

Properties and Effects of Water-Soluble Inhibitors on the Corrosion Rates of Structural Metals

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The effects of six commercial water-soluble inhibitor formulations on the corrosion rates of aluminum and steel in seawater were determined. Corrosion rates were measured by the weight loss of specimens following long-term immersion in artificial seawater containing inhibitors at the developer's recommended dosages. The effects of environmental changes on inhibitor behavior were also investigated by varying the seawater concentration in certain tests. Surface plasmon resonance (SPR) spectroscopy was investigated as a method to observe the inherent adherence and persistence of the inhibitors at a metal surface. Results show that the level of effectiveness of the test inhibitors varies significantly and is dependent on the nature of the metal being protected. While some inhibitors reduce the corrosion of steel by up to 80%, others actually increase the corrosion rate. Four of the six inhibitors were observed to increase aluminum pitting; the other two offered protection. Two of the inhibitors reduced the corrosion rates for the aluminum and steel. Surface plasmon resonance spectroscopy was able to detect and discriminate between inhibitors. These measurements show good correlation between the adherence of an inhibitor to a metal surface and its ability to reduce corrosion rates. Results of this study provide a firm measure of the levels of corrosion control that can be achieved by commercially available inhibitor formulations. They also provide a quantitative basis for comparison and selection of corrosion inhibitors for use in a variety of applications (i.e., metal holding tanks and cans, recirculation loops, and modified wash downs of outdoor equipment typically experiencing deterioration due to exposure to salt-containing environments).

Keywords corrosion inhibitors, seawater corrosion control, steel and aluminum corrosion rates, surface plasmon resonance spectroscopy and water soluble corrosion inhibitors

1. Introduction

A recent Federal Highway Administration report estimates that the annual cost of metallic corrosion in the United States is \$276 billion (Ref 1). Because it is clearly recognized that the cost of corrosion places a substantial burden on the economy, there is an urgent need for reliable data from which to choose appropriate methods for corrosion control and to evaluate their cost benefits. One approach to corrosion control is the insertion of small quantities of inhibitor agents in the proximity of metals exposed to aggressive environments (frequently containing some level of salinity). For example, inhibitors can be added to the contents of holding tanks and cans, boilers, oil well and refinery equipment, fuels, lubricants, and recirculation systems. Inorganic salts (phosphates, chromates, nitrites, silicates), amino compounds, imidazolines, and many other compounds have been used for corrosion inhibition. More recently, inhibiting additives are being explored for use in water sprays or rinses to provide residual protection to metal structures exposed to corrosive environments or to offset corrosion during wet-blast preparation of surfaces for coatings. This approach is

of particular interest to the military, whose operations require equipment to be periodically exposed to seawater-containing environments. Resulting corrosion damage places a large drain on readiness and life-cycle costs. This approach would also be applicable for use on vehicles and other equipment exposed to outdoor conditions, especially in coastal regions. Several water-soluble inhibitor formulations are commercially available; however, information concerning the nature of the active agent is considered proprietary and few quantitative data are available to assess the level of protection that can be achieved by their use. Furthermore, reliable estimates of their effectiveness in a rinsing application are limited by a poor understanding of their attraction to a metal surface and whether the effects will persist following washing or rewetting procedures.

Corrosion inhibitors may be classified in various ways (i.e., by chemistry, physical properties, or application), but in general the mechanisms for reducing corrosion rates fall into one of four categories: surface adsorption to produce a superficial barrier film only a few molecules thick, chemical reaction with a metal surface to form a thick visible protective coating, generation of a passive surface layer, and/or chemical reaction with the environment to form protective surface products or to remove aggressive components (Ref 2, 3). Any of these mechanisms can restrict diffusion of chloride or oxygen to the surfaces and thereby obstruct corrosion processes. Organic inhibitors tend to adsorb according to their charge or polarizability and the charge at the metal surface.

In this study, the fundamental properties of commercial water-soluble inhibitors relevant to their application for corrosion control were examined through a series of laboratory-scale studies. In particular, the ability of the additives to reduce corrosion processes, especially in variable saline conditions,

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and the degree of their attraction to metal surfaces were examined. The identity of the inhibiting species and the mechanisms for their action were unknown. Because corrosion rates depend upon a wide range of factors and normally exhibit high levels of variability, the present analysis was designed to draw upon the trends and correlations between various types of experimental data and a sufficiently large number of trials. In this way, it is possible to build a database of fundamental inhibitor behavior that can be exploited to support more reliable assessment of their potential benefits in use. The corrosion rates of metal samples immersed in artificial seawater containing recommended dosages of six additives were determined. Corrosion rates were measured as weight loss. Aluminum alloy 6061 and 1018 steel specimens were selected as representative of structural materials used in many applications. It is important to note that the experimental setup was not chosen to mimic conditions of use, but rather to isolate conditions that are controllable and to ensure the presence of the inhibitor additive around the metal. In this case, the inherent ability of the additive to affect corrosion processes of each metal in seawater could be observed. The experiments were repeated with diluted seawater to determine the effects of salinity on the inhibitor properties. The performances of some of the inhibitors were ranked in earlier work (Ref 4). The current study, however, includes a more exhaustive measurement of corrosion rates as well as testing of the relative levels of attraction of the inhibitors to a metallic surface.

Weight loss results were supplemented with another study involving surface plasmon resonance (SPR) spectroscopy. Surface plasmon resonance spectroscopy is a surface-sensitive optical reflectivity technique presently used for the study of the adsorption and character of organic and inorganic molecular layers (tens of angstroms thick) on metal surfaces. Surface plasmon resonance spectroscopy was used to examine the fundamental adherence tendency or sticking of the additive or its components to the metal surface. Surface plasmons are the aggregate of free-electron oscillations in a metallic film. When the free electrons are set to oscillate (resonate) with an incoming light source, light energy is absorbed that results in changes in the reflectivity of the incident beam off the surface. The resonant condition is very sensitive to the local refractive index at the surface, and so the adsorption of molecular species (whose character affects the refractive index) can be accurately detected. An understanding of the adhesion properties accompanying the additives will provide figures-of-merit for establishing inhibitor performance and important clues to the processes occurring at the metal surface. This work represents a preliminary analysis of adherence properties of inhibiting washes using a "surface specific" method based on optical reflectivity measurements. Such an approach is similar to that of Klenerman et al., who studied the deposit of oleic imidazoline derivatives on steel in seawater using second harmonic generation (SHG) reflectance measurements (Ref 5-7). In the current study, the authors used SPR to explore the natural attraction or tendency of the additives to adhere to and distribute over metal surfaces. Another aspect of this approach is that it is based on the use of features that provide for a statistical interpretation of the reflectivity measurements. This approach was applied in a series of studies concerning the analysis of

Table 1 Inhibitor additives, manufacturer's description, and recommended dilutions in seawater for rinse solutions

Additive	Manufacturer's description	Recommended dilution, mL/L (oz/gal)
INH1	Water additive for salt removal and corrosion inhibition	23.4 (2.5)
INH2	Water-based cleanser and degreaser that deposits a corrosion-resistant film on metals	10.2 (1.5)
INH3	Water additive for salt removal and corrosion inhibition	23.4 (2.5)
INH4	Water based, protects metals against corrosive effects of fresh water, salt water, and salt	15.6 (2.0) and 62.5 (8.0)
INH5	Water additive that provides a corrosion protective film on metals	62.5 (8.0) Note: This is 4× recommended
INH6	INH5 plus a general-purpose detergent, leaves a dry coating, protects against further exposure	62.5 (8.0)

Note: Commercial names of some of these inhibitors may be obtained by contacting the authors.

SHG measurements of reflectance from metal-electrolyte and thin-film interfaces (Ref 8, 9).

2. Experimental Procedures

2.1 Immersion Tests

Standard immersion tests, described in detail elsewhere (Ref 10), were used to determine the effects of the inhibitors on the corrosion rates of 6061 aluminum and 1018 steel specimens in seawater. Six commercial inhibitor additives, designated INH1 to INH6, were evaluated. The manufacturer's description of each additive and recommended dilution levels are given in Table 1. Note that the designations INH4(2) and INH4(8) represent two different concentrations of inhibitor INH4 (Table 1). Test samples were $2.54 \times 5.08 \times 0.32$ cm coupons (surface area approximately 30 cm²) sectioned from test metal panels. A 0.32 cm diameter hole was drilled at one end of each coupon to suspend it, using a nylon thread, from a plastic lid into a 200 mL glass jar. A 0.64 cm diameter hole was drilled into the top of the lid to allow access to air. All samples were rinsed sonically in methanol, dried, and stored in a desiccator until the tests were started. Figure 1 shows the experimental setup for the immersion tests.

Artificial seawater was prepared by adding 118.3 mL synthetic sea salt Instant Ocean (Aquarium Systems, Inc., Mentor, OH) to 3.785 L distilled water. This was adopted as full-strength or full-salinity seawater. Solutions of the artificial seawater containing the manufacturer's recommended wash-additive dosage were prepared. Exactly 200 mL of these solutions were added to the test jars. The metal samples were weighed, dipped in seawater for 2 min, and then suspended in the test solution for 12 weeks. Distilled water was added to the jars weekly to adjust for losses due to water evaporation. At the



Fig. 1 Test setup for evaluating the influence of inhibitor additives on corrosion processes in seawater; sample bottles from left to right, 1018 steel in $\frac{1}{4}$ and $\frac{1}{2}$ strength seawater and 6061 aluminum in $\frac{1}{4}$ and $\frac{1}{2}$ strength seawater

end of 12 weeks, the samples were removed from the solution, rinsed with distilled water, and the corrosion products removed following standard procedures (Ref 10). The samples were then thoroughly dried and weighed, and the change in weight was determined. Additional tests were performed by adding the manufacturer's recommended dosage of the inhibitor additive to stock solutions of artificial seawater diluted to half and quarter strength with distilled water. By this means, the salinity of the test solutions was varied. Each test was repeated in triplicate according to standard procedure and to assess reproducibility of the results (Ref 10). In addition to measuring the weight loss, the exposed samples were visually examined.

2.2 Surface Plasmon Resonance Spectroscopy

Surface plasmon resonance (SPR) spectroscopy was performed using a thin gold film coated with a layer of full-strength inhibitor additive. The same gold surface was used for all SPR experiments in this work. A 2.2 cm^2 cover glass was cleaned with a hot "piranha" solution (30:70 vol.% mixture of H_2O_2 and H_2SO_4). A 50 nm gold film was deposited onto the cover glass from a gold sample of 99.99% purity using a vacuum evaporator. Deposition was in a vacuum of 10^{-6} bar and at a rate of 0.02 to 0.04 nm/s. The gold film thickness was determined using a crystal oscillator. Inhibitor additive layers were applied to the gold-coated cover glass slip by spin coating each liquid additive at 8000 rpm for 60 s at room temperature. The gold substrate was washed rigorously with distilled water before a new inhibitor additive layer was applied. The additive-coated surface was then ready for SPR analysis. In some experiments, to investigate adherence under wash conditions, the additive-coated substrate was washed briefly with either distilled water or 1% NaCl from a wash bottle 5 min prior to performing SPR analysis. The SPR spectrometer used for analysis employed the Kretschmann configuration, which is shown in Fig. 2 (Ref 11). Here, a prism is used to couple the wave vectors of the incoming light beam with that of the plasmons. The glass prism was made of standard BK7 glass (90° , 17 mm high, 22×32 mm at the base, refractive index $n = 1.5$). Index matching fluid was used to index match the prism to the

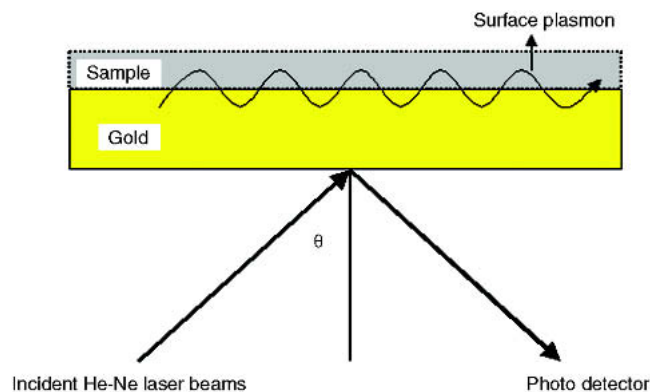


Fig. 2 Schematic diagram describing SPR measurement and interpretation of results

cover glass ($n = 1.51$). The SPR instrumentation consisted of a semiconductor diode laser (HeNe, 1.0 mW, p polarized at 632.8 nm) as the light source. The polarized light is incident on the prism and reflected back from the base of the prism onto a photo detector. Variable angles were selected by means of a stepper motor controlled goniometer with a resolution of 0.1° . The data acquisition was completely automated, with a typical SPR scan angle (40° to 80°) taking 8 min. Surface plasmon resonance scanning angle experiments used in this study follow reflectivity as a function of the angle of incidence of a light beam focused on a metal surface. Each measurement was repeated three times, and there was good consistency in the replicated results. Observed changes in reflectivity are used to examine the attraction and adherence of rinse additives or their constituents to the metal substrate. The specific mode of analysis adopted in this study is that used by Yee et al. (Ref 12-16) to study the nature of organic films on gold surfaces. In this study, a gold substrate was selected for SPR testing of all additives as well as the seawater control. The use of gold is preferable to isolate the inherent tendency of inhibitor additives to adhere to a metal surface. It is assumed that minimal electrochemical events will occur at a gold surface in the test solutions used, thus allowing the experiment to focus on changes due to adsorbed layers.

3. Experimental Results

3.1 Weight Loss

To illustrate the breadth of data collected in the weight-loss experiments, raw data for aluminum and steel specimens exposed to INH4 are shown in Table 2. For each sample, the sample number, inhibitor additive, dilution, strength of seawater, sample dimensions, sample weight before and after the test, difference in weight, and percent weight loss are reported. From the replicated percent weight loss, averages and standard deviations (SD) were calculated. Figures 3 and 4 show plots of the weight losses of aluminum and steel exposed to each of the inhibitor additives as a function of seawater strength. Error bars in these curves show the precision of the measurements. Figures 3(b) and 4(b) are amplifications of the curves for the inhibitors showing the greatest effects on corrosion rates for

Table 2 Illustration of data collected for each of the samples during weight loss studies

Sample No.	Inhibitor	Dilution, oz/gal	Strength of seawater, fraction	Sample dimensions, cm			Weight, g		Weight loss	
				Length	Width	Thickness	Before	After	g	%
6061 Aluminum: started: 09-12-02, ended: 12-12-02										
A2 No. 1	INH4	8	1/1	5.044	2.500	0.3	10.23243	10.23132	0.00111	0.01084
A2 No. 2	INH4	8	1/1	5.058	2.494	0.3	10.09982	10.09867	0.00115	0.01138
A2 No. 3	INH4	8	1/1	5.130	2.601	0.3	10.74316	10.74237	0.00079	0.00735
1018 Steel: started: 09-12-02, ended: 12-12-02										
S2 No. 1	INH4	8	1/1	5.070	2.615	0.3	29.95523	29.81346	0.14177	0.47327
S2 No. 2	INH4	8	1/1	5.205	2.595	0.3	29.69463	29.57896	0.11567	0.38953
S2 No. 3	INH4	8	1/1	5.093	2.606	0.3	29.75164	29.62976	0.12188	0.40965

Table 3 Average weight loss relative to seawater control

Seawater strength inhibitor	6061 Aluminum			1018 Steel		
	Full (1/1)	Half (1/2)	Quarter (1/4)	Full (1/1)	Half (1/2)	Quarter (1/4)
INH1	17.35	8.80	15.38	0.79	1.03	0.94
INH2	0.07	0.45	0.26	0.41	0.74	0.62
INH3	19.47	10.42	8.84	0.16	0.43	0.39
INH4 (2)	0.37	0.22	0.27	0.26	0.46	0.41
INH4 (8)	0.34	0.20	0.27	0.24	0.44	0.40
INH5	63.28	28.34	30.57	1.44	3.06	2.80
INH6	34.33	17.93	13.40	0.78	1.59	1.22

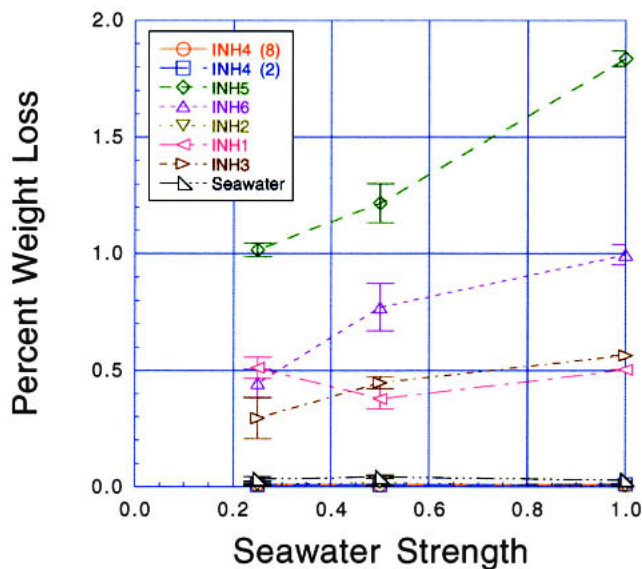
steel and aluminum. Percent weight loss relative to that in unaltered seawater was also determined as ratio of weight loss in additive to weight loss in seawater control. These results are presented in Table 3. Values of less than 1.0 imply that the inhibitor performed better than unaltered seawater; values greater than 1.0 imply that the inhibitor performed worse than seawater.

Several observations can be made from these tables and graphs. Comparing the effects of the inhibitors on the two metals, it can be seen that the results vary considerably among the test formulations and between the metals. For aluminum, there was a lower weight loss and fewer visible pits on samples exposed to INH2 and INH4 as compared with the seawater control. Significant increases in the size and number of pits, however, were observed for the other inhibitors tested. As an example, the number of pits on aluminum samples exposed to INH3 increased by a factor of 10 relative to seawater. For steel specimens, however, corrosion rates in the presence of three inhibitors (INH2, INH3, and INH4) were reduced. The best performance was observed for INH3 and INH4 where the rates decreased by 70% and 80%, respectively. For the other inhibitors the corrosion rates of steel were not significantly changed. In the case of INH5, however, a significant increase was observed. The results concerning the effect of the strength or salinity of the seawater on weight loss were ambiguous. For aluminum, the weight loss trend appears to increase with increasing seawater strength for some of the additives, but not for others. For steel, in additive-dosed seawater the weight loss does not appear to have any strong trend, as a function of seawater strength. A significant decrease is noted, however, from full to half strength for unaltered seawater. Additives that

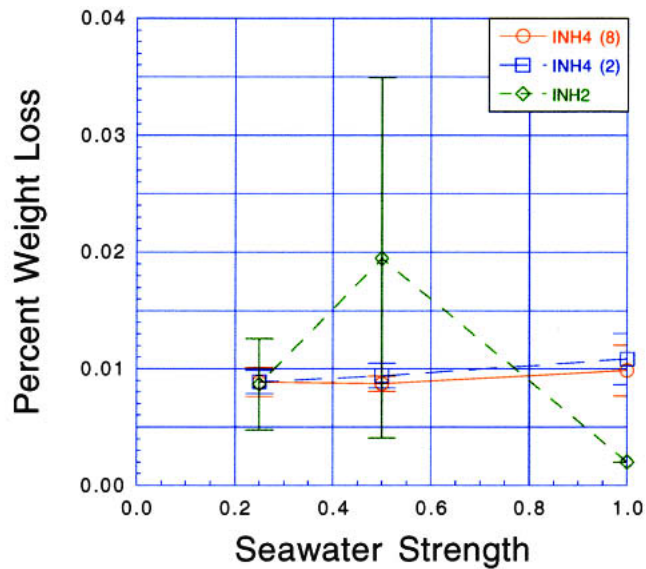
improved the corrosion behavior showed no particular trend with increasing seawater strength or salinity for both metals, or at the very least, the variations were within the error bars and hence statistically insignificant. INH2 and INH4 were found to reduce the corrosion rates of both metals. INH3 reduced the corrosion rate of steel but not the pitting of aluminum. There appears to be very little difference in the results between the two dosages of INH4 for both metals.

3.2 SPR Spectroscopy

Surface plasmon resonance spectra of the gold substrate, the gold substrate with and without additive coating, and the additive-coated substrate after washing with water and 1.0% NaCl are shown in Fig. 5 and 6. The curves are of the reflected light intensity, that is, the reflectivity function R , as a function of angle of incidence (the angle θ is shown in Fig. 2). As described previously, the procedures for substrate preparation and subsequent inhibitor additive coating of the substrate were the same for each of the measured SPR spectra. The data are presented in two sets, and a gold baseline was set for each as shown in Fig. 6(a) and (b). This is because the measurements were made on two different days, and this is reflected in the different scales for R . Factors contributing to variability of the SPR measurements are the relative levels of substrate surface roughness and inhomogeneities within the surface covering. An analysis of spectral features related to these factors would require calculations of the complex permittivities of the layer structures using inverse optical methods and is not within the scope of the present analysis (Ref 17). The data were further analyzed by noting the position (scan angle) and the amplitude of the minima in the spectra. These results are presented in Table 4. Referring to this table, the following observations can be made. Runs with the two sets of bare gold ("no wash") substrates are similar, the minima positions being near 46.4 and the amplitude ($-R$) of the minima being 0.46 for the first set and 0.57 for the second set. The "water wash" curves also have minima at the same angle as the "no wash" gold. The "NaCl wash" curves are significantly different in that minima are located at a higher scan angle and have smaller amplitudes than the no wash and wash conditions. The gold substrates coated with the inhibitors had different responses to SPR spectroscopy. The no wash curves for INH2, INH3, INH6, and INH4 showed no minima. The no wash curve for INH1 had a minima

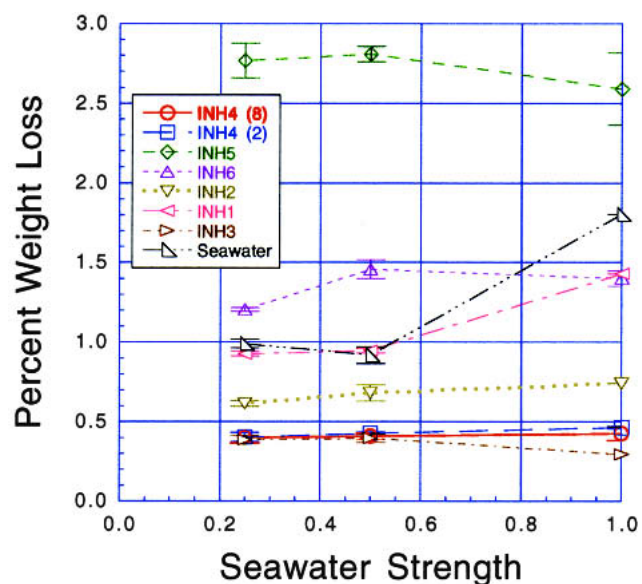


(a)

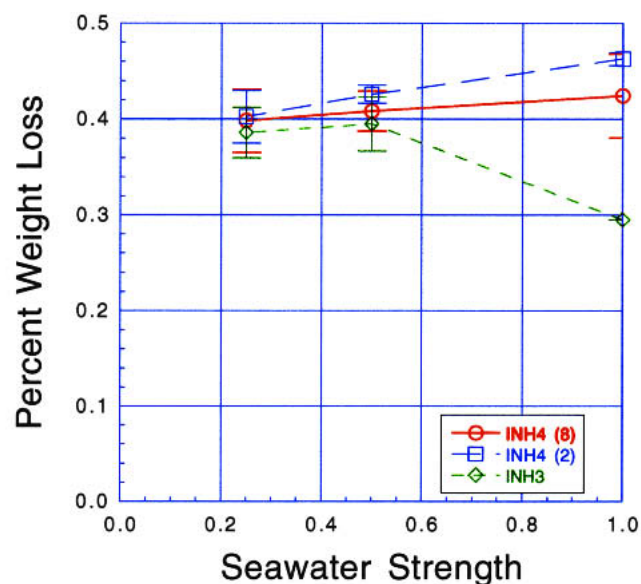


(b)

Fig. 3 (a) Effect of inhibitor additives and seawater control on the weight loss of 6061 aluminum as a function of seawater strength. (b) Graph amplifying effects observed with additives resulting in least weight loss. INH4(2) and INH4(8) designate different concentrations of INH4 (Table 1).



(a)



(b)

Fig. 4 (a) Effect of inhibitor additives and seawater control on the weight loss of 1018 steel as a function of seawater strength. (b) Graph amplifying effects observed with additives resulting in least weight loss. INH4(2) and INH4(8) designate different concentrations of INH4 (Table 1).

at a scan angle near that of bare gold, but with a somewhat reduced amplitude. The no wash curve for INH5 was at a significantly lower angle and had a significantly reduced amplitude from that of pure gold. After the water wash, the spectra for INH1, INH4, and INH6 were the same as those for bare gold. For INH2 and INH6, however, the minima after washing were shallower than that of bare gold, suggesting residual effects on the SPR signals. After the NaCl wash, minima appeared in all spectra. However, the position of the minima

shifted by different amounts from that of the bare gold and the amplitude varied somewhat.

4. Discussion

4.1 Weight Loss and Corrosion Rate

From a practical point of view, the weight-loss results clearly indicate the importance of making informed selections

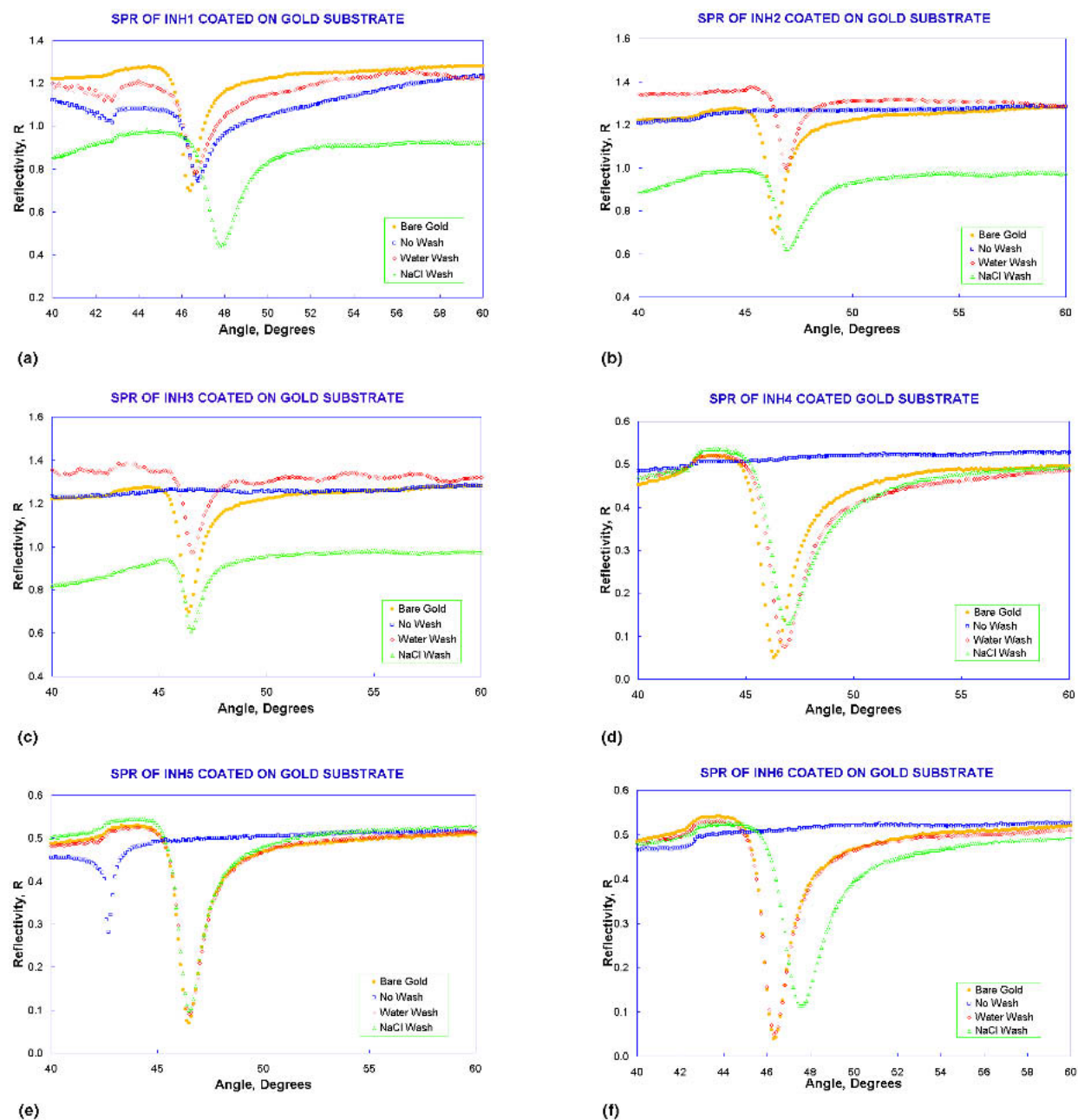


Fig. 5 Reflectivity curves. (a) INH1 on gold substrate. (b) INH2 on gold substrate. (c) INH3 on gold substrate. (d) INH4 on gold substrate. (e) INH5 on gold substrate. (f) INH6 on gold substrate

of inhibitors for metallic structures that will be used in a marine environment. For steel protected by INH2, INH3, and INH4, the corrosion rate in seawater is significantly reduced. In the case of INH1 and INH6, the corrosion rate of steel in seawater remains the same and for INH5 corrosion increases. For aluminum protected by INH2 and INH4, seawater corrosion is reduced; however pitting is increased for the other additives. It should be pointed out that only INH2 and INH4 would be suitable for consideration in protecting structures made of both steel and aluminum.

The corrosion rate of aluminum remained essentially constant with increase in seawater strength or salinity when im-

mersed in the unaltered seawater control. Seawater salinity independence, at least within the measurement error, was observed when INH4 of both dilutions, INH1 or INH2, was added to seawater. When INH3, INH6, or INH5 was added to seawater, the corrosion rate increased with increasing seawater strength. For steel, the corrosion rate decreased significantly (by 50%) as the salinity of seawater was decreased by half, but remained essentially the same with further reduction in salinity. It is possible that lower-strength seawater even without the additives can provide some benefit for steel when fresh water for a wash cycle is scarce. For steel, the presence of any of the additives in seawater appears to have produced no strong trends

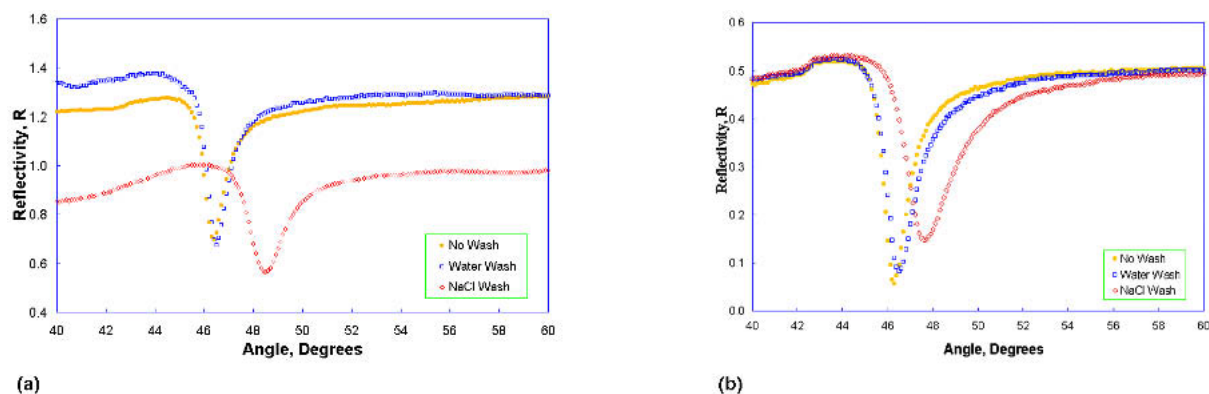


Fig. 6 (a) SPR reflectivity curve for bare gold substrate (baseline for curves in Fig. 5a, b, and c). (b) Reflectivity curves for bare gold substrate, run 2 (baseline for curves in Fig. 5d, e, and f)

Table 4 Analysis of SPR spectra giving position or scan angle, θ ($^{\circ}$) and amplitude or $(-R)$ of the minima

Substrate	Bare gold		No wash		Water wash		NaCl wash	
	θ ($^{\circ}$)	$(-R)$	θ ($^{\circ}$)	$(-R)$	θ ($^{\circ}$)	$(-R)$	θ ($^{\circ}$)	$(-R)$
Bare gold	46.5	0.57	46.5	0.70	48.5	0.44
INH1	46.4	0.56	46.8	0.33	46.6	0.41	47.9	0.54
INH2	46.5	0.57	None	None	47.0	0.36	47.0	0.39
INH3	46.4	0.56	None	None	46.6	0.36	46.6	0.35
Bare gold	46.3	0.46	46.5	0.44	47.7	0.39
INH4	46.3	0.47	None	None	46.7	0.45	46.8	0.40
INH5	46.5	0.46	42.7	0.17	46.5	0.44	46.5	0.45
INH6	46.4	0.50	None	None	46.4	0.48	47.6	0.42

None means no minima

with seawater strength. With some inhibitors, such as INH1, INH2, and INH4, there appears to be a mildly increasing trend. With others, for example, INH5 and INH3, there appears to be a mildly decreasing trend.

Analysis shows that for additives that worsen the corrosion response, the strength or level of salinity of seawater does influence weight loss in aluminum but not in steel. This is contrary to the observation that the level of salinity in unaltered seawater had no influence on aluminum, but did have an influence on steel. In this case, the seawater environment does affect the corrosion processes in aluminum but not in steel. It is possible that components in these inhibitors interact with seawater in such a manner as to produce the opposite effects observed on the two metals. For inhibitors that improve the corrosion response, the level of salinity had no significant effect on weight loss for either metal. This is a significant observation because it implies that seawater strength becomes less important when selecting a wash containing beneficial inhibitor additives.

In general, it is apparent that the action of the additive or its ingredients dominates the corrosion processes in both metals. Since additive ingredients are a trade secret, any explanation forwarded would be speculative. Relative to seawater control, some additives increase the corrosion rate by a large amount, while some decrease the corrosion rate by a large amount.

These results provide a ranking and some guidance for the practical use of the additives. A couple of inhibitors were found to produce lower corrosion rates in both metals. This is significant because it meets the need to identify wash additives that would be suitable for both metals.

In aluminum, pitting is the dominant corrosion mechanism. Pitting of aluminum is known to initiate by some action of the chloride ion, at very small concentrations, leading to the breach of the protective Al_2O_3 surface film. With inhibitor additives that markedly increase the corrosion rate, more numerous, larger, and deeper pits were observed on aluminum. These additives also show an increasing trend with increasing salinity. The extent of pitting, determined by examination, correlated well with the weight-loss results for the different additives.

4.2 SPR Spectrum Analysis Based on Statistical Feature Variables

The simplest interpretation of physical processes underlying SPR is to consider surface plasmons as surface waves propagating through a medium consisting of free electrons of a given density distribution and relative mobility. These surface waves are induced by an incident light beam of given wavelength and reside at the metal surface as shown in Fig. 2. The free electrons that support the surface plasmons are interpreted as moving in a polarizable and screening background, which is associated with the bulk metal substrate. Any external influence, which modifies the physical characteristics of this background or of the free-electron density distribution, will affect the characteristic mobility of the surface electrons and thus the oscillatory structure of the plasma waves. Specifically, there is a direct correlation between the absorptive part of the complex refractive index or absorbance character of a sample layer and the amplitude of the resonance minimum observed in the reflectivity as a function of angle of incidence (or of reflection) (Ref 12). It follows therefore that the amplitudes of plasma resonance minima may be adopted as a statistical feature whose magnitude may be correlated with the average adherence properties of adsorbates or of surface coatings in general. The theory of SPR combined with effective medium theories for representing the electromagnetic permittivity of the substrate and inhibitor coatings provides, in principle, a formulation for

the analysis of the different features associated with SPR spectra. These features would include, for example, relative shifts or broadening of SPR minima. This type of analysis would require, however, detailed information concerning the chemical composition of the inhibitor solutions, explicit knowledge of substrate surface roughness, the electronic nature of the adsorbed molecules, the extent of surface covering by adsorbed molecules, and the statistical character of inhomogeneities within the surface covering. In their analysis, the authors consider, therefore, only one feature of SPR spectra, the relative amplitude of the minimum of the reflectivity function, a quantity that may be correlated with the density distribution and mobility of free surface electrons (see Ref 12 for further discussion). The density distribution and mobility of surface electrons, in turn, may be correlated with the presence or absence of an inhibitor film on the substrate or with the relative average level of surface coverage by an inhibitor or with the relative ability of the inhibitor to adhere to the metal surface via some unique bonding mechanism. The amplitudes of the SPR minima are to be interpreted as statistical feature variables rather than “deterministic” spectral signatures to be correlated with known structure of the additives or their components.

From the SPR results (Fig. 5), it can be seen that the amplitudes of the SPR resonance minima associated with INH2, INH3, INH4, and INH6 are negligible or nonexistent. This “totally damped” response may be correlated with a surface coating layer that tightly adheres to the substrate. This implies a change in the density distribution of surface electrons that is sufficient for constraining, or rather, totally damping out any oscillations of the free electrons on the surface of the gold substrate. For INH1 and INH5 (Fig. 5a, e) the presence of a resonance minima correlates with no surface layer or one having a relatively weak adherence to the substrate. A weak adherence of the coating layer to the metal substrate such that surface electron mobility or availability is not reduced, implies that there is a minimal constraining of the oscillations of the free electrons on the surface of the gold.

Results of reflectivity curves corresponding to two different experimental trials involving washing of additive-coated substrates using fresh water or 1% NaCl are interesting. It can be seen that, after washing, the amplitudes of the SPR minima for the surface coated with the additives all obtain similar values relative to each other. In addition, these spectra all indicate a similar level of damping relative to the bare gold substrate. This consistency suggests that in each case water represents the dominant ambient medium at the gold interface. After washing with 1% NaCl, the amplitudes of almost all the SPR minima are large and shifted to a higher angle relative to those associated with bare gold. It is to be noted that for INH3 and others there does exist a nonnegligible level of damping of the SP resonance. This implies the persistence of some coating after washing with NaCl. It is further noted that there is actually amplification of some SP resonance amplitudes relative to bare gold. This enhancement of the resonance may be due to the presence of an electrolyte as the ambient medium at the gold surface. The cause of this effect, however, is not relevant to the authors’ present analysis. The significant feature in this analysis, indicating the presence of inhibitor, is the level of damping of the SP resonance relative to bare gold. These resonance

amplitudes are sufficient, therefore, for suggesting that the adsorbed layers have been washed off.

The trends observed in the SPR studies show reasonably good consistency with those of the weight-loss studies. INH1 and INH5 were observed, for all experimental trials, to have SPR spectra consistent with weak or no adherence of a surface film on the gold substrate. This result is consistent with the fact that these inhibitors do not reduce the corrosion rates of the metals. In fact, INH5 increases the corrosion rate of steel relative to unaltered seawater. INH1 also increases the corrosion of aluminum. Reflectivity curves for INH2, INH3, and INH4 and INH6 suggest the presence of a surface effect, and this correlates with cases in which the corrosion rates of aluminum and steel are reduced. After NaCl and water washes, the minima in the SPR curves become similar to that of gold except for the case of INH3, where, following the water wash, the minimum was not restored to that of gold. This suggests some surface species remain deposited. INH3 provided very good protection for steel but increased aluminum pitting. The corrosion rates of steel and aluminum increase relative to seawater in the presence of INH6. Although the SPR spectra for INH6 show evidence of physical adherence, apparently the adsorbed species increases rather than decreases corrosion rates.

5. Conclusions

The objective of this work was to obtain reliable measurements of the corrosion rates of representative aluminum and steel specimens exposed to seawater containing water-soluble corrosion inhibitors and to examine the adhesion and persistency of the inhibitors to a metallic surface. While these measurements cannot represent the environmental situation for all possible applications of inhibitors, they can be used to evaluate and rank benefits that can be achieved from their use. The most important findings of this study are:

- A significant result of this analysis is that it supports an increased confidence level concerning the overall concept of using inhibitor formulations or reductions in seawater concentration as a viable method of corrosion control. These results demonstrate a high degree of sensitivity to differences in the types of inhibitor additives and, further, a marked and statistically reliable reduction in corrosion due to the presence of inhibitor.
- Pitting of aluminum is increased for the majority of the inhibitors tested (INH1, INH3, INH5, and INH6) for all seawater concentrations. These additives should be avoided for use with aluminum parts. In the presence of INH4 and INH2, aluminum pits somewhat less than it does in seawater, and these additives may be recommended for aluminum.
- The corrosion rate of steel is reduced in lower-strength seawater. INH1, INH6, and INH5 provide poor protection to steel in seawater and these additives should be avoided. Significant reductions in corrosion rates are observed, however, for INH2, INH3 and INH4, and these additives may be recommended for steel.
- For structures containing both aluminum and steel parts, INH2 and INH4 may be used.

- It can be inferred that SPR measurements detect the intrinsic attraction of corrosion-inhibiting species at a metal surface. There is good correlation between additive adhesion and lower corrosion rates. The SPR measurements can be useful in monitoring the relative persistency of the additives following mechanical washing procedures.

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