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Effect of Inhibitor Treatment on Corrosion of Steel in a Salt Solution

Ramazan Kahraman, Huseyin Saricimen, Mesfer Al-Zahrani, and Salah Al-Dulaijan

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This study examined experimentally different chemicals for inhibition of steel corrosion in a simulated aqueous solution for the industrial marine atmosphere of the Arabian Gulf region. The literature reported various inhibitors that can help in protection against metal corrosion in aqueous environments. Among them, 10 inhibitors (calcium silicate, cyclohexylamine, n-methylcyclohexylamine, dicyclohexylamine nitrite, sodium benzoate, sodium nitrate, sodium nitrite, sodium phosphate, sodium dihydrogen orthophosphate, and magnesium nitrate hexahydrate) were obtained and corrosion resistance of inhibitor applied steel specimens were examined in the simulated solution (2 wt.% NaCl and 1 wt.% Na_2SO_4). Test specimens were prepared from locally produced reinforcing steel products. Treatment of steel with either dicyclohexylamine nitrite or sodium dihydrogen orthophosphate both at 10 mM concentration for 1 day at room temperature resulted in significant inhibition of corrosion. No significant improvement in corrosion inhibition was observed either with an increase in inhibitor concentration at room temperature or with an increase in inhibitor application temperature at 10 mM concentration. A further study is planned to examine the inhibition performances of the two inhibitors under actual atmospheric conditions in the Arabian Gulf region (industrial marine environment).

Keywords corrosion, dicyclohexylamine nitrite, dihydrogen orthophosphate, inhibitors, steel

1. Introduction

The weather in the Arabian Gulf region is hot and humid providing corrosive environment for mild steel. The atmospheric corrosion in the Gulf region is aggravated further by the high salinity of Gulf water resulting in the high rate of seasalt deposition. In addition, sulfur dioxide and carbonaceous deposits from burning fuel make the atmosphere in the Gulf region more corrosive. Various inhibitors that can help protect against metal corrosion in aqueous environments were reported in the literature. Among them are toluylalanine, cyclohexyl amine, methylcyclohexylamine, phenylthiourea, sodium benzoate, sebacic acid, sodium nitrite, calcium silicate, sodium phosphate, and sodium nitrate.

Saurbier et al.[1] compared 3-(toluyl)-N-(1,1-dimethyl-2-hydroxyethyl)-alanine, known as toluylalanine (TALA) $C_{15}H_{21}NO_4$, sebacte (seba) $C_{10}H_{18}O_4$, i-nonate (i-non) $C_9H_{18}O_2$, m-nitrobenzoate (m-nitro) $C_7H_5NO_4$, i-phthalate (i-phtha) $C_8H_6O_4$, benzoate (Benz) $C_7H_6NO_2$, and nitrite as inhibitors of corrosion in wet atmosphere. The most effective inhibition was obtained in solution with the passivating TALA. Some other inhibitors reported to be effective against corrosion are TPI-4[2], $NaNO_2$-water solution,[3] five-membered polynitrogen heterocycles,[4] amines such as cyclohexyl amine,[5] ethanolamine,[6] sulfonates and phosphorous-containing organic compounds,[7] imidazole derivatives,[8] and fatty acid esters.[9] Some commercial coolants are also used as atmospheric corrosion inhibitors.[10] Chromates are effective as atmospheric inhibitors (for aerospace aluminum alloys); however, they are identified to be carcinogenic and their use therefore is not recommended.[11,12] Non-chromate inhibitor formulations such as borate, molybdate, dihydrogen orthophosphate, and silicate were studied for aluminum aircraft.[12]

Thiophenol was reported to serve as a good inhibitor (studied at concentrations of 1 mM, 10 mM, 100 mM) for the corrosion of iron and mild steel in acidic solutions.[13,14] However, thiophenols have not been given much attention as inhibitors due to their obnoxious odor and low solubility in acidic solutions.[13].

The influence of the concentration of electrolyte anions on the efficiency of acid-based inhibitors for steel in the neutral solution was studied using anodic and cathodic polarization at a rotating disk electrode. The N-ethyl-morpholine of a q-benzoyl alcanoic acid and benzoic acid were used as inhibitors. Both inhibitors were found to inhibit the anodic partial reaction. The inhibition effect was more pronounced at low electrolyte concentration.[15]

The corrosion inhibiting performance of a tertiary amine possessing two carboxylic acid groups (N coco-amine-2-proprionic acid) was studied on initially clean and pre-corroded mild steel. High levels of efficiency were found of the inhibitor at a concentration level of 10 ppm.[16]

The influences of inhibitor concentrations for orthodihydrogen orthophosphate mixed with polydihydrogen orthophosphate were studied on steel. The total concentration of two inhibitors was 15 mg/L. The corrosion rate, which was 1.9

Ramazan Kahraman, Chemical Engineering Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia; and **Huseyin Saricimen, Mesfer Al-Zahrani**, and **Salah Al-Dulaijan,** Research Institute King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia. Contact e-mail: kahraman@kfupm.edu.sa.

Table 1 Typical Composition of Steel Used in the Present Investigation (Residual* Elements by wt.%)

C	Si	Mn	P	S	Cu	Cr	Mo	Ni	Sn	V	Nb
0.34	0.18	1.23	0.12	0.11	0.048	0.022	0.012	0.020	0.002	0.004	0.005

* The balance is Fe.

miles per year (mpy) at 0% of orthodihydrogen orthophosphate, decreased to 0.3 mpy at 60% of orthodihydrogen orthophosphate but then increased up to 1.8 mpy when orthodihydrogen orthophosphate concentration increased to 100%.[17]

The objective of the current study was to select, through accelerated laboratory tests, candidate inhibitor(s) for examination against atmospheric corrosion of mild steel under actual atmospheric conditions in a further study. For this purpose, several inhibitors (calcium silicate, cyclohexylamine, n-methylcyclohexylamine, dicyclohexylamine nitrite, sodium benzoate, sodium nitrate, sodium nitrite, sodium phosphate, sodium dihydrogen orthophosphate, and magnesium nitrate hexahydrate) were obtained and examined in a simulated solution of 2% NaCl and 1% Na_2SO_4.[18]

2. Experimental

2.1 Test Specimens

Test specimens that were 1 in. long were prepared from locally produced 12 mm (diameter) deformed hot rolled quenched steel bars. A typical chemical analysis of the steel used in the study is given in Table 1. It has pearlitic and ferritic microstructure inside with tempered martensitic rim of about 1 mm thick at its circumference. The specimens were threaded at one cross sectional side to fit them in the working electrode rod of the electrochemical cell. They were washed prior to the study using soap and water, followed by ultrasonic cleaning in acetone and methanol before drying.

2.2 Inhibitor Application

Solutions of inhibitors in distilled water were prepared in desired concentrations using magnetic mixing. Inhibitor application of specimens to be protected was conducted by immersing the specimens in the inhibitor solution for a specified period of time (1 day) at room temperature. Then the specimen was placed in the corrosive solution for evaluation of the effectiveness of inhibitor in slowing down corrosion.

2.3 Inhibitor Performance Analysis

The effect of inhibitors on the corrosion of steel specimens in a simulated environment was evaluated by electrochemical technique in a standard test cell. The cell was a vessel containing the solution electrolyte and electrodes. The solution electrolyte was distillate water with dissolved salts. The salt solution contained 2% sodium chloride (NaCl) and 1% sodium sulfate (Na_2SO_4) to simulate industrial marine atmosphere.[18] The steel specimens were the working electrodes in the electrochemical test cell. A graphite electrode functioned as the auxiliary electrode while a standard saturated calomel electrode (SCE) was used as the reference electrode. The working, auxiliary and reference electrodes were connected to a potentiostat (Model 273A, EG&G PARC, Princeton, NJ). The potentiostat was controlled by a microcomputer through corrosion software (Model 352, EG&G PARC). The corrosion rates were measured using linear polarization resistance (LPR) and Tafel techniques. The input data for Tafel and polarization runs are given in Table 2. From appropriate plots, corrosion current density (I_{corr}), corrosion potential (E_{corr}), polarization resistance (R_p), and corrosion rates were determined.

3. Results and Discussion

3.1 Preliminary Screening Tests to Determine the Inhibitor Concentration to Use in Comparing Inhibitor Performances

A few preliminary electrochemical tests were performed on untreated (control) steel and on steel after treatment by solutions of several inhibitors at different concentrations to be able to come up with a satisfactory concentration to use in comparing the corrosion inhibition performances of various inhibitors. Representative results are presented in Fig. 1 and 2. As seen here (and also in the cases not shown here), 10 mM concentration was found to be sufficient for significant corrosion inhibition for the inhibitor solutions examined.

3.2 Performance Analysis Tests on Several Inhibitors

The following inhibitors were screened through corrosion tests in the simulated solution (2 wt.% NaCl + 1 wt.% Na_2SO_4):

1. Calcium silicate
2. Cyclohexylamine
3. N-methylcyclohexylamine
4. Dicyclohexylamine nitrite
5. Sodium dihydrogen orthophosphate
6. Sodium benzoate
7. Sodium nitrate
8. Sodium nitrite
9. Sodium phosphate
10. Magnesium nitrate hexahydrate

Inhibitor application of specimens to be protected was conducted by inserting the specimens in the inhibitor solution at 10 mM concentration for 1 day at room temperature (23 ± 2 °C).

The results of the Tafel runs (in a simulated solution of 2 wt.% NaCl + 1 wt.% Na_2SO_4) are tabulated in Table 3. As mentioned earlier, the Tafel constants β_{anode} and $\beta_{cathode}$, which were obtained in Tafel runs, were used to determine the corrosion rates through the linear polarization resistance tests.

The average corrosion rates of the steel specimens treated by various inhibitors are presented in Fig. 3 and compared with that of the control (untreated) specimen. As seen, treatment of steel with dicyclohexylamine nitrite resulted in the best inhibition of corrosion followed by the inhibitor sodium dihydrogen orthophosphate. Corrosion inhibition performances of sodium benzoate and sodium nitrite were similar and little better than that of sodium nitrate. Treatment by N-methylcyclohexylamine did not cause a significant decrease in corrosion rate of steel. The candidate inhibitors calcium silicate, cyclohexylamine, sodium phosphate, and magnesium nitrate hexahydrate were found to be corrosive and increased, rather than decreased, the corrosion rate of steel in the simulated solution.

3.3 Screening of Inhibitor Application Conditions for the Selected Inhibitors

As a result of the first screening tests, dicyclohxylamine nitrite (organic) and sodium dihydrogen orthophosphate (inorganic) were selected for further investigation.

Table 2 Input Data for Tafel and LPR Electrochemical Techniques

	Input Data	
	Tafel	LPR
Minimum potential	−25 mV	−10 mV
Maximum potential	+25 mV	+10 mV
Scanning rate	0.1 mV/s	0.1 mV/s
β_{anode}	…	From the Tafel test
$\beta_{cathode}$	…	From the Tafel test
Sample area	Depends on the sample	Depends on the sample
Sample density	7.87 g/cm^3	7.87 g/cm^3
Equivalent weight	27.89	27.89

3.3.1 Inhibitor Application at Room Temperature. The second screening tests were carried out to determine the concentration at room temperature that the inhibitors are most effective. For this purpose the inhibitors were tested using the same methods at 1.0, 10, and 100 mM concentrations in the case of dicyclohxylamine nitrite (preparation of higher concen-

Table 3 Results of the Tafel Runs in the Simulated Solution of 2 wt.% NaCl + 1 wt.% Na_2SO_4

Specimens (Treated With the Following Inhibitors)	Run No.	β_{anode}	$\beta_{cathode}$
Control (no inhibitor treatment)	1	0.084	0.426
	2	0.068	0.720
	3	0.067	0.721
Calcium silicate	1	0.060	0.678
	2	0.090	1.013
	3	0.072	0.862
Cyclohexylamine	1	0.081	0.715
	2	0.077	0.869
	3	0.094	0.850
N-methylcyclohexylamine	1	0.040	1.140
	2	0.069	0.720
	3	0.045	0.692
Dicyclohexylamine nitrite	1	0.036	0.838
	2	0.042	0.547
	3	0.043	0.358
Sodium dihydrogen orthophosphate	1	0.031	0.644
	2	0.036	0.618
Sodium benzoate	1	0.063	0.121
	2	0.061	0.121
Sodium nitrate	1	0.067	0.122
Sodium nitrite	1	0.066	0.122
Sodium phosphate	1	0.088	1.250
	2	0.127	1.235
	3	0.035	0.711
Magnesium nitrate hexahydrate	1	0.075	0.527
	2	0.085	0.574
	3	0.073	0.435

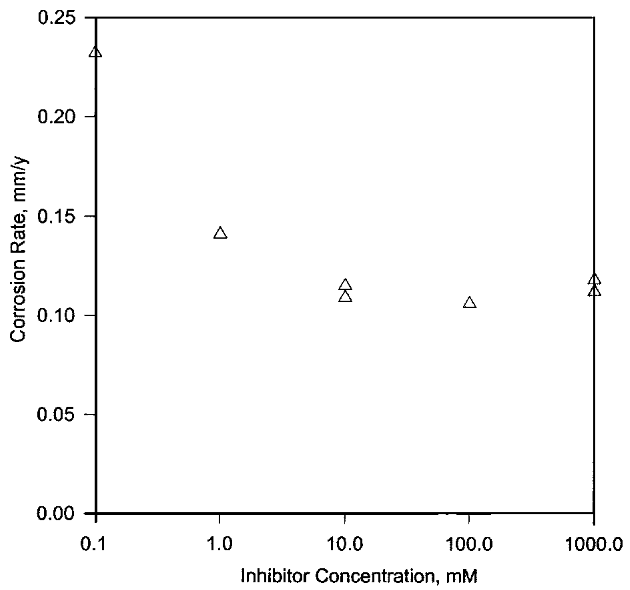

Fig. 1 Corrosion rate versus inhibitor concentration for steel treated with sodium benzoate for 1 day at room temperature

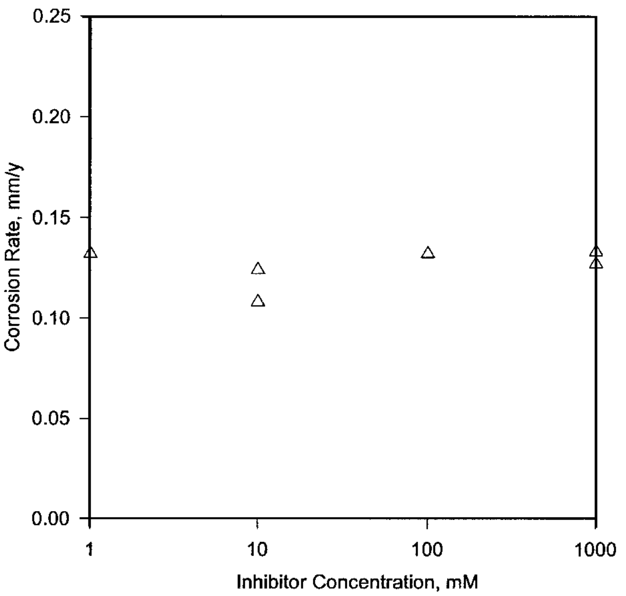

Fig. 2 Corrosion rate versus inhibitor concentration for steel treated with sodium nitrate for 1 day at room temperature

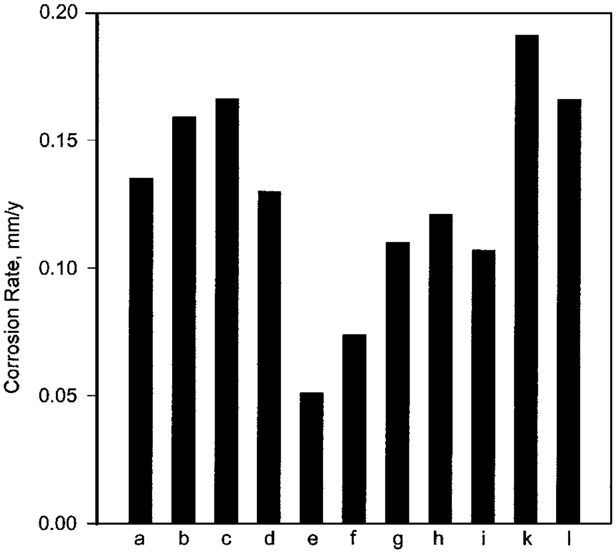

Fig. 3 Corrosion rates in a simulated solution of 2 wt.% NaCl and 1 wt.% Na_2SO_4 of untreated control specimen **(a)** and specimens treated in solution of calcium silicate **(b),** cyclohexylamine **(c),** N-methylcyclohexylamine **(d),** dicyclohexylamine nitrite **(e),** sodium dihydrogen orthophosphate **(f),** sodium benzoate **(g),** sodium nitrate **(h),** sodium nitrite **(i),** sodium phosphate **(k),** and magnesium nitrate hexahydrate **(l)**

trations was not possible) and at 1.0, 10, 100, and 1000 mM concentrations in the case of sodium dihydrogen orthophosphate.

The results showed that the selected two inhibitors are most effective near 10-100 mM concentration (Fig. 4 and 5).

3.3.2 Inhibitor Application at Elevated Temperatures. In the third screening tests, the inhibitors at a concentration of 10 mM were tested for the most effective inhibitor application temperature. They were tried at three different temperatures: 200, 400, and 600 °C. The results, which are compiled in Table 4 and 5, did not show any improvement with an increase in application temperature. In fact, corrosion rate increased with rising temperature.

Therefore, room temperature was selected for inhibitor application of steel specimens in further planned studies under atmospheric conditions.

4. Conclusions

- Treatment of steel with dicyclohexylamine nitrite at a concentration of 10 or 100 mM for 1 day at room temperature resulted in significant inhibition of corrosion in the simulated aqueous solution of 2% NaCl + 1% Na_2SO_4. Preparation of dicyclohexylamine nitrite solutions at higher concentrations was not possible.
- Treatment of steel with 10 or 100 mM sodium dihydrogen orthophosphate (for 1 day at room temperature) also resulted in significant corrosion inhibition in the simulated salt solution. Higher (1000 mM) or lower (1 mM) inhibitor concentrations caused an increase in corrosion rate of steel.

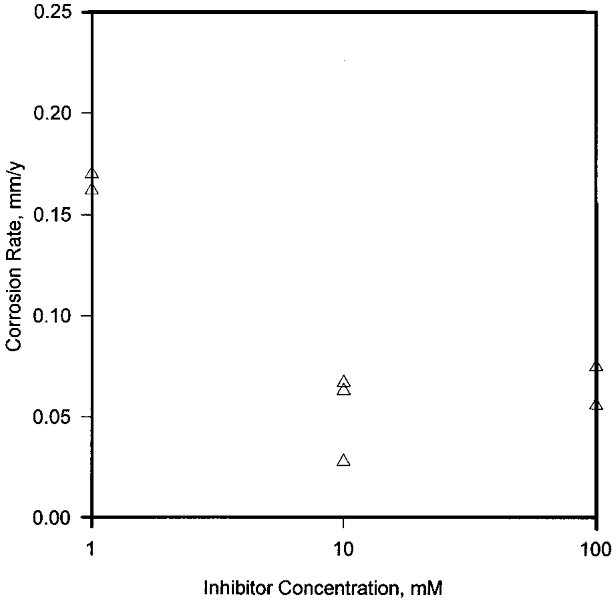

Fig. 4 Corrosion rate versus inhibitor concentration for steel treated with dicyclohexylamine nitrite for 1 day at room temperature

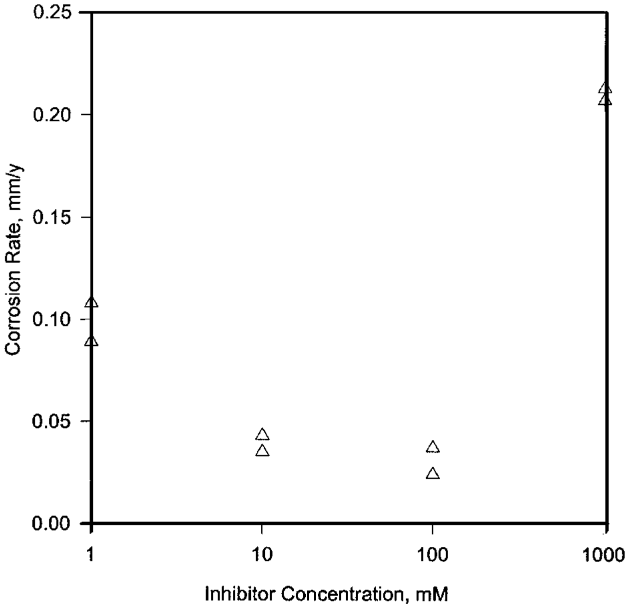

Fig. 5 Corrosion rate versus inhibitor concentration for steel treated with sodium dihydrogen orthophosphate for 1 day at room temperature

- Application of the inhibitors at a higher temperature than room temperature did not improve their performance.

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Table 4 Electrochemical Tests on Steel Specimens Treated by Dicyclohexylamine Nitrite at Elevated Temperatures: Corrosion Rates in a Simulated Solution of 2 wt% NaCl and 1 wt% Na_2SO_4

Inhibitor Temp., °C	Run No.	Surface Area, cm^2	Corrosion Potential, V	R_p, kΩ-cm^2	I_{corr}, μA/cm^2	Corrosion Rate	
						mpy	mm/y
200	1	9.802	−0.644	2.391	11.01	4.618	0.117
	2	9.588	−0.658	2.109	11.35	5.236	0.133
400	1	9.296	−0.628	3.71	5.571	2.57	0.065
	2	9.962	−0.622	2.253	9.175	4.233	0.108
600	1	9.707	−0.72	2.256	18.37	8.473	0.215
	2	9.566	−0.644	2.683	15.44	7.126	0.181

Table 5 Electrochemical Tests on Steel Specimens Treated by Sodium Dihydrogen Orthophosphate at Elevated Temperatures: Corrosion Rates in a Simulated Solution of 2 wt.% NaCl and 1 wt.% Na_2SO_4

Inhibitor Temp., °C	Run No.	Surface Area, cm^2	Corrosion Potential, V	R_p, kΩ-cm^2	I_{corr}, μA/cm^2	Corrosion Rate	
						mpy	mm/y
200	1	9.584	−0.664	2.125	9.364	4.32	0.110
	2	10.03	−0.672	2.358	8.43	3.889	0.099
400	1	9.452	−0.672	2.197	14.71	6.788	0.172
	2	9.746	−0.68	2.092	15.45	7.128	0.181
600	1	9.694	−0.748	1.839	16	7.381	0.187
	2	9.337	−0.748	1.53	11.924	8.876	0.225

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