

N. GOUDARZI*, M. PEIKARI*, M. REZA ZAHIRI*, H. REZA MOUSAVI*

ADSORPTION AND CORROSION INHIBITION BEHAVIOR OF STAINLESS STEEL 316 BY ALIPHATIC AMINE COMPOUNDS IN ACIDIC SOLUTION

ADSORPCJA I HAMOWANIE KOROZJI STALI NIERDZEWNEJ 316 PRZEZ ALIFATYCZNE ZWIĄZKI AMINOWE W KWAŚNYM ROZTWORZE

Gravimetric and electrochemical measurements were performed to investigate the effectiveness of an aliphatic amine compound with trade name of Armohib 28. It was found that the percentage inhibition efficiency increased with the increase of the compound concentration. Polarization curves indicate that the inhibitor under investigation acts as cathodic type which retards the rate of corrosion reactions by adsorbing on to the steel surface according to Langmuir adsorption isotherm. The activation energy and thermodynamic parameters were calculated and analyzed. The data obtained from electrochemical impedance spectroscopy (EIS) were analyzed to model the corrosion inhibition process through equivalent circuit.

Keywords: Corrosion inhibitor, Armohib 28, Stainless steel 316

W celu zbadania skuteczności alifatycznego związku aminowego o nazwie handlowej Armohib 28 przeprowadzono pomiary grawimetryczne i elektrochemiczne. Stwierdzono, że procentowa skuteczność hamowania wzrosła wraz ze wzrostem stężenia związku. Krzywe polaryzacji wskazują, że badany inhibitor działa jak inhibitor typu katodowego, który opóźnia szybkość reakcji korozji adsorbując na powierzchni stali według izotermi adsorpcji Langmuira. Energia aktywacji i parametry termodynamiczne zostały obliczone i analizowane. Dane uzyskane z elektrochemicznej spektroskopii impedancyjnej (EIS) wykorzystano do modelowania procesu hamowania korozji przy użyciu obwodu zastępczego.

1. Introduction

SX 316 is an improved version of SX 304, with the addition of molybdenum and slightly higher nickel content. The resultant composition of SX 316 gives the steel much increased corrosion resistance in many aggressive environments. Because of its superior corrosion and oxidation resistance, good mechanical properties and fabricability, SX 316 has applications in many sectors of industry include tanks and storage vessels for corrosive liquids, specialized process equipment in the chemical, food, paper, mining, pharmaceutical, and petroleum industries [1]. To improve its corrosion resistance to a completely safe level, the use of corrosion inhibitors is suggested. Review including extensive listing of various types of organic compounds as corrosion inhibitor of stainless steels has been published. These are usually organic compounds containing Oxygen, Nitrogen, Sulfur and Phosphorous and are characterized by high molecular weight, and in particular by setero-chemical struc-

tures and the presence of polar groups. Inhibitors protect the SS surface by effective adsorption and/or chemical bonding interaction through the hetero atoms with the corroding surface, thus giving a non-conducting protective layer on the surface [1-9].

In the present investigation, the corrosion inhibiting behavior of an organic compound with trade name of Armohib 28 was investigated on stainless steel type 316 in acidic solution. To prove the effectiveness of this compound as corrosion inhibitor, gravimetric and electrochemical methods were used.

2. Experimental procedures

2.1. Test specimens

Test specimens were produced from austenitic stainless steel SX 316 with the bellow chemical composition (wt %):

* DEPARTMENT OF TECHNICAL INSPECTION ENGINEERING, PETROLEUM UNIVERSITY OF TECHNOLOGY, ABADAN, IRAN. PETROLEUM UNIVERSITY OF TECHNOLOGY, NORTH BOVARDEH, MOALLEM STREET, ABADAN, KHUZESTAN, IRAN

1.33% Si, 1.2% Mn, 19.11% Cr, 11.00% Ni, 2.37% Mo and balance Fe.

For the gravimetric and electrochemical measurements, pre-treatment of the surface of specimens was carried out by mechanically grinding with 220, 400, 600, 800 and 1000 grades of emery papers, degreasing with acetone and rinsing with bi-distilled water just before tests.

2.2. Solution preparation

The solutions were prepared using analytical reagent grade chemicals and double distilled water. The pH of the solutions was adjusted using ammonia within 3.5 to 4.0. The volume of the test solutions was 200 ml and no attempt were made to deareate them. According to the previous studies on determination of suitable solutions for acid cleaning of stainless steel the bellow composition was considered for single and multiple steps cleaning of SX 316 in acid electrolytes. The considered solution showed the best cleaning efficiency in removing scales from SS surface in previous works.

Citric acid 3% containing ammonium bifluoride 1% as co-solvent [10].

The concentration range of the inhibitor employed was 100 to 700 ppm.

2.3. Inhibitor

Armohib is the trade name of some types of inhibitors which are aliphatic nitrogen compounds retarding the corrosive effects of acids on metals. They offer low cost, dependable protection over a wide range of temperature. Acid attack on metals can be retarded by incorporating small amount of these chemicals with the acid. Since the Armohib compounds are all liquid, readily soluble in acids, non-staining and do not precipitate on standing, they are easy to use. Armohib 28 is a mixture of amines with the general formula of R-NH₂. From the process of atmospheric distillation of Armohib 28, it was found that R can be C₃H₇, C₄H₉, C₅H₁₁, and C₆H₁₃ [11]. For these compounds it is clear that the adsorption on the metal surface is the initial step in inhibition. The adsorption inhibitor is related to the presence of hetero atoms such as nitrogen and long hydrocarbon chain length in their molecular structure. Generally a stronger co-ordination bond causes higher inhibition efficiency. Table 1 shows some physical properties of Armohib 28.

TABLE 1
Physical properties of Armohib 28 [11]

Name	Formula	Appearance	Specific gravity	Flash point
Armohib 28	Aliphatic nitrogen compound	Brown liquid	0.925 gr/cm ³	32°C

2.4. Test methods

2.4.1. Weight loss

For weight loss measurements, the weighed specimens with surface area of 6 cm² were exposed in 200 ml of Citric acid 3% solutions containing Ammonium bifluoride 1% with and without the different concentrations of investigated aliphatic compound for 3 days at 80°C. After exposure, the specimens were washed, dried and weighed. The inhibition efficiency (%IE) was calculated using the formula

$$IE(\%) = [CR_0 - CR/CR_0] \times 100 \quad (1)$$

Where CR₀ and CR are the corrosion rates in the absence and presence of the inhibitor, respectively.

2.4.2. Polarization tests

The effect of addition of increasing concentrations of Armohib 28 and increasing temperature on the potentiodynamic polarization curves of SX 316 in acidic solution was studied. For electrochemical measurements, SX 316 specimen, which was embedded in polyester resin, having a geometric area of 1 cm² was used. The polarization studies were carried out in Citric acid 3% solution containing Ammonium bifluoride 1% at room temperature using an electrochemical work station (Auto Lab Model PGSTAT302N). The potentiodynamic current – potential curves were recorded by changing the electrode potential automatically from –450 to 500 mV (relative to reference electrode potential) with the scan rate of 1 mVs⁻¹ and the corresponding corrosion current were recorded. Before test, the working electrode was immersed in test solution for 24 h until we obtained a steady state open circuit. A Platinum foil and a Silver/Silver-Chloride electrode (Ag/AgCl) were used as counter and reference electrode, respectively. The inhibition efficiency was calculated using the relation

$$IE(\%) = [I_{corr}^{\circ} - I_{corr}/I_{corr}^{\circ}] \times 100 \quad (2)$$

Where I_{corr}^o and I_{corr} are the corrosion current densities in the absence and presence of the inhibitor, respectively.

The obtained data were used to achieve the best adsorption isotherm.

2.4.3. Electrochemical impedance spectroscopy

Impedance measurements were carried out at the E_{corr} using the same equipment as for the polarization measurements. After immersion of the specimen for a period of 24 h, prior to each measurement, which proved sufficient for E_{corr} to attain a stable value, the AC current frequency range from 100 KHz to 5 mHz with a

10 mV peak-to-peak sine wave as the excitation signal were applied.

Since R_{ct} is inversely proportional to current density, it can be used to calculate the inhibition efficiency from the formula

$$IE(\%) = [R_{ct} - R_{ct}^{\circ}/R_{ct}] \times 100 \quad (3)$$

Where R_{ct}° and R_{ct} are the charge transfer resistances in the absence and presence of inhibitor, respectively.

3. Results and discussion

3.1. Weight loss

The values of corrosion rate and inhibition efficiency calculated for different concentrations of the investigated compound by weight loss method are reported in Table 2. From these results it was found that, in general, as the concentration of the inhibitor was increased, the percentage inhibition efficiency was also increased. This behavior could be attributed to the increase of the surface area covered by the adsorbed molecules of the inhibitor with the increase of its concentration [12].

TABLE 2
Corrosion rate and inhibition efficiency of SX 316 steel in free and inhibited acid solutions at 80°C

Armohib 28 Conc. (ppm)	Corrosion Rate (mpy)	IE (%)
0	35	–
100	24	31
300	18.5	47
500	14	60
700	9	74

3.2. Polarization measurements

3.2.1. Effect of inhibitor concentration

Fig. 1 shows typical polarization curves of SX 316 in acidic solution devoid of and containing increasing concentrations of Armohib 28. The corrosion parameters of SX 316 steel in free and inhibited solutions were obtained from the curves of Fig. 1 and given in Table 3.

An inspection of the results obtained from Table 3 reveals that, the increasing in the concentration of the additive shows the following:

- I. The polarization curves shift toward more negative potential and lower current density values upon the addition of inhibitor. This behavior reflects the inhibitive action of Armohib 28 which is attributed to the adsorption on to the steel surface [24].
- II. Cathodic Tafel lines are shifted to more negative potentials relative to the blank solution. This means that the inhibitor under investigation acts as cathodic type [17]. The decreasing trend of E_{corr} confirms this state. According to Riggs and others, the classification of a compound as an anodic or cathodic inhibitor is feasible when the potential displacement is at least 85 mV in relation to that measured for the blank solution. From data of Table 3 it can be observed that the displacement is at least 136 mV with respect to E_{corr}° . Therefore Armohib 28 is definitely cathodic type inhibitor [18].
- III. The values of β_c were changed with increasing inhibitor concentration, which indicates the influence of Armohib 28 on the kinetics of hydrogen evolution reaction. The parallel cathodic Tafel curves showed that the hydrogen evolution was activation controlled and the reduction mechanism was not affected by the presence of inhibitor [16].

TABLE 3
Corrosion parameters of SX 316 steel in free and inhibited acid solutions at 25°C

Concentration (ppm)	I_{corr} (μ A/cm ²)	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	IE (%)	Surface Coverage θ
0	1.344	-30	99	102	–	–
100	0.883	-166	113	111	35	0.35
300	0.5781	-223	110	107	57	0.57
500	0.3541	-178	116	115	74	0.74
700	0.08921	-240	120	99	93	0.93

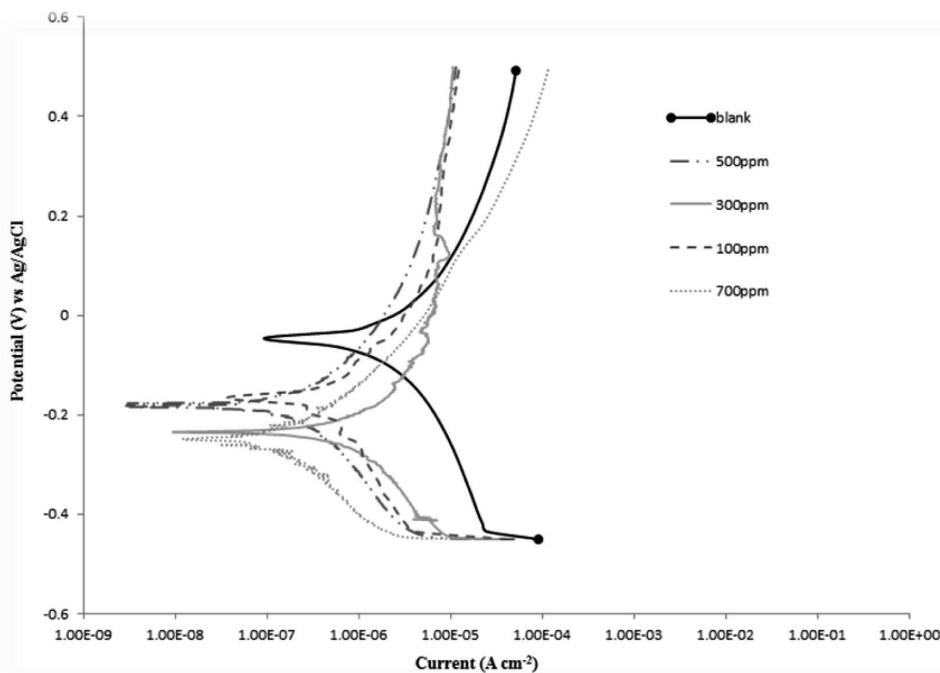


Fig. 1. Polarization curves of SX 316 steel in free and inhibited acid solutions at 25°C

3.2.2. Effect of temperature

The effect of temperature on the various corrosion parameters I_{corr} , θ , and IE were studied in Citric acid 3% containing ammonium bifluoride 1% at temperature range 25-65°C in absence and presence of optimum concentration of Armohib 28 (700 ppm).

Variation of temperature has almost no effect on the general shape of the polarization curves. Similar curves were obtained at high temperature as shown in Fig. 1, and the results were listed in Table 4.

TABLE 4

The effect of temperature on the corrosion parameters of SX 316 steel in free and inhibited acid solutions

Temperature (°C)	blank	Armohib28 (700ppm)		
	I_{corr} (μ A/cm ²)	I_{corr} (μ A/cm ²)	θ	IE (%)
25	1.344	0.06576	0.95	95
35	1.858	0.2332	0.87	87
50	3.586	1.325	0.63	63
65	7.155	3.455	0.52	52

An investigation of Table 4 shows that the values of I_{corr} increased by increasing temperature. As temperature increases, adsorption and inhibition decrease. So this type of inhibitor is not suitable for elevated temperatures.

The activation energy of the corrosion process can be calculated using the following equation

$$K = A \exp(-E_a/RT) \tag{4}$$

Where E_a is the activation energy, A is the frequency factor, T is the absolute temperature, R is the gas constant and K is the rate of metal dissolution reaction and is directly related to corrosion current density I_{corr} . Plotting $\log I_{corr}$ vs $1/T$, the values of E_a can be calculated from the slopes of straight lines obtained from Fig. 2. The values of E_a obtained for blank and inhibited solutions are shown in Table 5. The presence of Armohib 28 increases the activation energy of steel indicating strong adsorption of the inhibitor molecules on the steel surface and the presence of this additive induces energy barrier for the corrosion reaction [25].

TABLE 5

Activation parameters of the dissolution reaction of SX 316 steel in acidic media in the absence and presence of inhibitor

	E_a (KJ/ mol)	ΔH^* (KJ/ mol)	ΔS^* (KJ/mol)
blank	15.48	13.96	-33.48
Armohib 28 (700 ppm)	25.19	34.62	25

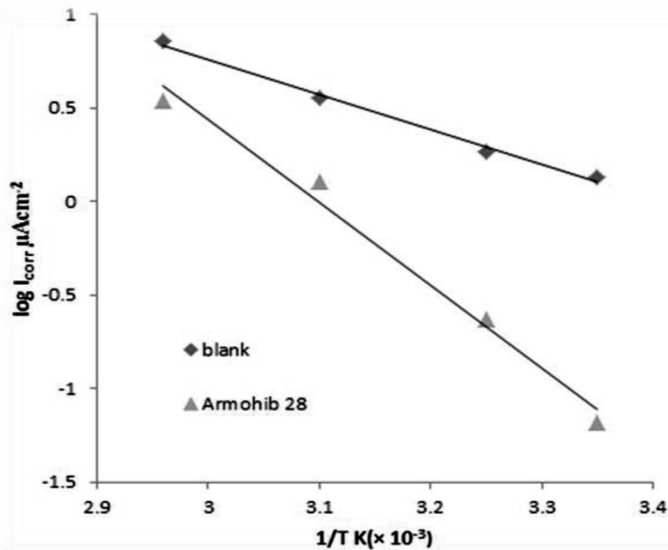


Fig. 2. Arrhenius plots ($\log I_{corr}$ vs $1/T$) for free and inhibited solutions

The enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) for the corrosion of stainless steel in acidic medium can be obtained by applying the transition-state equation [21].

$$\log \frac{W}{T} = \left[\left(\log \frac{R}{hN} \right) + \left(\frac{\Delta S^*}{2.303R} \right) \right] - \frac{\Delta H^*}{2.303RT} \quad (5)$$

Where h is the Planck's constant and N is the Avogadro's number. A plot of $\text{Log} (I_{corr}/T)$ against $(1/T)$ was made for the blank and inhibited solutions with a slope of $-\Delta H^*/2.303R$ and an intercept of $\log(R/hN) + \Delta S^*/2.303R$ (Fig. 3).

Positive signs of the enthalpy reflect the endothermic nature of the steel dissolution process.

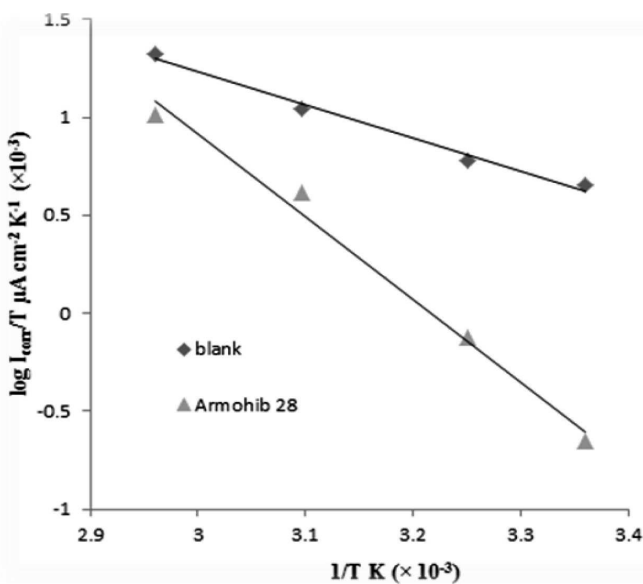


Fig. 3. Transition-state plots of the blank and inhibited solutions

3.2.3. Adsorption isotherm

Basic information on the interaction between the inhibitor and the stainless steel surface can be provided by the adsorption isotherm. The surface coverage (θ) of different concentrations of inhibitor in acidic media have been evaluated from polarization measurements, using the equation

$$\theta = [I_{corr}^{\circ} - I_{corr}/I_{corr}^{\circ}] \quad (6)$$

The values of θ are listed in Table 3.

Attempts were made to fit these values to various isotherms including Frumkin, Langmuir, Temkin, and so on. By far the best fit was obtained with Langmuir isotherm which represented in Fig. 4. This Langmuir model has been used for other inhibitor systems [14, 15, and 22]. According to this isotherm, θ is related to the inhibitor concentration C_{inh} via

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \quad (7)$$

Where K_{ads} is the adsorption equilibrium constant. According to this isotherm, we assume that the inhibitor forms a mono (-molecule) layer on the steel surface, and there is no interaction between the adsorbed species on the electrode surface and the energy of adsorption is independent on the surface coverage [1, 3].

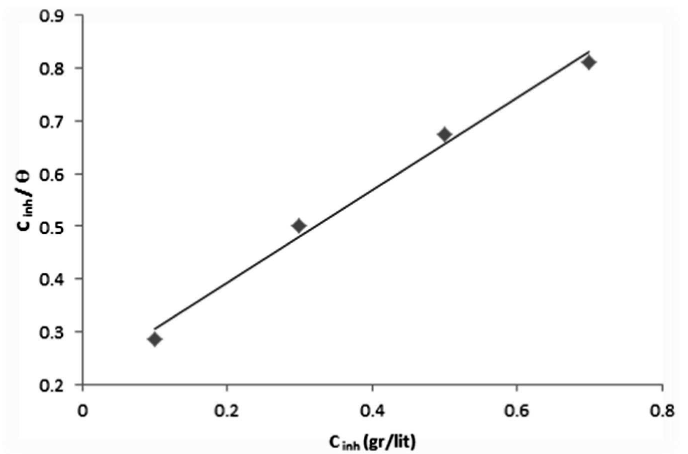


Fig. 4. Langmuir adsorption isotherm for SX 316 steel in acid solution containing different concentration of Armohib 28 at 25°C

The free energy of adsorption ΔG_{ads} can be evaluated using equation. 8, where one molecule of water is replaced by one molecule of inhibitor.

$$\Delta G_{ads} = -RT \ln K_{ads} \quad (8)$$

For a certain range of inhibitor concentration and temperature where mono layer adsorption occurs, the Langmuir adsorption isotherm may be expressed by

$$\text{Log}(\theta/1 - \theta) = \log A + \log C - \Delta H/2.303RT \quad (9)$$

Where T is absolute temperature, A is independent constant, C is inhibitor concentration, R is gas constant, ΔH is heat of adsorption and θ is surface coverage by the inhibitor molecules [1, 3, and 23]. Plot $\log(\theta/(1-\theta))$ vs $(1/T)$ at constant additive concentration of 700 ppm is shown in Fig. 5. The slope of the linear part of the curve is equal to $-\Delta H/2.303R$ from which the average heat of adsorption ΔH_{ads} can be calculated.

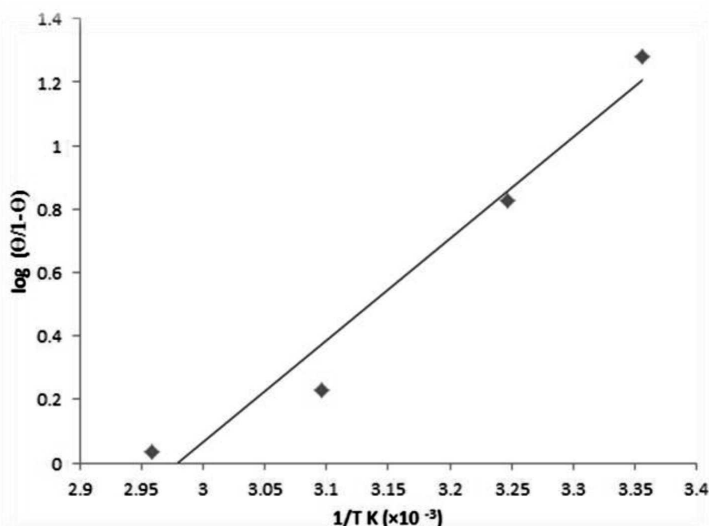


Fig. 5. Plot of $\log(O/(1-O))$ vs $(1/T)$ for SX 316 steel in acidic solution

Standard adsorption entropy of investigated compound can be calculated from the thermodynamic relation

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \quad (10)$$

TABLE 6

Thermodynamic parameters for the adsorption of Armohib 28 on SX 316 steel

Temperature (°C)	K_{ads}	ΔG_{ads} (KJ/mol)	ΔH_{ads} (KJ/mol)	ΔS_{ads} (KJ/mol)
25	4.82	-13.85	-77.24	-214
35	4.82	-14.32	-77.24	-204
50	4.82	-15	-77.24	-193
65	4.82	-15.7	-77.24	-182

Table 6 shows these thermodynamic parameters of adsorption. The negative value of ΔH_{ads} reflects the exothermic characteristic of adsorption, while negative sign of ΔG_{ads} indicates that the adsorption of Armohib 28 compound on the steel surface is a spontaneous process. In all cases, negative values of entropy of adsorption were obtained and range between -214 and -182. The negative values are indicative of increase in the system order. In fact before the adsorption of inhibitor onto the steel surface, inhibitor molecules freely move in the

bulk solution, but with the progress in the adsorption, inhibitor molecules were orderly adsorbed on to steel surface, as a result entropy decreases.

3.3. Electrochemical impedance spectroscopy

Nyquist plots of SX 316 steel in Citric acid 3% containing Ammonium bifluoride 1% in the absence and presence of various concentrations of Armohib 28 are given in Fig. 6. The shape of these impedance spectra did not present perfect semicircles. The Nyquist curve contains a single capacitive semicircle for blank and all concentration range studied. The standard Randles' circuit model was used and is shown in Fig. 7. The solution resistance R_s , constant phase element parameters (Q_{dl} , n), and charge transfer resistance R_{ct} were fitted, and their values are listed in Table 7.

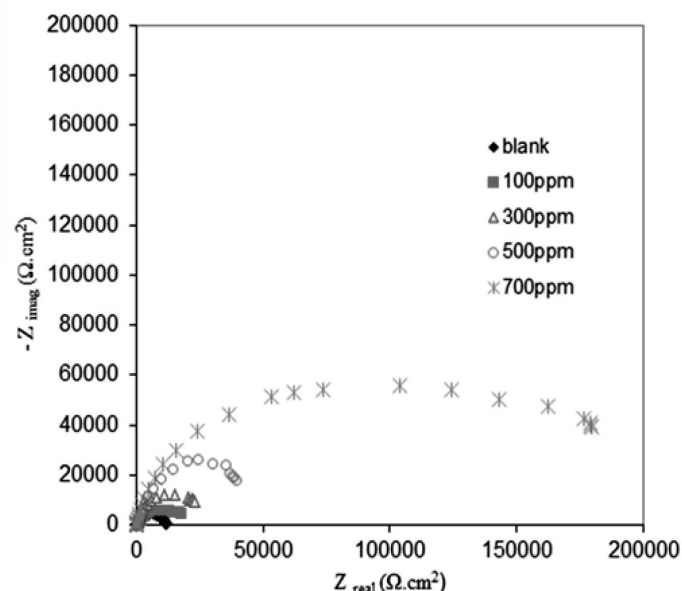


Fig. 6. Nyquist plots of 316 SS in free and inhibited acid solutions at 25°C

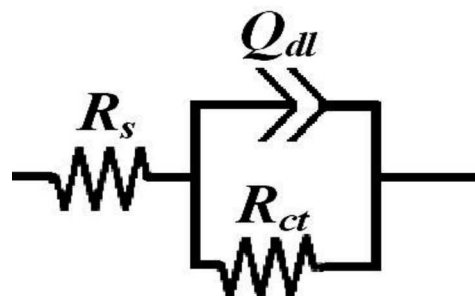


Fig. 7. Equivalent circuit used to fit the EIS data

TABLE 7
Results of fitting procedure of EIS spectra recorded for SX 316 steel immersed in free and inhibited acid solutions

Conc. (ppm)	R_s ($\Omega \cdot \text{cm}^2$)	R_{ct} ($\Omega \cdot \text{cm}^2$)	$Q_{dl} \times 10^6$ ($\Omega^{-1} \text{cm}^{-2} \text{Sn}$)	n	IE (%)
0	8.05	9054	900	0.8	
100	8	16130	500	0.7	43
300	10	22873	370	0.85	60
500	12.5	39505	230	0.85	77
700	12.5	180440	100	0.85	95

It is seen that addition of inhibitor increases the values of R_{ct} and reduces Q_{dl} . At the highest concentration of 700 ppm, R_{ct} increased markedly and inhibition efficiency has reached the highest value of 95%. The change in R_{ct} and C_{dl} values was caused by the gradual adsorption of the organic molecules on the steel surface decreasing the extent of corrosion reactions. The increase in R_{ct} is attributed to formation of the barrier film which prevented acidic medium from attacking the steel surface. The values of C_{dl} are always smaller in the presence of the inhibitor than in its absence as a result of the effective adsorption of Armohib 28 [19, 20].

4. Conclusions

- The results proved that Armohib 28 compound displayed good corrosion inhibition for SX 316 steel in Citric acid solution containing Ammonium bifluoride.
- The inhibition performance was found to improve as the concentration of compound increases, and decline as the temperature increases.
- The results of potentiodynamic polarization measurements demonstrated that the compound under investigation acts as cathodic type inhibitor.
- The adsorption of Armohib 28 compound on the steel surface obeys a Langmuir adsorption isotherm, indicating that the main inhibition process occurs via adsorption and the adsorption of this compound leads to the formation of a mono-layer on the surface. The negative values of ΔG_{ads} obtained from this study indicate that the compound was strongly adsorbed on the electrode surface.
- The results of EIS measurements indicated that, as the concentration of the inhibitor increases, the charge transfer resistance is increased, while the double layer capacitance is decreased.

Acknowledgements

The authors wish to express their appreciation and gratitude to Professor I. Danaee for his advice and long lasting collaboration.

this work is financially supported by Imam Khomeini Oil Refining Company of Shazand.

REFERENCES

- [1] A.Y. El-Etre, *Appl. Surf. Sci.* **252**, 8521 (2006).
- [2] M. Abdallah, *Mater. Chem. Phys.* **82**, 786 (2003).
- [3] M. Abdallah, *Corros. Sci.* **44**, 717 (2002).
- [4] A.S. Fouda, M. Abdallah, S.M. Al-Ashrey, A.A. Abdel-Fattah, *Desal.* **250**, 237 (2009).
- [5] G.O. Ilievbare, G.T. Burstein, *Corros. Sci.* **45**, 1545 (2003).
- [6] A.S. Fouda, H.A. Mostafa, H.M. El-Abbasy, *J. Appl. Electrochem.* **40**, 163 (2010).
- [7] E.V. Filimonov, A.I. Shcherbakov, *Prot. Metals.* **36**, 332 (2000).
- [8] S.H. Sahand, A.A. Ismail, N.A. Mahmoud, *J. Mater. Sci.* **27**, 5706 (1992).
- [9] A.K. Satpati, P.V. Ravindran, *Mater. Chem. Phys.* **109**, 352 (2008).
- [10] L. Li, P. Caenen, M. Daerden, D. Vaes, G. Meers, C. Dhondt, J. Celis, *Corros. Sci.* **47**, 1307 (2005).
- [11] E.W. Flick, *Corrosion Inhibitors, an Industrial Guide*, Noyes Publication, New Jersey, 1993.
- [12] R. Tuir, M. Cenoui, M. El Bakri, M. Ebn Touhami, *Corros. Sci.* **50**, 1530 (2008).
- [13] S.A. Abd El. Maksoud, A.S. Fouda, *Mater. Chem. Phys.* **93**, 84 (2005).
- [14] M. Christov, A. Popova, *Corros. Sci.* **46**, 1613 (2004).
- [15] Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, A. Cherqaoui, D. Takky, *Appl. Surf. Sci.* **252**, 8178 (2006).
- [16] Z. Tao, S. Zhang, W. Li, B. Hou, *Ind. Eng. Chem. Res.* **49**, 2593 (2010).
- [17] M.A. Migahed, *Mater. Chem. Phys.* **93**, 48 (2005).
- [18] E.S. Ferreira, C. Giacomelli, F.C. Giacomelli, A. Spinelli, *Mater. Chem. Phys.* **83**, 129 (2004).
- [19] W. Li, Q. He, C. Pei, B. Hou, *Electrochim. Acta.* **52**, 567 (2007).
- [20] T. Kosec, D.K. Merl, I. Milosev, *Corros. Sci.* **50**, 1987 (2008).
- [21] S.A. Umoren, O. Ogbobe, I.O. Igwe, E.E. Ebenso, *Corros. Sci.* **50**, 1998 (2008).
- [22] V.R. Saliyan, A.V. Adhikari, *Corros. Sci.* **50**, 55 (2008).
- [23] I.K. Putilova, S.A. Balezin, Y.P. Barasanik, *Metallic Corrosion Inhibitors*, Program Press, Oxford, 1960.
- [24] M. Sahin, G. Gece, S. Bilgic, *Appl. Electrochem.* **38**, 809 (2008).
- [25] F. Bentiss, L. Lebrini, M. Lagrenee, *Corros. Sci.* **47**, 2915 (2005).