Chemical Bulletin of “Politehnica” University of Timisoara, ROMANIA
Series of Chemistry and Environmental Engineering

Chem. Bull. "POLITEHNICA" Univ. (Timisoara) *Volume 59(73), 1, 2014*

Expired Zosyn Drug as Corrosion Inhibitor for Carbon Steal in Sodium Chloride Solution

M. Dan*, N. Vaszilcsin*, M. Labosel* and B. Pancan**

* University Politehnica Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, 300223, Parvan 6, Timisoara, Romania, e-mail: nicolae.vaszilcsin@upt.ro

**Aurel Vlaicu University, Arad, 310130 – Arad, Romania

Abstract: In this paper, the possibility to use expired zosyn as corrosion inhibitor for carbon steel in sodium chloride aqueous solution was investigated. The inhibitory effect has been studied by several methods : weight loss measurements, linear polarization, Tafel plots method for the kinetic parameters determination, scanning electron microscopy, all of them providing complete information about the inhibition mechanism. Furthermore, the inhibitory efficiency has been studied as a function of temperature.

Keywords: zosyn, expired drugs, corrosion inhibitor, inhibitory efficiency.

1. Introduction

Corrosion of metals and alloys remains a sensitive issue at both industrial and economic point of view, it is also an important topic of scientific research. Losses of metals and alloys produced by corrosion represent about one third of world production. The use of corrosion inhibitors to reduce the dissolution process of metals and alloys is one of the most economical and practical method used in the corrosion protection [1,2].

A study of expired drugs used as corrosion inhibitors is an attractive field of research due to its usefulness in various industries [3,4]. Exploitation of drugs can significantly reduce emissions of contaminants from expired drugs in the environment and the need for corrosion inhibitors obtained by conventional methods. Also, expired drugs confer a high inhibitory efficiency due to their structure and large molecular volume [5].

Globally, inadequate depositing of expired drugs has a negative impact on the environment and population health. A wide range of antibiotics have been identified to fulfill the conditions of corrosion inhibitors and tested for corrosion prevention: ampicillin, tetracycline, penicillin V, streptomycin [6].

The aim of this work is to investigate the possibility of using expired zosyn as corrosion inhibitor for carbon steel in sodium chloride aqueous solution.

Zosyn consists of a mixture of piperacillin ($C_{23}H_{27}N_5O_7S$) and tazobactam ($C_{10}H_{12}N_4O_5S$) at the mass ratio 2 g /0.25 g.

The corrosion process reduction of carbon steel in the presence of expired drugs can be attributed to the adsorption of inhibitor molecules on the methal surface blocking the active sites or depositing corrosion products.

The substitutional adsorption of an inhibitor to the adsorbed water molecules ($H_2O_{(ads)}$) is represented by the following equation [8]:

$$Zosyn_{(sol)} + nH_2O_{(ads)} \rightarrow Zosyn_{(ads)} + nH_2O_{(sol)} \quad (1)$$

where $Zosyn_{(sol)}$ and $Zosyn_{(ads)}$ are piperacillin/ tazobactam molecules in the aqueous solution, respectively in adsorbed state and *n* is the number of water molecules replaced by inhibitor .

2. Experimental

2.1. Materials

The working electrode was a cylindrical disc cut from a carbon steel sample with the elemental composition presented in table 1.

To determine the inhibitor effect of zosyn on the corrosion rate of carbon steel in sodium chloride aqueous solution different concentrations of the expired drugs, between 10^{-6} and 10^{-3} M,have been used. All concentrations are based on the amount of piperacillin in the test solutions. The corrosive media was prepared from sodium chloride (Merck, 99.9%). The chemical structures of piperacillin ($C_{23}H_{27}N_5O_7S$) and tazobactam ($C_{10}H_{12}N_4O_5S$) are presented in figure 1 [5].

TABLE1. Elemental composition of the carbon steel samples

Element	Fe	C	Si	Mn	P	S	Cr	Ni
wt%	96.98	0.4184	0.2510	0.7920	0.0132	0.0335	1.162	0.029
Element	Mo	Cu	Al	Ti	V	Co	Nb	W
wt%	0.2123	0.0234	0.0229	<0.004	0.0124	0.0222	<0.001	<0.010

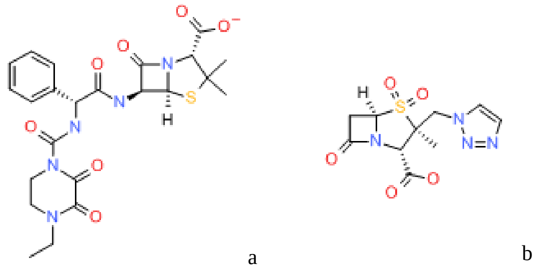


Figure 1. Chemical structures of piperacillin (a) and tazobactam (b) [5].

2.2. Methods

Cyclic voltammetry, linear polarization and weight loss methods were used in order to notice the inhibitive properties of zosyn on the carbon steel corrosion process. The surface morphology of corrosion samples has been characterized by scanning electron microscopy (SEM) using a FEI INSPECT S microscope, before and after corrosion tests.

Electrochemical measurements were performed in a typical glass cell consisted of the carbon steel specimen with 1 cm^2 exposed area as working electrode (WE), two graphite counter electrodes (CE), and a Ag/AgCl electrode as reference .

Electrochemical studies were carried out using a BioLogics SP150 potentiostat galvanostat. All potentials were referred to the saturated Ag/AgCl reference electrode. Before each experiment the test solutions were deaerated by bubbling high purity nitrogen. The carbon steel electrode was abraded with different grit emery papers, cleaned in ultrasonic bath, washed with distilled water and finally dried. The electrode potential was allowed to stabilize 60 min before starting the measurements.

3. Results and Discussion

3.1. Cyclic voltammetry method

The preliminary information about how zosyn expired can influence the corrosion process of carbon steel are pointed by its electrochemical behavior in sodium chloride media emphasised by cyclic voltammetry.

In figure 2 (dE/dt= 500 mVs^{-1}) and 3 (dE/dt= 5 mVs^{-1}) there are showen cyclic voltammograms recorded on Pt as working electrode, in 3.5% NaCl solutions without and with lowest and highest concentrations of zosyn used in corrosion tests. The base curve obtained in a blank solution presents the characteristics of polarization curves drawn in sodium chloride solutions. On the anodic branch of the voltammogra one can distinct the peak corresponding to chlorine evolution reaction as well as the plateau characteristic for oxygen release.

On the backward scan one can observe a cathodic peak at 1.0 V/AgAgCl associated with the oxidation of superficial remanent oxygen also at more negative potentials then -1.0 V/AgAgCl, the increasing current can be associated with hydrogen evolution reaction. The addition of expired zosyn in the electrolyte leads to a decrease of the current for chlorine evolution reaction.

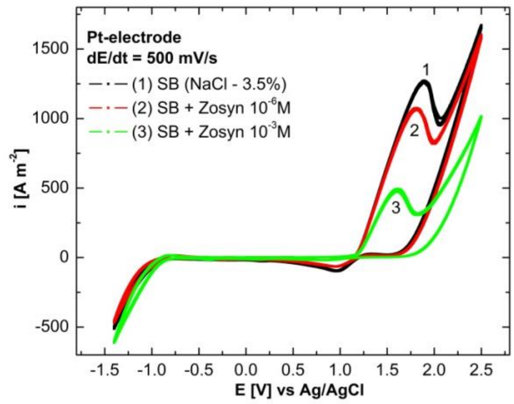


Figure 2. Cyclic voltammograms on Pt electrode in 3.5% NaCl in the absence/presence of zosyn, scan rate 500 mV s^{-1}

The pronounced anodic peak from figure 2, whose height is proportional to the concentration of zosyn in test solutions when the CVs are recorded at 500 mV s^{-1} scan rate, has approximately the same intensity at 5 mV s^{-1} scan rate for all three test solutions. Also, the presence of inhibitor in test solutions reduces the cathodic and anodic currents.

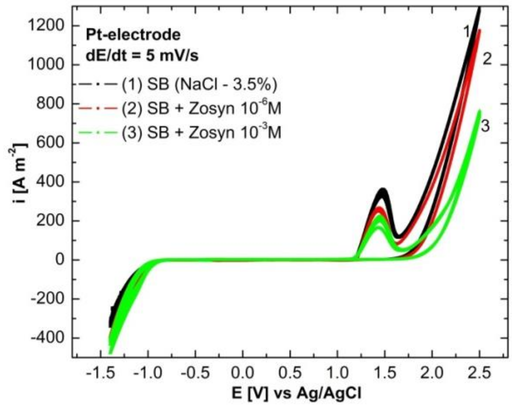


Figure 3. Cyclic voltammograms on Pt electrode in 3.5% NaCl in the absence/presence of zosyn, scan rate 5 mV s^{-1}

In order to identify how zosyn expired influences the electrode processes, polarization curves where recorded separately at higher sensitivity, in cathodic domain as well as in anodic one.

According to figures 4 and 5, the hydrogen and oxygen evolution reactions in 3.5% sodium chloride solution in the presence of zosyn are inhibited due to the adsorption on carbon steel surface of piperacillin and/or tazobactam molecules. The effect is more obvious as the zosyn concentration in corrosive media is 10^{-3} M.

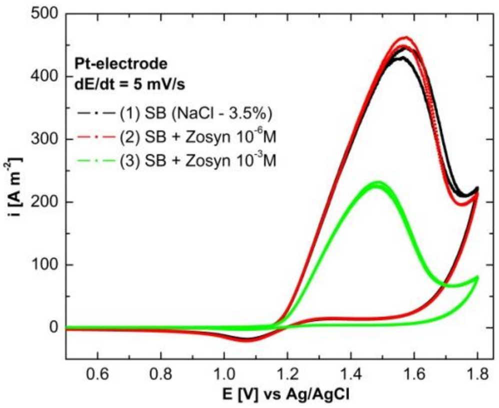


Figure 4. Cyclic voltammograms on Pt electrode for anodic polarization in 3.5% NaCl in the absence/presence of zosyn, scan rate 5 mV s^{-1}

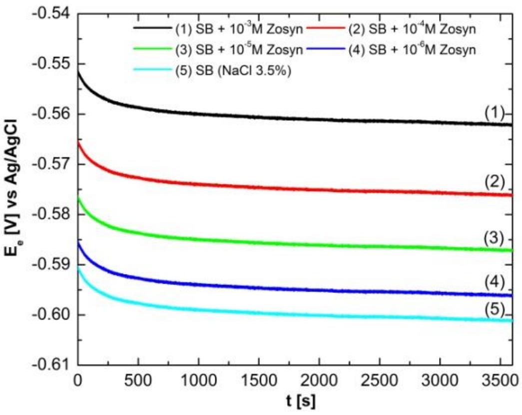


Figure 6. Open circuit potential for carbon steel electrode in 3.5% NaCl in the absence/presence of zosyn

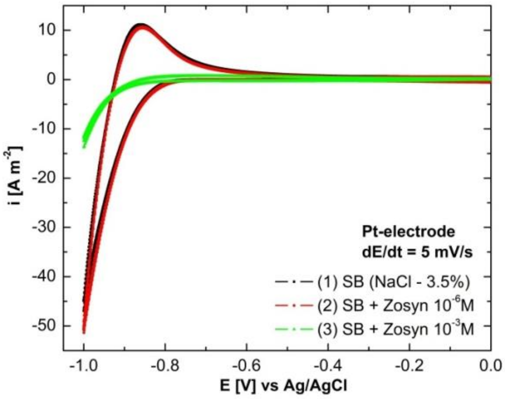


Figure 5. Cyclic voltammograms on Pt electrode for anodic polarization in 3.5% NaCl in the absence/presence of zosyn, scan rate 5 mV s^{-1}

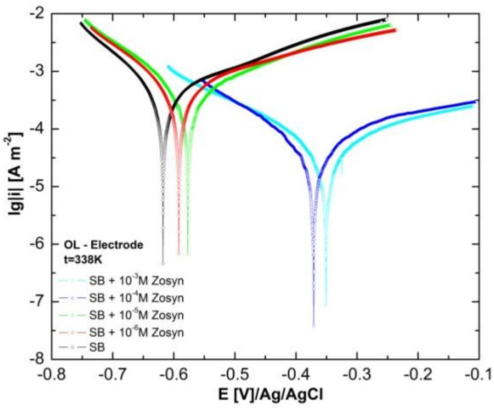


Figure 7. Linear polarization curves on carbon steel electrode in 3.5% NaCl in the absence/presence of zosyn, scan rate 1 mV s^{-1}

3.2. Linear polarization method

The expired zosyn effect on corrosion of carbon steel was studied in 3.5% NaCl corrosive environment by applying successive investigation methods presented above. These were applied after about 1 hour, sufficient time to install an electrode equilibrium or quasi-equilibrium state, as shown in figure 6.

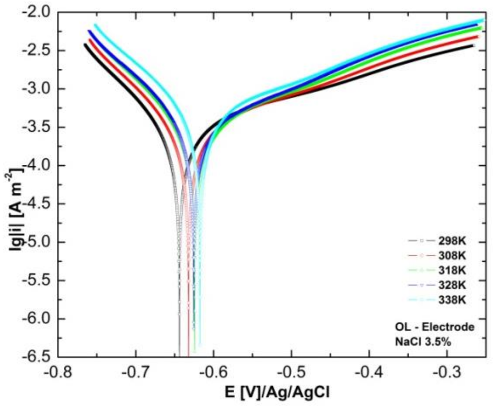
In solutions with different concentrations of inhibitor, carbon steel electrode equilibrium potential is shifted to more positive values, a phenomenon that can be attributed to the adsorption of piperacillin and tazobactam molecules or corrosion products deposition on the electrode surface.

The manner in which Zosyn acts as corrosion inhibitor for carbon steel in sodium chloride solution and its effect on the corrosion rate can be estimated by different procedures, one of the most used being Tafel polarization method. The potentiodynamic polarization curves recorded without and with various concentrations of Zosyn are shown in figure 7.

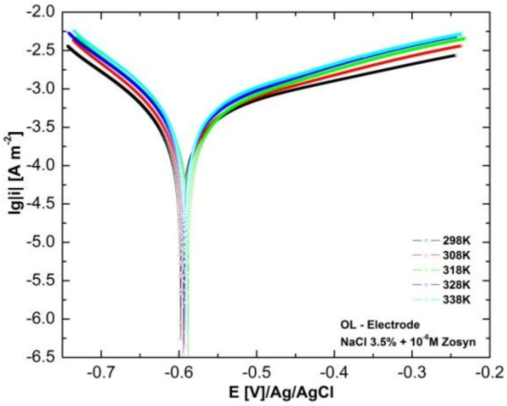
The Tafel curves presented in figure 7 show that zosyn significantly influences both processes: the cathodic process of hydrogen evolution reaction and the anodic process of dissolution/passivation of the metal. As the concentration of the inhibitor is higher the diminution of the cathodic current is more pronounced, suggesting that zosyn acts by adsorption on steel surface.

To investigate how the temperature affects the corrosion process, polarization curves of carbon steel in 3.5% NaCl were determined at various temperatures (298–338 K) in the absence and presence of inhibitor at different concentrations. The results obtained for carbon steel samples in NaCl solution without inhibitor and with 10^{-6}M zosyn are showen in figure 8.

Analysis of results from Table 2 reveals that the corrosion rate decreases and hence inhibition efficiency (*IE*) increases as the temperature increases. This indicates that the rising of temperature increases the inhibition process, and the highest inhibition efficiency has been obtained with 10^{-3} M Zosyn at 338 K.



a)



b)

Figure 8. Linear polarization curves on carbon steel electrode for anodic polarization in 3.5% NaCl in the absence (a) and presence of 10^{-6}M zosyn, at different temperatures, scan rate 1 mV s^{-1}

Numerical values of the corrosion current density (i_{corr}) variation, corrosion potential (E_{cor}), anodic Tafel slope (b_a) and cathodic Tafel slope (b_c) and polarization resistance (R_p), as a function of zosyn concentrations, at various temperatures were obtained from polarization profiles by extrapolating potentiodynamic curves using BioLogics software.

The inhibition efficiency (*IE*) and surface coverage (θ) have been calculated using equations (2) and (3). All obtained values are presented in Tables 2.

$$IE(\%) = \left(\frac{i^{o}_{corr} - i^{inh}_{corr}}{i^{o}_{corr}}\right) \times 100 \qquad (2)$$

$$\theta = \frac{i^{o}_{corr} - i^{inh}_{corr}}{i^{o}_{corr}} \qquad (3)$$

where i^{0}_{corr} and i^{inh}_{corr} are the uninhibited and inhibited corrosion current densities, respectively.

From the results presented in Table 2, one can see that by increasing the inhibitor concentration, the corrosion rate is diminished in sodium chloride solution and inhibition efficiency is elevated. On the other hand, one can conclude that at lowest inhibitor concentrations in the test solution, the diminution of the corrosion rate is caused by the merely blocking of the reaction sites on carbon steel surface without interfering the anodic and cathodic reactions. In these circumstances the inhibitor doesn't cause significant changes in the anodic and cathodic Tafel slopes. This suggest that zosyn behaves as a mixed-type inhibitor. and can be classified as adsorptive-type [10].

TABLE 2. Polarization parameters for the corrosion of carbon steel in 3.5% NaCl in the absence/presence of zosyn

Electrolyte	T [K]	i_{cor} [μA cm^{-2}]	E_{cor} [V]	$-b_c$ [V dec^{-1}]	b_a [V dec^{-1}]	R_p [Ω]	v_{cor} [mm an^{-1}]	*IE* [%]	θ
SB (NaCl 3.5%)	298	240.9	-0.601	0.115	0.212	54.85	2.88	-	-
	308	277.8	-0.594	0.107	0.173	36.08	3.32	-	-
	318	298.1	-0.602	0.111	0.252	51.07	3.57	-	-
	328	323.9	-0.591	0.119	0.232	46.21	3.88	-	-
	338	365.5	-0.587	0.122	0.186	33.8	4.37	-	
SB + 10^{-6} M Zosyn	298	225.3	-0.648	0.097	0.245	57.53	2.69	6.48	0.06
	308	256.6	-0.638	0.099	0.257	56.31	2.95	7.63	0.08
	318	270.8	-0.627	0.105	0.246	50.3	3.34	9.16	0.09
	328	290.9	-0.624	0.109	0.23	46.83	3.48	10.19	0.10
	338	312.2	-0.618	0.111	0.257	38.97	4.11	14.58	0.15
SB + 10^{-5} M Zosyn	298	214.6	-0.537	0.132	0.218	729	2.59	10.92	0.11
	308	241.3	-0.545	0.13	0.213	59.9	3.01	13.14	0.13
	318	252.2	-0.558	0.136	0.194	52.37	3.26	15.40	0.15
	328	268.5	-0.589	0.124	0.212	47.72	3.57	17.10	0.17
	338	295.9	-0.577	0.128	0.183	37.87	4.02	19.04	0.19
SB + 10^{-4} M Zosyn	298	54.9	-0.337	0.282	0.355	1562	0.518	77.21	0.77
	308	53.6	-0.344	0.288	0.334	974	0.541	80.71	0.81
	318	51.1	-0.395	0.216	0.31	620	0.595	82.86	0.83
	328	52.8	-0.383	0.219	0.331	717	0.655	83.70	0.84
	338	53.6	-0.351	0.213	0.328	668	0.696	85.34	0.85
SB + 10^{-3} M Zosyn	298	50.8	-0.338	0.225	0.254	948	0.393	78.91	0.79
	308	45.7	-0.418	0.198	0.201	620	0.415	83.55	0.84
	318	40.9	-0.449	0.188	0.23	509	0.55	86.28	0.86
	328	37.7	-0.437	0.176	0.227	428	0.607	88.36	0.88
	338	32.6	-0.394	0.163	0.149	519	0.677	91.08	0.91

3.3. Weight loss method

Gravimetric measurements of carbon steel discs samples immersed in 100 mL 3.5% NaCl in the absence and presence of different Zosyn concentrations after 240 hours of immersion time at 298 K, were chosen to compare inhibition efficiency at selected concentrations. As expected, weight loss of carbon steel samples are decreased in the present of expired drug with increase of the concentration. This means that Zosyn acts as an efficient inhibitor.

The corrosion rate of carbon steel (W_{corr}) was determined using the relation (4) and the inhibition efficiency (*IE*) and surface coverage (θ) with equations (5) and (6):

$$W_{corr} = \frac{W_1 - W_2}{S \times t} \quad (4)$$

where W_1 and W_2 are the initial and final mass of the samples in mg, *S* is the total surface area in cm^2 and *t* is the exposure time in h.

$$IE(\%) = \left(1 - \frac{W_{corr}}{W_{corr}^0}\right) \times 100 \quad (5)$$

$$\theta = 1 - \frac{W_{corr}}{W_{corr}^0} \quad (6)$$

where W_{corr} and W_{corr}^0 are the weight loss in the presence and the absence of inhibitor, respectively.

TABLE.3. The inhibition efficiency and surface coverage obtained by weight loss method

Zosyn conc. [M]	W_{corr} [mg cm^{-2} h^{-1}]	*IE* [%]	θ
SB	0.49	-	
1×10^{-6}	0.44	9.91	0.10
1×10^{-5}	0.41	16.53	0.17
1×10^{-4}	0.12	71.80	0.72
1×10^{-3}	0.04	90.42	0.90

The data presented in table 3 show that inhibitor efficiency reaches to appreciable values for concentrations of Zosyn bigger then 10^{-4} M.

3.4. Surface analysis

SEM analysis was performed to investigate the surface morphology of the carbon steel after immersion in 3.5% NaCl in the absence (figure 9) and the presence of 10^{-3} M (figure 10) for 240 h at 298 K. Damaged surface was observed in the absence of inhibitor due to high dissolution rate of iron in NaCl solution.

The samples surface was protected by adsorption of inhibitor molecules that form a protective film, or due to complex compounds between iron and piperacillin and tazobactam molecules. The comparing of micrographs recorded at same magnification for both samples suggest that corrosion process of carbon steel is inhibited which is confimed by the weight loss measurement, cyclic voltammetry and polarization results.

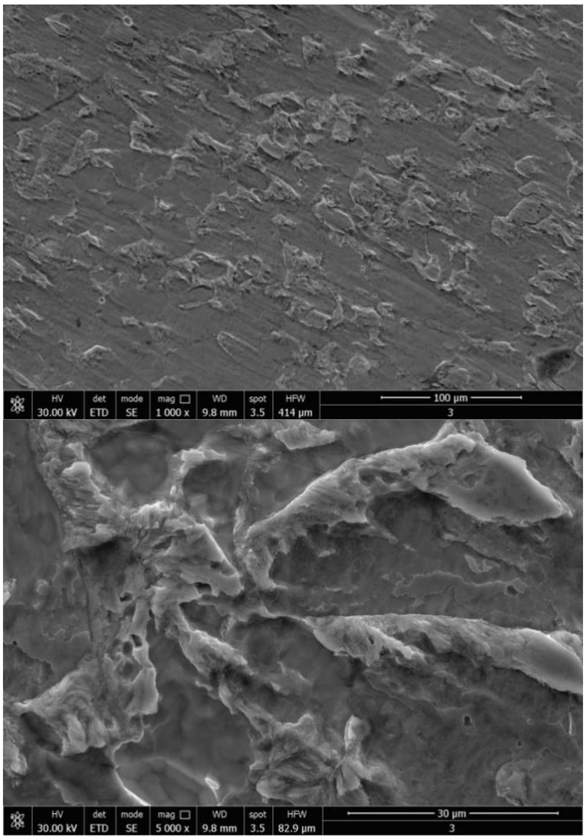


Figure 9. SEM images obtained on carbon steel after 240 h immersion time in NaCl 3.5% at different magnification.

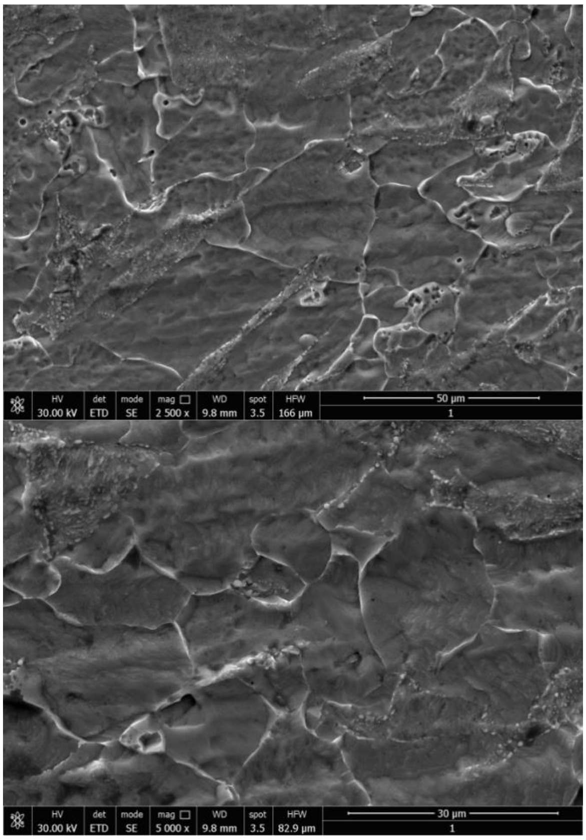


Figure10. SEM images obtained on carbon steel after 240 h immersion time in NaCl 3.5% with 10^{-3} M Zosyn.

4. Conclusions

Inhibition efficiency of zosyn expired drugs has been studied by two different methods: weight loss and linear polarization, all giving comparable results. This drug exhibited excellent inhibition performance as a mixed-type inhibitor for carbon steel in sodium chloride solutions at concentrations bigger then 10^{-4} M.

Zosyn expired act as efficient corrosion inhibitors in 3.5% NaCl solution and it exhibit a maximum inhibition efficiency of 91%. SEM micrographs showed that the inhibitor molecule form a good protective film on the carbon steel surface.

The good inhibition efficiencies obtained in sodium chloride solution makes them a suitable alternative as environmentally friendly corrosion inhibitors in deicing solutions in which the main ingredient is sodium chloride.

REFERENCES

1. Schweitzer P.A., Fundamentals of Corrosion, CRC Press Taylor and Francis Group, Boca Raton FL, USA, **2010**.
2. Roberge P.R., Corrosion Engineering, McGraw Hill, New York, **2008**.
3. Gece G., *Corrosion Science*, 53, **2011**, 3873-3898.
4. Vaszilcsin N., Ordodi V. and Borza A., *International Journal of Pharmaceutics*, 431, **2012**, 241-244.
5. Bobina M., Kellenberger A., Millet J.P., Muntean C. and Vaszilcsin N., *Corrosion Science*, 69, **2013**, 389-395.
6. Abdallah M., *Corrosion Science*, 46, **2004**, 1981-1996.
7. Sudhish K.S., Ashish K.S., Ishtiaque A. and Quraishi M.A., *Matterials Letters*, 63, **2009**, 819-822.
8. Hazazi O.A., *International Journal of Latest Research in Science and Technology*, 4(2), **2015**, 138-143.
9. http://livertox.nih.gov/FourthGenerationPenicillins. htm#structure
10. Suaad M.H., Al-Majidi, Uday H.R., Al-Jeilawi, Khulood A.S. and Al-Saadie, *Iraqi Journal of Science*, 54(4), **2013**, 789-802.

Received: 13 May 2014
Accepted: 10 June 2014