INHIBITION EFFECT OF SOME COMMERCIAL CORROSION INHIBITORS ON MILD STEEL IN 7.0 M PHOSPHORIC ACID

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ABSTRACT. Corrosion tests were carried out in order to find the best inhibitor for the protection of steel pipelines used in H_3PO_4 and fertilizers industry. The corrosion inhibition efficiency of five commercial inhibitors was investigated on mild steel by using electrochemical methods (EIS and polarization curves) in a 7M H_3PO_4 solution (pH 0.5). The efficiency of best corrosion inhibitors was tested at different concentrations.

Key words: mild steel, corrosion inhibitors, electrochemical impedance spectroscopy, polarization curves, inhibitor efficiency, phosphoric acid.

INTRODUCTION

Phosphoric acid is widely used in the production of fertilizers and surface treatment of steel such as surface cleaning, chemical and electrolytic polishing, coloring, etching, removal of oxide film, phosphating and passivating [1]. Most of the acid is produced from phosphate rocks by the so-called dihydrate wet process, equivalent to 7.0 M H_3PO_4 (about 35% H_3PO_4) [2]. Most of the industrial equipment is made of steel that can be damaged by the contact with this acidic solution; this is why it is imperative to protect the steel materials used in the phosphoric acid industry.

The use of inhibitors is one of the most practical methods for protecting metals or alloys from corrosion [3]. There is a wide variety of organic compounds used as corrosion inhibitors for steel in H_3PO_4 media: thiosemicarbazones [4], hydroxyquinoline derivatives [5], triazole derivatives [6 - 8], imidazoles [9], tetraalkylammonium salts [10], "green compounds" such as plant extracts [11 - 13], guar gum [14] etc., but to find new efficient corrosion inhibitors remains of major interest.

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In this context, the aim of this paper is to investigate the corrosion of mild steel in 7.0 M H_3PO_4 solution (pH 0.5) in the absence and in the presence of three commercial products from Nalco Products, USA, (3DT177, 3DT179, Nalco 73413). The effect of these inhibitors was compared with that of Galoryl IC20 (produced by ArrMazz Chemicals SAS, USA) and Corrogard (Able Westchem, Australia). The protective effect of inhibitors at different concentrations was investigated by electrochemical methods (polarization measurements and electrochemical impedance spectroscopy).

RESULTS AND DISCUSSION

Open circuit potential

In order to determine the corrosion behavior of carbon steel in corrosive media 7M H_3PO_4 (pH = 0.5) in the absence and in the presence of corrosion inhibitors, the experiments were started by recording the open circuit potential (OCP) of the samples in time. The OCP values were situated between -0.370 V and -0.410 V vs. $Ag/AgCl/KCl_{sat}$ and become relatively constant after 1h.

Electrochemical impedance spectroscopy

Nyquist impedance spectra were recorded immediatly after OCP monitoring in the corrosive solution (pH 0.5) in the presence of inhibitors and the obtained results were compared with those without inhibitors (Figure 1). In all cases, a pure capacitive behavior of the systems was noticed. The electrical equivalent circuit used to fit the experimental spectra was $R_e(QR_p)$, where R_e is the corrosion solution resistance and the couple Q-R_p, represents the constant phase element corresponding to the double layer capacity and the polarization resistance, respectively. The polarization resistance corresponds to the corrosion reaction at the metal substrate / solution interface, which contains charge transfer resistance, double layer resistance, film resistance and other accumulations at the metal / solution interface [15]. As the main contribution is that of the charge transfer resistance, we assumed that R_p in our case can be practically assimilated to the charge transfer resistance, R_{ct}. The values of C_{dl} were calculated using the equation $C_{dl} = (R^{1-n}Q)^{1/n}$, where n reflects the depressed feature of the capacitive loop in Nyquist diagram $(0 < n \leq 1)$ which is generally attributed to the frequency dispersion, as well as to inhomogeneities, roughness of metal surface and mass transport process [16]. The obtained results for all the analysed samples are presented in Table 1. The chi squared (χ^2) values were of order 10^{-4}.

Analyzing the Table 1 data it can observed that in the case of using 0.2 mL/L of inhibitors, an increase of the charge transfer resistance, R_{ct}, can be noticed, but this increase is not significant. Best results were obtained in the case of Corrogard and Nalco 73413.
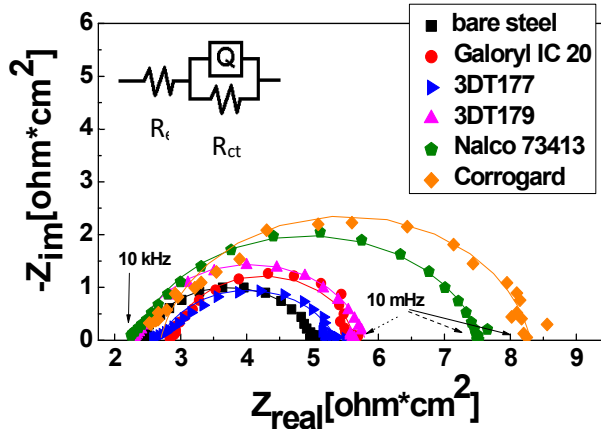

Figure 1. Nyquist impedance diagrams for the steel electrodes recorded in 7M H_3PO_4 solution (pH 0.5), in the absence and in the presence of corrosion inhibitors (c = 0.2 mL/L) after 1h at OCP; the lines represent fitted data

Table 1. The electrochemical impedance parameters estimated by fitting the experimental impedance data from Figure 1.

Inhibitors	R_e [$\Omega \cdot cm^2$]	R_{ct}[a] [$\Omega \cdot cm^2$]	C_{dl}[b] [mF/cm^2]	n_{dl}[c]
No inhibitors	2.42	2.596	1.211	0.836
3DT177	2.25	3.387	0.790	0.878
3DT179	2.88	2.742	0.946	0.924
Galoryl IC20	2.67	2.686	1.033	0.781
Corrogard	2.69	5.612	0.591	0.888
Nalco 73413	2.29	5.267	0.679	0.821

[a]The standard error for R_{ct} values was between 0.77% - 2.16%; [b]The standard error for Q values was between 2.34% - 5.42%; [c]The standard error for n_{dl} values was between 1.02% - 2.27%

Next, in an attempt to optimize the results, the inhibitors with the best inhibition efficiencies (Corrogard and Nalco 73413) were tested at different concentrations. As before, the experiments started with the measurement of the open-circuit potential (OCP) of the steel electrodes for a period of 1 hour, followed by the recording of EIS spectra.

Figure 2 shows the Nyquist plots obtained for all analyzed steel samples, in the presence of Corrogard and Nalco 73413 at concentrations of 0.2 mL / L, 0.4mL / L, 0.6 mL / L and 0.8 mL / L. All the plots contain depressed semicircles reflecting a pure capacitive behavior. The results obtained both in the absence and in the presence of inhibitors can be suitably represented by using only one time constant circuit and the parameters obtained for all samples are shown in Table 2.
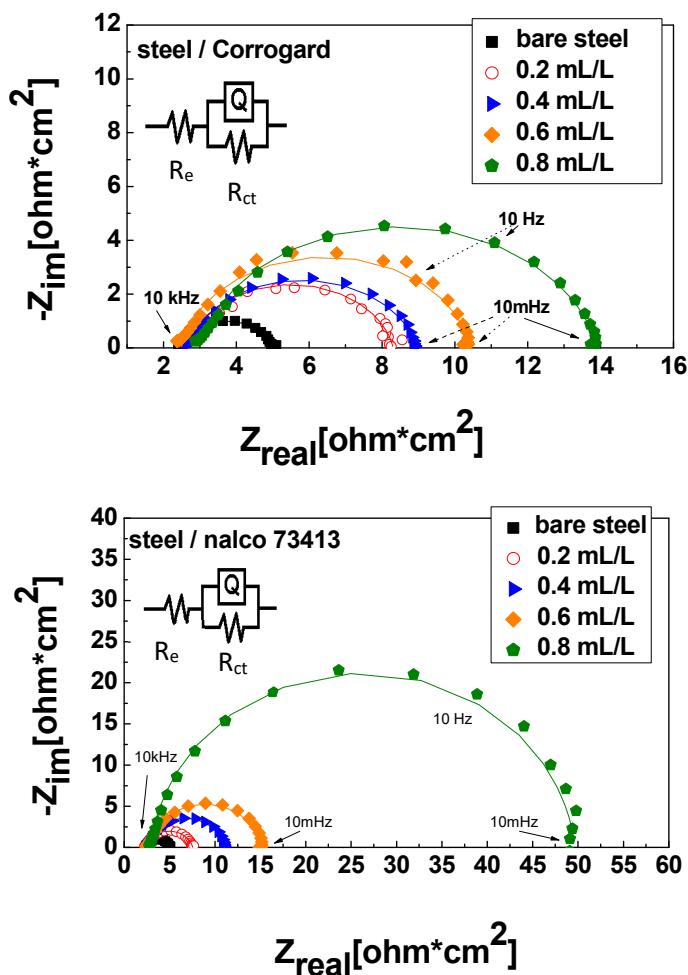

Figure 2. Nyquist impedance diagrams for the steel electrodes in 7M H_3PO_4 solution (pH 0.5), in the presence of the corrosion inhibitors Corrogard and Nalco 73413 at different concentrations; the lines represent fitted data

Table 2. The electrochemical impedance parameters estimated
by fitting the experimental impedance data from Figure 2.

Inhibitors	C_{inh} [mL / L]	R_e [$\Omega*cm^2$]	R_{ct} [$\Omega*cm^2$]	C_{dl} [mF/cm^2]	n_{dl}
-	0	2.42	2.596	1.211	0.837
Corrogard	0.2	2.69	5.612	0.591	0.889
	0.4	2.63	6.345	0.588	0.855
	0.6	2.48	7.937	0.565	0.899
	0.8	2.99	10.92	0.544	0.878
Nalco 73413	0.2	2.29	5.267	0.717	0.872
	0.4	2.50	8.524	0.679	0.886
	0.6	2.47	12.85	0.576	0.864
	0.8	2.86	49.36	0.515	0.885

[a]The standard error for R_{ct} values was between 1.41% - 2.75%; [b]The standard error for Q values was between 3.39% - 5.61%; [c]The standard error for n_{dl} values was between 0.97% - 1.53%

From the data presented in Table 2, it can be concluded that, as expected, the protective effect of the inhibitors depends on their concentration and generally, the corrosion resistance slightly improved as their concentration increased.

Polarization measurements

To determine the polarization resistance of the electrodes, linear polarization curves were recorded, in the potential domain of ± 20 mV *vs*. OCP. The polarization resistance (R_p) values, for each electrode, was calculated with the formula: $R_{p(\Delta E \to 0)} = \dfrac{\Delta E}{\Delta i}$, (1), and are shown in Table 4. The protection efficiency of the inhibitors on steel was determined either with the formula: $IE[\%] = \dfrac{R_p^{inh} - R_p^0}{R_p^{inh}} \cdot 100$, (2), where R_p^{inh} and R_p^0 are the polarization resistances in presence and in the absence of inhibitors, respectively, or with the formula , $IE[\%] = \dfrac{i^0 - i^{inh}}{i^0} \cdot 100$ (3), where i^{inh} and i^0 are the corrosion current densities in presence and in the absence of inhibitors, respectively.

In order to determine the kinetic parameters of the corrosion process, potentiodynamic polarization curves were recorded in the potential range of ± 200 mV vs. OCP (Figure 3), after OCP recording during 1h. The Tafel interpretation of the polarization curves provided the results presented in Table 3.
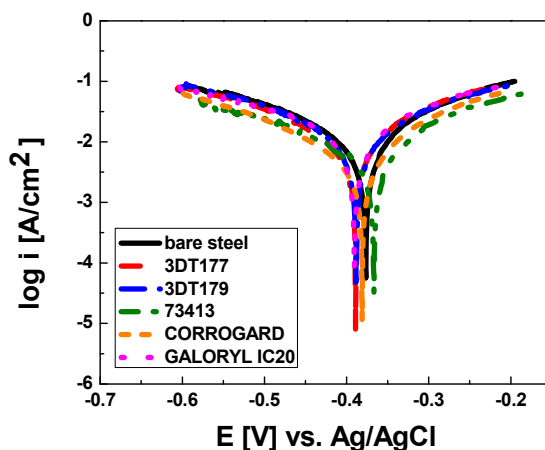
Figure 3. The polarization curves (± 200 mV *vs.* OCP) for the steel immersed in 7M H_3PO_4 (pH = 0.5) at 0.2 mL/L concentration of inhibitors; scan rate, 10 mV / min.

Table 3. Corrosion process parameters in the absence and in the presence of the examined inhibitors at 0.2 mL/L concentration.

Inhibitors	OCP [mV *vs* RE]	E_{cor} [mV *vs* RE]	i_{cor} [mA/cm^2]	β_a [mV/dec]	β_c [mV/dec]	IE [%]
Bare steel	-396	-393	17.62	236	344	-
3DT177	-408	-395	12.82	156	192	27.22
3DT179	-410	-381	14.72	323	372	16.44
Galoryl IC20	-439	-391	15.74	217	201	10.66
Corrogard	-402	-384	12.05	178	255	31.60
Nalco 73413	-378	-373	12.58	232	302	28.55

β_a and β_c are the Tafel coefficients

The analysis of the data led to the conclusion that in the case of all tested corrosion inhibitors, a slight decrease of the corrosion current densities can be noticed, even if the inhibition efficiency (IE) was not satisfactory.

In an attempt to see if responsible for this situation was the concentration of the additives, the inhibitors with the highest inhibition efficiency (Corrogard and Nalco 73413) were tested at different concentrations: 0.2 mL / L, 0.4mL / L, 0.6 mL / L and 0.8 mL / L and the corresponding polarization curves are presented in Figure 4.
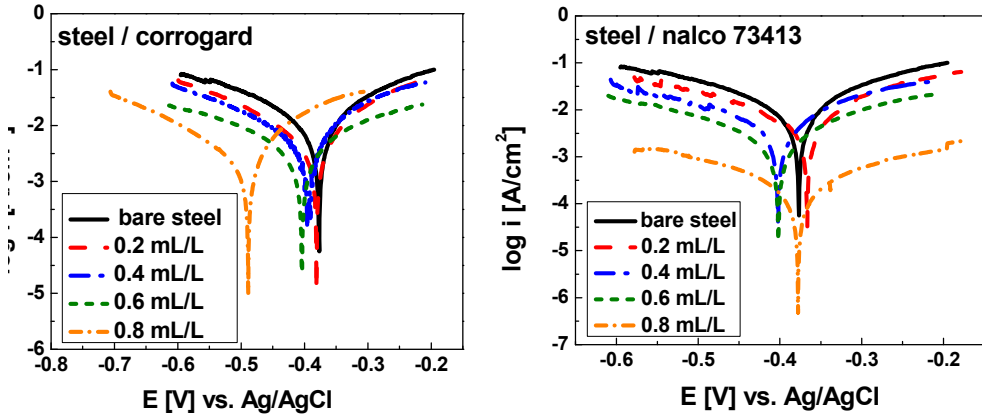
Figure 4. The polarization curves (± 200 mV vs. OCP) for the S235 steel immersed in 7M H3PO4 (pH = 0.5) at different concentrations of inhibitors; scan rate, 10 mV / min.

Both branches of the polarization curves are influenced by the inhibitors, proving that they act as mixed-type inhibitors. The Tafel interpretation of the polarization curves led to the results presented in Table 4.

Table 4. Kinetic parameters of the corrosion process in 7M H_3PO_4 at different concentrations of inhibitors Corrogard (1) and Nalco 73413 (2)

Inh	C_{inh} [mL/L]	OCP [mV vs RE]	E_{cor} [mV vs RE]	i_{cor} [mA/cm²]	β_a [mV/dec]	- β_c [mV/dec]	R_p [Ωcm²]	IE [%]	
								i_{cor}	Rp
-	0	-396	-393	17.62	236	344	6.73	-	-
1	0.2	-402	-384	12.05	177	255	10.86	32.09	38.02
	0.4	-410	-414	10.16	205	283	10.51	42.32	36.01
	0.6	-415	-416	5.57	472	930	21.27	68.37	68.36
	0.8	-508	-501	4.57	159	247	17.57	74.06	61.70
2	0.2	-378	-373	12.58	232	302	11.11	28.55	38.77
	0.4	-408	-404	10.14	351	628	13.51	42.46	49.66
	0.6	-409	-408	4.21	281	380	25.25	76.07	73.47
	0.8	-378	-375	0.44	424	420	284.09	97.45	97.63

It can be observed, especially in the case of Nalco 73413, a significant increase of the inhibition efficiency in parallel with the inhibitors' concentration. The highest efficiency was noticed at 0.8 mL/L, when a decrease of the

corrosion current density with two orders of magnitude was observed in comparison with the absence of the additive. The same trend was observed in the case of Corrogard, but its effect was not so important.

Both inhibitors act as mixed-type inhibitors. The inhibition effect comes from the reduction of the reaction area on the surface of the corroding metal after inhibitor adsorption [17]. The surface coverage θ of the electrode surface at different inhibitor concentrations, calculated from the equation $\theta = IE/100$, suggests an incomplete coverage of the electrode surface with inhibitor molecules, which explains their moderate effect.

The beneficial effect of inhibitors was put in evidence also by visual inspection of the corroded surfaces of the electrodes (Figure 5). It can be observed that in case of bare steel, the corrosion products layer is not uniform, with severely corroded areas, while in the case of using corrosion inhibitors, the aspect of the samples is uniform and the presence of rust is not visible.
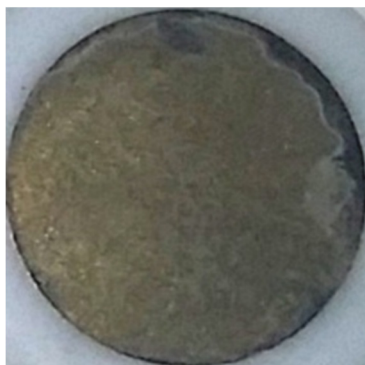
Bare steel

Corrogard
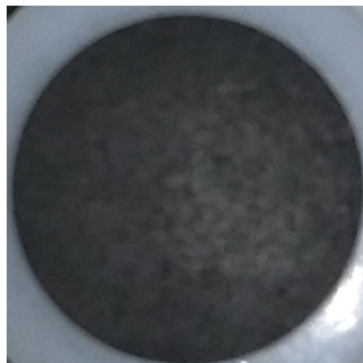
Nalco 37413

Figure 5. Influence of the inhibitors (c = 0.2 mL/L) on the aspect of the steel electrodes immersed in 7M H_3PO_4 solution after corrosion tests

CONCLUSIONS

In terms of practical use, based on electrochemical investigations, all inhibitors tested in the present work can be used as inhibitors against steel corrosion in concentrated phosphoric acid. The best was Nalco 37413.

The protective effect of the inhibitors is moderate, depends on their concentration and generally, the corrosion resistance improved as their concentration increased.

All investigated compounds act as a mixed-type inhibitor, and the inhibition is caused by geometric blocking effect of the surface. EIS spectra exhibit only one capacitive loop which indicates that the corrosion reaction is controlled by the charge transfer process.

Further investigations to assess the corrosion morphology and to elucidate the mechanism for the inhibition of mild steel corrosion in $7M\ H_3PO_4$ acidic media are required.

EXPERIMENTAL

Materials and solutions

The commercial inhibitors used in the experiments were Nalco 73413, two phosphino succinic oligomer derivatives (3DT177, 3DT179) from Nalco Products USA, and two other products, namely Galoryl IC20 (ArrMazz Chemicals SAS, USA) and Corrogard (Able Westchem, Australia). The inhibitors were dissolved in the corrosive solution at different concentrations: 0.2 mL / L, 0.4mL / L, 0.6 mL / L, 0.8 mL / L.

Mild steel samples (0.22% C, 0.85% Mn, 0.055% P, 0.055% S and Fe balance) were used in the experiments. The working electrodes - WE were cut from a steel bar (S = 0.5 cm^2) mounted in Teflon; a copper rod was attached for electrical contact.

Prior to electrochemical tests, the steel samples were ground using different emery papers up to 2000 grade, washed with distilled water and degreased with acetone, after that were dried at room temperature.

Experimental methods

The electrochemical corrosion measurements were performed on a PC – controlled electrochemical analyzer PAR 2273 (Princeton Applied Research, USA) using a three electrodes cell containing a working electrode (steel), a saturated Ag/AgCl/KCl electrode as reference electrode, and a

platinum counter electrode. The electrolyte solution for corrosion measurements was acidic 7M H_3PO_4 (pH = 0.5).

The open circuit potential for steel immersed in the corrosive solution was monitored during 1 hour. Then, electrochemical impedance spectroscopy spectra (EIS) were recorded in the frequency ranging from 10 kHz – 10 mHz with a disturbance voltage of ± 10 mV at 30 points/decade. The impedance data were fitted with a R(QR) equivalent electrical circuit, using the ZSimpWin V3.21 software.

After the EIS measurement was finished, polarization curves were recorded immediately by scanning in a potential range of ± 20 mV (for polarization resistance determination) and of ± 200 mV *vs.* open circuit potential, (for Tafel interpretation) with a scan rate of 10 mV / min. The testing temperature was kept at 20 °C.

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