Organic Corrosion Inhibitors for Mild Steel in Aerated Near-Neutral Chloride Solutions

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SUMMARY
Over 120 organic compounds have been investigated as potential corrosion inhibitors for mild steel in simulated engine coolants. A relationship has been found between the corrosion potential $E_{corr}$ and inhibitor performance ($R_p$). With straight chain alkyl carboxylates, maximum inhibition was found for $C_6 - C_{10}$ monocarboxylates and $C_{11} - C_{12}$ dicarboxylates. Polarization curves for selected inhibitors and the $E_{corr} - R_p$ relationship suggest that these compounds are most effective at the anodic dissolution. The inhibitor effectiveness of sebacate was found to be unaffected by stirring or the presence of corrosion products.

1. INTRODUCTION
Automotive cooling systems are generally protected against metallic corrosion by the addition of corrosion inhibitors (1). Because of increasing concern over health, safety and environmental pollution, many existing inhibitor formulations are becoming untenable. In recent years, much work has been done on the development of low toxicity organic inhibitors (2, 3).

Due to the presence of more than one metal in automotive cooling systems, single inhibitors are rarely used and all formulations incorporate inhibitors intended for the protection of an individual metal. As ferrous metals such as mild steel are always found in juxtaposition with copper and aluminium, knowledge of the effects of inhibitors on mild steel corrosion is essential. This arises because practical experience shows that a good inhibitor for one metal may actually accelerate the corrosion of another metal. Also, the failure to adequately inhibit the corrosion of one metal may intensify the attack on another (4).

Though many "broadbrush" surveys on the corrosion inhibiting properties of compounds have been reported, most have been carried out in strongly acid media. Studies on mild steel in aerated near-neutral Cl-containing media, which may behave quite differently, are comparatively scarce (5, 6). Frequently, inhibitors that are efficient in acidic solutions are of little or no use in near-neutral media because of the different corrosion mechanism(s) involved (7). In aerated near-neutral media, the metal surface is oxide(s) covered and the cathodic reaction is the reduction of dissolved oxygen rather than $H_2$. Furthermore, changes in protonation or complexation may alter inhibitor behaviour. For these reasons it was considered essential to conduct a wide ranging survey of organic compounds under near-neutral mildly saline conditions typical of many engine coolant fluids in Australia.

2. EXPERIMENTAL
All solutions were prepared with high purity water (Millipore Milli-Q System). Inhibitors were laboratory grade reagents used as supplied. All other reagents were analytical reagent grade. The test solutions were, when possible, aerated near-neutral Cl-containing media, which may behave quite differently. Frequently, inhibitors that are efficient in acidic solutions are of little or no use in near-neutral media because of the different corrosion mechanism(s) involved (7). In aerated near-neutral media, the metal surface is oxide(s) covered and the cathodic reaction is the reduction of dissolved oxygen rather than $H_2$. Furthermore, changes in protonation or complexation may alter inhibitor behaviour. For these reasons it was considered essential to conduct a wide ranging survey of organic compounds under near-neutral mildly saline conditions typical of many engine coolant fluids in Australia.

Electrochemical measurements were made using a PAR 173 Potentiostat, a PAR 175 Programmer and a Bryans 2600 A3 X-Y Chart Recorder. Voltamograms were taken after the stationary electrode had been allowed to corrode under open circuit conditions for 18 h in a continuously aerated solution at 25.0 ± 0.5°C. Measurements to determine the Polarization resistance ($R_p$) were measured by the Stern-Geary method scanning at 0.1 mV/s over a range of ± 100 mV centred at the corrosion potential ($E_{corr}$). To determine the extent of inhibition, $E_{corr}$ was first recorded with scan reversal at -1200 mV. Potential-time measurements were also made to determine the effect of sebacate on corroded (18 h at $E_{corr}$) steel.

3. RESULTS AND DISCUSSION
3.1 Relationship between Corrosion Potential and Polarization Resistance
Approximately 120 organic compounds were investigated as possible mild steel corrosion inhibitors. Fig. 1 shows a plot of $E_{corr}$ against $R_p$ for these compounds; the heavy point marked 1 corresponds to the uninhibited solution. The data in Fig. 1 establish a clear relationship between $E_{corr}$ and $R_p$. Inhibitors with $E_{corr}$ more positive than -150 mV (vs. Ag/AgCl) were very effective, with the electrode disks retaining their well polished condition throughout the experiments. Compounds with $E_{corr}$ values more negative than -500 mV were very poor inhibitors resulting in the coverage of the electrode surface with a thick, loosely adherent nonprotective oxide layer. Moderate inhibitors (-500 mV < $E_{corr}$ < -150 mV) frequently allowed localized attack with brownish corrosion products deposited around the corrosion pits whilst the remainder of the electrode surface area remained bright. This type of attack is common with mild steel corrosion in Cl-containing media.

![Fig. 1. Relationship between corrosion potential and polarization resistance for mild steel in a medium containing various inhibitors: (1) no inhibitor, (2) morpholine, (3) benzotriazole, (4) phthalate, (5) s-nitro-m-phthlate, (6) sebacate, or (7) sodium nitrite.](image)

That the corrosion rate decreases (increasing $R_p$) as $E_{corr}$ becomes more positive, irrespective of the type of compound, indicates that all compounds examined are predominantly anodic inhibitors. That is, they function mainly by suppressing the anodic reaction with a minimum or no effect on the cathodic reaction. This is contrary to the view that, in aerated near-neutral media, corrosion of mild steel can be effectively inhibited only by suppressing the stirring controlled reaction of oxygen reduction (9, 10).

The observed $E_{corr}-R_p$ relationship provides an experimental justification for the developing commercial practice (11) of using corrosion potential measurements to monitor automotive coolant corrosivity.

3.2 Straight Chain Alkyl Carboxylates as Inhibitors
Previous studies have found that the inhibition of straight chain monocarboxylates towards copper and aluminium corrosion improved markedly with chain length (12). However, only a limited range of chain lengths were investigated so we sought to establish the limits of this effect. The measurements were also extended to include the alkyl dicarboxylates. The results are summarized in Table 1 and Fig. 2.

3.2.1 Monocarboxylates ($C_nH_{2n+1}COO^-$)
Short chain length ($0 < n < 5$) monocarboxylates are either mildly corrosive (formative, $n = 0$) or weak inhibitors. However, as the chain length increases, inhibitor effectiveness rises abruptly at $n = 6$ remaining high up to $n = 10$ before declining dramatically for $n > 11$. 

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Table 1. Inhibition efficiency toward mild steel corrosion of straight chain mono- and di-carboxylates

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>Inhibition Efficiency</th>
<th>n=3</th>
<th>n=8</th>
<th>n=11</th>
<th>n=16</th>
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<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.40</td>
<td>1.25</td>
<td>1.15</td>
<td>1.05</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>0.77</td>
<td>0.64</td>
<td>0.52</td>
<td>0.50</td>
<td>0.43</td>
</tr>
<tr>
<td>5</td>
<td>-1.04</td>
<td>-1.04</td>
<td>-1.04</td>
<td>-1.04</td>
<td>-1.04</td>
</tr>
</tbody>
</table>

* Data in the inhibited solution, smooth and broken lines are 1767 and 1.00 log [M], respectively.
* Data in the uninhibited solution, the smooth curve will be much more reliable and data are rarely available.
* Smoothed curve.

Fig. 2. Effect of carbon chain length on the inhibition properties toward mild steel of straight chain monocarboxylates (•) and dicarboxylates (+).

Clearly, the hydrophobicity of the carboxylates plays a vital role in determining inhibitor effectiveness. Given that the pKa (and presumably the metal complexing ability for which few data are available) of these species is little affected by the carbon chain length (Table 1), the observed effect is almost certainly due to the enhanced surface adsorption with increasing chain length (14). The dramatic fall of inhibitor effectiveness at n=11 is consistent with increasing micelle formation in the solution (15) reducing the surface coverage; the carboxylate concentration (0.005 x 10^-1 M) is below the saturation limit for n=11. The apparent decrease in effectiveness with increasing micellization contrasts with the surfactant-type inhibitors, i.e., substituted aminocarboxylic or sulphonic acids, whose micellar clusters rather than monomolecular entities have proved active in protecting mild steel in a simulated cooling environment (16).

The present data clearly show an optimum range of carbon chain length (n=6–10) for maximum inhibition of mild steel corrosion with straight chain monocarboxylates. This is consistent with the range n=7–9 deduced from simple short term test data (5) and shows there is no advantage in using longer chain carboxylates as inhibitors.

3.2.2. Dicarboxylates (C_2OOC(CH_2)_nCOO)

As for the monocarboxylates, the short chain alkyl dicarboxylates are either corrosive (oxalate, n=0) or weak inhibitors (Table 1, Fig. 2). The corrosive nature of oxalate is probably associated with its complexing ability towards Fe^{3+} and Fe^{2+} in solution (13). Again as n increases so does inhibitor effectiveness although rather more smoothly than for the monocarboxylates. Good protection is obtained from adipate (n=4) but, more importantly and in marked contrast to the monocarboxylates, the dicarboxylates show no decline in effectiveness with increasing n at least up to n=12 (1,12-dodecane dicarboxylate), the longest chain dicarboxylate studied. These data are consistent with long term weight loss test data which showed good inhibition of mild steel corrosion for n=3–8 (the longest chain length studied (6)). If micelle formation is responsible for the reduced inhibitor efficiency of the monocarboxylates at n=11, the dicarboxylates data suggest a low level of micelle formation in the solution. This agrees well with the markedly decreased tendency of the dicarboxylates to form micelles as a result of charge repulsions (17) (note that at pH 8.4 used in this study virtually all of the dicarboxylates will be present as di-negative ions, see pKa data in Table 1).

The present data show that for dicarboxylates little benefit is gained by increasing the carbon chain length beyond 8 (sebacate) but also that a catastrophic loss in inhibitor activity does not occur. Interestingly, as for the monocarboxylates, the inhibiting properties of the dicarboxylates appear to be unrelated to the pKa's.

3.3 Polarization Curves

As mentioned above, the E_{corr}-R_p relationship (Fig. 1) suggests that the compounds studied are predominantly anodic inhibitors. To get a better insight into their inhibition mechanism(s), wide range polarization curves were recorded. Five compounds were selected to represent three types of inhibition behaviour. The sebacate (6 in Fig. 1) and 5-nitro-m-phthalate (5 in Fig. 1) represent the good inhibitor type, the phthalate (4) and benzotriazole (3) represent moderate inhibitors whereas morpholine (2) represents the weak inhibitor type. For comparison, the widely used and effective inorganic inhibitor NaN_3 (7), was also studied. The relevant electrochemical data for these compounds are gathered into Table 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Inhibitor</th>
<th>E_{corr}</th>
<th>R_p</th>
<th>Inhibition</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>none</td>
<td>-465</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>morpholine</td>
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<td>benzotriazole</td>
<td>-104</td>
<td>2.07</td>
<td>51</td>
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<tr>
<td>4</td>
<td>phthalic acid*</td>
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<tr>
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</tr>
<tr>
<td>6</td>
<td>5-nitro-m-phthalic acid*</td>
<td>64</td>
<td>1340</td>
<td>99</td>
</tr>
<tr>
<td>7</td>
<td>sodium nitrite</td>
<td>22</td>
<td>1220</td>
<td>99</td>
</tr>
</tbody>
</table>

* sodium salt

Table 2. Corrosion data for mild steel with selected inhibitors

Fig. 3. Potentiodynamic anodic and cathodic polarization curves for mild steel in a medium containing no inhibitor (- - - -), morpholine (-----), benzotriazole (-- -- --), phthalate (- - - -), 5-nitro-m-phthalate (-----), or sebacate (- - - -).
Fig. 3 shows the potentiodynamic polarization curves recorded for mild steel in the uninhibited solution and in the solutions containing compounds 2, 3, 4, 5 and 6. In the uninhibited solution, the cathodic polarization curve was seen to exhibit a well-defined plateau between -800 mV and -950 mV, due to the reduction of dissolved oxygen (18). The rise in the current at potentials more negative than -1000 mV corresponds to H₂ evolution. In the presence of morpholine the cathodic plateau was only slightly visible but well defined plateaus were observed for benzotriazole, phthalate and sebacate between -600 mV and -950 mV, with slightly higher limiting current densities compared with the uninhibited solution. Virtually no cathode plateau was observed with 5-nitro-m-phthalate, presumably due to the reduction of NO₃ group. The H₂ evolution for all solutions was very similar. In summary, these organic compounds have little or no effect on the rate of oxygen reduction, the dominant cathodic reaction during corrosion in cooling water systems.

In contrast, the anodic branch of the polarization curves (Fig. 3) reveal characteristic differences depending on the inhibitor properties. In the uninhibited solution, the anodic polarization curve shows active corrosion without any current plateau indicating the absence of a protective film. The current density eventually approaches a limiting value of ca. 18.5 mA cm⁻² (Fig. 3), presumably as a result of diffusion control, by some soluble species at the electrode surface. With morpholine, the anodic curve was similar to that in the uninhibited solution. When benzotriazole was present, the anodic polarization curve was shifted toward lower currents.

As would be expected, the good inhibitor phthalate slows the anodic reaction further showing little current flow at applied potentials negative of -100 mV vs. Ag/AgCl consistent with the formation of a passive film. The sudden increase in the anodic current at ca. -60 mV is indicative of the breakdown of the passive film on the mild steel surface by pitting corrosion. Even better protection of mild steel is provided by 5-nitro-m-phthalate which gives a current density of ca. 0.4 μA cm⁻² (cf. ca. 3μA cm⁻² for phthalate) in the passive region, with pitting occurring at +20 mV. With sebacate, the protection of the passive film was further improved. The passive current density remained at ca. 0.4 μA cm⁻² but the pitting potential (Epit) was shifted to +140 mV.

In summary, the data in Fig. 3 show conclusively that all of the organic compounds studied are anodic inhibitors and have little effect on the oxygen reduction reaction. This contradicts the views (9, 10) that effective inhibition of mild steel corrosion in aerated near-neutral media can be achieved only by cathodic inhibitors.

3.4 Effects of Solution Stirring on Corrosion and Pitting Potentials

Coolant flow is one of the factors affecting the corrosion rate and inhibitor performance. Some movement of coolant solution seems desirable to ensure adequate amounts of inhibitor at the liquid-metal interface. However, high flow rates can either be beneficial, by helping to maintain inhibitor concentrations in stagnant areas, or detrimental, by sweeping away protective films. Because the C₆ dicarboxylate, sebacate, shows considerable promise as an inhibitor, it was used to study solution stirring effects.

The dependence of ECorr and Epit for a mild steel disk electrode on rotation is shown in Fig. 4. Without inhibitor, a pronounced effect of rotation speed (solution stirring) can be seen. That ECorr becomes more positive with increasing rotation speed suggests that the cathodic reaction becomes faster. This behaviour is typical of a corrosion process with a mass transfer (i.e. stirring) controlled cathodic reaction (19). Under the present circumstances, this is most likely to be the reduction of dissolved oxygen. With sebacate added, the effect of rotation speed is insignificant (Fig. 4), consistent with the presence of a protective film. As changes in rotation speed do not affect Epit in the inhibited solution, it can be concluded that pit nucleation must occur inside the micropores of the passive film, whose dimensions and shapes preclude effective contact with the bulk solution (20).

The lack of influence of stirring on the sebacate system suggests that the passive film is equally protective in stagnant and circulating systems which is a very desirable property for an automotive coolant inhibitor.

3.5 The Effect of Sebacate on Corroded Mild Steel

Clean metallic surfaces (as generally used in laboratory studies) are not normally encountered in cooling water systems, most being covered with corrosion products such as oxides. Thus, for practical applications, an inhibitor must be able to prevent the further corrosion of corroded surfaces.

Fig. 5 shows ECorr for a mild steel electrode as a function of time after the addition of disodium sebacate. These data show from the rapid positive shift of ECorr (cf. Fig. 1) that the addition of reasonable concentrations of sebacate can spontaneously passivate corroded mild steel. Given the fact that 5.00 x 10⁻⁴ M sebacate can protect abraded mild steel completely, the increased sebacate requirement (ca. 3 x 10⁻³ M) for achieving passivation may be explained in terms of surface heterogeneity which is definitely greater on the corroded than on the abraded surface. Nevertheless, the form of the potential rise undoubtedly suggests that the passivation reaction is a three-step process.

That the initial rapid potential rise in Fig. 5 is dependent on sebacate concentration and stirring (21) probably reflect the specific adsorption of sebacate onto the corroded surface. Bohnsack et al. (22) believe Fe(III) oxyhydrates (FeOOH) are responsible for the adsorption of anions such as PO₄³⁻ and sebacate may behave similarly. Whatever the process is, it is followed by further steps probably within the surface film, which ultimately transforms the porous non-protective film into a passivating one. These later processes, evidenced by the second sharp rise in ECorr followed by a gently increasing plateau, are nearly independent of both the sebacate concentration and solution stirring (21).

It is planned to further investigate the nature of these processes, however, the present data clearly show that sebacate is effective in preventing further corrosion of corroded mild steel.
4. CONCLUSIONS

The inhibition properties of a large number of organic compounds toward mild steel have been studied by electrochemical methods in simulated engine coolants. These data show that the corrosion potential is a good criterion for predicting inhibitor effectiveness. The inhibitor properties of straight chain alkyl carboxylates show a definite dependence on the carbon chain length. Maximum effectiveness was found for \( C_5-C_{10} \) monocarboxylates and \( C_5-C_{12} \) dicarboxylates. Unlike the dicarboxylates, the higher monocarboxylates show a marked decline in inhibition. This is believed to be a reflection of their tendency to form micelles. The \( E_{corr}-R_p \) relationship and the polarization curves of selected organic compounds suggest that such compounds, contrary to previous thinking, are anodic rather than cathodic inhibitors on mild steel. Sebacate shows consistently good inhibiting properties towards mild steel under the test conditions and is capable of inhibiting even precorroded steel surfaces.

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