ISSN : 0974 - 7486 Volume 10 Issue 2

Materials Science

An Indian Journal

Full Paper

MSAIJ, 10(2), 2014 [57-71]

Corrosion inhibition and antimicrobial activity of some ethoxylated sulphanilamides on carbon steel in acidic medium

Dalia E.Mohamed*, Mohamed A.Abbas, Nesreen A.Fatthallah, Marwa R.Mishrif

Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, (EGYPT)

E-mail : daliaemam99@yahoo.com

ABSTRACT

Sulfanilamide was ethoxylated with three degrees of ethylene oxides giving S_1, S_2 and S_3 compounds. Corrosion behavior of carbon steel specimens in 1 M HCl solution was studied for the three sulfanilamides using weight loss technique. Temperature effect on the corrosion behavior was studied in the temperature range 298–333 K. The associated activation energy of corrosion and other thermodynamic parameters were calculated. The results showed that, the inhibition efficiency values increase with increasing inhibitor concentration, ethylene oxide units (to a certain extent) and with decreasing temperature. Finally, these sulfanilamides were tested for their antimicrobial activities against some microorganisms causing microbial biofilm.

KEYWORDS

Carbon steel;
Weight loss;
Acid corrosion;
Adsorption isotherm;
Kinetic parameters.

INTRODUCTION

Carbon steel is one of the most important alloys used in several fields of industry. It can be exposed to corrosion when exposed to aggressive environmental conditions, especially in environment containing Cl^- ions. As Cl^- ion is an active one, it forces oxide formation on metal surface by being adsorbed as an alternative on metal surface[1]. This increases the corrosion rate of metal. Acid solutions are widely used for removal of undesirable scale and rust in many industrial processes. Among the commercially available acids, the most frequently used one is hydrochloric acid. Inhibitors are generally used in these processes to control metal dissolution as well as the consumption of acid[2,3]. Most of acid corrosion inhibitors are organic compounds containing electronegative atoms (such as, N, S, P, O, etc.), unsaturated bonds (such as, double bonds or triple bonds, etc.) and plane conjugated systems including all kinds of aromatic cycles[4-7]. These inhibitors can adsorb on the metal surface by blocking the active sites and thereby decreasing the corrosion rate.

The choice of optimal inhibitor should be based on three considerations: (i) it should have a convenient synthesis from inexpensive raw materials, (ii) the presence of phosphorus, nitrogen, oxygen, sulphur and multiple bonds in the inhibitor molecule is required for its efficiency and (iii) its toxicity towards the environment must be negligible[8].

Slime on surfaces is the usual manifestation of a phenomenon called "microbiofouling". In other words, slime forming microorganisms are the biofoulants. Biofouling generally leads to biocorrosion[9-11]. It occurs in a wide range of industrial processes and in all of them it is a

nuisance, sometimes a very expensive one. Basically, in microbiofouling (or microbial fouling) the processes occur as follows: microorganisms colonize surfaces, sequester nutrients from the water phase and convert them into metabolites and new biomass. Cooling systems and industrial plants frequently offer large surface areas, which invite colonization and subsequent use of biodegradable substances, leading to an extent of biofilm development that interferes with process parameters or product. All these phenomena are subsumed under the term "biofilm"[12]. Cooling tower systems are considered to be ideal places for microbial growth. These microorganisms include algae, bacteria, cysts, and viruses. It has been shown that *Pseudomonas* genus members form or associate with biofilms[13,14]. Marine organisms like *Escherichia coli* and *Pseudomonas aeruginosa* have been found to be involved in the biofouling process. Moreover, in industrial settings, unwanted biofilms of *Staphylococcus aureus* is responsible for the biofouling of cooling-water towers, water pipelines, membrane unit or food-processing plants[15].

Uncontrollable biological growth causes fouling, loss of heat exchange capacity, equipment failure and energy wastage. Therefore, it is important to understand the different types of microbiological growths found in cooling water to be controlled correctly.

In this study, synthesis of ethoxylated sulfanilamides with different number of ethylene oxides was carried out. Then, evaluation of these sulfanilamides as corrosion inhibitors and as biocides was investigated, where the influence of inhibitors concentration and temperature on the corrosion rate was studied in aqueous 1.0 M hydrochloric acid solutions using carbon steel as the working electrode. Finally, antimicrobial activity of the three ethoxylated sulfanilamides against some representatives of the microorganisms causing biofilm (microbiofouling organisms) was detected.

MATERIALS AND METHODS

Three ethoxylated sulfanilamides with 2, 12 and 20 ethylene oxide units were prepared. Sulfanilamide was charged into a closed reaction vessel with 0.3 gm sodium metal "Na metal" as a catalyst and heated to 150 – 180 °C (423-453 K) with continuous stirring while passing a stream of nitrogen gas through the system for 2 minutes then replaced by ethylene oxide stream. The reaction was carried out for different intervals of time after which the apparatus was filled with nitrogen, cooled and the reaction vessel was weighed. The difference in weight indicated the amount of the ethylene oxide consumed in the reaction from which the number of moles of ethylene oxide was calculated[16-18]. The total number, n, of ethylene oxide groups were = 2, 12 and 20 and the resulted products can be simplified as (S_1, S_2 and S_3) respectively. The product was then neutralized with HCl, dissolved in isopropanol, then salted out with supersaturated NaCl solution. The organic layer was then separated and the isopropanol was distilled off. The ethoxylated product obtained showed a brown viscous liquid appearance.

The chemical structures of the synthesized inhibitors were confirmed by FTIR and ^{1}H-NMR spectroscopy.

Weight loss measurements

The corrosive solution (1 M HCl) was prepared by appropriate dilution of analytical grade 37% HCl with double distilled water. Tests were performed on steel specimens of a rectangular form (7 cm x 2 cm x 0.2 cm and average weight = 37.5 gm). Prior to all measurements, the steel specimens of composition (0.15-0.2 wt%C; 0.6-0.9 Mn wt%; 0.05 Si wt%; 0.04 P wt % and the reminder is Fe) were abraded with different emery papers (grade 320-600-800-1000-1200), degreased with acetone, then washed with double distilled water and finally dried between two filter papers. After weighing accurately, the specimens were immersed in 150 ml hydrochloric acid with and without addition of different concentrations (0.4, 0.8, 1.2, 1.5 and 1.9 mM) of the tested inhibitors at different temperatures (298,303, 313, 323 and 333 K). After the required immersion time (6 hours), the tested specimens were removed, washed with double distilled water, dried by a jet of air and finally weighed.

Antimicrobial bioassay

Microorganisms

Some representatives of microorganisms causing microbial biofilm (microbial fouling) in cooling water systems and cooling towers were tested. The tested organisms were bacterial: (i) Gram positive bacteria- *Sta-*

phylococcus aureus, NCTC-7447 and (ii) Gram negative bacteria- *Pseudomonas aeruginosa*, NCTC-10662 and *Escherichia coli*, NCTC-10416.

Nutrient broth media were used for cultivation and maintenance of the tested bacteria. The nutrient broth composition (gm/L) was: Peptone, 5.0 gm; NaCl, 5.0 gm; Yeast extract, 2.0 gm and Beef extract,1.0 gm)[19].

Test solutions

Different concentrations of each of the three ethoxylated sulfanilamides (S_1, S_2 and S_3) were prepared from stock solutions[20-21] using distilled water. Tested concentrations were 0.5, 1.0, 1.5, 2.0 and 2.5 ppm for each one at different time intervals: 0 time, 24 hrs, 48 hrs, 72 hrs and 96 hrs.

Growth measurements

Minimum inhibitory concentration (MIC) determination

MIC of the three tested sulfanilamides against selected bacterial strains obtained from The National Collection of Type Cultures (NCTC) was carried out. 1mL of bacterial suspension was inoculated in 1 mL of Mueller Hinton Broth (Difco) containing the tested compounds from 2-fold dilutions. The final inoculum was approximately 1 x 10^5 viable bacteria/mL and the final volume was 2 mL. Inoculated tubes were incubated at 35 ºC for 18 - 21 hrs. Readings were made visually (by observed turbidity). The MIC was defined as the lowest concentration of antimicrobial agent showing complete inhibition of growth. The growth of the tested strains was estimated from a method based on turbidity (optical density) measurements[22-23].

The turbidity of the bacterial suspensions was measured (as absorbance) at 600 nm using the JENWAY 6300 spectrophotometer. The procedure for preparing bacterial suspensions of the desired concentrations was standardized by adjusting the turbidity of the initial stock suspensions. Optical density was calculated as optical density per milliliter (i.e., growth). The inhibition percentage was concluded from the following equation[24]:

$$\% \text{ Viable cells } (I) = O.D_T \times 100 / O.D_C \quad (1)$$

where, $O.D_T$ = Test optical density and $O.D_C$ = Control optical density.

This method is based on the principle that as the growth proceeds, cell number increases, leading to a proportional increase in the optical density of the medium.

RESULTS AND DISCUSSION

Characterization of the synthesized inhibitors

The chemical structures as well as the molecular weights of the prepared sulfanilamides are shown in TABLE 1 and confirmed by FTIR (TABLE 2) and ^{1}H NMR spectra (TABLE 3).

FTIR spectra

FTIR spectra of the synthesized S_1, S_2 and S_3 compounds are shown in TABLE 2, The presence of two bands in the vicinity of 2941 and 2884 cm^{-1} were assigned to stretching vibration of the —CH_2 groups in S_1, while a band appeared at 2876 in case of both S_2 and S_3 compounds. The peaks at 1090, 1089 and 1106 cm^{-1} (for S_1, S_2 and S_3 respectively), are due to C-O stretching group, indicating the formation of the ether bond due to the condensation of ethylene oxides. In case of S_1, there was an overlap between the peaks of

TABLE 1 : Designation and molecular weights of the ethoxylated sulfanilamides (S_1, S_2 and S_3)

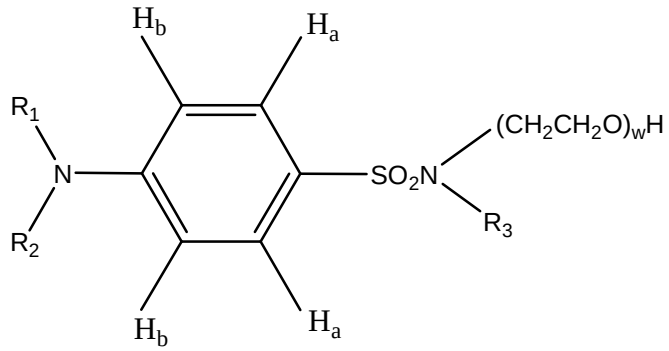
Sulfanilamide	Chemical Structure	Molecular Weight
S_1		260
S_2		702
S_3		1053

TABLE 2 : FTIR spectroscopic analysis of the ethoxylated sulfanilamides (S_1, S_2 and S_3)

Fct. Gp.	I.R.(KBr) Bands (ν cm^{-1})		
	S_1	S_2	S_3
C-H_{st}.	2941 & 2884	2876	2876
C-H_{Sciss}.	1448	1458	1456
ν_s (S=O)	1148	1119	1106
ν_{as} (S=O)	1311	1324	1326
C-O-C	1090	1089	1106
OH	3367	3373	3384
NH	3367	-	-
NH_2 Aromatic	3367	-	-

TABLE 3 : ^{1}H-NMR spectral data of the ethoxylated sulfanilamides S_1, S_2 and S_3

Sulfanilamides	^{1}H-NMR (TMS) spectra data (δ)ppm
S_1	(2.70-2.72,2H,NH_2), (5.95 ,1H, NH), (4.75-4.78,1H, OH), (3.03-3.16, 2H, SO_2 N $\underline{CH_2}CH_2O$), (3.34-3.56, 2H, SO_2 N CH_2CH_2O $\underline{CH_2}$ CH_2), (6.59-6.66, Ha Ar), (7.38-7.47, H_b Ar).
S_2	(4.54, 1H , OH), (3.17, 2H, SO_2 N $\underline{CH_2}CH_2O$), (3.19-3.26,2H, SO_2 N CH_2CH_2O $\underline{CH_2}$ CH_2), (3.27-3.58, 2H ,N $\underline{CH_2}CH_2O$), (6.53-6.82, Ha Ar), (7.40-7.53, H_b Ar).
S_3	(4.52-4.53,1H , OH),(3.17,2H, SO_2 N $\underline{CH_2}CH_2O$), (3.19-3.27,2H , SO_2 N CH_2CH_2O $\underline{CH_2}$ CH_2), (3.32-3.56,2H , N $\underline{CH_2}CH_2O$), (6.66-6.69 ,H_a Ar), (7.45-7.48, H_b Ar).

OH, NH and NH_2 giving one broad peak at 3367 cm^{-1}.

^{1}H NMR spectra

^{1}H NMR spectra of the synthesized compounds are shown in TABLE 3, where the data confirmed the expected hydrogen proton distribution in the synthesized compounds. In compound S_1, the peaks appeared at δH" (3.03-3.16) and (3.34-3.56) were assigned to the –CH_2- groups of (SO_2 N $\underline{CH_2}CH_2O$) and (SO_2 N CH_2CH_2O $\underline{CH_2}CH_2$) respectively. Also, the peaks appeared at (2.70-2.72) were assigned to NH_2 group, while those appeared at 5.95 & 4.75-4.78 were assigned to NH & OH groups respectively. The chemical shift values of compounds S_2 & S_3 were clarified in TABLE 3, the values obtained were nearly the same for the three prepared compounds except the presence of NH and NH_2 groups which only appeared in S_1.

where R_3 = H in case of S_1 R_3 = $(CH_2CH_2O)_z$ in case of S_2 and S_3 ; R_1 = R_2 = H in case of S_1 R_1 = $(CH_2CH_2O)_x$ in S_2 and S_3; R_2 = $(CH_2CH_2O)_y$ in S_2 and S_3 x + y + w + z = 12 units in case of S_2; x + y + w + z = 20 units in case of S_3 w = 2 in case of S_1

Corrosion inhibition application

Effect of chemical structure

Good performance of the ethoxylated sulfanilamides (S_1, S_2 and S_3) as corrosion inhibitors for carbon steel in 1.0 M HCl solutions can be attributed to the presence of π-electrons of the aromatic ring, lone pairs of electrons of O, N and S-atoms in their structures, which can act as adsorption centers for the inhibitor molecules on the metal surface[25]. Figure 1, shows the inhibition efficiencies of the inhibitors at different concentrations, from which we concluded that, the inhibition efficiency order is S_2 > S_3 > S_1. This can be explained on the basis of the presence of one S-atom, two N-atoms and 12 O-atoms in S_2 compound, which favors its greater adsorption on the steel surface, while S_1 contains one S-atom, two N-atoms and only 2 O-atoms. So, the main conclusion is that the presence of ethylene oxide units (nonionic chain length) in the inhibitor molecules increases their inhibiting efficiencies. On the other hand, S_3 has slightly lower inhibition efficiency than S_2 although it contains 20 ethylene oxide units, meaning that the higher increase in the number of the ethylene oxide units may lead to a decrease in the inhibition efficiency values, this can be attributed to the coiling effect of the large chain leading to a reduction in the adsorption process, which in turn leads to a decrease in the inhibition efficiency values of S_3. This result goes in agreement with other investigators[26].

Effect of inhibitor concentration

Corrosion inhibition efficiencies η_w (%) and surface coverage (θ) were calculated according to the following equations[27]:

$$\eta_w\ (\%) = 100\ (\text{“}W\text{-”}W_i)/\ \text{“}W \quad (2)$$

$$\theta = (\text{“}W\text{-”}W_i)/\ \text{“}W \quad (3)$$

where, “W and “W_i are the weight loss of carbon steel in the absence and presence of the inhibitors, respectively.

The values of inhibition efficiencies obtained from weight loss measurements were plotted against different concentrations of the prepared inhibitors at differ-

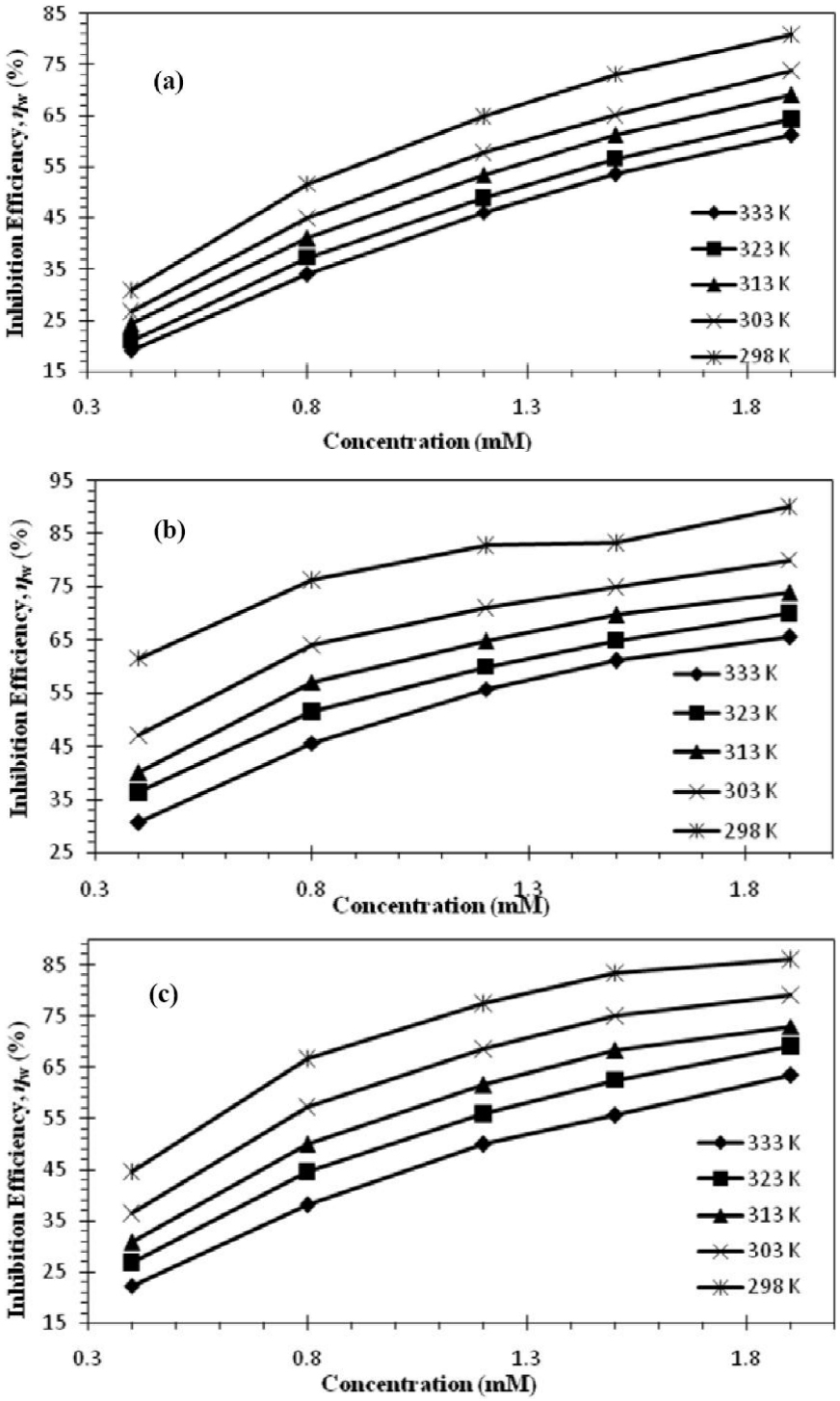


Figure 1 : Relationship between the inhibition efficiency and concentration at different temperatures for compounds a) S_1, b) S_2 and c) S_3.

ent temperatures Figure 1. Data showed that, the corrosion inhibition efficiencies for the prepared inhibitors increased with increasing inhibitor concentrations TABLE 4. It can be seen also that corrosion rate values decreased as the concentration of inhibitor increased. This result is due to the fact that the adsorption amount and coverage of inhibitors on carbon steel surface increases with inhibitor concentration.

Effect of temperature

The temperature effect on the rate of dissolution of carbon steel in 1.0 M HCl containing different concen-

Full Paper

TABLE 4 : Corrosion rate (k), surface coverage (θ) and corrosion inhibition efficiency (η_w %) for carbon steel in absence and presence of the prepared inhibitors in 1M HCl from weight loss measurements at various temperatures.

inhibitors	Conc. of inhibitors (mM)	298°C			303°C			313°C			323°C			333°C	
		Θ	K (mg.cm^{-2}h^{-1})	$\eta_{w\%}$	θ	K (mg.cm^{-2}h^{-1})	$\eta_{w\%}$	θ	K (mg.cm^{-2}h^{-1})	$\eta_{w\%}$	θ	K (mg.cm^{-2}h^{-1})	$\eta_{w\%}$	θ	K (mg.cm^{-2}h^{-1})	$\eta_{w\%}$
Blank			0.14			0.16			0.21			0.27			0.32	
S1	0.4	0.30	0.10	30.770.26	0.12	26.670.24		0.16	24.240.21		0.21	21.050.19		0.26	19.05	
	0.8	0.51	0.07	51.610.44	0.09	44.940.41		0.13	41.030.37		0.17	37.210.34		0.21	34.04	
	1.2	0.64	0.05	64.860.57	0.07	57.830.53		0.10	53.330.48		0.14	48.980.46		0.17	46.15	
	1.5	0.73	0.04	73.170.65	0.05	65.220.61		0.08	61.220.56		0.12	56.600.53		0.15	53.57	
	1.9	0.80	0.03	80.850.73	0.04	73.790.69		0.07	69.090.64		0.10	64.410.61		0.13	61.29	
S2	0.4	0.61	0.06	61.540.47	0.09	47.060.40		0.13	40.000.36		0.17	36.36 0.3		0.22	30.77	
	0.8	0.76	0.03	76.190.64	0.06	64.000.57		0.09	57.140.51		0.13	51.610.45		0.18	45.71	
	1.2	0.82	0.03	82.760.71	0.05	71.010.64		0.08	64.860.60		0.11	60.000.55		0.14	55.81	
	1.5	0.83	0.02	83.330.75	0.04	75.000.69		0.07	69.770.64		0.10	64.940.61		0.13	61.22	
	1.9	0.90	0.01	90.00 0.8	0.03	80.000.74		0.06	74.000.70		0.08	70.000.65		0.11	65.52	
S3	0.4	0.44	0.08	44.440.36	0.11	36.360.30		0.15	30.770.26		0.20	26.670.22		0.25	22.22	
	0.8	0.66	0.05	66.670.57	0.07	57.140.50		0.11	50.000.44		0.15	44.440.38		0.20	38.10	
	1.2	0.77	0.03	77.420.68	0.05	68.570.61		0.08	61.540.55		0.12	55.81 0.5		0.16	50.00	
	1.5	0.83	0.02	83.330.75	0.04	75.000.68		0.07	68.180.62		0.10	62.500.55		0.14	55.56	
	1.9	0.86	0.02	86.000.79	0.04	79.000.73		0.06	73.000.69		0.08	69.000.63		0.12	63.33	

trations of inhibitors at different temperatures (298,303, 313, 323 and 333 K) was studied to calculate the thermodynamic parameters. The values of inhibition efficiency decreased with increasing temperature as shown in Figure 1 and TABLE 4, so the effect of these inhibitors appears to be solution temperature dependent. This fact can be attributed to the decrease in the strength of adsorption process at high temperatures, which led to desorption of the inhibitor molecules from the steel surface, meaning that, greater area of metal will be exposed to aggressive solution. This behavior suggests the formation of an adsorptive film of a physical character.

Thermodynamic parameters for the corrosion process

Thermodynamic parameters are important to study the inhibitive mechanism. The thermodynamic functions for dissolution of carbon steel in the absence and in the presence of various concentrations of the inhibitors were obtained by applying the Arrhenius and the transition state equations[28-31].

It is found that almost all the regression coefficients between ln *k* and 1/*T* (Figure 2), are very close to 1, indicating a good linear relationship between ln *k* and 1/*T*. This means that the carbon steel corrosion in hydrochloric acid can be elucidated using the kinetic model.

The rate of corrosion (*k*) was calculated by the following equation:

$$k = W / S\,t \quad (4)$$

where *W* is the average weight loss of three parallel carbon steel sheets, *S* is the total area of the specimen and *t* is the immersion time.

The activation energy of the metal dissolution reaction was calculated using Arrhenius equation[32].

$$\ln k = - E_a / RT + \text{Constant} \quad (5)$$

where *R* is the universal gas constant; *k* is the average corrosion rate and *T* is the absolute temperature.

Plots of ln the corrosion rate (k) against the reciprocal of the absolute temperature (1/*T*) were drawn graphically to obtain the activation energy, E_a from the slope of this plot.

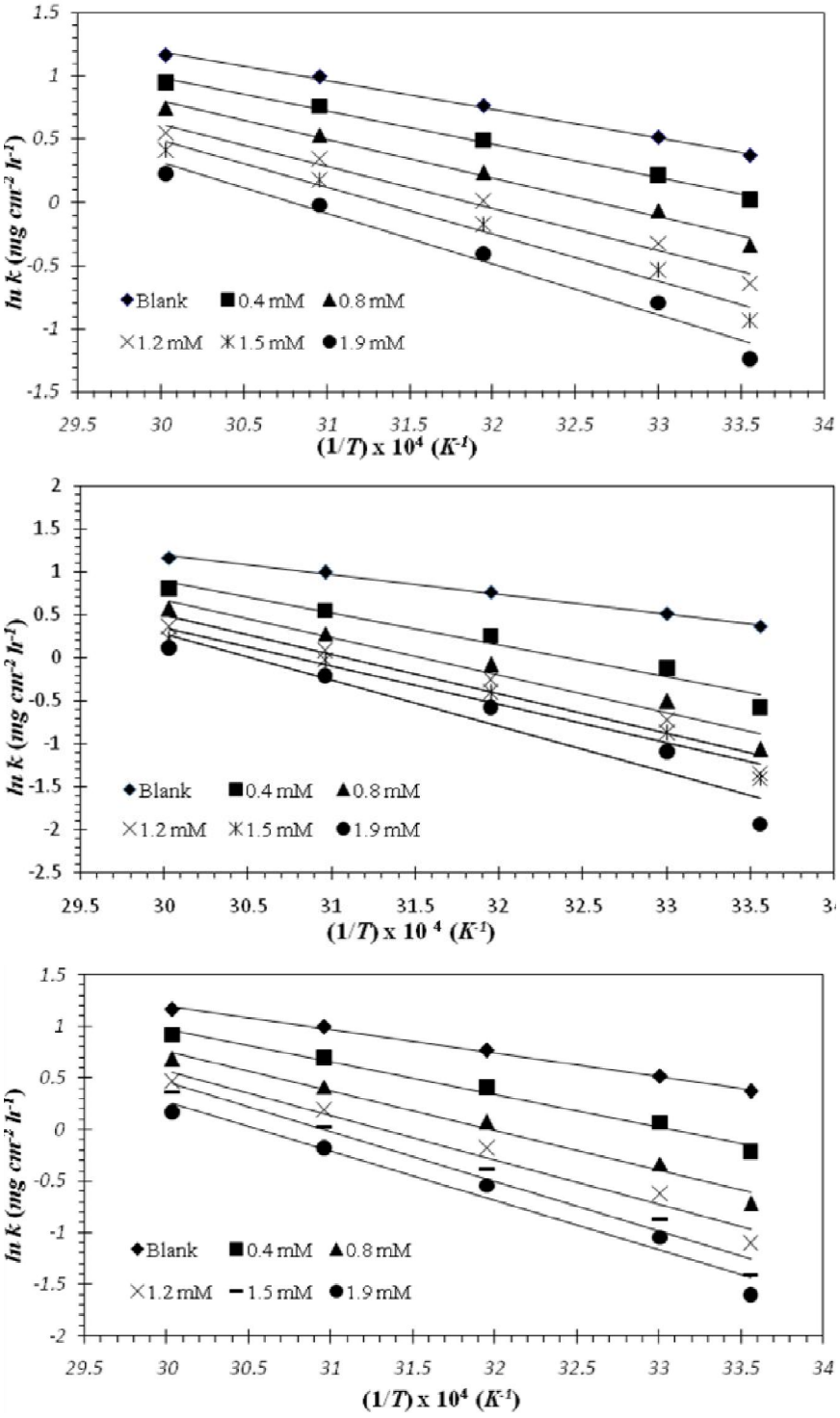


Figure 2 : Arrhenius plots of ln k versus 1/T for carbon steel dissolution in 1M HCl in the absence and the presence of different concentrations of the inhibitors a) S_1, b) S_2 and c) S_3 at different temperatures.

From the Arrhenius plots Figure 2, the obtained data reveal that the increase of activation energy in presence of the inhibitor indicated that a physical adsorption (electrostatic) occurs in the first stage[33]. This behavior was because corrosion primarily occurs at surface sites free of adsorbed inhibitor molecules, and the increase in activation energy leads to an increase in the energy barrier for the carbon steel corrosion[34]. From TABLE 5, it can be found that, the E_a values in absence of the prepared inhibitors were less than in their presence and

that, the E_a values increased by increasing the concentration of the inhibitors. The higher E_a value in the inhibited solution can be correlated to the increased thickness of the electrical double layer, which enhances the activation energy of the corrosion process. In other words, the increase in the activation energy increases the energy barrier which tries to prevent the corrosion process and enhances the inhibition process.

and S_3 compounds. Such variation is concerned with the phenomenon of ordering and disordering of the inhibitor molecules at the electrode surface. The negative values of ΔS^* also suggest an increasing in ordering takes place in going from reactants to the metal/solution interface, which is the driving force for the adsorption of inhibitors onto the carbon steel surface[37].

TABLE 5 : The values of activation parameters E_a, "H* and "S* of the prepared inhibitors on carbon steel in 1M HCl

Surfactant	Conc. (mM)	Correlation Coefficient, R^2 (ln k # 1/T)	E_a (kJ mol^{-1})	Correlation Coefficient, R^2 (ln k/T # 1/T)	?H* (kJ mol^{-1})	?S* (J mol^{-1} K^{-1})
Blank	0	0.997	18.83	0.995	16.21	-187.26
	0.4	0.994	22.03	0.993	19.41	-179.34
	0.8	0.988	25.17	0.985	22.56	-171.51
S_1	1.2	0.982	27.74	0.978	25.12	-165.30
	1.5	0.975	30.70	0.970	28.08	-157.52
	1.9	0.973	33.26	0.968	30.65	-151.29
	0.4	0.962	30.90	0.954	28.28	-153.57
	0.8	0.958	36.34	0.951	35.30	-139.08
S_2	1.2	0.943	37.91	0.934	34.30	-135.86
	1.5	0.958	36.91	0.951	41.87	-140.06
	1.9	0.919	44.49	0.91	41.87	-117.93
	0.4	0.986	26.16	0.982	23.54	-167.11
	0.8	0.981	32.04	0.977	29.43	-151.23
S_3	1.2	0.970	35.81	0.965	33.19	-141.49
	1.5	0.972	40.07	0.968	37.45	-122.96
	1.9	0.967	39.72	0.962	37.11	-132.28

Figure 3 shows the Arrhenius plots from the transition state theory and the values thus obtained from this figure are recorded in TABLE 5.

Enthalpy and entropy of activation ($\Delta H^*$and ΔS^*) were calculated from the transition state theory[35,36].

$$ln(k/T) = [ln(R/N_A h) + (\Delta S^*/R)] - \Delta H^*/RT \quad (6)$$

where N_A is Avogadro's number and h is Planck's constant.

The plot of ln (k/T) versus 1/ T yielded straight lines with a slope of (-ΔH^*/ R) and an intercept of [ln (R/ $N_A h$) + (ΔS^*/ R)].

Inspection of data listed in TABLE 5 reveals that, the activation parameters (E_a and ΔH^*) of dissolution of carbon steel in 1M HCl in presence of the inhibitors are higher than that in their absence. On comparing the values of the entropy of activation (ΔS^*), it is clear that less negative values are obtained in presence of S_1, S_2

Adsorption isotherm

Basic thermodynamic information on interaction between inhibitor molecules and metal surface can be provided by adsorption isotherm. The type of inhibitor adsorption (chemisorption or physisorption) can be determined using thermodynamic data obtained from isotherms.

In order to obtain adsorption isotherm, the surface coverage values (θ) for different concentrations of the prepared sulfanilamides in 1M HCl solution have been obtained from weight loss measurements and tested graphically for fitting a suitable adsorption isotherm. The plot of C/ θ versus C (Figure 4) gave a linear relationship with correlation coefficient of 0.9998 and the slope closed to 1 providing that the adsorption of the prepared sulfanilamides obeys Langmuir adsorption isotherm, which is presented by the following equation:

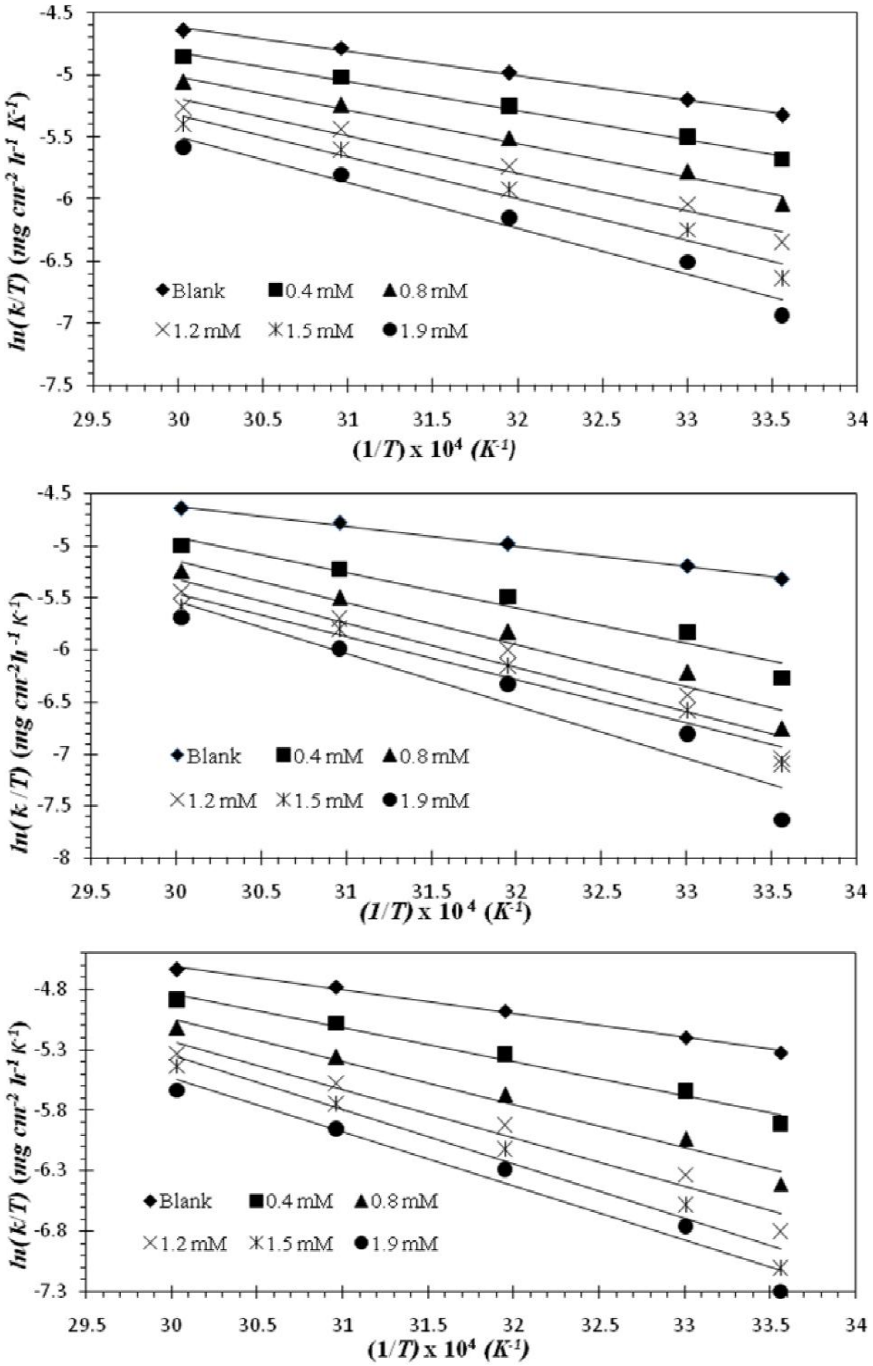


Figure 3 : Arrhenius plots of ln k/T versus 1/T for carbon steel dissolution in 1M HCl in absence and presence of different concentrations of the inhibitors a) S_1, b) S_2 and c) S_3 at different temperatures (to obtain ΔH^* from the slope and ΔS^* from the intercept).

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

where C is the inhibitor concentration, θ is the degree of coverage on the metal surface and K_{ads} is the equilibrium constant for the adsorption-desorption process.

The value of the equilibrium constant, K_{ads} can be calculated from the reciprocal of the intercept of the isotherm line[38].

The slopes of the straight lines obtained from the plots of Langmuir isotherm for S_1, S_2 and S_3 are all near the unity especially S_2. The order of increasing the slope is as follows $S_1 < S_3 < S_2$. This order proves the good performance of S_2 in covering the steel surface protecting it from the corrosive environment.

The adsorption-desorption equilibrium constant

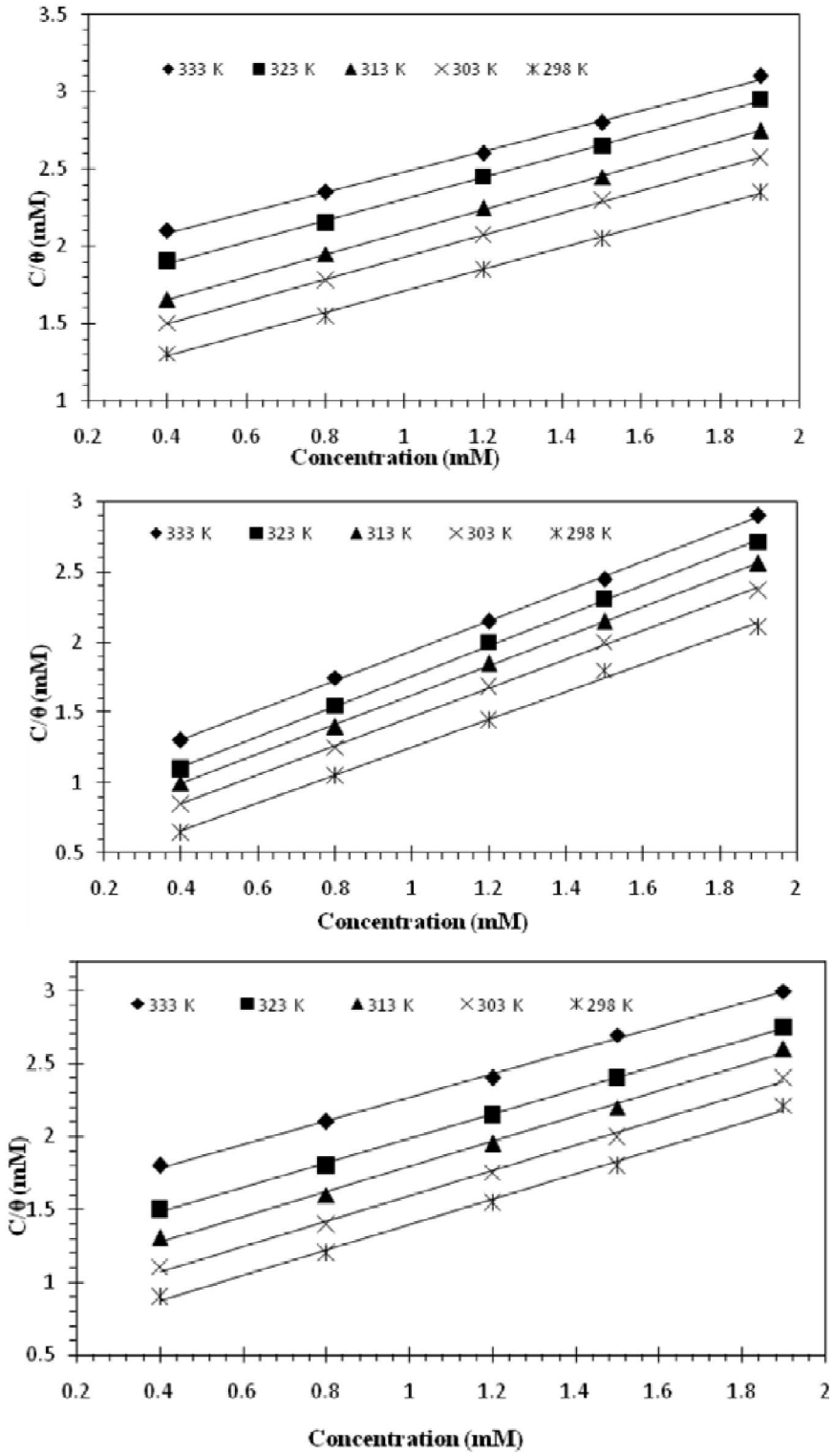


Figure 4 : Langmuir adsorption isotherm for the inhibitors a) S_1, b) S_2 and c) S_3 on carbon steel surface in 1 M HCl at different temperatures.

(K_{ads}) is related to the standard free energy of adsorption (ΔG^0_{ads}) by the equation:

$$\Delta G^o_{ads} = -RT \ln (55.5\ K_{ads}) \quad (8)$$

where R is the universal gas constant; T is the absolute temperature and the value 55.5 is the molar concentration of water in solution in mol dm^{-3}. The enthalpy of adsorption (H^o_{ads}) was calculated from the Gibbs-Helmholtz equation[39]:

$\Delta G^{o}_{ads} / T = (\Delta H^{o}_{ads} / T) + A$ (9)

where A is a constant. The variation of "G^{o}_{ads} / T with 1/ T gives a straight line with a slope that equals (ΔH^{o}_{ads}). Then the standard adsorption entropy (ΔS^{o}_{ads}) was obtained using the thermodynamic basic equation: ΔS_{ads} = $(\Delta G_{ads} - \Delta H_{ads}) / T$ (10)

TABLE 6 shows negative values of ΔG^{o}_{ads}. The absolute values of ΔG^{o}_{ads} are less than -40 kJ mol^{-1}. Indicating that there are electrostatic interaction between the inhibitor molecules and the metal surface (physisorption, physical adsorption)[38,40].

cal or a chemical interaction is the adsorption enthalpy. Figure 5 shows the variation of "GÚ$_{ads}$ / T with 1/T which gives a straight line with a slope equals to ÄH_{ads} and correlation coefficients equal to 0.928, 0.998 and 0.998 for S_1, S_2 and S_3 respectively, indicating a good relationship. It is clear that,ΔG_{ads} / T decreases linearly with 1/T. The negative values of ÄH_{ads} indicates that, the adsorption of the prepared inhibitors was an exthothermic process. Generally, an exothermic adsorption process signifies either physisorption or chemisorption while endothermic process is attributable un-

TABLE 6 : Thermodynamic parameters for the adsorption of the prepared inhibitors at different temperatures

Inhibitors	Temperature (K)	Correlation Coefficient, R^2 (C/θ # C)	Slope	K_{ads} (mol^{-1})	? G^{o}_{ads} (kJ mol^{-1})	Correlation Coefficient, R^2 (? G^{o}_{ads} # 1/T)	? H^{o}_{ads} (kJ mol^{-1})	? S^{o}_{ads} (J mol^{-1} K^{-1})
	333	0.998	0.6618	548.85	-28.58			-58.49
	323	0.999	0.7026	623.05	-28.07			-58.69
S_1	313	0.999	0.7303	734.21	-27.62	0.928	-9.107	-59.16
	303	0.999	0.7213	827.13	-27.04			-59.19
	298	0.999	0.7026	943.40	-27.05			-60.22
	333	0.999	1.0547	1128.03	-30.58			-36.99
	323	0.999	1.0787	1496.33	-30.42			-37.64
S_2	313	0.999	1.0503	1781.58	-29.87	0.998	-18.26	-37.08
	303	0.999	1.027	2320.72	-29.58			-37.35
	298	0.999	0.9914	2777.78	-30.38			-40.68
	333	0.997	0.8096	684.46	-29.19			-33.74
	323	0.999	0.8394	855.43	-28.97			-34.08
S_3	313	0.999	0.8659	1054.30	-28.63	0.998	-17.96	-34.08
	303	0.999	0.8671	1336.01	-28.33			-34.22
	298	0.999	0.8694	1538.46	-28.67			-35.94

The high values of K_{ads} for the studied ethoxylated sulfanilamides indicated stronger adsorption on the carbon steel surface in 1.0 M HCl solution. The higher the K_{ads} value (≥□ 100 M^{-1}), the stronger and more stable adsorbed layer is formed, which increases the inhibition efficiency[37]. The investigated compounds follow the order $S_1 < S_3 < S_2$ with K_{ads} range values (548.85-943.40 M^{-1}) < (684.46-1538.46 M^{-1}) < (1128.03-2777.78 M^{-1}) respectively. The values of K_{ads} decreased as temperature increased (TABLE 6), which indicates the presence of a rearrangement and detachment of the corrosion inhibitor molecules from the metallic surface with a consequent decay in inhibitor efficiency[41].

Another parameter that has been used to determine whether a process may be associated to a physi-

equivocally to chemisorption. In the present work, enthalpy absolute values were lower than 41.8 kJ mol^{-1} (9.107 kJ mol^{-1} for S_1, 18.26 kJ mol^{-1} for S_2 and 17.96 kJ mol^{-1} for S_3) which indicates that; physisorption was the process under control. The negative values of entropy (TABLE 6) suggest that adsorption is coupled with a decrease in the system disorder due to the adsorption of inhibitor on the steel surface. Correlation coefficients equal to 0.928, 0.998 and 0.998 for S_1, S_2 and S_3 respectively, indicating the good relationship.

Antibacterial assessment of ethoxylated sulfanilamides

The antimicrobial activities of the three ethoxylated sulfanilamides against *Staphylococcus aureus*,

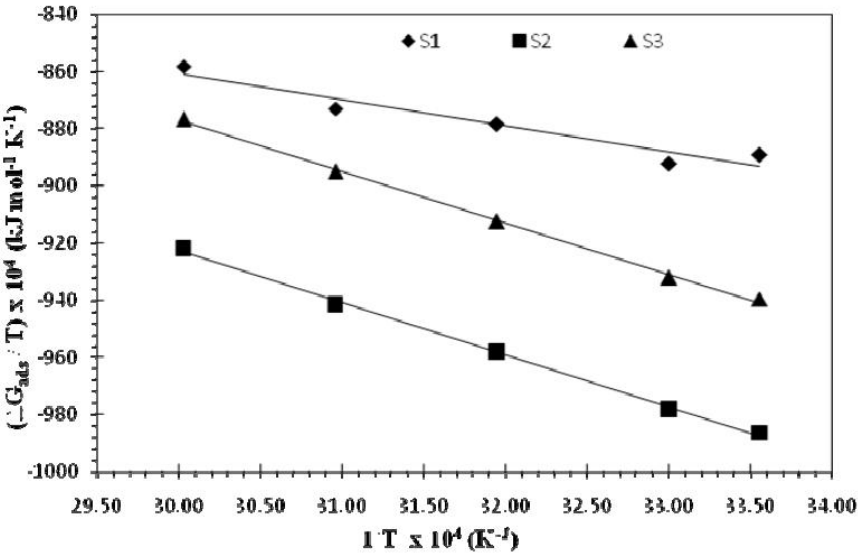


Figure 5 : The Relationship between $\Delta G_{ads}/T$ and 1/T for carbon steel in 1.0 M HCl solution containing different concentrations of compounds S_1, S_2 and S_3

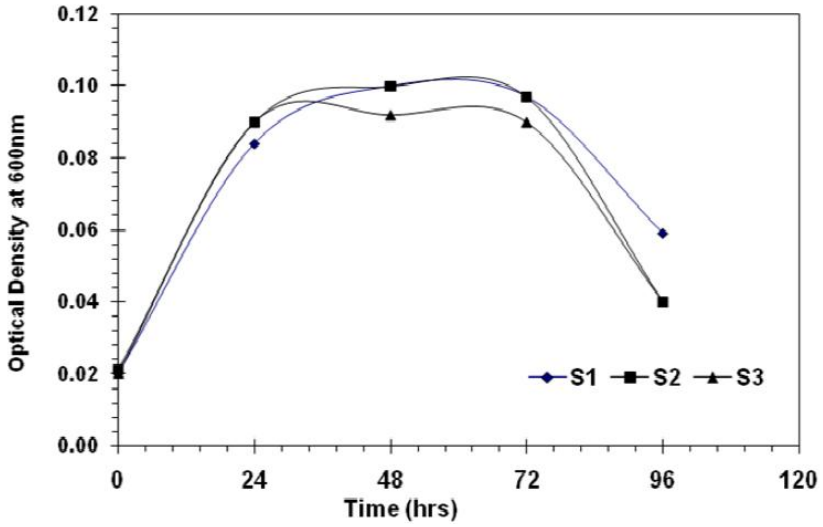


Figure 6 : Antimicrobial activity of the three ethoxylated sulfanilamides S_1, S_2 and S_3 against Staphylococcus Aureus

Pseudomonas aeruginosa and *Escherichia coli* were evaluated by optical density method mentioned previously. A control test was carried out without sulfanilamides.

For *Staphylococcus aureus* S_3 showed the highest activity, whereas S_1 was the highest antimicrobial agent against *Escherichia coli*. In case of *Pseudomonas aeruginosa*, the higher activity belonged to the sulfanilamides S_1 and S_2 equally (Figures 6-8). From the data obtained, it can be concluded that, in gram positive bacteria, the antibacterial activity increased as the ethoxylation units increased, and almost vice versa for gram negative bacteria.

The activity of the three sulfanilamides against the tested organisms was determined depending on the start point of the decline phase of the growth curve plotted.

Concerning mode of action, the sulfanilamides are known to act as competitive enzyme inhibitors and block the biosynthesis of the vitamin folic acid in bacterial cells which is crucial to cell biochemistry. Folic acid is clearly necessary for the survival of bacterial cells. A possible explanation for these observations may lie in the significant differences in the outer layers of Gram-negative and Gram- positive bacteria. Gram-negative bacteria possess an outer membrane and a unique periplasmic space not found in Gram- positive bacteria[42,43]. The resistance of Gram-negative bacteria towards antibacterial substances was related to the hydrophilic surface

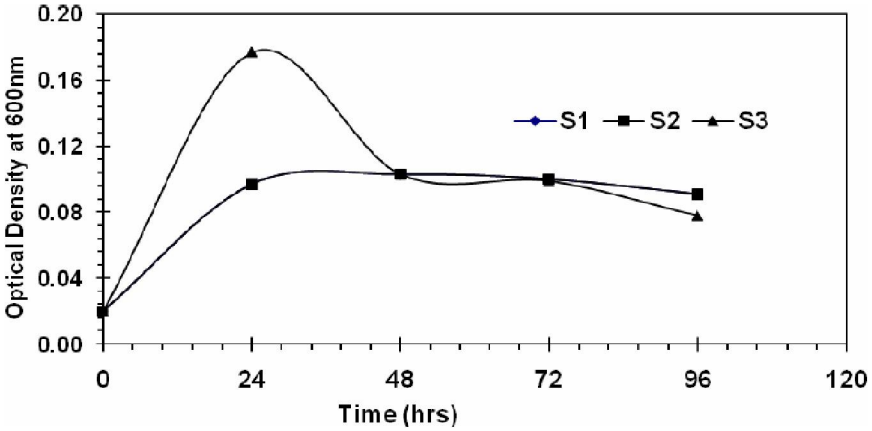


Figure 7 : Antimicrobial activity of the three ethoxylated sulfanilamides S_1, S_2 and S_3 against Pseudomonas Aeruginosa

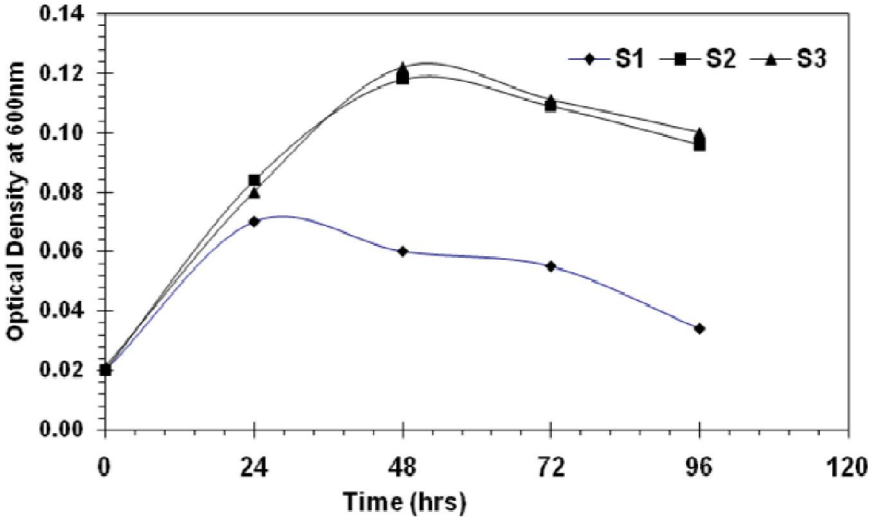


Figure 8 : Antimicrobial activity of the three ethoxylated sulfanilamides S_1, S_2 and S_3 against E. Coli

of their outer membrane which was rich in lipopolysaccharide molecules, presenting a barrier to the penetration of numerous antibiotic molecules and was also associated with the enzymes in the periplasmic space, which are capable of breaking down the molecules introduced from outside[44, 45]. Gram-positive bacteria do not have such an outer membrane and cell wall structure. Antibacterial substances can easily destroy the bacterial cell wall and cytoplasmic membrane, resulting in leakage of the cytoplasm and its coagulation[46].

CONCLUSION

In this study, the inhibition property of S_1, S_2 and S_3 was tested using weight loss technique. According to the results, the prepared compounds are good inhibitors in 1M HCl. Adsorption of the inhibitor molecule onto carbon steel surface obeys Langmuir isotherm. The protection efficiency increased with increasing inhibitor concentration, but decreased slightly with the rise of temperature. The calculated activation energy values indicated that, adsorbed inhibitor molecules create a physical barrier to charge and mass transfer for metal dissolution and hydrogen reduction reaction.

Selection of these compounds as corrosion inhibitors was based on the facts that these compounds contain lone pair of electrons on the N, S and O atoms through which it can adsorbed on the metal surface.

The antimicrobial activity results indicate that (a) S_3 showed relatively better activity against Gram- positive bacteria than Gram- negative bacteria, and (b) S_1, S_2 & S_3 antibacterial activity increased proportionately to the increasing length of the carbon chain between NH groups in case of Gram- negative bacterium *E. coli* which is in agreement with the results of Ozbek[47]. Regarding the highest sensitivity of *Pseudomonas*

aeruginosa, S_1 is the more active sulfanilamide.

REFERENCES

[1] S.Z.Yao, X.H.Jiang, L.M.Zhou, Y.J.Lv and X.Q.Hu; Mater.Chem.and Phys., **104**, 301 **(2007)**.

[2] M.G.Hosseini, M.Ehteshamzadeh, T.Shahrabi; Electrochim.Acta, **52**, 3680 **(2007)**.

[3] J.Aljourani, K.Raeissi, M.A.Golozar; Corros.Sci., **51**, 1836 **(2009)**.

[4] K.S.Jacob, G.Parameswaran; Corros.Sci., **52**, 224 **(2010)**.

[5] Y.Tang, X.Yang, W.Yang, Y.Chen and R.Wana; Corros.Sci., **52**, 242 **(2010)**.

[6] P.Lowmunkhong, D.Ungthararak, P.Sutthivaiyakit; Corros.Sci., **52**, 30 **(2010)**.

[7] R.Hasanov, S.Bilge, S.Bilgiç, G.Gece, Z.Kýlýç; Corros.Sci., **52**, 984 **(2010)**.

[8] R.F.Godec; Electrochim.Acta, **52**, 4974 **(2007)**.

[9] S.Borenstein; Handbook, Woodhead Publishing Ltd., Cambridge, 113–160 **(1996)**.

[10] I.B.Beech, V.Zinkevich, L.Hanjangsit, R.Gubner, R.Avci; Biofoul., **15**, 3 **(2000)**.

[11] I.B.Beech, J.A.Sunner, K.Hiraoka; Internat. Microbiol., **8**, 157 **(2005)**.

[12] R.M.Donlan; Emerging Infectious Diseases, **8**, 881 **(2002)**.

[13] J.W.Costerton, P.S.Stewart, E.P.Greenberg; Sci., **284**, 1318 **(1999)**.

[14] Y.Liua, W.Zhanga, T.Sileikaa, R.Wartaa, N.P.Cianciottob; A.Packmana, Biofoul., **25**, 241 **(2009)**.

[15] A.K.Lee, D.K.Newman, Appl.Microbiol.Biotech., **62**, 134 **(2003)**.

[16] W.Hreczuch, Trathnigg B.Dziwinski, K. Pyzalski; J.Surfact.Deterg., **4**, 167 **(2001)**.

[17] A.M.Al-Sabagh, M.E.Abdul-Raouf, R.Abdel-Raheem; Colloids and Surfaces A: Physicochem. Eng.Aspects, **251**, 167 **(2004)**.

[18] E.Y.Sheu, O.C.Mullins; Asphaltenes: Fundamentals and Applications, Plenum Press, New York, **(1995)**.

[19] R.M.Atlas; Handbook of microbiological media, 3rd Edition, CRC Press LLC, New York, **(2004)**.

[20] Charlotte Bailey, Vicki Barwick; Laboratory Skills, Training Handbook, **(2007)**.

[21] Chemiasoft; Guide to Preparation of Stock Standard Solutions, **(2011)**.

[22] E.Lancaster, A.Villanova; National Committee for Clinical Laboratory Standard, Pensnylvania 19085, USA, **(2000)**.

[23] S.Bellú, E.Hure, M.Trapé, M.Rizzotto; Quim.Nova, **26**, 188 **(2003)**.

[24] S.Mageswari, K.Subramanian; J.Appl.Poly.Sci., DOI: 10.1002/app.36462, **(2012)**.

[25] T.Du, J.Chen, D.Cao; J.Mater.Sci., **36**, 3903 **(2001)**.

[26] N.A.Negm, A.M.Al Sabagh, M.A.Migahed, H.M.Abdel Bary, H.M.El Din; Corros.Sci., **52**, 2122 **(2010)**.

[27] A.M.Badawi, M.A.Hegazy, A.A.El-sawy, H.M.Ahmed, W.M.Kamel; Mater.Chem.and Phys., **124**, 458 **(2010)**.

[28] A.Ostovari, S.M.Hoseinieh, M.Peikari, S.R.Shadizadeh, S.Hashemi; Corros.Sci., **51**, 1935 **(2009)**.

[29] Z.Wei, P.Duby, P.Somasundaran; J.Colloid Interface Sci., **259**, 97 **(2003)**.

[30] X.H.Li, S.D.Deng, H.Fu, G.N.Mu; Corros.Sci., **50**, 2635 **(2008)**.

[31] N.M.Guan, L.Xueming, L.Fei; Mater.Chem.and Phys., **86**, 59 **(2004)**.

[32] N.A.Negm, M.F.Zaki, M.M.Said, S.M.Morsy; Corros.Sci., **53**, 4233 **(2011)**.

[33] H.A.Sorkhabi, B.Shaabani, D.Seifzadeh; Appl.Surf.Sci., **249**, 408 **(2005)**.

[34] L.G.Qiu, Y.Wu, Y.M.Wang, X.Jiang; Corros.Sci., **50**, 576 **(2008)**.

[35] D.K.Yadav, B.Maiti, M.A.Quraishi; Corros.Sci., **52**, 3586 **(2010)**.

[36] M.A.Hegazy, A.S.El-Tabei, A.H.Bedair, M.A.Sadeq; Corros.Sci., **54**, 219 **(2012)**.

[37] I.Ahamad, R.Prasad, M.A.Quraishi; Corros.Sci., **52**, 933 **(2010)**.

[38] E.S.Meresht, T.S.Farahani, J.Neshati; Corros.Sci., **54**, 36 **(2012)**.

[39] A.K.Singh, M.A.Quraishi; Corros.Sci., **52**, 152 **(2010)**.

[40] I.B.Obot, N.O.Obi-Egbedi, S.A.Umoren; Corros.Sci., **51**, 1868 **(2009)**.

[41] E.A.Flores, O.Olivares, N.V.Likhanova, M.A.D.Aguilar, N.Nava, D.Guzman-Lucero, M.Corrales; Corros.Sci., **53**, 3899 **(2011)**.

[42] H.Nikaido, Cellular, Molec.Biology, F.C.Neidhardt, (Ed.); American Society for Microbiology Press, Washington, D.C., **(1996)**.

[43] C.F.Duffy, R.F.Power; Inter.J.Antimicrob.Agents, **17**, 527 **(2001)**.

[44] A.D.Russell; J.Appl.Bacteriology, **71**, 191 **(1991)**.

[45] Y.Gao, M.J.van Belkum, M.E.Stiles; Appl.and Environ.Microbiology, **65**, 4329 **(1999)**.

[46] D.Kalemba, A.Kunicka; Current Med.Chem., **10**, 813 **(2003)**.
[47] N.Ozbek, H.Katýrcýoglu, N.Karacan, T.Baykal; Bioorg.& Med.Chem., **15**, 5105 **(2007)**.