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Study of corrosion inhibition of C38 steel in 1 M HCl solution by polyethyleneiminemethylene phosphonic acid

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Abstract A new class of corrosion inhibitors, namely, polyethyleneiminemethylene phosphonic acid (PEIMPA), was synthesized and its inhibiting action on the corrosion of C38 steel in 1 M HCl at 30 °C was investigated by various corrosion monitoring techniques such as weight loss measurements, potentiodynamic polarization, linear polarization resistance (Rp), and surface analysis (SEM and EDX) which are used to characterize the steel surface. Weight loss measurements revealed that the presence of PEIMPA increases the inhibition efficiency by decreasing the corrosion rate. Tafel polarization study showed that the inhibitor acts as a mixed-type inhibitor. Adsorption of PEIMPA on the carbon steel surface was found to obey the Langmuir isotherm. Some thermodynamic functions of dissolution and adsorption processes were also determined and discussed. The SEM results showed the formation of protective film on the mild steel surface in the presence of PEIMPA. The results obtained from different tested techniques were in good agreement.

Keywords Corrosion \cdot Inhibition \cdot C38 steel \cdot Phosphonic acid

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Introduction

Study of organic corrosion inhibitor is an attractive field of research due to its usefulness in various industries. Acid is widely used in various industries for the pickling of ferrous alloys and steels. Because of the aggressive nature of the acid medium, the inhibitors are commonly used to reduce acid attack on the substrate metal. Most of the reported corrosion inhibitors are organic compounds containing O, N, S, and P [1-14] in their structures. The phosphoric functions are considered to be the most effective chemical group against corrosion process [15]. The use of organic phosphonic acids to protect carbon steel against corrosion has been the subject of various works [16-26]. Aminomethyl-phosphonic acids are excellent sequestering agents for electroplating, chemical plating, degreasing, and cleaning. It was shown that piperidin-1-yl-phosphonic acids (PPA) and (4phosphono-piperazin-1-yl) phosphonic acid (PPPA) are used to reduce the corrosion of iron in a NaCl medium, even if PPPA is more efficient than PPA [27]. In the present investigation, the influence of polyethyleneiminemethylene phosphonic acid (PEIMPA) as a corrosion inhibitor of carbon steel in 1 M HCl has been systematically studied by weight loss measurements, potentiodynamic polarization studies, and surface analysis (SEM, EDX). Results are reported and discussed.

Experimental

Polyethyleneiminemethylene phosphonic acid polymer was synthesized (see Scheme 1) from commercially available Lupasol P (polyethylenimine) according to the Moedrizer–Irani reaction [28]. The synthesis was





Scheme 1 Synthesis of polyethyleneiminemethylene phosphonic acid from Lupasol P

performed in distilled water under microwave irradiation. In a quartz reactor, a mixture of polyethylenimine (Lupasol P, 80 mmol, 3.44 g), phosphorous acid (80 mmol, 6.68 g), and hydrochloric acid-water (1:1) solution (12 mL) was vigorously stirred and then irradiated (150 W) in a glass cylinder reactor for 1 min. A formaldehyde aqueous solution (160 mmol) was added and irradiated for 8 min.

Then, the precipitation was washed with distilled water to remove unreacted reagents. Finally, phosphonic-modified Lupasol P was washed three times with distilled water and ethanol. After drying, the solid was further pulverized to give a brown powder.

The structure and purity were identified and characterized by elemental microanalysis (Table 1) and ¹H, ¹³C, and ³¹P NMR spectroscopy. The spectra showed the expected signals due to the polyethylenimine skeleton and methylene phosphonic units as matched to the proposed structure (Scheme 1).

NMR spectral data: ¹H NMR d (ppm): 4.92 (N–CH₂); 2.33 (CH₂–P); 1.6 NH. ¹³C NMR d (ppm): 82.16 (N–CH₂), 52.1 (CH₂–P). ³¹P NMR d (ppm): 3.91. The presence of phosphonic acid was confirmed by FTIR measurement: the polymer displays characteristic bonds for P–O–C at 1050 cm⁻¹, P–OH at 2372, and 2338 cm⁻¹ 189 and P = O at 1172 cm⁻¹.

Elemental microanalysis suggests the structure made of fragment of the phosphonic acid polymer, corresponding after calculation to x = 5 and y = 9 (Scheme 1).

A 1 M HCl solution was prepared from an analytical reagent grade of HCl 37% and double-distilled water and was used as corrosion media in the studies. Note that the solubility of polyethyleneiminemethylene phosphonic acid is very high in this medium.

For the weight loss measurements, the experiments were carried out in the solution of 1 M HCl (uninhibited and inhibited) on carbon steel containing 0.30-0.35% C, 0.15-0.35% Si, 0.035% S, 0.5-1.0% Mn, and 0.035% P.

Sheets with dimensions $20 \text{ mm} \times 10 \text{ mm} \times 2 \text{ mm}$ were used. They were polished successively with different grades of emery paper up 1200 grade. Each run was carried out in a glass vessel containing 100 ml test solution. A clean weight mild steel sample was completely immersed at an inclined position in the vessel. After 4 h of immersion in 1 M HCl with and without the addition of inhibitor at different concentrations, the specimen was withdrawn, rinsed with double-distilled water, washed with acetone, dried, and weighed. The weight loss was used to calculate the corrosion rate in milligrams per square centimeter per hour.

Electrochemical experiments were carried out in a glass cell (CEC/TH Radiometer) with a capacity of 500 ml. A platinum electrode and a saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode. The working electrode was in the form of a disc cut from mild steel under investigation and was embedded in a Teflon rod with an exposed area of 0.5 cm². Potentiodynamic polarizations were conducted in an electrochemical measurement system (VoltaLab 21) which comprises a PGP201 potentiostat, a personal computer, and VoltaMaster4 software. The polarization resistance measurements were performed by applying a controlled potential scan over a small range typically ± 15 mV with respect to Ecorr with a scanning rate of 0.5 mV s^{-1} . The resulting current is linearly plotted vs. potential, the slope of this plot at Ecorr being the polarization resistance (Rp). Corrosion current densities were determined by extrapolating the cathodic Tafel regions from the potentiodynamic polarization curves to the corrosion potential. The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -700 to -300 mV with the same scanning rate (0.5 mV s⁻¹) under static on the same electrode without any surface treatment. All experiments were carried out in freshly prepared solution at constant temperatures.

mental s of	Microanalysis	%C	%H	%N	%O	%P
iminemethylene cid	Found	30.8112	7.6250	13.2519	29.3535	18.9574
	Calculated $(x = 5, y = 9)$	30.6631	6.6989	13.5359	29.8342	19.2679

Table 1Elemicroanalysipolyethylenephosphonic a

Inhibition efficiencies P % were calculated as follows: Weight loss measurement:

$$P\% = \frac{w - w'}{w} \times 100 \tag{1}$$

where w and w' are the corrosion rate of steel due to the dissolution in 1 M HCl in the absence and the presence of definite concentrations of inhibitor, respectively.

Linear polarization measurement:

$$P\% = \frac{R'_{p-}R_p}{R'_p} \times 100$$
(2)

where R_p and R'_p are the values of linear polarization in the absence and presence of the inhibitor, respectively.

Polarization measurement:

$$P\% = \frac{I_{\rm corr} - I'_{\rm corr}}{I_{\rm corr}} \times 100$$
(3)

where i_{corr} and i'_{corr} are the corrosion current densities in the absence and the presence of the inhibitor, respectively.

For all methods, the tests were performed in non-deaerated solutions under unstirred conditions.

The surface morphology of the samples before and after adding PEIMPA inhibitor in the medium 1 M HCl after 1 day of immersion was observed by scanning electron microscope (SEM) Quanta 200 FEG coupled with EDX analysis.

Results and discussion

Weight loss measurements

The gravimetric measurements of mild steel in 1 M HCl in the absence and presence of various concentrations of PEIMPA investigated were determined after 4 h of immersion at 30 °C.

Table 2 gives values of the corrosion rates and percentage inhibition efficiency calculated from the weight loss measurements for different concentrations of PEIMPA.

 Table 2
 Corrosion rates and inhibition efficiencies of PEIMPA at different concentrations in 1 M HCl

Conc. (ppm)	$V_{\rm corr} \ ({ m mg} \ { m cm}^{-2} \ { m h}^{-1})$	P (%)
1 M HCl	0.703	_
100	0.195	72.15
200	0.120	82.93
300	0.104	85.07
400	0.093	86.69
500	0.069	90.11

Inspection of this table shows that the inhibition efficiency increases with increasing inhibitor concentration. The optimum concentration required to achieve this efficiency is found to be 500 ppm. The inhibition of corrosion of carbon steel by the investigated inhibitor can be explained in terms of adsorption on the metal surface. It is generally assumed that the adsorption of the inhibitor at the metal/solution interface is the first step in the mechanism of inhibition in aggressive media.

This compound can be adsorbed on the metal surface by the interaction between lone pair of electrons of hetero atoms and the metal surface. This process is facilitated by the presence of vacant orbitals d of low energy in iron atom, as observed in the transition group metals. Moreover, the formation of positively charged protonated species in acidic solutions facilitates the adsorption of the compound on the metal surface through electrostatic interactions between the organic molecules and the metal surface [29].

Polarization measurements

Figure 1 shows the polarization curves of mild steel in 1 M HCl, blank solution, and in the presence of different concentrations (100–500 ppm) of PEIMPA. With the increase of PEIMPA concentrations, both anodic and cathodic currents were inhibited. This result shows that the addition of PEIMPA inhibitor reduces anodic dissolution and also retards the hydrogen evolution reaction. We note that the corrosion potential varies slightly after the addition of the inhibitor at different concentrations.

Table 3 shows that an increase in inhibitor concentration is resulted in increased inhibition efficiency. It is evident from the results that the I_{corr} values decrease considerably in the presence of inhibitor and that the maximum decrease in I_{corr} coincides with the optimum concentration of



Fig. 1 Polarization curves of carbon steel in 1 M HCl in the presence of different concentrations of PEIMPA at 30 $^{\circ}C$



Conc. (ppm)	$E_{\rm corr}$ vs. SCE (mV)	$i_{\rm corr} ({\rm mA.cm}^{-2})$	$R_{\rm p} \; (\Omega.{\rm cm}^2)$	$b_{\rm c} \ ({\rm mV} \ {\rm dec}^{-1})$	$P(i_{\rm corr})$ (%)	$P(R_{\rm p})(\%)$
1 M HCl	-501	1.94	12.98	156	-	-
100	-486	0.567	68.13	143	70.77	80.94
200	-512	0.359	73.54	146	81.49	82.34
300	-497	0.343	81.77	186	82.31	84.12
400	-511	0.336	99.04	134	82.68	86.89
500	-515	0.302	104.50	153	84.43	87.57

Table 3 Potentiodynamic polarization parameters for corrosion of carbon steel in 1 M HCl with various concentrations of PEIMPA at 30 °C

inhibitor. Linear polarization technique was performed in 1 M HCl with various concentrations of PEIMPA. The corresponding polarization resistance (R_p) values of carbon steel in the absence and in the presence of different inhibitor concentrations are also given in Table 3. It is apparent that R_p increases with increasing inhibitor concentration. The inhibition percentage (P %) calculated from R_p values is also presented in Table 3. We remark that P % increases with increasing concentration of inhibitor and attains 87% at 500 ppm. The inhibition efficiencies of PEIMPA obtained by potentiodynamic polarization and by polarization resistance methods are in good agreement, particularly, at high concentrations.

For anodic polarization, it can be seen from Fig. 1 that, in the presence of PEIMPA at all concentrations, two linear portions were observed. When the anodic potentials increases, the anodic current increases at a slope of b_{a1} in the low polarization potential region. After passing a certain potential $E_{\rm u}$, the anodic current increases rapidly and dissolves at a slope of b_{a2} in the high polarization region. This behavior was already documented for iron in acid solutions [30-33]. The rapid increase of anodic current after $E_{\rm u}$ may be due to the desorption of PEIMPA molecules adsorbed on the electrode. This means that the inhibition mode of PEIMPA depends on electrode potential. In this case, the observed inhibition phenomenon is generally described as corrosion inhibition of the interface associated with the formation of a bidimensional layer of adsorbed inhibitor species at the electrode surface [34]. Note that the potential $E_{\rm u}$ is also denoted $E_{\rm 1}$ in Bartos and Hackerman's paper [30]. Figure 1 shows also that, at potentials higher than $E_{\rm corr}$, PEIMPA affects the anodic reaction. This result indicates that PEIMPA exhibits both anodic and cathodic inhibition effects.

Adsorption isotherm

The adsorption of the organic compounds can be described by two main types of interaction: physical adsorption and chemisorption that are influenced by the charge nature of the metal, the type of the electrolyte, and the chemical structure of the inhibitor.





Fig. 2 Langmuir adsorption isotherm of PEIMPA on the carbon steel surface in 1 M HCl from potentiodynamic measurements

The adsorption isotherm can give information on the metal-inhibitor interaction. The adsorption isotherm can be derived from the curve surface coverage against inhibitor concentration. Surface coverage θ was estimated as in Eq. 5. The θ values for different inhibitor concentrations are tested by fitting to various isotherms. So far, the best fit was obtained with the Langmuir isotherm. According to this isotherm, θ is related to concentration inhibitor C via

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{4}$$

where *C* is the concentration of inhibitor, *K* is the adsorptive equilibrium constant, and θ is the surface coverage and calculated by the following equation [6, 35, 36]:

$$\theta = 1 - \frac{I_{\rm corr}}{I'_{\rm corr}} \tag{5}$$

where I'_{corr} is the corrosion current density in uninhibited acid and I_{corr} is the corrosion current density in inhibited acid.

Plotting C/ θ vs. C yields a straight line, as shown in Fig. 2. The linear correlation coefficient (r) is almost equal to 1 (r = 0.9999) and the slight deviation of the slope



Fig. 3 Polarization curves for C38 steel electrode in 1 M HCl (a) and in HCl+ 500 ppm of PEIMPA (b) at different temperatures

(1.14) from the unity is attributable to molecular interactions in the adsorbed layer which corresponds to the observed physical adsorption mechanism [37]. The adsorptive equilibrium constant (*K*) value is 6.22×10^5 -L mol⁻¹. The free energy of adsorption ΔG°_{ads} of the inhibitor on mild steel surface can be determined using the following relation:

$$K = \frac{1}{55.5} \exp\left(\frac{\Delta G_{\text{ads}}}{RT}\right) \tag{6}$$

where *R* is the gas constant (8.314 J K⁻¹ mol⁻¹), *T* is the absolute temperature (*K*), and the value 55.5 is the concentration of water in solution expressed in *M*. The ΔG°_{ads} value calculated is -37.90 kJ mol⁻¹. The negative values of ΔG°_{ads} indicate that the adsorption of inhibitor molecule onto steel surface is a spontaneous process. In general, it is well known that the values of $-\Delta G^{\circ}_{ads}$ of the order of -20 kJ mol⁻¹ or lower indicate a physisorption; those of order of -40 kJ mol⁻¹ or higher involve charge sharing or

a transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption). In the present study, the value of ΔG°_{ads} is about between -20and -40 kJ mol⁻¹, probably mean that the adsorption mechanism of the PEIMPA on steel in 1 M HCl solution is both physisorption and chemisorption.

Noticeably, it is generally accepted that physical adsorption is the preceding stage of chemisorption of inhibitors on metal surface [38]. It was reported that in this domaine, the surface charge of steel at $E_{\rm corr}$ in HCl solution is expected to be positive. Thus, the anions are first adsorbed on the steel surface creating an excess negative charge, which, in turn, facilitates physical adsorption of the inhibitor cations [39]. Accordingly, the Cl⁻ and phosphonate ions adsorb and the surface becomes negatively charged. Due to the electrostatic attraction, the protonated PEIMPA molecules are adsorbed on carbon steel surface (physisorption).

Along with electrostatic force of attraction, inhibitor also adsorbs on the carbon steel surface through chemical adsorption. The adsorption of free molecules could take place via interaction of the unshared pairs of electrons of nitrogen and oxygen atoms of the $-PO(OH)_2$ group and the vacant *d*-orbitals of iron atoms.

Therefore, inhibition takes place through both physisorption and chemisorption. However, chemisorption has no substantial contribution [12]. Indeed, the PEIMPA molecules are easily protonated to form ionic forms in acid solution. It is logical to assume that in this case, the electrostatic cation adsorption is mainly responsible for the protective properties of this compound.

Effect of temperature

To investigate the mechanism of inhibition and to determine the activation energy of the corrosion process, polarization curves of steel in 1 M HCl were determined at various temperatures (303-333 K) in the absence and presence of 500 ppm of PEIMPA. Representative Tafel polarization curves for C38 steel electrode in 1 M HCl without and with 500 ppm at different temperatures are shown in Fig. 3a, b. Similar polarization curves were obtained in the case of the other concentrations of PEIMPA (not given). The analysis of these figures reveals that raising the temperature increases both anodic and cathodic current densities, and consequently, the corrosion rate of C38 steel increases. The corresponding data are given in Table 4. In the studied temperature range (303–333 K), the corrosion current density increases with increasing temperature both in uninhibited and inhibited solutions and the values of the inhibition efficiency of PEIMPA decrease with the increase of temperature.



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Milieu	<i>T/</i> (°C)	$E_{\rm corr}/({\rm mVvSCE})$	$i_{\rm corr}/({\rm mA/cm}^2)$	$b_{\rm c}/({\rm mV/dec})$	P/(%)
1 M HCl	20	-466	1.46	198	_
	30	-501	1.94	156	_
	40	-459	2.83	193	_
	50	-457	4.01	196	_
500 ppm PEIMPA	20	-462	0.160	180	89.04
	30	-515	0.302	134	84.34
	40	-486	0.562	175	80.15
	50	-485	1.052	188	73.81
	Milieu 1 M HCl 500 ppm PEIMPA	Milieu T/(°C) 1 M HCl 20 30 40 50 50 500 ppm PEIMPA 20 30 40 50 50	Milieu $T/(^{\circ}C)$ $E_{corr}/(mVvSCE)$ 1 M HCl 20 -466 30 -501 40 -459 50 -457 500 ppm PEIMPA 20 -462 30 -515 40 -486 50 -485	Milieu $T/(^{\circ}C)$ $E_{corr}/(mVvSCE)$ $i_{corr}/(mA/cm^2)$ 1 M HCl 20 -466 1.46 30 -501 1.94 40 -459 2.83 50 -457 4.01 500 ppm PEIMPA 20 -462 0.160 30 -515 0.302 40 -486 0.562 50 -485 1.052 -485 1.052	Milieu $T/(^{\circ}C)$ $E_{corr}/(mVvSCE)$ $i_{corr}/(mA/cm^2)$ $b_c/(mV/dec)$ 1 M HCl 20 -466 1.46 198 30 -501 1.94 156 40 -459 2.83 193 50 -457 4.01 196 500 ppm PEIMPA 20 -462 0.160 180 30 -515 0.302 134 40 -486 0.562 175 50 -485 1.052 188

Figure 4 and 5 present the Arrhenius plots of the natural logarithm of the current density vs. 1/T, for 1 M solution of hydrochloride acid, without and with the addition of PEIMPA and $\ln(i_{corr}/T)$ with reciprocal of the absolute temperature, respectively. Straight lines with coefficients of correlation (c.c.) high to 0.99 are obtained for the supporting electrolyte and PEIMPA.

The values of the slopes of these straight lines permit the calculation of the Arrhenius activation energy, E_{a} , according to

$$\ln I_{\rm corr} = -\frac{E_{\rm a}}{RT} + \ln A \tag{7}$$

where R is the universal gas constant and A is the Arrhenius factor.

In addition, from transition-state plot according to the following equation:

$$\ln\left(\frac{I_{\rm corr}}{T}\right) = \frac{-\Delta H_{\rm a}^{\circ}}{RT} + B \tag{8}$$

where ΔH_{a}° is the enthalpy of activation and B is a constant.

The E_a and $\Delta H^{\circ}a$ values were determined from the slopes of these plots. The calculated values of E_a and ΔH_a



Fig. 4 Arrhenius plots of log icorr vs. 1/T without and with 500 ppm of PEIMPA



Fig. 5 $\ln(i_{corr}/T)$ vs. 1/T for C38 steel dissolution in 1 M HCl in the presence of PEIMPA at 500 ppm

in the absence and the presence of PEIMPA at 500 ppm are given in Table 5. Inspection of these data reveals that the increase in E_a in the presence of the inhibitor may be interpreted as physical adsorption. Indeed, a higher energy barrier for the corrosion process in the inhibited solution is associated with physical adsorption or weak chemical bonding between the inhibitor species and the steel surface [22, 40]. Szauer and Brand explained that the increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the carbon steel surface with the increase in temperature. A corresponding increase in the corrosion rate occurs because of the greater area of metal that is consequently exposed to the acid environment [41].

The enthalpy of activation values is found to be positive in the absence and presence of inhibitor and reflects the endothermic mild steel dissolution process. It is evident from Table 5 that the value of ΔH°_{a} increased in the presence of PEIMPA than the uninhibited solution indicating protection efficiency. This suggested the slow dissolution and hence lower corrosion rate of mild steel [2, 7]. This result permits verifying the known thermodynamic equation between E_a and ΔH°_a [42]:

Table 5 Apparent activation energy E_a and activation enthalpy ΔH°_{a} of dissolution of C38 steel in 1 M HCl in the absence and presence of 500 ppm PEIMPA

Milieu	$E_{\rm a} ({\rm kJ} {\rm mol}^{-1})$	$\Delta H^{\circ}a \ (kJ \ mol^{-1})$	$E_{\rm a} - \Delta H^{\circ} {\rm a} ~({\rm kJ}~{\rm mol}^{-1})$
1 M HCl	26.82	24.21	2.61
500 ppm PEIMPA	49.32	46.71	2.61



element	70 masses
iron	88.74
carbon	4.60
oxygen	4.13
chlorine	0.41

Fig. 6 SEM and EDX data of C38 steel immersed in 1 M HCl solution for 24 h







element	% masses
iron	76.36
oxygen	7.20
carbon	4.01
chlorine	2.76
Phosphor	0.30
nitrogen	0.50

Fig. 7 SEM and EDX data of C38 steel immersed in 1 M HCl+ 500 ppm PEIMPA for 24 h



$$E_{\rm a} - \Delta H \circ {\rm a} = RT.$$

Surface examination by SEM/EDX

Figure 6 shows the scanning electron micrographs of C38 after immersion for 24 h in 1 M HCl solution. The specimen surface in Fig. 6 appears to be roughened extensively by the corrosive environment and the porous layer of corrosion product is present. The EDX spectra show the characteristics peaks of some of the elements constituting of the steel sample after 24 h immersion in 1 M HCl without inhibitor, which reveals the presence of oxygen and iron, suggesting, therefore, the presence of iron oxide/ hydroxide.

When PEIMPA was added into the corrosion test solution (Fig. 7), a smooth surface was noticed traducing a good protection effect of the corrosion inhibitor by a formation of a thick and compact film. This may be intercepted by the adsorption of these inhibitors on the electrode surface.

In the presence of PEIMPA inhibitor, the EDX spectra show additional lines of nitrogen and phosphorus, due to the adsorbed layer of inhibitor that covered the electrode surface. In addition, the Fe peaks are decreasing in relation to the uninhibited steel surface sample. This diminution of the Fe lines occurs because of the overlying inhibitor film.

These results confirm those from weight loss and polarization measurements, which suggest that a protective film was formed over the metal surface and hence retarded both anodic and cathodic reactions.

Conclusion

On the basis of this study, the following conclusions can be drawn:

- PEIMPA shows a very good activity of preventing corrosion of carbon steel in 1 M HCl.
- Inhibition efficiency of PEIMPA varies directly with the concentration and inversely with the temperature.
- Potentiodynamic polarization experiments reveal that PEIMPA acts as mixed-type inhibitor.
- The adsorption of PEIMPA on the metal surface follows Langmuir isotherm.
- The corrosion inhibition is probably due to the adsorption of PEIMPA on the metal surface and blocking its active sites by the phenomenon of physical and chemical adsorptions.
- The weight loss, linear polarization, and polarization curves are in good agreement.

• SEM and EDX techniques reveal that the inhibitor molecules form a good protective film on the steel surface and confirm the result obtained by gravimetric and polarization methods.

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