



Synergistic effect of an expired antibiotic with potassium iodide on mild steel corrosion in 1N HCl

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Abstract

The synergistic effect of the expired Amoxicillin antibiotic (EA), with potassium iodide (KI) on mild steel corrosion in 1N HCl was studied at different temperatures (25, 35, 45 and 55 °C); using the potentiodynamic polarization, the electrochemical impedance spectroscopy (EIS), the method of zero charge potential (PZC) and the scanning electron microscopy (SEM). The results show that the synergy (5.10⁻² M KI + 1800 ppm E.A) indicates a cooperative adsorption; it acts as a mixed inhibitor. Steel surface is positively charged. The adsorption process obeys to Langmuir isotherm; the molecules are physico-chemisorbed. Best inhibitor efficacies were obtained at 25°C for Amoxicillin alone (80%) and Synergy (91.17%). The adsorption process was spontaneous and endothermic. SEM micrographs confirm the obtained results.

Keywords: Mild steel; corrosion; inhibitor; synergy; expired amoxicillin

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1. Introduction

Organic inhibitors are often used against metals corrosion in acid medium. Heterocyclic organic compounds, composed of atoms such as (N, S, O, etc.), generally have a good inhibition efficacy [1,2]. This inhibition efficacy can be improved by the addition of one or more inhibitors in the corrosive medium. This phenomenon is known by the synergistic effect [3], which was subject of several scientific studies. Ouchenane *et al.*, studied the inhibition synergistic effect by the hydroxy-ethylene diphosphonic acid (HEDP) and yttrium ions (Y⁺³) on A37 steel corrosion in 0.5 M NaCl. Inhibition efficacy was improved (75%) with 200 ppm Y⁺³ addition. While it was only 48% at 10 ppm HEDP alone [4]. The inhibition effect, of halide ions in combination with organic inhibitors in acid medium, increases the inhibition efficacy, respectively: I⁻>Br⁻>Cl⁻. Most influence of the iodide ions is often attributed to their large ionic radius, high hydrophobicity and low electronegativity compared with other halides [5]. Therefore, the iodide ions influence, on copper corrosion inhibition in 1M HNO₃, with 10⁻⁴ M l-methionine, improved the inhibition efficacy from 95.75% to 98% [6]. Ahmed. Y. Musa *et al.* studied the effect of KI potassium iodide addition at 6.02 mM in synergy with phthalazone (PTO) at 1mM as a corrosion inhibitor of mild steel in 1M HCl. Inhibition efficacy increased from 79% to 87% [7]. Steel corrosion inhibition in 1M HCl was investigated using 1000

ppm natural honey. Maximum obtained efficacy is 79.4%, while with 0.1M KI addition, it increased to 93.29% [8]. The 5.10⁻³M KI influence on the corrosion inhibition of carbon steel in 0.5 M H₂SO₄ was studied by Farag *et al.*, with 5.10⁻³ M of 2-Pyrazinecarboxamide (PCA) and gave 92.6% inhibition efficacy instead of 78.8% [9]. Whereas with 5.10⁻³M de 3-(4-cyanophenylazo)-2,4-pentanedione (L), maximum inhibition efficacy (95.86%) was obtained with a ratio [KI]/[L]=1 [10]. Recently, several studies showed that drugs have inhibitory properties for various metals protection from corrosion, due to their heterocyclic structures like organic inhibitors and their electron densities [11]. Furthermore, other previous studies showed that halides increase the inhibition efficacy of some drugs [12]. Nnabuk *et al.*, studied mild steel corrosion inhibition in 0.1M H₂SO₄ by 13.10⁻⁴ M Ampicillin alone and in combination with KI. The 6.10⁻² M KI addition increased the inhibition efficacy from 89.96% to 95.37% [13]. Obot studied the synergistic effect of Nizoral (NZR) with KI on mild steel corrosion in 0.1 M H₂SO₄. The 5.10⁻³M KI concentration improves the inhibition efficacy up to 63.7%, whereas it was only 25.6% at 10⁻² M NZR alone [14]. Barbituric acid (BA) was studied as mild steel corrosion inhibitor in 1M H₃PO₄, the results show that 7.87.10⁻³ M KI addition to 10⁻⁵M (BA) increased the inhibition efficacy from 88% to 93% [15].

After the expiry date, drugs retain at least 90% of their original properties but their medicinal use is limited due to professional restrictions and liability issues [16]. Therefore, for economic and environmental reasons several expired drugs were used as corrosion inhibitors of different metals [17]. Recently, expired Ethambutol was used as mild steel corrosion inhibitor in 0.5M HCl. The maximum inhibition efficacy obtained was 97.6% at 1000 ppm [18]. Singh *et al.*, investigated the corrosion inhibitor effect of mild steel in 1M HCl, an expired anti-tuberculosis drug (isoniazid), and the maximum efficacy obtained was more than 95% at 200 ppm [19]. The use of the expired Acetazolamide as mild steel corrosion inhibitor in hydrochloric acid was studied by Chaudhari *et al.*, and the maximum efficacy obtained was 93% at 500 ppm [20]. Expired Ambroxol was studied as mild steel corrosion inhibitor in 1M hydrochloric acid, and the maximum efficacy achieved was 93.35% at 9% (v/v) [21]. In our laboratory, we studied the expired Amoxicillin (E.A) as a green corrosion inhibitor of mild steel in 1N HCl; maximum obtained efficacy was 81.61% at 1800 ppm (E.A) [22]. In this context, to enhance the E.A and the development of a new inhibiting formulation that is at once effective, economical and environmentally friendly; we investigated the inhibition synergistic effect of steel corrosion in 1N HCl, by expired Amoxicillin (E.A.), in synergy with potassium iodide (KI). We used stationary electrochemical technics (potentio-dynamic polarization) and transitory (Electrochemical Impedance Spectroscopy (EIS) and the method of potential of zero charge (PZC)) as well as microscopic observations (SEM). The temperature effect was studied without and with E.A and the synergy (E.A+KI).

2. Materials and methods

The material used as working electrode was mild steel whose composition in mass percentage is 0.17 C, 0.59 Si, 1.60 Mn, 0.04 P and 97.60 Fe. The study medium was a hydrochloric acid (HCl) solution at 1N without and with E.A and potassium iodide. The inhibitor studied was expired amoxicillin; its chemical structure is shown in Figure 1. The electrochemical study was carried out in 1N hydrochloric acid using Gamry interface 1000 Potentiostat/Galvanostat connected to a conventional cell of three electrodes: a reference electrode (Ag/AgCl), a platinum counter electrode made of plate and a study steel working electrode, with 0.5cm² contact surfaces, and Gamry Echem Analyst software. The working electrode undergoes a pre-treatment before each test, consisting of a polishing by abrasive paper with different granulometries (SiC: 800, 1200, 2400 and 4000), followed by a rinsing with distilled water, then a degreasing with acetone and finally a drying.

The experiments were performed at different temperatures namely: 25, 35, 45 and 55 °C. Where temperature was controlled by a thermostatic bath without agitation. Potentiodynamic curves were obtained in a range Benachour *et al.*, 2020

of ± 500 mV relative to corrosion potential with 1 mV/s scanning speed. The inhibition efficacy is calculated according to equation (1).

$$IE(\%) = \left(\frac{i_{corr}^{\circ} - i_{corr}}{i_{corr}^{\circ}} \right) \times 100 \quad (1)$$

Where: i_{corr}° and i_{corr} are the respective densities values of steel corrosion current without and with inhibitor. The electrochemical impedance diagrams were achieved in a frequency range 100 KHz to 10mHz, with 10mV amplitude. The inhibitor efficacy is calculated according to equation (2).

$$IE(\%) = \left(\frac{R_{ct} - R_{ct}^{\circ}}{R_{ct}} \right) \times 100 \quad (2)$$

Where: R_{ct}° and R_{ct} are the charge transfer resistances without and with inhibitor, respectively. The characterization of mild steel surface was made by scanning electron microscopy (SEM) after 1hour immersion in different study media.

3. Results and discussions

3.1. Characterization of the inhibitor (FTIR)

Amoxicillin was used 6 months after its expiry date; we firstly made FTIR analysis of expired and unexpired Amoxicillin to determine existing functional groups: OH (alcohol) at 3500cm⁻¹; OH (carboxylic acid) at 3300cm⁻¹; NH₂ (primary amine)(3000-2500) cm⁻¹; C=O (carboxylic acid) at 1750 cm⁻¹; C=O (amide) at 1650 cm⁻¹; C=C (aromatic) at 1500 cm⁻¹; C-O at 1245 cm⁻¹; C-S at 915 cm⁻¹; and C-H (aromatic) at 840 cm⁻¹ [23,24]. According to figure 2, it can be noted that the E.A keeps the same characteristic bands as the U.A but with different intensities. Which proves that E.A has similar properties to U.A ones. Similar results were obtained by Dohare *et al.* with expired tramadol [25].

3.2. Synergistic effect

We have studied the KI effect at different concentrations (10⁻³, 5.10⁻³, 10⁻² and 5.10⁻² M) on E.A inhibition efficacy in 1N HCl (Figure 3a). We have noticed that KI concentration increase rises the capacitive loop and the inhibition efficacy which increased in turn until 91.17% at 5. 10⁻² M KI, whereas, it was only 81.61% without KI.

In order to choose the best synergy, we also studied the E.A concentration influence on mild steel corrosion inhibition in 1N HCl solution containing 5.10⁻² M KI (Figure 3b). We observed that the capacitive loop increased with the increase in the E.A concentration. This corrosion process was controlled by the charge transfer phenomenon.

From Table 1, we noted that 5.10⁻² M KI addition increases R_{ct} values and decreases the CPE ones compared to the solution containing E.A. The R_{ct} values rise is attributed to the improvement of increased E.A adsorption on metal surface due to synergy effect by iodide ions. This co-adsorption leads to a recovery rate increase thus inducing

to an inhibition efficacy improvement [26]. The CPE decrease may be related to local dielectric constant decrease and/or a thickness augmentation of the formed layer on steel surface. As a result of water molecules displacement initially adsorbed on surface by E.A. molecules and iodide ions [27]. Therefore, it is clearly that the inhibition efficacy increased significantly with synergy (E.A+KI) compared to those obtained with E.A and KI individually. The process taking place at the electrode/electrolyte interface can be modeled by an equivalent electrical circuit illustrated in Figure 4.

3.3. Potential of zero charge method (PZC)

The iodide ions effect on E.A molecules adsorption was studied by the potential of zero charge method. The curve obtained represented a parabola whose maximum corresponded to the potential of zero charge $E_{pzc} = -0.530V/Ag/AgCl$ (figure 5). The rational corrosion potential of Antropov (E_r) was calculated from the following equation:

$$E_r = E_{ocp} - E_{pzc} \quad (3)$$

The value of $E_r = +0.77V$, this leads us to conclude that steel surface was positively charged, which indicated that anions adsorption was favored. Similar result was reported previously [28].

3.4. Synergy parameter (s)

The synergy parameter (s) was calculated by the following relation of Aramaki and Hackerman [29]:

$$s = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}} \quad (4)$$

Where: θ_{1+2} and θ'_{1+2} are the recovery rates of the calculated and measured surface, respectively.

θ_{1+2} was calculated according to the equation (5):

$$\theta_{1+2} = \theta_1 + \theta_2 - \theta_1 \cdot \theta_2 \quad (5)$$

Where:

- i. θ_1 : Recovery rate of ion iodide surface at $5.10^{-2}M$.
 - ii. θ_2 : Recovery rate of E.A. surface at 1800 ppm.
 - iii. θ'_{1+2} : Recovery rate of the synergy surface.
- According to Aramaki *et al.*, the synergy effect of two inhibitors was determined by two types of adsorption:
- i. Competitive adsorption ($s < 1$): both inhibitors were adsorbed competitively on different sites of metal surface.
 - ii. Cooperative adsorption ($s > 1$): one of the inhibitors was chemisorbed on metal surface and the other was physisorbed on the first.

The value of synergy parameter was greater than the unity ($s=1.34$). This indicated that synergy was cooperative. Similar result was obtained by Obot *et al.*, studying the synergetic effect between an antifungal drug (clotrimazole) and potassium iodide [30].

3.5. Adsorption isotherms

To understand the interactions between E.A molecules with $5.10^{-2}M$ KI on mild steel surface; we tested several adsorption isotherms according to their equations: (6), (7), (8) (9), (10), and (11):

$$\text{Frumkin} \quad \frac{\theta}{1-\theta} e^{(-2a\theta)} = K_{ads} C_{inh} \quad (6)$$

$$\text{Temkin} \quad e^{-2a\theta} = K_{ads} C_{inh} \quad (7)$$

$$\text{Langmuir} \quad \frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (8)$$

$$\text{Freundlich} \quad \log \theta = \log K_{ads} + n \log C \quad (9)$$

$$\text{Flory - Huggins} \quad \log \frac{\theta}{C} = \log K_{ads} + a \log(1 - \theta) \quad (10)$$

$$\text{El - Awady et al.} \quad \log \left(\frac{\theta}{1-\theta} \right) = \log K' + y \log C \quad (11)$$

Where: K_{ads} is the equilibrium constant of the adsorption process; θ is the recovery rate on metal ($\theta = E/100$), a is the molecular interaction parameter, $1/y$ is the inhibitor molecules number occupying an active site where K the binding constant is given by: $K = K^{(1/y)}$ [31]. According to different isotherms plots, the E.A adsorption with $5.10^{-2}M$ KI in 1N HCl obeys the Langmuir isotherm (Figure 6) whose regression coefficient ($R^2 = 0.9975$) is very close to the unity compared with other isotherms. The adsorption equilibrium constant (K_{ads}) is related to standard free energy of adsorption (ΔG_{ads}°) by Gibbs equation:

$$\Delta G_{ads}^{\circ} = -RT \ln (1000 K_{ads}) \quad (12)$$

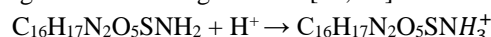
Where R: perfect gas constant ($R = 8,314 J K^{-1}mol^{-1}$), T: temperature (K). The value (1000) is water concentration (g/l).

Generally, the values $\Delta G_{ads}^{\circ} \leq -20 kJ.mol^{-1}$ are related to electrostatic interactions between charged molecules and charged metal, which indicated that the adsorption mode was a physical type (physisorption), whereas the values $\Delta G_{ads}^{\circ} \geq -40 kJ.mol^{-1}$ were due to charge transfer processes between organic molecules and metal surface, this indicated that the adsorption mode was a chemical type (chemisorption).

In our study, $\Delta G_{ads}^{\circ} = -26.03 kJ.mol^{-1}$. The ΔG_{ads}° negative value indicated the E.A adsorption process spontaneity with KI in 1N HCl on metal surface. This value also indicated that the adsorption was a physio-chemisorption type [32]

3.6. Inhibition mechanism

In the hydrochloric acid solution, E.A. can exist in cationic species form in other words protonated species according to the following reaction [33, 34]:



From the obtained results in this study, steel surface with synergy (E.A+KI) was positively charged. Thus, the adsorption of E.A. on positive surface was difficult. Strong chemisorption of iodide ions on metal surface allowed the adsorption of E.A. protonated molecules by the Coulomb attraction on metal surface, where iodide ions were already chemisorbed by forming a stable complex by electrostatic

interactions. The latter leads to higher surface recovery rate. In addition to physical adsorption, E.A molecules were chemically adsorbed directly on steel surface. Chemical adsorption occurred from interactions (acceptor-donor) between free electron pairs of heteroatoms (N, O and S), π electrons multiple bands and d iron vacant orbitals [35].

3.7. Temperature effect and thermodynamic parameters

In order to understand better, the inhibition mechanism and to determine thermodynamic parameters. We studied temperature effect by plotting potentiodynamic polarization curves of mild steel in 1N HCl without and with E.A. alone at 1800 ppm, then in synergy with 5.10^{-2} M KI at temperatures 25; 35; 45 and 55 °C (Figure 7).

The corrosion current densities, the corrosion potentials and the inhibition efficacies of E.A. and in synergy (E.A+KI) according to temperature are grouped in Table 2 where we observe that minimum current density was obtained at 25 °C with E.A. alone and its synergy with KI, inducing inhibition efficacy increase up to 80% and 90.17%, respectively. At the temperatures 35; 45 and 55 °C, the inhibition efficacy decreases in both inhibited solutions, may be due to the inhibitor film desorption of mild steel surface [36].

The Arrhenius equation (Eq.13) representation from which we calculated the activation energy of different solutions by drawing the straight-line $\log i_{corr}=f(1/T)$ shown in figure 8.

$$\log i_{corr} = - \frac{E_a}{2.303RT} + \log A \tag{13}$$

Where:

- i. i_{corr} : corrosion current density (A.cm⁻²)
- ii. A: Arrhenius constant
- iii. E_a : activation energy (kJ.mol⁻¹)
- iv. R: constant of perfect gases (J.mol⁻¹.K⁻¹)
- v. T: Absolut temperature (K)

The second representation of Arrhenius equation (Eq.14) allows the determination of the variation of standard

enthalpy activation (ΔH_a°) and the variation of standard entropy activation (ΔS_a°).

$$\ln \left(\frac{i_{corr}}{T} \right) = \ln \left(\frac{R}{Nh} \right) + \left(\frac{\Delta S_a^\circ}{R} \right) - \left(\frac{\Delta H_a^\circ}{RT} \right) \tag{14}$$

Figure 9, illustrates the variation of $\ln i_{corr}/T$ versus $\frac{1}{T}$ in

1N HCl without and with addition of E.A. alone and in synergy (E.A+KI). The straight lines obtained have a slope equal to $\left(-\frac{\Delta H_a^\circ}{R} \right)$ and an intercept of $\left(\ln \frac{R}{Nh} + \frac{\Delta S_a^\circ}{R} \right)$. The ΔH_a° and ΔS_a° calculated values are gathered in Table 3.

From Table 3 show that the activation energy values calculated with E.A. and the synergy (E.A+KI) are higher than that of uninhibited solution. This indicated that the adsorption was of physical type [37]. In addition, the activation energy values were less than 80 kJ.mol⁻¹, which confirmed this adsorption type [38]. The $\Delta H_a^\circ > 0$ values indicated that steel dissolution was endothermic [39]. The ΔS_a° negative values with E.A. alone and in synergy (E.A+KI) signify a molecular disorder decrease caused by the formation of metal/adsorbed species complex. This implies the steel dissolution decrease inducing the inhibition efficacy increase [40].

3.7. Micrographs (SEM)

Figure 10 shows micrographs obtained by scanning electron microscopy of mild steel surface immersed in 1N HCl without and with E.A, KI and (E.A+KI). From figure 10.a, show that the surface was rough and corroded under generalized form due to acid attack. While with E.A (figure 10.b), KI (figure 10.c) and (E.A+KI) (figure 10.d), it was noted that the surface roughness decreased by the appearance of an inhibitor film whose observed thickness increased significantly in following order: KI<E.A<E.A+KI. Which confirmed the obtained results by the electrochemical methods used, and are expressed in inhibition efficacy.

Table 1 Electrochemical parameters deduced from mild steel Nyquists in 1N HCl without and with E.A, KI and their synergies

[KI] (M)	[E.A] (ppm)	R_s ($\Omega.cm^2$)	R_{ct} ($\Omega.cm^2$)	CPE ($\mu F.cm^{-2}$)	n	Θ	IE (%)
1N HCl		2.226	146.5	267.7	0.844	-	-
-	1800	1.639	794.3	137.2	0.798	0.816	81.61
10^{-3}	1800	1.645	895	100.5	0.898	0.836	83.63
5.10^{-3}	1800	1.512	1013	96.12	0.856	0.855	85.53
10^{-2}	1800	1.733	1325	91.25	0.845	0.889	88.94
5.10^{-2}	1800	1.984	1800	74.25	0.821	0.911	91.17
5.10^{-2}	-	2.643	226.4	159.9	0.781	0.352	35.29
5.10^{-2}	1200	2.854	550	182.1	0.790	0.733	73.36
5.10^{-2}	1400	2.147	698	170.4	0.803	0.791	79.01
5.10^{-2}	1600	2.525	1000	146.5	0.821	0.854	85.40
5.10^{-2}	1800	1.984	1800	74.25	0.871	0.911	91.17

Table

Solutions	Parameters	t (°C)	E_{corr} (mV/Ag/AgCl)	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	$-bc$ (mV.dec ⁻¹)	E (%)
1N HCl		25	-457.5	497.4	100.1	-
		35	-447.7	645	122.5	-
		45	-434.2	923	111.6	-
		55	-423.8	1015	160.4	-
1N HCl +1800ppm E.A.		25	-463.0	99.45	108.0	80.00
		35	-452.6	245.5	124.7	61.93
		45	-441.7	372.1	117.7	59.69
		55	-444.4	580.7	140.0	42.78
1N HCl +1800ppm E.A. + 5.10 ⁻² M KI		25	-453.0	40.2	123.5	91.17
		35	-432.1	258.1	138.1	60.00
		45	-438.7	415.35	136.9	55.10
		55	-439.0	517.5	134.2	49.01

2

Electrochemical parameters deduced from mild steel polarization curves in different media and at different temperatures, as well as the calculated inhibitor efficacies

Table.3 Thermodynamic parameters of mild steel in 1N HCl without and with the addition of E.A. and the synergy (E.A.+KI)

Solutions Parameters	1N HCl	1800ppm E.A	1800ppm E.A+ 5.10 ⁻² M KI
E_a (kJ.mol ⁻¹)	20.43	48.37	50.95
ΔH_a° (kJ.mol ⁻¹)	95.31	85.79	87.25
$-\Delta S_a^\circ$ (J.mol ⁻¹ .K ⁻¹)	132.42	160.96	163.83

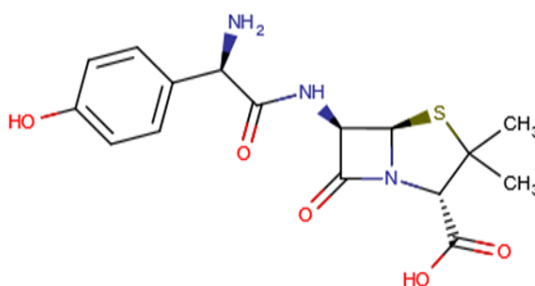


Figure1: Amoxicillin chemical structure

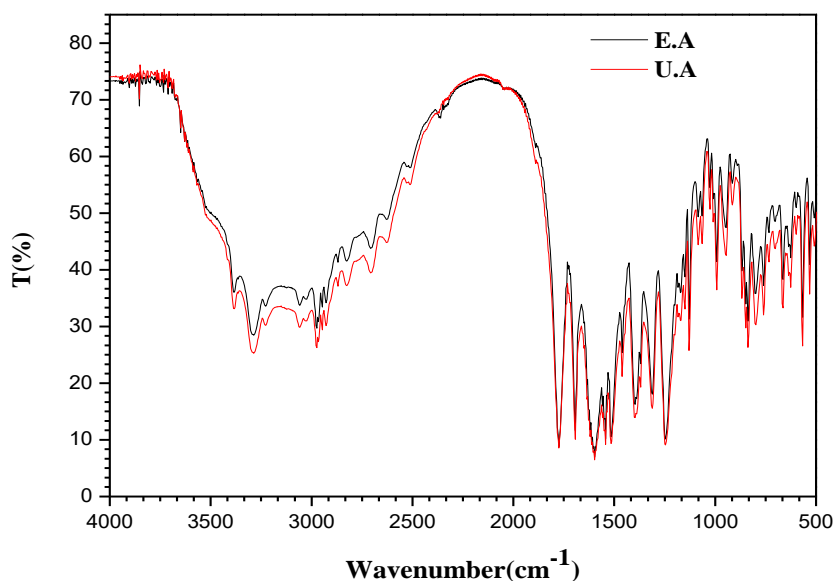


Figure 2: FTIR spectrum of unexpired Amoxicillin (U.A) and expired Amoxicillin (E.A)

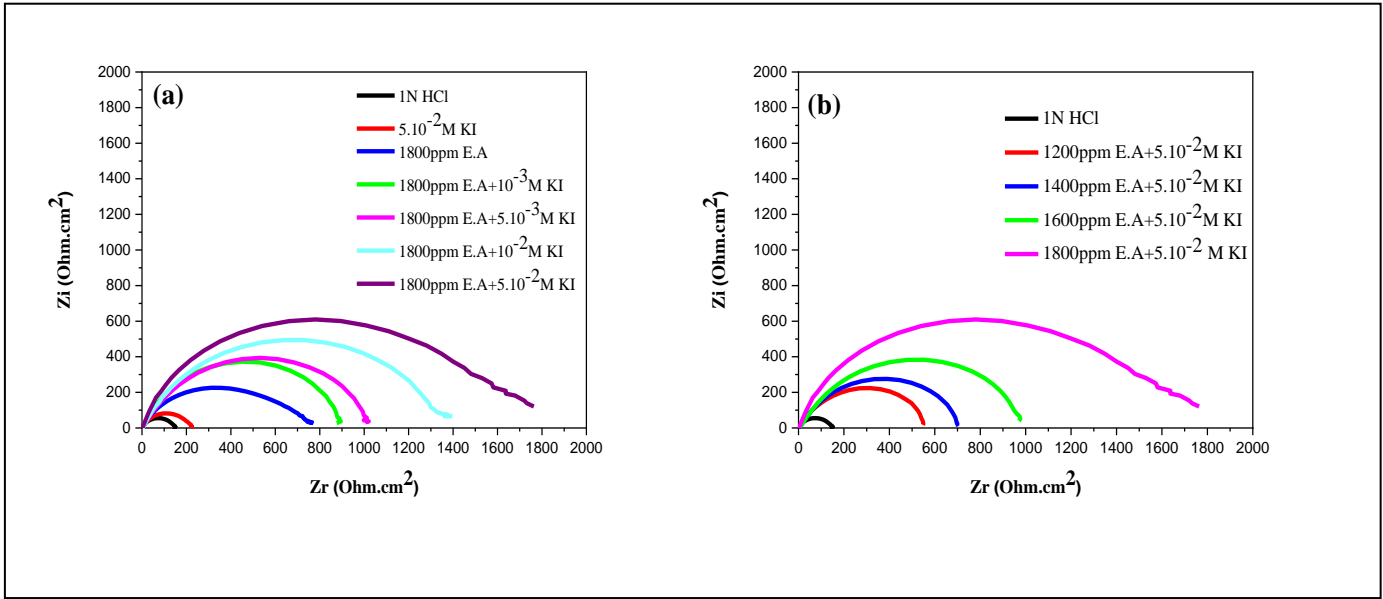


Figure 3: Nyquist curves of mild steel in 1N HCl (a) KI concentration influence (b) E.A concentration influence

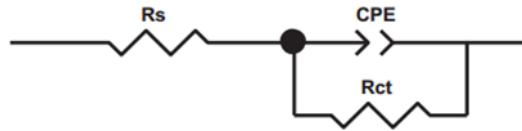


Figure 4: Equivalent electrical circuit corresponding to metal/solution interface

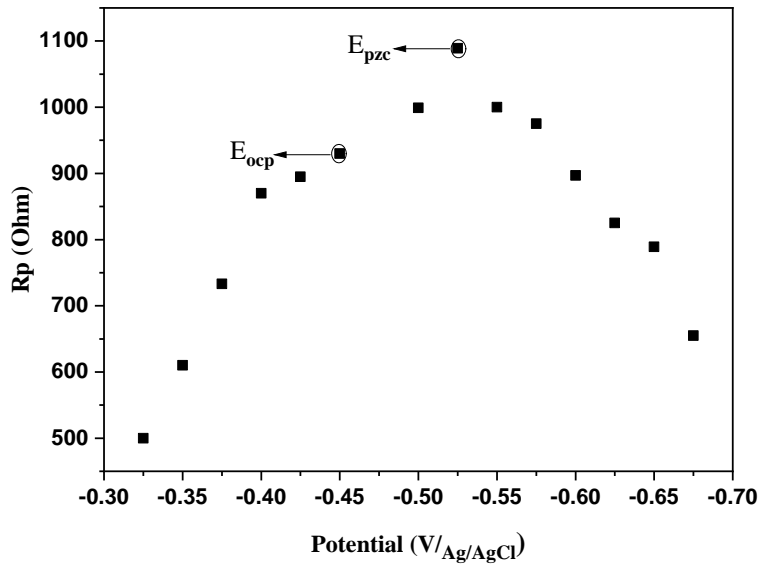


Figure 5: Polarization resistance according to steel potential in 1N HCl with synergy (1800ppm E.A+5.10⁻² M KI)

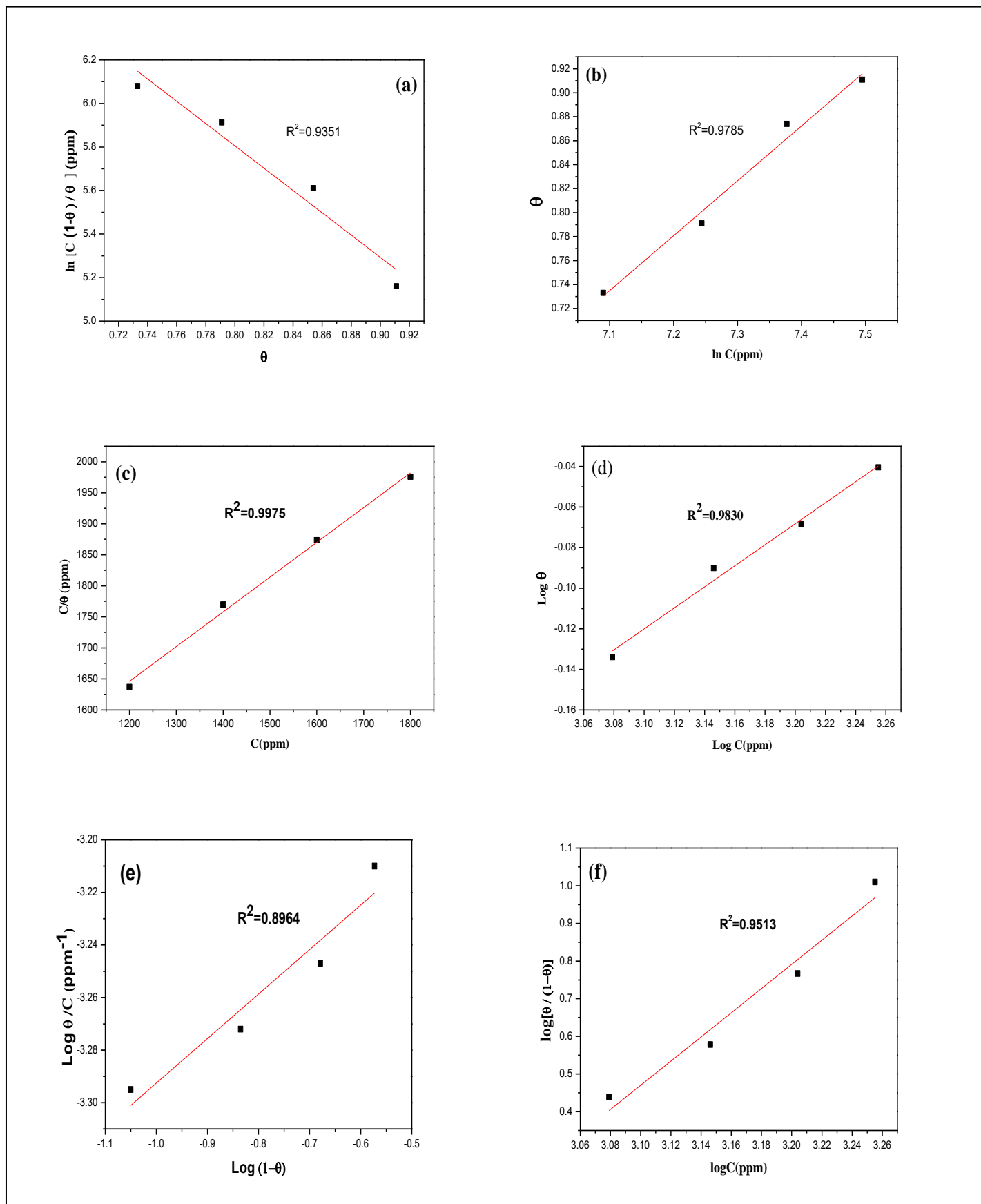


Figure 6: Different adsorption isotherms (a) Frumkin (b) Temkin (c) Langmuir (d) Freundlich (e) Flory-Huggins and (f) El-Awady *et al.* of synergy (E.A+KI) in 1N HCl

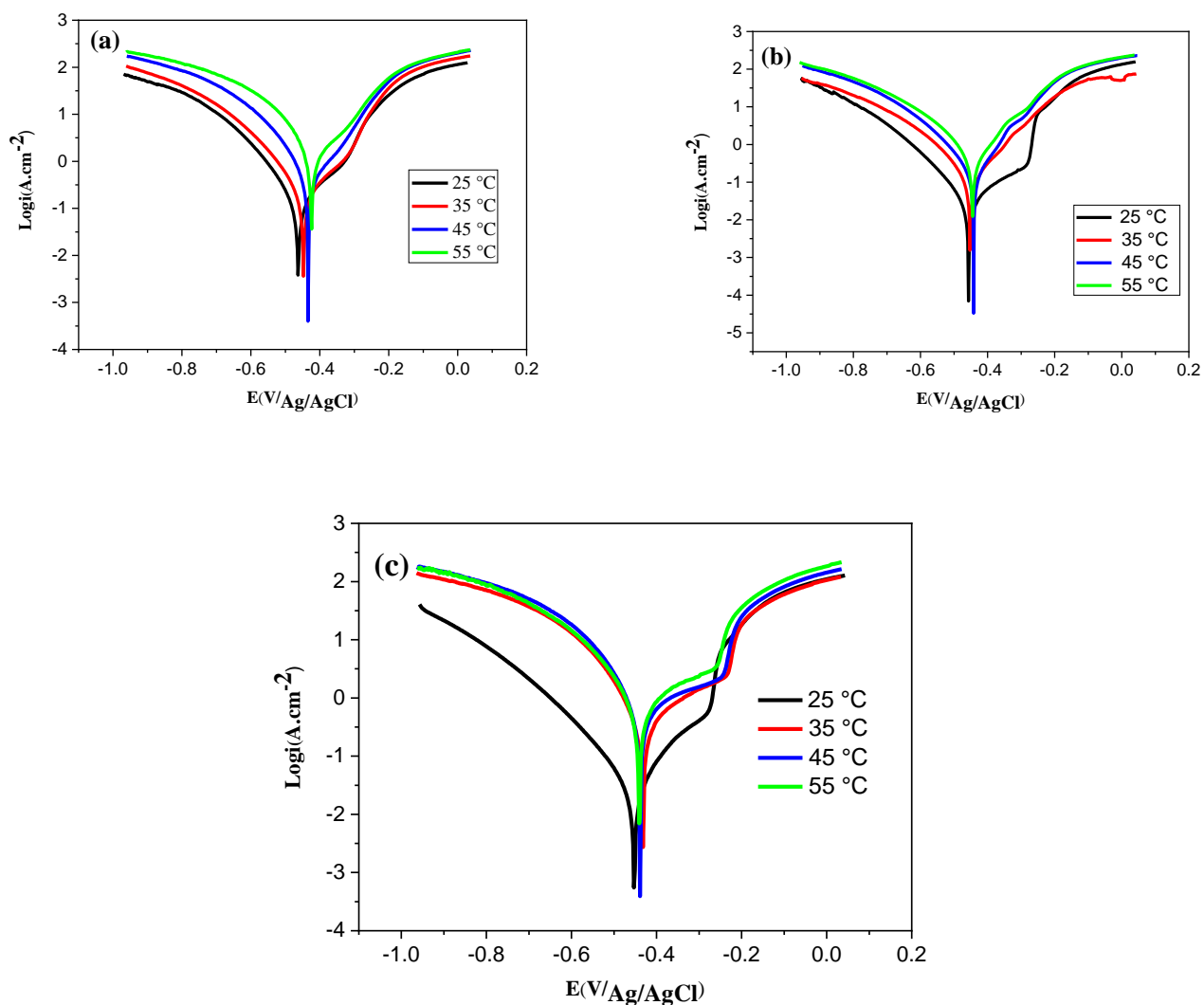


Figure 7: Steel polarization curves at different temperatures in (a) 1N HCl (b) 1N HCl+1800ppm E.A. (c) 1N HCl+1800ppm E.A.+5.10⁻² M KI

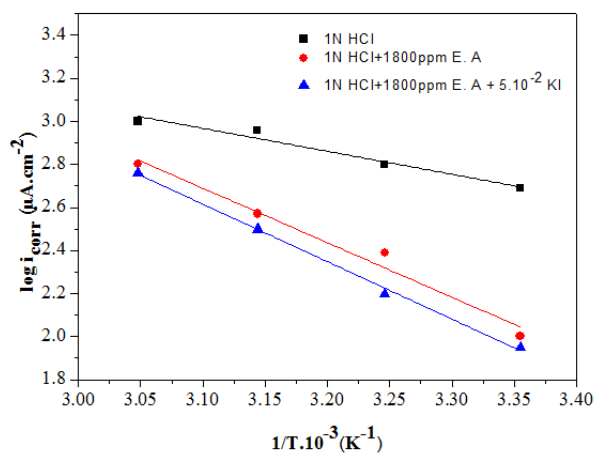


Figure 8: Arrhenius plots of $\text{log} i_{\text{corr}}$ according to $1/T$ mild steel in 1N HCl without and with addition of E.A. alone and in synergy (E.A+KI)

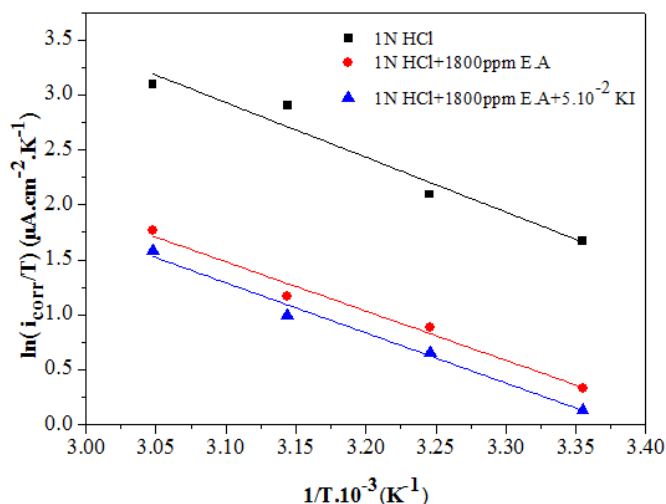


Figure 9: Arrhenius plots of $\ln(i_{corr}/T)$ according to $1/T$ mild steel in 1N HCl without and with addition of E.A. alone and in synergy (E.A+KI)

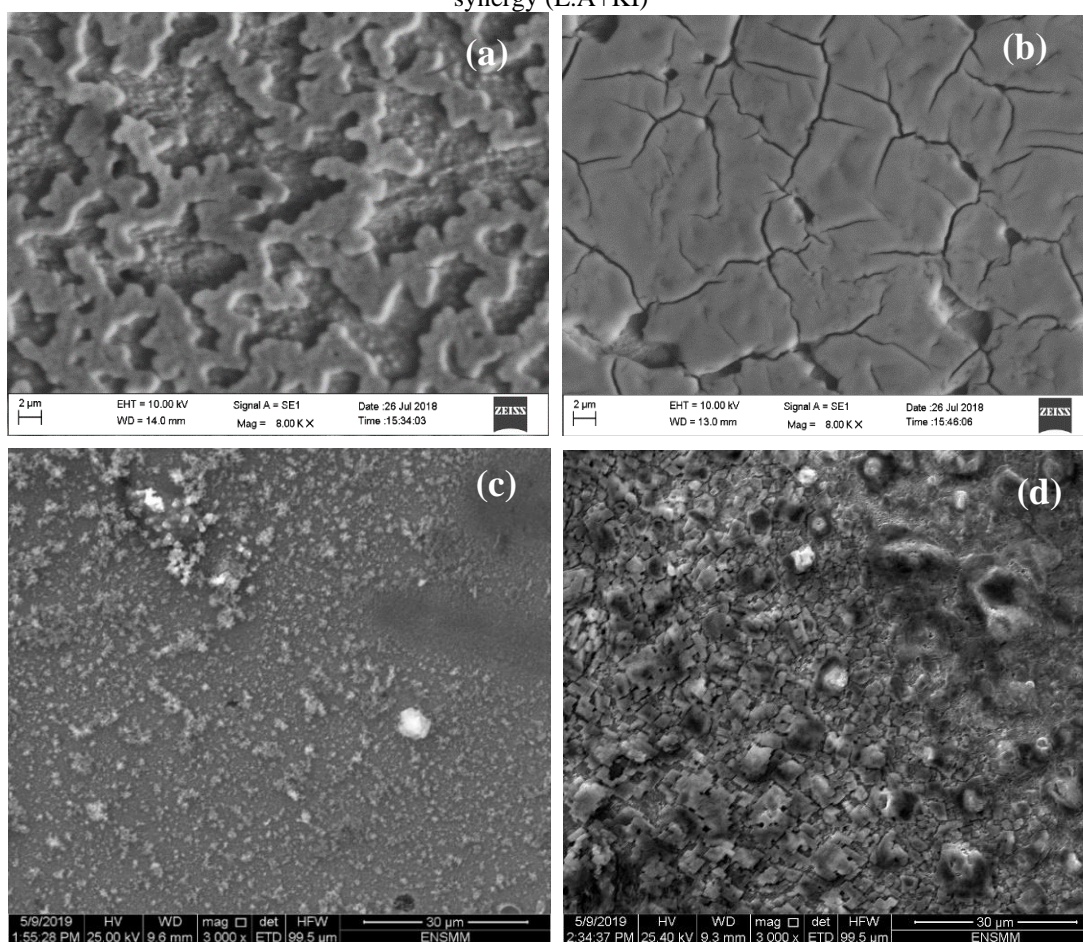


Figure 10: Micrographs (SEM) of mild steel surface (a) in 1 N HCl, (b) in 1N HCl+1800 ppm E.A. (c) in 1N HCl+5.10⁻²M KI and (d) in 1N HCl+1800 ppm E.A.+5.10⁻²M KI

4. Conclusions

- i. The addition of 5.10⁻² M KI improved the E.A. inhibitor properties at 1200, 1400, 1600 and 1800 ppm.
- ii. Competitive adsorption of the synergy (1800 ppm E.A.+5.10⁻²M KI).
- iii. Steel surface was positively charged allowing the adsorption of iodide ions that form intermediate bridges between E.A. protonated molecules and metal surface.
- iv. The adsorption was a physi-chimisorption type, endothermic reaction and obeyed the Langmuir isotherm.
- v. The synergy (E.A+KI) acted as a mixed inhibitor; Best inhibition efficacies were obtained at 25 °C

for Amoxicillin alone (80%) and in synergy (91.17%).

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