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Adsorption and inhibitive impact of 5-[4-(dimethylamino) benzylidene]-1,3-dimethylbarbituric acid on carbon steel corrosion in molar hydrochloric acid solution

ABSTRACT

The inhibiting impact of ecofriendly 5-[4-(dimethylamino) benzylidene]-1,3-dimethylbarbituric acid in 1 M HCl on the corrosion for carbon steel has been examined via “weight loss (WL) method, potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS), electrochemical frequency modulation (EFM) tests”. The attained outcomes exhibit that the investigated compound is excellent inhibitor and its inhibition efficiency (%IE) rises by raising concentration and decreases by raising the temperature. The adsorption of 5-arylidene barbituric acid on the surface of C-steel follows Langmuir isotherm. The adsorption process of the investigated compound is spontaneous and considered as of chemisorption and physisorption type. PP curves revealed that the 5-arylidene barbituric acid derivative is mixed-type inhibitor. Moreover, EIS results confirmed the adsorption of the investigated compound on C-steel surface via increasing on charge transfer resistance (R_{ct}). The IE% of this inhibitor reached to 86.9% at concentration 21×10^{-6} M according to PP method. Finally, the experimental and theoretical results are in good harmony.

***Keywords**: Carbon steel, HCl, EFM, EIS, 5-Arylidene barbituric acid derivative.*

1. INTRODUCTION

Acidic media are generally applied for elimination of unwanted scale and corrosion in several industrial procedures. By monitoring metal dissolution attributable to acidic exposure, so inhibitors are commonly applied within these operations [1]. Organic inhibitors today do the inhibition of corrosion well than the inorganic inhibitors [2]. Organic compounds are kind of acidic inhibitors including hetero atoms for example oxygen , sulfur, and nitrogen. Amongst, organic inhibitors have several advantages for instance low value, low poisonousness, high inhibition efficiency, and easy to organize [3-6]. Generally, heterocyclic organic compounds are applied to the corrosion inhibition on copper [7] aluminum [8-10], iron [11-16] and also other metals [17-18] within diverse corrosion media. A review of the literature on acid corrosion inhibitors reveals that they work by adsorbing to the metal's surface.

This effect may be caused by electrostatic attraction between the charged metal and the charged inhibitor molecules, (ii) dipole-type interaction between uncharged electron pairs in the inhibitor and the metal, (iii) electron-interaction with the metal, or (iv) a combination of the aforementioned [19]. Pyrimidine is a six-membered heterocyclic aromatic compound with two nitrogen atoms at positions 1 and 3. The chemistry of pyrimidine derivatives is crucial in medicine, agrochemicals, and a variety of biological activities. Many well-known commercial medications contain pyrimidine derivatives, such as Uramustine, Piritrexim, Isetionate, Tegafur, Floxuridine, Fluorouracil, Cytarabine, and Methotrexate. Furthermore, the pyrimidine skeleton is found in a wide range of natural products, including nucleic acids, vitamins, enzymes, chlorophyll, haemoglobin, and hormones. “Ansari el al [20] investigate the corrosion protection of mild steel by four PPDs namely 5-phenyl-1,3,5,6,8-pentahydro-pyrimido[4,5-d] pyrimidine-2,4,7-trione (PPD-4), 5-(4-methoxyphenyl)-1,3,5,6,8-pentahydropyrimido [4,5-d] pyrimidine-2,4,7-trione (PPD-3), 5-phenyl-1,3,5,6,8-pentahydro-7-thioxo-pyrimido[4,5-d] pyrimidine-2,4-dione (PPD-2), and 5-(4-methoxyphenyl)-1,3,5,6,8-pentahydro-7-thioxo-pyrimido

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[4,5-d] pyrimidine-2,4-dione (PPD-1) in 1M HCl solution and they found the percentage inhibition efficacy 88-97.1% at 400 mg L^{-1}". Numerous pyrimidine derivatives have been synthesized and studied their suitability for corrosion inhibition of variety of steel samples in acidic medium. The effect of many pyrimidine derivatives namely, 2-aminopyrimidine, 4,6-dihydroxypyrimidine,2,4-diaminopyrimidine, 2,4-diamino-6-hydroxypyrimidine, 2,4,6-triaminopyrimidine, 4,6-diamino-2-mercaptopyrimidine [21,22], 2,6-dimethylpyrimidine-2-amine, *N*-Benzylidene-4,6-dimethylpyrimidine-2-amine and 2-[(3,6-Dimethyl pyridimine-2-ylimino)methyl]-4-nitrophenol [23] in 2M HCl; thymine, uracil, thymidine and uridine [24], 4,6-dihydroxy-2-mercaptopyrimidine[25], 5-(3,4,5-trimethoxybenzyl) pyrimidine-2,4-diamine [26], benzylidene-pyrimidin-2-yl-amine, (4-methyl-benzylidene)-pyrimidine-2-yl-amine and (4-chloro-benzylidene)-pyrimidine-2-yl-amine [27], 4-((4,6-dimethylpyrimidin-2-ylimino)-methyl) chlorobenzene, 4-((4,6-dimethylpyrimidin-2-ylimino)methyl)-*N,N*- dimethylaniline, 4-((4,6-dimethylpyrimidin-2-ylimino)methyl)phenol [28], ethyl (2-amino-5-methyl[1,2,4]-triazolo[1,5-*a*]pyrimidin-7-yl)acetate, ethyl (5-methyl[1,2,4] triazolo [1,5-*a*]pyrimidin-7-yl)-acetate [29], The efficacy of the organic compounds including hetero atoms as corrosion inhibitors in acidic solutions for C-steels is well recognized [30-34]. Pyrimidines and their derivatives are important because they are available in nature, particularly in the nucleobases present in nucleic acids, and many of them have been discovered to be beneficial in chemotherapy [35]. Currently in use as anticancer, antifungal, and antibacterial medicines are pyrimidine-containing chemotherapeutics [36]. Furthermore, in HCl and H_2SO_4 solutions, several pyrimidine derivatives were found to be efficient corrosion inhibitors for steel [37].

The purpose of this work is to study the impact of 5-[4-(dimethylamino) benzylidene]-1,3-dimethylbarbituric acid as ecofriendly inhibitor for C-steel in 1M hydrochloric acid solution by applying WL, PP, EIS, EFM tests. The investigated 5-arylidene barbituric acid derivative is not reported as a corrosion inhibitor for steel in the literature.

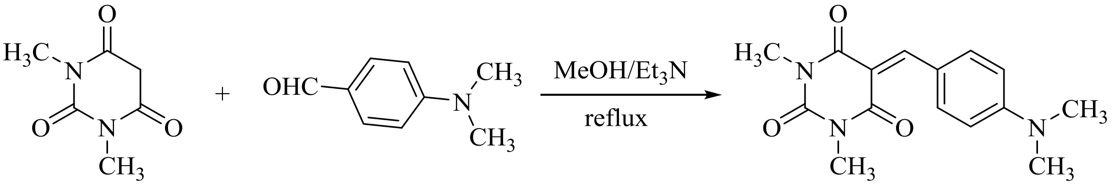
2. MATERIALS AND METHODS

2.1. Materials

Chemical conformation of C-steel samples in weight percentage are carbon (0.200%); manganese (0.350%); phosphor (0.024%); chromium; sulfur (0.003%); and balance iron.

2.2. Inhibitor

5-Arylidene barbituric acid derivative (**3)** was prepared as outlined in scheme 1. The detailed information of 5-[4-(dimethylamino) benzylidene]-1,3-dimethylbarbituric acid (**3**) was prepared on treatment of 1,3-dimethylbarbituric acid (**1**, 2.5 mmol) with 4(N,N-dimethylamino) benzaldehyde (**2**, 2.5 mmol) in 20mL methanol at reflux, in the presence of triethyl amine as a catalyst to afford compound 3 as an orange-red solid in 91% yield, mp 239–241 °C (EtOH/ EtOAc). Lit. mp 240-242 ^{o}C [38, 39]. IR (KBr) v' 3082 (sp^2 C-H stretch), 2922, 2871 (sp^3 C-H stretch), 1713, 1659, 1651 (CO stretch), 1608, 1570, 1558 (C=C stretch) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz); δ 3.15 (s, 3H, 2N-Me), 3.40 (s, 6H, 2N-Me), 6.71 (d, J = 9.3 Hz, 2H, 1,4-disubstituted benzene), 8.41 (d, J = 9.3 Hz, 2H, 1,4-disubstituted benzene), 8.43 (s, 1H, methine-H). Molecular Formula $C_{15}H_{17}N_3O_3$ (287.31)



Scheme 1. Synthetic route of the 5-aryldine barbituric acid derivative

Šema 1. Sintetički put derivata 5-arildin barbiturne kiseline

2.3. Aqueous solutions

The corrosive solutions, 1M hydrochloric acid were prepared by dilution of the analytical grade 37% hydrochloric acid via bi-distilled water, and the concentration ranges of applied inhibitors are 1×10^{-6} - 21×10^{-6} M.

2.4. Weight loss (WL) method

Seven identical pieces of C-steel have 2.5 × 2.0 × 0.06cm^2 are polished by abrasive paper (grades 320–1200) then washed by bi-distilled water. The pieces were weighted and submerged in 100 ml beaker including 100 ml of hydrochloric acid without and with diverse concentrations of the examined inhibitor.

Corrosive acid solutions are wide open to air. After each 30 min, pieces were ejected, cleaned, dry up, then weighed perfectly for 3h. The θ, and IE % of the examined inhibitors are calculated from the subsequent equation [40]:

$$IE\% = \theta x 100 = \left[1 - \frac{W}{W^{o}}\right] x 100 \qquad (1)$$

where, W° and W are the values of the average weight loss without and with adding of the inhibitor, separately.

2.5. Electrochemical techniques

Electrochemical measurements are taken within traditional three electrode glass cell including saturated calomel electrode (SCE) linked with fine "Luggin capillary, platinum counter electrode and working electrode is carbon steel with a square cut shape and surface area of 1.0×1.0 cm^2. PP curves are established through altering the electrode potential automatically from -1000 to +00 mV vs. OCP with a sweep rate of 1 mVs^{-1}. Stern-Geary method [41] applied the definition of corrosion current is achieved via deducing on cathodic and anodic Tafel lines to a point which provides log i_{corr} and the resulting E_{corr} for inhibitor free acid and to any concentration of inhibitor". Thereafter i_{corr} can be applied to examine of θ and IE % as subsequent:

$$IE\% = \Theta \ x \ 100 = [1 - i_{corr(inh)} / i_{corr(free)}] \qquad (2)$$

where, "$i_{corr(free)}$ and $i_{corr(inh)}$ are the corrosion current densities at the absence and existence of inhibitor", separately.

EIS are applied within range of frequency from 100kHz to 10mHz and 10mV amplitude peak-to-peak at Ocp. The θ and the IE% achieved from the impedance calculation were assessed through the next equation:

$$IE\% = \theta x 100 = \left[1 - \frac{R^{o}_{ct}}{R_{ct}}\right] x 100 \qquad (3)$$

where, "R^{o}_{ct} and R_{ct} are the resistance of charge transfer at the absence and existence of inhibitor", separately.

EFM tests were accomplished via dual frequencies "2 and 5Hz with base frequency 0.1Hz, consequently the wave shape repeats subsequently at 1s. The large peaks located in the intermodulation spectra were utilized to assess the corrosion current density (i_{corr}), the Tafel slopes (β_a and β_c) and CF-2 & CF-3" [42,43], the %IE and θ were assessed from Equation (2).

All electrochemical experiments are ready solution at 25 ±1°C. The potential of electrode can be permitted until become stable 30 min prior to start the measurements. All electrochemical experiments were done at 25 ±1°C and accomplished via Gamry (PCI4/ 750G) Potentiostat/Galvanostat/ZRA. This includes Gamry Framework for controlling and Echem Analyst5.58 software for data analysis and plotting.

3. RESULTS AND DISCUSSION

3.1. Weight loss (WL) method

The WL-time diagrams for the corrosion of C-steel in 1 M hydrochloric solution before and after addition of diverse concentrations of the investigated compound are displayed within Fig. 1. Fig. 1 demonstrates that the values of WL for C-steel with 1M hydrochloric acid solution lies higher than in inhibitor and the WL decreases as inhibitor dose rises; It meaning the strengthens of corrosion inhibition by increasing the inhibitor concentration as listed in Table (1) .This explains the adsorption of inhibitor molecule on the C-steel surface, i.e. the C-steel surface is shielded from the aqueous media through creation of protecting film on this surface [44, 45].

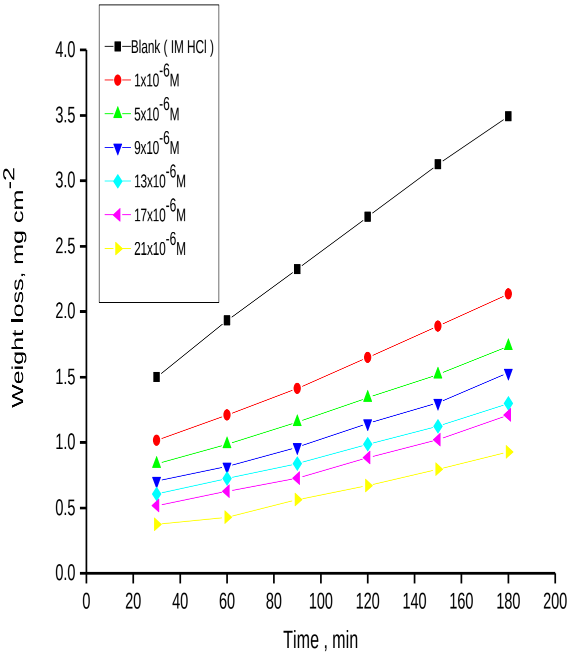


Figure 1. Time-WL bends for C-steel in 1M HCl in the absence and presence of diverse doses of 5-Arylidene barbituric acid derivative at 25°C

Slika 1. Vreme-VL se savija za C-čelik u 1M HCl u odsustvu i prisustvu različitih doza derivata 5-ariliden barbiturne kiseline na 25°C

Table 1 Variation of %IE with altered doses of investigated 5-Arylidene barbituric acid derivative at 25^{o}C from WL measurements at 120 min dipping in 1M HCl.

Tabela 1. Varijacija %IE sa izmenjenim dozama ispitivanog derivata 5-ariliden barbiturne kiseline na 25^{o}C iz VL merenja na 120 min potapanjem u 1M HCl.

%IE	CR (mg cm^{-2} min^{-1})	Conc. (M)
---	0.028	---
35.7	0.018	1x10^{-6}
46.4	0.015	5x10^{-6}
57.1	0.012	9x10^{-6}
60.7	0.011	13x10^{-6}
67.9	0.009	17x10^{-6}
75.0	0.007	21x10^{-6}

3.2. PP studies

Figure 2 illustrates the Tafel polarization diagrams for C-steel in 1 M hydrochloric acid in the absence and existence of 5-Arylidene barbituric acid derivative dose at 25^{o}C. “From Fig.2, it is obvious that anodic metal dissolution and cathodic H_2 reduction reactions were controlled when examined 5-Arylidene barbituric acid derivative was added to 1 M HCl solution also this inhibition was more obvious through rising dose of inhibitor. Table 2 illustrates that i_{corr} declines via addition of the inhibitor and through raising their doses. Furthermore, E_{corr} does not change clearly, and this exhibits that the examined derivative is considered as mixed-type inhibitor [46]. Moreover, Tafel slopes [β_a, β_c] are almost constant indicating that the two reactions (i.e., anodic metal dissolution and cathodic hydrogen reduction) were slightly affected without altering mechanism of dissolution [47, 48].

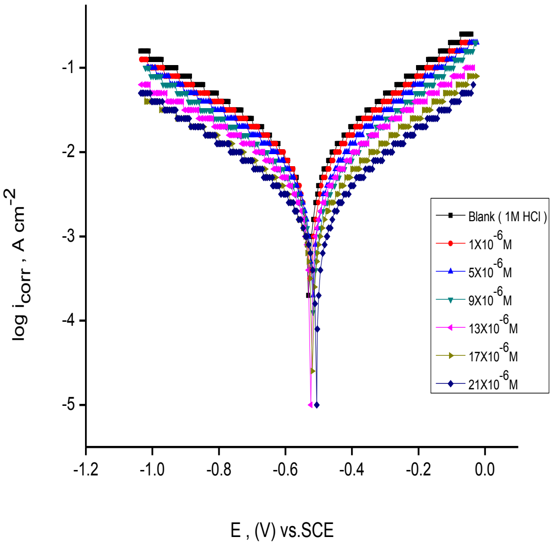


Figure 2. PP diagrams for dissolution of C-steel in 1M HCl in the attendance and absence of altered doses of 5-Arylidene barbituric acid derivative at 25ºC.

Slika 2. PP dijagrami za rastvaranje C-čelika u 1M HCl uz prisustvo i odsustvo izmenjenih doza derivata 5-ariliden barbiturne kiseline na 25^{o}C

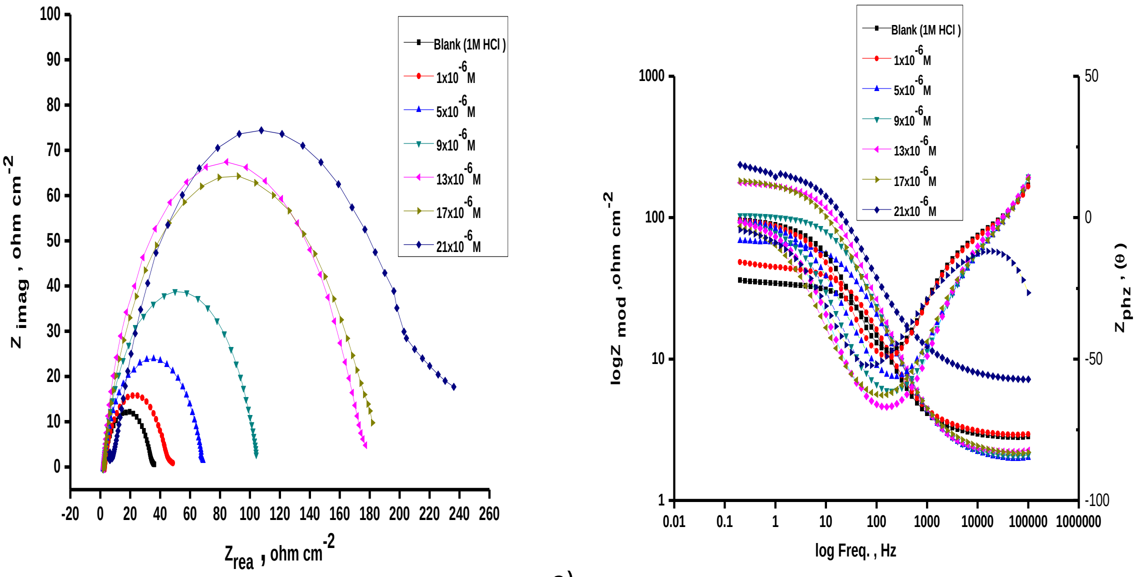
Table 2. Corrosion parameters of C-steel electrode in 1M HCl solution containing altered doses of 5-Arylidene barbituric acid derivative at 25 ^{0}C from PP technique.

Tabela 2. Parametri korozije C-čelične elektrode u 1M rastvoru HCl koji sadrži izmenjene doze derivata 5-ariliden barbiturne kiseline na 25^{0}C iz PP tehnike.

Conc., M	-E$_{corr}$ mV, vs. SCE	i$_{corr}$ (mA cm^{-2})	β_c mV dec $^{-1}$	β_a mV dec $^{-1}$	θ	%IE	CR mmy-1
1 M HCl	587	422	42	22	---	---	220.6
1x10^{-6}	586	300	32	41	0.412	41.2	137.2
5x10^{-6}	564	253	46	33	0.563	56.3	115.8
9x10^{-6}	574	203	85	54	0.658	65.8	92.9
13x10^{-6}	567	152	116	70	0.716	71.6	69.3
17x10^{-6}	566	117	106	76	0.797	79.7	53.5
21x10^{-6}	541	84.0	83	57	0.869	86.9	38.7

3.3. EIS studies

The impact of the doses of inhibitor on the impedance of C-steel in 1M HCl at 25ºC is produced in Fig. 3 [a, b]. “Curves show identical kind of Nyquist bends for C-steel with existence of diverse doses of the investigated inhibitor. Presence of single semi-circle displayed the single charge transfer procedure through dissolution which is unaltered with the existence of inhibitor compound. Deviations from ideal circular form are frequently signalize to the frequency dispersal of impedance interfacial which occurs because of impurities, surface coarseness, grain limits, dislocations, forming of porous layers and adsorption of derivatives, also homogenized on the surface of electrode [49, 50]. Observation of these data detected from all impedance graphs contains of large capacitive circle by only time constant of capacitive with Bode–phase graphs (Fig.3b). The electrical equivalent circuit is displayed in Fig.4 and it applied for examine achieve impedance data. This circuit involves R_{ct}, C_{dl} also the solution resistance (R_s). Fit excellent through this model can be gained through experimental data. EIS outcomes in Table 3 distinguished that C_{dl} values declines as well as R_{ct} values rises by rising doses of inhibitor". It is because of the exchange of the adsorbed water molecules with the inhibitor molecules on the surface of metal, declining the metal dissolution reaction [51, 52]. The diminishing in "C_{dl} can be caused by a drop in the local dielectric constant and/or a rise in the thickness of the double layer electrical suggested that inhibitor molecules function through adsorption at the metal and solution interface [53]. The precision of fitting outputs was assessed using a chi-square test for goodness of fit; the tiny chi-square values (Table 4) obtained for all of the outcomes suggest that the fitted results are very close to the experimental findings. %IE gained from EIS studies are close to those inferred of PP studies".



a) b)

Figure 3. Nyquist (a) and Bode (b) plots for C-steel in 1M HCl at altered doses of 5-Arylidene barbituric acid derivative at 25°C

Slika 3. Nyquist (a) and Bode (b) krive za C-čelik u 1M HCl pri izmenjenim dozama derivata 5-ariliden barbiturne kiseline na 25°C

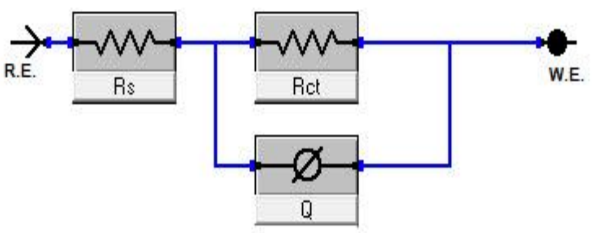


Figure 4. Electrical equivalent circuit model utilized to fit the results of impedance

Slika 4. Model električnog ekvivalentnog kola koji se koristi za uklapanje rezultata impedance

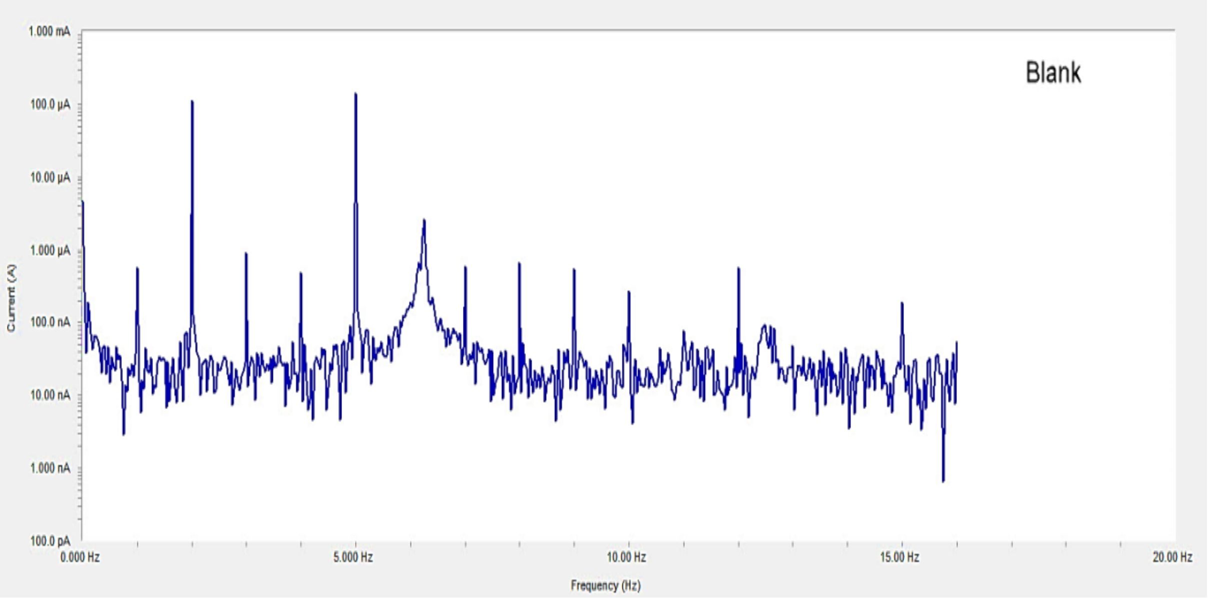
Table 3 EIS data of C-steel in 1M HCl and in existence of altered doses of investigated 5-Arylidene barbituric acid derivative at 25 ºC.

Tabela 3. EIS podaci za C-čelik u 1M HCl i postojanje izmenjenih doza ispitivanog derivata 5-ariliden barbiturne kiseline na 25 şC.

Conc., M	**C_{dl} (μF cm^{-2})**	**R_{ct} (ohm cm^2)**	**θ**	**%IE**
1M HCl	117.9	31.7	---	---
1x10^{-6}	97.2	42.6	0.256	25.6
5x10^{-5}	90.4	65.96	0.528	51.8
9x10^{-5}	84.9	101.4	0.688	68.8
13x10^{-6}	79.4	168.4	0.811	81.1
17x10^{-6}	69.3	176.0	0.821	82.1
21x10^{-6}	66.2	224.0	0.859	85.9

3.4. EFM studies

EFM spectra intermodulation for C-steel in 1M hydrochloric acid solution before and after adding 21x10^{-6}M of 5-Arylidene barbituric acid derivative is displayed in Fig. 5. The bigger peaks were applied to examine i_{corr}, β_c, β_a, CF-2 and CF-3. “Those electrochemical factors are concurrently specified then recorded in Table 4. It can be viewed from this Table 4, the values of i_{corr} diminish with existence of various doses of 5-Arrylidene barbituric acid derivative than with existence only of 1M HCl in situation of C-steel. The obtained Causality factors for the examined data are in excellent quality with their theoretical (2 &3) values”.



21x10^{-6}M of 5-Arylidene barbituric acid derivative

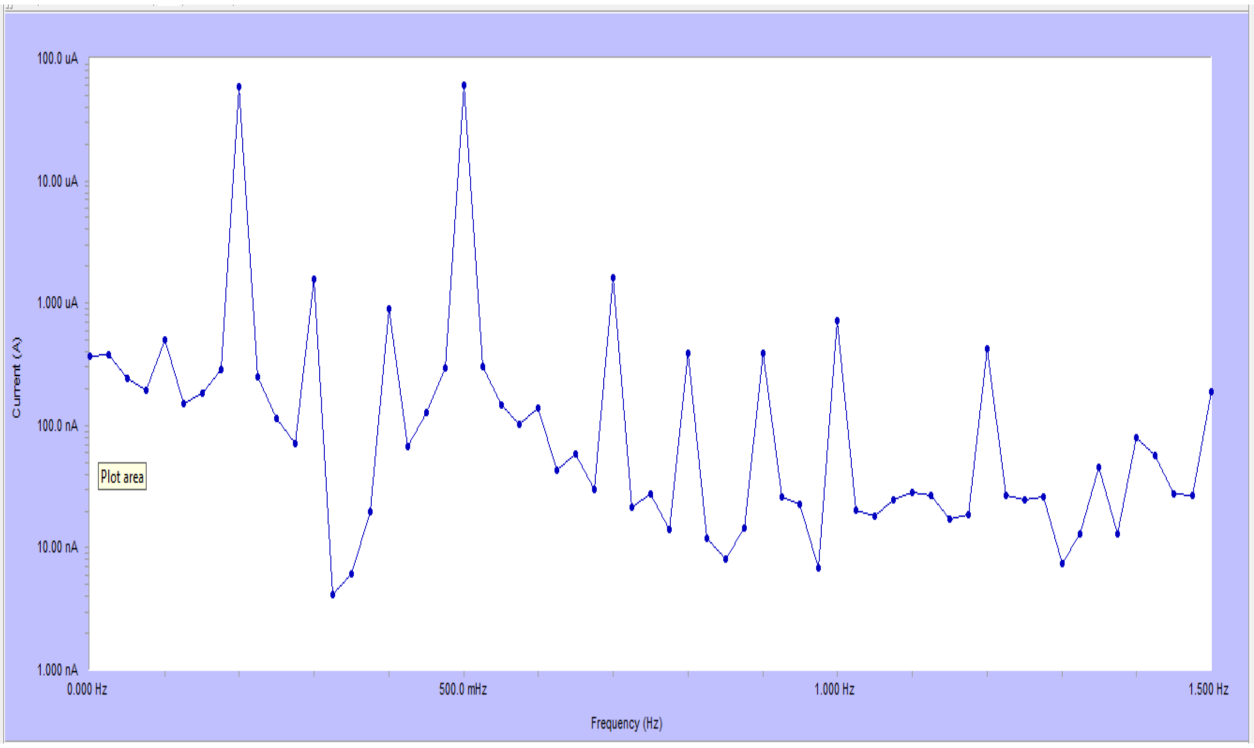


Figure 5. EFM spectra for C–steel in 1M HCl with and without 21x10^{-6} M of 5-Arylidene barbituric acid derivative at 25^{o}C

Slika 5. EFM spektri za C–čelik u 1M HCl sa i bez 21k10^{-6} M derivata 5-ariliden barbiturne kiseline na 25^{o}C

Table 4. EFM parameters for C-steel in 1M HCl solution and existence of altered doses of 5-Arylidene barbituric acid derivative at 25°C

Tabela 4. EFM parametri za C-čelik u rastvoru 1M HCl i postojanje izmenjenih doza derivata 5-ariliden barbiturne kiseline na 25°C

Conc., (M)	**i_{corr} (µA cm^{-2})**	**β_1 (mVdec^{-1})**	**β_2 (mVdec^{-1})**	**CF-2**	**CF-3**	**CR mmy^{-1}**	**% IE**
1M HCl	808.5	113	164	2.09	1.75	370.2	---
1x10^{-6}	505.1	98	134	2.03	2.96	231.8	37.5
5x10^{-6}	375.4	112	119	2.01	3.1	171.5	53.6
9x10^{-6}	219.1	95	108	2.01	2.83	100.2	72.9
13x10^{-6}	140.2	88	150	1.93	3.32	64.1	82.7
17x10^{-6}	132.6	101	104	1.37	2.22	56.5	83.6
21x10^{-6}	129.1	125	158	1.99	2.62	58.9	84.1

3.5. Effectiveness of temperature

Temperature impact on the rate of corrosion of C-steel in 1 M HCl including diverse concentration of the investigated inhibitor can be examined via WL method at temperature ranges of 25 to 55°C (Table 5). The Outcomes discovered that, by raising the temperature the rate of corrosion rises and declines with dose of this compound rises for the investigated inhibitor.

Table 5. Data of WL measurements for C-steel in 1M HCl solution with and without altered doses of 5-Arylidene barbituric acid derivative at 25 – 55°C

Tabela 5. Podaci merenja WL za C-čelik u 1M rastvoru HCl sa i bez izmenjenih doza derivata 5-ariliden barbiturne kiseline na 25 – 55°C

Inhibitor	**Conc., (M)**	**Temp. (°C)**	**CR)mg cm^{-2} min^{-1})**	**θ**	**%IE**
5-Arylidene barbituric acid derivative	Blank 1 M HCl	25	0.028	----	----
		35	0.033	----	----
		45	0.039	----	----
		55	0.045	----	----
	1x10^{-6}	25	0.018	0.357	35.7
		35	0.023	0.286	28.6
		45	0.030	0.212	21.2
		55	0.036	0.187	18.7
	5x10^{-6}	25	0.015	0.493	46.4
		35	0.019	0.399	39.9
		45	0.026	0.329	32.9
		55	0.031	0.306	30.6
	9x10^{-6}	25	0.012	0.569	57.1
		35	0.016	0.496	49.6
		45	0.022	0.427	42.7
		55	0.027	0.398	39.8
	13x10^{-6}	25	0.011	0.628	60.7
		35	0.015	0.545	54.5
		45	0.019	0.491	49.1
		55	0.023	0.469	46.9
	17x10^{-6}	25	0.009	0.671	67.9
		35	0.012	0.626	62.6
		45	0.017	0.544	54.4
		55	0.021	0.519	51.9
	21x10^{-6}	25	0.007	0.754	75.0
		35	0.009	0.707	70.7
		45	0.014	0.628	62.8
		55	0.018	0.603	60.3

The activation energy (E^*_{a}) can be examined by applying Arrhenius equation:

$$k = A e^{\frac{-E_a^*}{RT}} \qquad (4)$$

where, “A is Arrhenius constant and k is rate of corrosion. Straight lines are displayed in Fig. 6.and their linear regression (R^2) are nearer to 1 and E^*_a can be obtained from the slope. Table 6 displayed that the value of E^*_a for uninhibited solution is lower than inhibited solution, supposing that the dissolution of C-steel is slow within existence of inhibitor [54]. This is recognized from Eq. 10 the higher values of E^*_a cause lower corrosion rate owing to construction of protecting film on the C-steel surface acting as an energy barrier of the C-steel corrosion [55-57]. Entropy and enthalpy of activation (ΔS^*, ΔH^*)” of the corrosion procedure were reckoned from the transition state theory:

$$k = \left[\frac{RT}{Nh}\right] e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^*}{RT}} \qquad (5)$$

where, “N Avogadro's number and h Planck’s constant. The graphs of log k/T versus 1/T of C-steel with 1M hydrochloric acid solution at diverse doses from examined compound, provides straight lines as displayed in Fig.7 for the inhibitor. The thermodynamic parameters are list in Table 6 show that ΔH^* values are positive signalize that the steel dissolution process is endothermic process”. High and negative values of ΔS^* assume that activated complex found in an association form more than dissociation form.

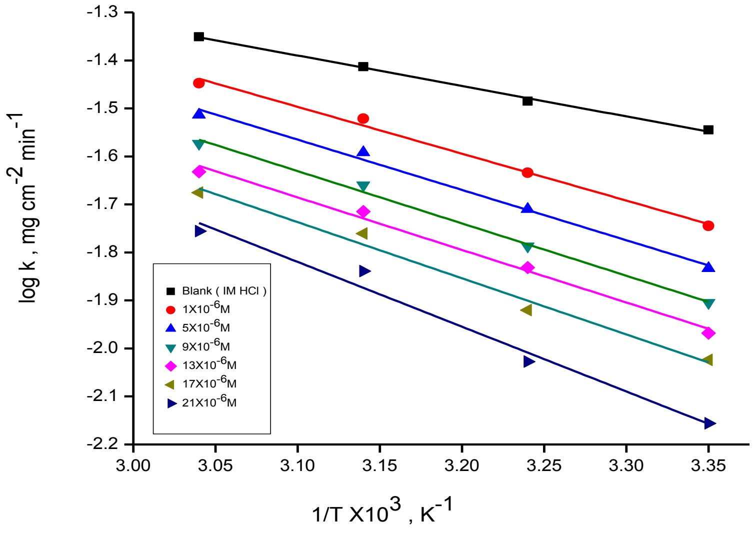


Figure 6. Log k – 1/T curves for C-steel dissolution in 1M HCl in the absence and existence of altered doses of 5-Arylidene barbituric acid derivative

Slika 6. Log k – 1/T krive za rastvaranje C-čelika u 1M HCl u odsustvu i postojanju izmenjenih doza derivata 5-ariliden barbiturne kiseline

Table 6 Activation parameters for dissolution of C-steel in the absence and existence of altered doses of 5-Arylidene barbituric acid derivative in 1M HCl

Tabela 6. Aktivacioni parametri za rastvaranje C-čelika u odsustvu i prisustvu izmenjenih doza derivata 5-ariliden barbiturne kiseline u 1M HCl

	Activation parameters				
Regression Coefficient (R^2)	**ΔS^*,- J $mol^{-1}K^{-1}$**	**ΔH^*, kJ mol^{-1}**	**E_a^*, kJ mol^{-1}**	**Conc. M**	**Inhibitors**
0.9941	108.6	9.6	12.2	1M HCl	
0.9875	90.3	16.1	18.7	$1x10^{-6}$	5-Arylidene barbituric acid derivative
0.9867	87.3	17.5	20.1	$5x10^{-6}$	
0.9915	86.1	18.3	20.9	$9x10^{-6}$	
0.9849	86.9	18.4	20.9	$13x10^{-6}$	
0.9743	83.4	19.8	22.4	$17x10^{-6}$	
0.9655	74.3	23.3	25.8	$21x10^{-6}$	

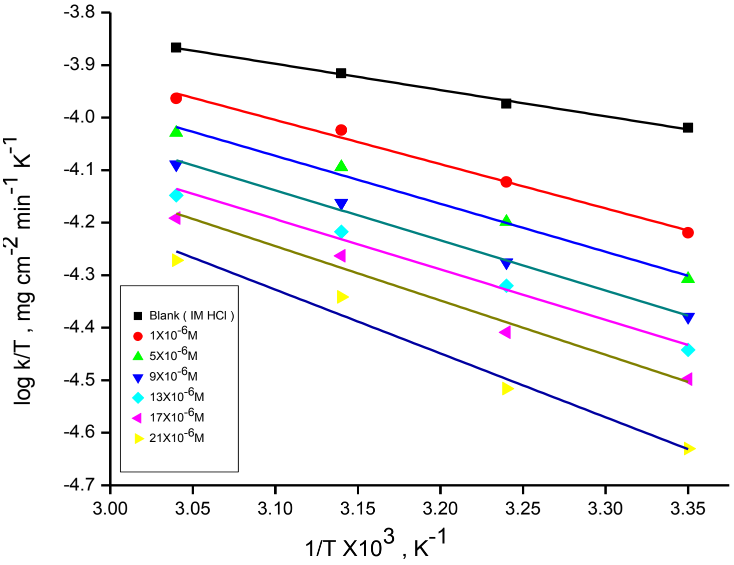


Figure 7. Log k/T – 1/T curves for C-steel dissolution in 1M HCl and existence of altered doses the investigated 5-Arylidene barbituric acid derivative

Slika 7. Log k/T – 1/T krive za rastvaranje C-čelika u 1M HCl i prisustvu izmenjenih doza ispitivanog derivata 5-ariliden barbiturne kiseline

3.6. Adsorption Isotherm

Organic compounds are inhibited the metal corrosion through adsorption on surface of metal. The adsorption procedure is considered as single replacement process of adsorbed water molecules (x) by a single inhibitor molecule [58, 59].

$$I_{(aq)} + xH_2O_{(sur)} \rightarrow I_{(sur)} + xH_2O_{(aq)} \quad (6)$$

As well, “the adsorption affords data about interaction between the adsorbed molecules and the surface of metal. The values of θ for diverse doses of the analyzed inhibitor at various temperatures have been applied to describe the most suitable adsorption isotherm to define adsorption procedure. Outcomes of the studied inhibitor are suitable with Langmuir adsorption isotherm. Fig 8 displays the plotting of C/θ versus C at 25°C to examined inhibitor”. Those schemes provided straight lines with unit slope signalized that adsorption of examined derivatives on C-steel surface confirmed Langmuir equation [60].

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

where, “C is the inhibitor concentration and K_{ads} is adsorption equilibrium constant” associated to the free energy of adsorption ΔG_{ads} as appear [61]:

$$K_{ads} = \frac{1}{55,5} e^{\frac{-\Delta G_{ads}}{RT}} \quad (8)$$

where, “T is the absolute temperature R is the universal gas constant and 55.5 is the concentration of water on the metal surface in M. The values of K_{ads} and ΔG^o_{ads} for 5-arylidene barbituric acid derivative are listed within Table 7. The increase in the negative value of ΔG^o_{ads} indicates that 5-Arylidene barbituric acid derivative was strongly adsorbed onto the C-steel surface in a stable state and that the adsorption process was spontaneous. Furthermore, the values of ΔG^o_{ads} are -32.5 and -33.0 kJ mol^{-1} indicate that the adsorption of 5-arylidene barbituric acid derivative on C-steel is mixed type i.e., physisorption and chemisorption, but mainly physisorption because the E^*_a values increases in presence of inhibitor than in its absence and % inhibition decreases by raising temperature [62].

Table 7. Equilibrium constant and adsorption free energy of investigated 5-Arylidene barbituric acid derivative adsorbed on C-steel surface at 25ºC

Tabela 7. Konstanta ravnoteže i energija bez adsorpcije ispitivanog derivata 5-ariliden barbiturne kiseline adsorbovanog na površini C-čelika na 25ºC

Langmuir isotherm				
R^2	Slope	$-\Delta G^\circ_{ads.}$, kJ mol^{-1}	K_{ads} x10^{-5}, M^{-1}	Inhibitor
0.9713	1.259	41.3	3.12	5-Arylidene barbituric acid derivative

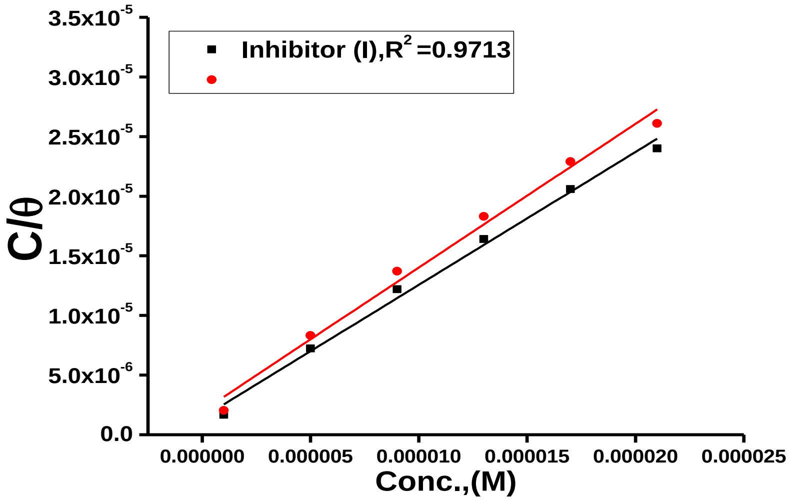


Figure 8. Langmuir isotherm plots for C-steel in 1M HCl containing various doses of 5-Arylidene barbituric acid derivative at 25°C

Slika 8. Langmuir-ove izoterme za C-čelik u 1M HCl koji sadrži različite doze derivata 5-ariliden barbiturne kiseline na 25°C

3.7. Mechanism of adsorption and inhibition

The adsorption of inhibitor on the steel surface can be used to suggest an inhibitory mechanism. “In general, a single adsorption mode between the inhibitor and the metal surface is impractical due to the complicated nature of adsorption and inhibition of a specific inhibitor”. “Based on the chemical structures of 5-ABAs they may adsorb on the active site of a C-steel surface in the current system. As a result, the inhibitory phenomenon may be affected by the following adsorption”:

(i) Because of the neutral O atoms in 5-ABAs, they may be protonated in an acid solution as: (5-ABAs) + xH$^+$ → [5-ABAsH]$^{x+}$

As a result, 5-ABAs exist as [5-ABAsH]$^{x+}$ in acidic solutions. “Because Cl$^-$ may adsorb on metal surfaces [63] they provide an excess negative charge in the solution, favoring cation adsorption”. The negatively charged metal surface may absorb [5-ABAsHx]$^{x+}$. In other words, there might be a synergistic relationship between adsorbed Cl$^-$ and protonated inhibitor [64].

(ii) “In addition to physical adsorption, 5-ABAs can be adsorbed on metal surfaces using the chemisorption mechanism, which involves the formation of coordinate bonds between the lone electron pairs of the O and S atoms and the empty orbital of Fe atoms, strengthening the combination in tension between the inhibitor molecule and the electrode surface”

(iii) It is widely believed that the heterocyclic ring is the primary adsorption center of heterocyclic compounds. “Because of the heterocyclic ring, 5-ABAs contain a lot of p-electrons, and they may be adsorbed on the metal surface because to donor–acceptor interactions between the p-electrons of the heterocyclic ring and the unoccupied d-orbitals of Fe [65].

4. CONCLUSIONS

5-Arylidene barbituric acid derivative is considered as good inhibitor for the corrosion of C-steel in 1M HCl as approved by the experimental studies. The adsorption of 5-Arylidene barbituric acid derivative on C-steel surface is followed Langmuir isotherm and deemed as mixed type but mainly physisorption. PP results revealed that the investigated 5-Arylidene barbituric acid derivative hindered anodic and cathodic reactions jointly (i.e., mixed type inhibitor). The values of C_{dl} decline and R_{ct} rise compared to blank solution when the inhibitor is existed, confirming the adsorption of inhibitor molecule on the surface of C-steel.

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IZVOD

ADSORPCIJSKI I INHIBITORSKI UTICAJ 5-[4-(DIMETILAMINO) BENZILIDEN] - 1,3-DIMETILBARBITURNE KISELINE NA KOROZIJU UGLJENIČNOG ČELIKA U MOLARNOM RASTVORU HLOROVODONIČNE KISELINE

Inhibicijski uticaj ekološki prihvatljive 5-[4-(dimetilamino) benziliden]-1,3-dimetil barbiturne kiseline u 1M HCl na koroziju ugljeničnog čelika je ispitan pomoću metoda gubitka težine (VL), potenciodinamičke polarizacije (PP), elektrohemijske impedansne spektroskopije (EIS) i testova elektrohemijske frekvencijske modulacije (EFM). Postignuti rezultati pokazuju da je ispitivano jedinjenje odličan inhibitor i da se njegova efikasnost inhibicije (%IE) povećava povećanjem koncentracije i smanjuje povećanjem temperature. Adsorpcija 5-ariliden barbiturne kiseline na površini ugljeničnog čelika prati Langmuirovu izotermu. Proces adsorpcije ispitivanog jedinjenja je spontan i smatra se hemisorpcionim. PP krive su otkrile da je derivat 5-ariliden barbiturne kiseline inhibitor mešovitog tipa. Štaviše, rezultati EIS-a su potvrdili adsorpciju ispitivanog jedinjenja na površini ugljeničnog čelika kroz povećanje otpora prenosa naelektrisanja (Rct). IE% ovog inhibitora dostigao je 86,9% pri koncentraciji 21×10^{-6} *M prema PP metodi. Konačno, eksperimentalni i teorijski rezultati su u dobroj harmoniji.*

Ključne reči: *ugljenični čelik, HCl, EFM, EIS, derivat 5-ariliden barbiturne kiseline*

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