH levels of 2.5, 5.5 and 8.0 in 0.01M NaCl.<sup>10</sup> Using electrospray mass spectroscopy it was found that the spectra from La(4-OHcin)<sub>3</sub> in the NaCl solution consisted predominantly of five different species; LaCl<sub>4</sub><sup>-</sup>, La(4-OHcin)Cl<sub>3</sub><sup>-</sup>, La(4-OHcin)<sub>2</sub>Cl<sub>2</sub><sup>-</sup>, La(4-OHcin)<sub>3</sub>Cl<sup>-</sup> and La(4-OHcin)<sub>3</sub><sup>-</sup>. At each pH level and concentration of La(4-OHcin)<sub>3</sub> the proportions of these species varied, which appeared to strongly correlate with the corrosion

inhibition performance observed. For instance, with 600 ppm of La(4-OHcin)<sub>3</sub> the association of the La gradually shifted from being mostly associated with 4-OHcin to being mostly associated with Cl anion, as the pH was reduced from 8.0 to 2.5 (Figure 7). Correspondingly, the inhibition efficiency also reduced as the pH reduced (Table 1). Interestingly, at a pH of 2.5, with the amount of La(4-OHcin)<sub>3</sub> reduced there was disproportionately less La(4-OHcin)<sub>3</sub> species in solution as compared to [LaCl<sub>4</sub>]<sup>-</sup>. This was accompanied by a marked decrease in inhibition efficiency (Table 1). At low pH, lanthanum chlorides are the predominant species but as pH and/or concentration increases, lanthanum complexes increasingly form. NMR chemical spectroscopy of <sup>139</sup>La supports this observation further. As confirmed by inhibition efficiencies, the presence of these rare-earth and the carboxylate complexes leads to a higher level of protection than the individual carboxylate anion or [LaCl<sub>4</sub>]<sup>-</sup> anion. These results confirm the importance of the rare earth being complexed with the carboxylate. When this complex persists in solution, the two components are incorporated into a protective surface film leading to a decreased corrosion tendency of the mild steel, even in aggressive chloride environments.

The structures of the 2-, 3- and 4-hydroxycinnamate investigated by Lee are shown in Figure 8. The large differences in corrosion inhibition were again due to the changes in speciation in solution.<sup>12</sup> Whilst these structural changes are very subtle, the change of rare earth to cerium resulted in increased solubility, while the 2- and 3-hydroxycinnamate led to changes in the steric effects. These property changes then alter the bonding of the carboxylate to the rare earth and the steel surface.



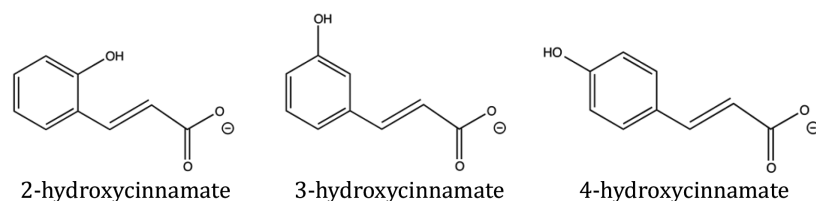
**Figure 6:** The mechanism proposed by Forsyth et al. for (a) coordination of rare-earth metal-organic carboxylate to iron on the metal surface, and (b) the components of the resulting surface film. Reproduced with permission from CSIRO Publishing.<sup>3</sup>



**Figure 7:** Mass spectrum of 600 ppm  $\text{La}(4\text{-OHCin})_3$  as a function of pH where (a) is solution at pH 2.5, (b) pH 5.5, and (c) pH 8.0. Reproduced with permission from J. Electrochem. Soc., 159, C181 (2012). Copyright 2012, The Electrochemical Society.

Interestingly, even in the  $\text{CO}_2$  saturated solution in which Nam et al. reported the inhibition behaviour of different RE carboxylate compounds, it is likely that different speciation in solution might exist.<sup>8</sup> However, even in this case, the results indicated similar behaviour to that in the chloride-contaminated solutions in which Ce was the worst performing of the same  $\text{RE}(4\text{-OHCin})_3$  compounds, with Pr showing the lowest corrosion rate.

Furthermore, Deacon et al. compared the speciation and corrosion performance of  $\text{La}(4\text{-OHCin})_3$  to  $\text{La}3\text{-(4-hydroxyphenyl)propionate}$ .<sup>21</sup> The propionate structure differs from the cinnamate in that it has no carbon double bond on its aliphatic chain. They found that the propionate complex showed no useful corrosion inhibition. It was also found that this complex readily dissociated in solution, which results in the absence of any synergy between



**Figure 8:** Chemical structures for 2-, 3- and 4-hydroxycinnamate.

the rare earth and the carboxylate as a corrosion inhibitor.

There is still much to understand about the structure-function relationships in these carboxylate-based inhibitor compounds, with scope to improve their protective properties further for steel in various corrosive environments.

#### 4 Conclusion

The development of corrosion inhibitors based on carboxylate complexes has shown that subtle changes in the structure can lead to major changes in their ability to protect mild steel surfaces. For instance, changing the position of the hydroxy group on the hydroxycinnamate anion resulted in significant changes in the corrosion inhibition. Similarly, a change in rare-earth metal or the organic cation can also affect a compound's performance. This means that a corrosion inhibitor that performs well in a particular chemical environment may not necessarily perform to the same level if that environment is changed. For example, as the pH of the environment is changed, the relative performance of the inhibitor compounds can change depending on the solubility and speciation. The speciation of these complexes in solution is important and more work to determine the effect of different rare-earth metals as well as organic cations in particular environments is required, so that these compounds can be optimized for a specific purpose. Furthermore, there is a need to understand the solubility and leaching of these inhibitor compounds from polymer coatings, as many applications will involve the incorporation of such compounds in paint coatings.

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