Dedicated to the memory of Professor Margareta Avram
on the remembrance of her 100th anniversary

COMMERCIAL AQUEOUS ADDITIVES USED AS ECO-FRIENDLY CORROSION INHIBITORS FOR CARBON STEEL IN NATURAL SEAWATER

Simona CAPRARESCU,[a] Violeta PURCAR[b,*] and Cristina MODROGAN[c]

[a]University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Inorganic Chemistry, Physical Chemistry and Electrochemistry Department, 1-7 Polizu St., 011061, Bucharest, Roumania, scaprarescu@yahoo.com
[b]National Research&Development Institute for Chemistry and Petrochemistry ICECHIM, Splaiul Independentei no. 202, 6th district, 060021, Bucharest, Roumania, purcarvioleta@gmail.com
[c]University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Analytical Chemistry and Environmental Engineering Department, 1-7 Polizu St., 011061, Bucharest, Roumania, c_modrogan@yahoo.com

The aim of the present study was to evaluate the effectiveness of the different commercial aqueous additives (flavors of pineapple and of strawberry) on corrosion of carbon steel in natural seawater using the weight loss measurement and potentiostatic polarization method, at room temperature. The effect of different amount of inhibitors (commercial aqueous additives) on the corrosion rate (CR) and inhibition efficiency (IE %) were also investigated. Experimental results indicated that the inhibition efficiency increases with increasing amount of inhibitor. Maximum inhibitor efficiency of 39.39 % was obtained at 6 mL of the commercial aqueous additive with flavor of pineapple, after 14 days. It was found that the commercial aqueous additives acted as good adsorption inhibitor for the corrosion of carbon steel in natural seawater. Furthermore, the corroded samples of carbon steel were examined using an optical microscope.
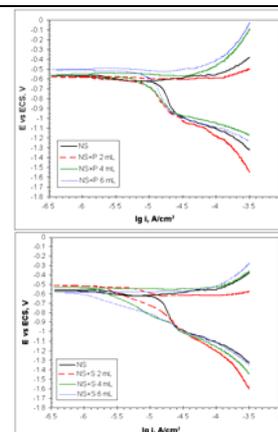
INTRODUCTION

Carbon steel due to its excellent properties (*i.e.* versatile, malleable and ductile, relatively low price) was used in many applications, such as: in marine applications, nuclear power and fossil fuel power plant, transportation, chemical processing, mining, structural purposes in bridges and buildings, pipelines and couplings gates, parts of automobiles, axles, gears, shafts, rails, fridges and washing machines.[1–4]

Corrosion, a major problem in local and industrial applications, is generally defined as the gradual destruction of materials by chemical reaction with their environment.[4–7]

In the last years, have been reported many studies on the corrosion of carbon steel and its alloys in seawater environments.[8–12] The use of inorganic or organic substances, solid or liquid, called "inhibitors" is one of the most practical and cost effective methods of controlling metallic corrosion, especially in the environment like

---
* Corresponding author: purcarvioleta@gmail.com

seawater.[8–13] Some extracts, obtained through simple extraction processes of plants parts (lives, roots, seeds, flowers, fruits, stem), were successfully used for corrosion protection due to their advantages, such as: are inexpensive, readily available, eco-friendly, are biodegradable, do not contain heavy metals or other toxic compounds, good corrosion inhibition ability.[14–16]

The aim of the present work was to study the effect of different corrosion inhibitors for carbon steel in natural seawater for 14 days using weight loss and electrochemical polarization curve measurements. The effect of amount of inhibitors on the corrosion rate and the inhibition efficiency of carbon steel in free and inhibited natural seawater was also investigated.

RESULTS AND DISCUSSION

The assessment of the effectiveness of corrosion inhibitors on the samples of carbon steel was done using weight loss measurements and potentiostatic polarization method. For weight loss measurements, the samples of carbon steel have been extensively employed for long-term immersion test (336 h). In order to evaluate the corrosion of samples of carbon steel, corrosion rate and corrosion inhibitor efficiency (percentage) were calculated.

Corrosion rate (CR) for the samples was calculated following equation (1):[1,2,6–17]

$$Cr = \frac{W_0 - W_1}{A \cdot t},\qquad(1)$$

where: Cr – corrosion rate, g/m²h; W_0 – initial weight of carbon steel coupon, g; W_1 – final weight of carbon steel, m²; t – the time of exposure (hrs).

The inhibitor efficiency (IE %) was calculated using equation (2):[1,2,6-17]

$$IE \quad (\%) = \frac{Cr_0 - Cr_1}{Cr_0} \times 100,\qquad(2)$$

where: Cr_0 – corrosion rate in the absence of inhibitor and Cr_1 – corrosion rate in the presence of inhibitor, g/m²h

Weight loss measurements

The corrosion rate (CR) and inhibition efficiency (IE %) values obtained by weight loss data, in different corrosion medium, are indicated in Table 1.

The extent of reduction in corrosion rate is seen to increase with increase in the amount of commercial aqueous additives (Table 1). The results indicated that the value of corrosion rate of carbon steel in natural seawater without inhibitors was higher when aqueous additives (inhibitors) were used. Inhibition efficiency increases with increasing amount of commercial aqueous additives, and the maximum IE % of 39.39 % was obtained at 6 mL of aqueous additives with flavor of pineapple. The reduction in the weight loss could be attributed to the mixture of various constituents.

Potentiostatic polarization curve

The polarization curves for the carbon steel electrode in natural seawater, in the absence and in the presence of various amounts of commercial aqueous additives are given in Fig. 1 and Fig. 2.

It can be seen from Fig. 1 and Fig. 2 that both anodic and cathodic Tafel slopes were significantly changed when the inhibitors were added in the natural seawater, indicating that the inhibition mechanism took place by coverage the available anodic and cathodic active sites on the metal surface.[16] Moreover, the addition of the commercial aqueous additives shifts the polarization curves towards electropositive values of the potential, especially for pineapple flavor, indicating that the inhibitors acted as mixed-type inhibitors. Olawale *et al.*[4] reported that the presence of active constituents on the metal surface, whose activity increases with the increase in concentration of the extract hence, leads to the formation of a protective film, thus reducing the corrosion of the metal.

Table 1

The values of CR and IE for samples of carbon steel in the different corrosion medium

Medium of corrosion	Amount of commercial aqueous additives, mL	CR, g/m² h	IE, %
NS	0	0.2046	–
NS+P	2	0.1674	18.18
	4	0.1488	27.27
	6	0.1240	39.39

Table 1 (continued)

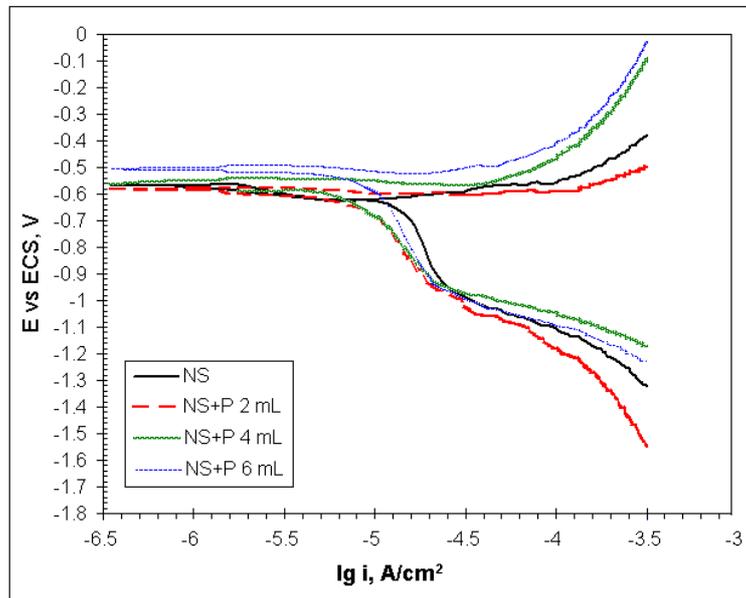|			
NS+S	2	0.1736	15.15
	4	0.1550	24.24
	6	0.1302	36.36

Fig. 1 – Potentiostatic polarization curves of the carbon steel in natural seawater (NS) in the absence and in the presence of different amounts of commercial aqueous additive with flavor of pineapple (P).
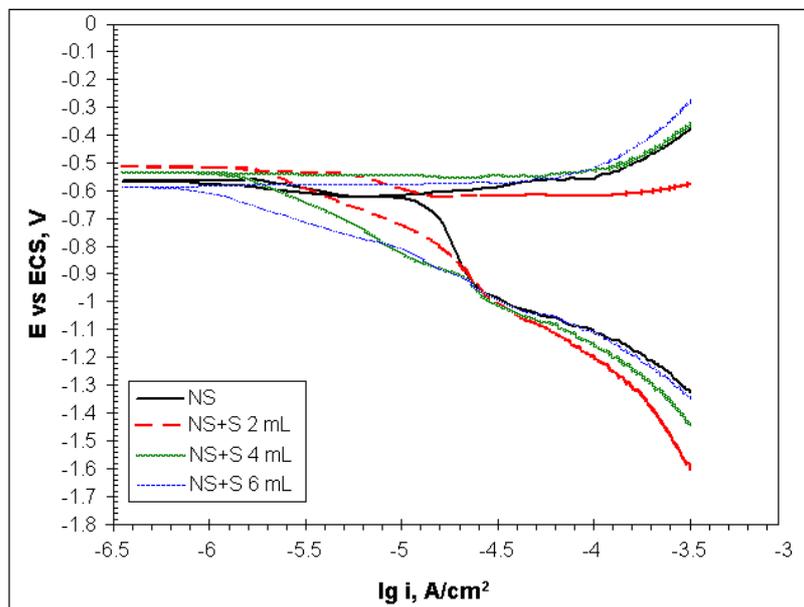

Fig. 2 – Potentiostatic polarization curves of the carbon steel in natural seawater (NS) in the absence and in the presence of different amounts of commercial aqueous additive with flavor of strawberry (S).

The potentiostatic parameters (corrosion potential (E_{corr}) and corrosion current density (i_{corr})), obtained by extrapolation of the linear Tafel segments of the anodic and cathodic curves are presented in Table 2.

The results presented in the Table 2 indicate that the inhibition efficiency (IE) increase with increasing amounts of the inhibitors. The best value of IE (35.44 %) was obtained in the case of pineapple flavor at higher values of the amount of 6 mL.

Table 2

Electrochemical parameters calculated from polarization
measurements on carbon steel in natural seawater + different amounts of inhibitors at 25°C

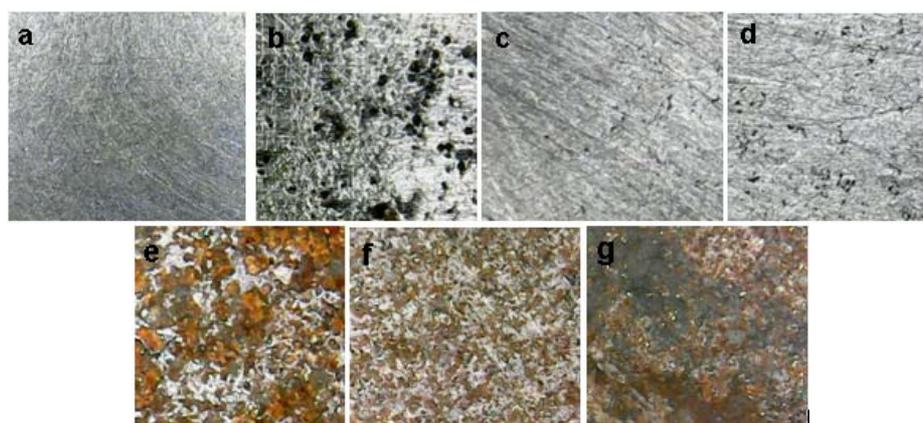| Medium of corrosion	Amount of commercial aqueous additives, mL	E_{corr}, mV/ECS	i_{corr}, $\mu A/cm^2$	IE, %
NS	0	-882	30.90	-
NS+P	2	-850	25.12	18.71
	4	-822	22.39	27.54
	6	-781	19.95	35.44
NS+S	2	-861	29.51	4.50
	4	-838	26.92	12.88
	6	-810	25.12	18.71

Figure 3 - Surface morphologies of the carbon steel: a) blank; b) corroded carbon steel in NS; c) corroded carbon steel in NS+P (6 mL); d) corroded carbon steel in NS+S (6 mL); f) corroded carbon steel in NS with corrosion products; f) corroded carbon steel in NS+P (6 mL) with corrosion products; g) corroded carbon steel in NS+S (6 mL) with corrosion products.

Surface examination of carbon steel

Morphological surfaces of samples of carbon steel were examined before and after exposure in the natural seawater for 336 hours without and with inhibitor (Fig. 3).

The image shows that the corrosion reaction does not take place homogenously over the surface of carbon steel in natural seawater without and with inhibitors (Fig. 3 b-d). However, the surface was remarkably protected by commercial aqueous additives (inhibitors) in comparison the solution without inhibitors (Fig. 3 f, g). The good corrosion inhibition of the commercial aqueous additives may due to the presence of a mixture of various components (*i.e.* tannins, alkaloids, flavonoids, carbohydrates, amino acids, proteins) which form adsorbed films on the metal surface. It is very difficult to determine what components present in commercial aqueous additives contribute to inhibit corrosion.

It can be observed that the attack of corrosion was high for the sample of carbon steel in the natural seawater in comparison with samples tested in the natural seawater with inhibitors. The images show that the active sites have been covered on the metal surface as a result of inhibitor molecules (Fig. 3 f, g). Moreover, a film formation was observed to be populated around the substrate. Also, it was reported in literature[16–19] that the chloride ions in seawater, correlated mainly to the NaCl, $MgCl_2$ and KCl content, can contribute to the increase of the corrosion rate of steel and to the breakdown of passive film (*e.g.* ferrous oxide) on the surface of the steel. On the other hand, the oxygen could be distributed all over the surface, which indicates corrosion products of oxide film on the surface, while the important element, Fe, covered uniformly the surface.[16–19]

EXPERIMENTAL

Materials

Natural seawater (NS) was taken from the Constanța area, Roumania (Fig. 4) and stored in closed glass containers. All the corrosion tests were conducted without and with different amounts of commercial aqueous additives (flavors of pineapple (P) and of strawberry (S)) (Senzor Planet, Roumania) at room temperature (25°C).

Fig. 4 – Image of seawater from the Constanța area.

Table 3

Chemical composition (in wt%) of carbon steel

C	Mn	Si	Cr	S	P	Fe
0.21	2.5	0.35	0.16	0.04	0.29	Balance

The small rectangular carbon steel coupons (thickness of 0.46 mm) were used in this research. The chemical composition of carbon steel is given in Table 3.

All surfaces of the coupons were ground clean using silicon carbide grinding paper starting with grit P120 and finishing with grit P400, rinsed with bi-distilled water, degreased with sodium carbonate (powder, Sigma-Aldrich), washed with bi-distilled water and dried with ethanol to remove residual water. Afterwards, the coupons were weighed accurately before and after all corrosion tests using an analytical balance (Kern KB, Germany, accuracy of 0.001 g).

Weight loss measurements

Rectangular carbon steel coupons (16 mm x 15 mm) were mechanically cut and immersed in the corrosion medium for gravimetric method. The carbon steel specimens were totally immersed into beakers containing 20 mL of natural seawater without and with various amount of the inhibitor (2, 4 and 6 mL). After corrosion test the coupons were taken out, cleaned using a solution of ammonium citrate in order to eliminate the corroded and extraction layer on the metal surface, dried at room temperature and then weighed accurately at analytical balance. Corrosion rate and corrosion inhibitor efficiency (percentage) were calculated to evaluate the corrosion of samples of carbon steel.

Potentiostatic polarization measurements

For potentiostatic polarization measurements were used two carbon steel coupons (anode and cathode) with size 1.5 cm x 1.6 cm. The test solution contains: 70 mL of natural seawater and different amount of commercial aqueous additives (2, 4 and 6 mL). The potentiostatic polarization measurements were carried out using a conventional glass cell (U shape) at room temperature. The values of potential were measured from 5 to 5 minutes.

CHARACTERIZATIONS

The reference electrode was a saturated calomel electrode (SCE), which was connected at a digital multimeter (AXIOMET AX-100, Germany). A DC power supply (AXIOMET AX-3005D, Germany) and a rotary potentiometer (Piher, 50K, 5 kΩ, 200 mW) were used to fixed values of current intensity between 1-900 µA.

An optical digital microscope (Media-Tech MT4096, USB, magnification 100x) was employed to analyze the morphology of the carbon steel surface. Images of the samples were recorded before and after 336 h exposure time in corrosion medium without and with commercial aqueous additives.

CONCLUSIONS

Weight loss and potentiostatic polarization results indicate that the commercial aqueous additives studied acted as corrosion inhibitors in natural seawater for carbon steel.

The presence of the inhibitors leads to a decrease in the corrosion rate, observed for both applied methods (weight loss and potentiostatic polarization). The best value of corrosion rate $(0.1240 \text{ g/m}^2\text{h})$ was obtained for commercial aqueous additive with flavor of pineapple, at maximum amount of inhibitor of 6 mL.

Inhibition efficiency increases with increasing amount of inhibitors. The maximum IE % of 39.39 % was obtained at 6 mL of commercial aqueous additive with flavor of pineapple, after 336 h.

The morphological image showed that the carbon steel coupons immersed into medium without inhibitor corroded more than the carbon steel which was immersed into medium with

inhibitor. The introduction of the inhibitors into natural seawater results in the formation of films on the carbon steel surface, which effectively protects the steel from corrosion.

REFERENCES

1. R. A. Prabhu, T. V. Venkatesha, A. V. Shanbhag, G. M. Kulkarni and R. G. Kalkhambkar, *J. Corros. Sci.*, **2008**, *50*, 3356-3362.
2. W. B. Wan Nik, F. Zulkifli, M. M. Rahman and R. Rosliza, *Int. J. Basic Appl. Sci.*, **2011**, *11*, 75-80.
3. F. Branzoi, V. Branzoi and A. Stanca, *Rev. Roum. Chim.*, **2016**, *61*, 837-850.
4. O. Olawale, O. F. Adekunle, A. A. Adesoji and O. A. Sunday, *Anal. Univ. "EFTIMIE MURGU"*, **2016**, *1*, 1453-7397.
5. G. Hart Kalada, K. Orubite-Okorosaye and O. James Abodsede, *Int. J. Adv. Res. Chem. Sci.*, **2017**, *4*, 32-40.
6. V. Branzoi and F. Branzoi, *Rev. Roum. Chim.*, **2002**, *47*, 1193-1203.
7. S. Caprarescu, C. Modrogan, V. Purcar, A. M. Dancila and R. C. Fierascu, *Rev. Chim.*, **2019**, *70*, 1140-1143.
8. F. O. Aramide, *Leonardo J.Sci.*, **2009**, *5*, 47-52.
9. A. U. Malik, S. Ahmad and I. Andijani, *J. Corros. Sci.*, **1995**, *3*, 1521-1535.
10. R. E Melchers, *Corros. Sci.*, **2005**, *47*, 2391-2410.
11. V. R. Mohan and A. Nishanthini, *Asian Pac. J. Trop. Biomed.*, **2012**, *2*, 1701-1706.
12. H. Möller, E. T. Boshoff and H. Froneman, *J. South Afr. Inst. Min. Metall.*, **2006**, *106*, 585-592.
13. G. Hart Kalada, K. Orubite-Okorosaye and O. James Abodsede, *Int. J. Adv. Res. Chem. Sci.*, 2017, *4*, 32-40.
14. A. Y. Eltre, *J. Colloid Interface Sci.*, **2007**, *3*, 578-583.
15. A. Ismail, *ARPN J. Eng. Appl. Sci.*, **2016**, *11*, 8710-8714.
16. L. Nnanna, G. Nnanna, J. Nnakaife, N. Ekekwe and P. Eti, *Int. J. Mater. Chem.*, **2016**, *6*, 12-18.
17. M. M. Martin, *Ind. Chem. Process Analysis Design*, Elsevier, **2016**.
18. S. Gadang Priyotomo, L. Nuraini and S. Prifiharni, *J. Eng. Technol. Sci.*, **2017**, *49*, 770-784.
19. R. Yamamoto, Y. Kawana, R. Minagawa and H. Sasamoto, *Am. J. Plant Sci.*, **2011**, *2*, 35-42.