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Polarization, EIS and EN Studies to Evaluate the Inhibition Effect of Vanillin as Environment-friendly Inhibitor on Carbon Steel in Hydrochloric Acid Solution

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ABSTRACT

Vanillin is an interesting corrosion inhibitor because of its safe use and high solubility in water. The effect of vanillin on the corrosion inhibition of carbon steel in 1.0 M hydrochloric acid solution has been studied using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) techniques. The effect of temperature on the rate of corrosion in the absence and presence of vanillin was also studied. Some thermodynamic parameters were computed from the effect of temperature on corrosion and inhibition processes. Adsorption of vanillin was found to obey Langmuir adsorption isotherm. Furthermore, in this paper the electrochemical noise (EN) technique under open circuit conditions was employed for the quantitative evaluation of corrosion inhibition. This was done by using the standard deviation of partial signal (SDPS) for calculation of the amount of noise charges at the particular timescale range, thereby obtaining the inhibition efficiency (IE) of an inhibitor. These IE values show a reasonable agreement with those obtained from potentiodynamic polarization and EIS measurements.

Keywords: Vanillin; Electrochemical Noise; Wavelet Analysis; Inhibition Efficiency; Electrochemical Impedance Spectroscopy

INTRODUCTION

The inhibition of steel in acid solutions by different types of organic inhibitors has been extensively studied. Inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media. However, the use of these compounds has been questioned lately, due to the several negative effects they have caused in the environment. Thus, the development of the environment-friendly corrosion inhibitors of natural source and non-toxic type has been considered to be more important and desirable [1, 2]. Among these compounds, vanillin (4-hydroxy-3-methoxy benzaldehyde) offers interesting possibilities for corrosion inhibition [2-12]. Vanillin (Fig. 1) is one of the most widely used and important flavoring materials worldwide. It has many advantages such as low cost, non-toxicity, high solubility in water and easy production. The annual production capability in the world can reach to 12,000 ton [13].

A very promising method for the

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investigation and monitoring of corrosion is the recording and analysis of the electrochemical noise (EN) data [14-24]. EN is defined as the fluctuations of potential or current originating from the localized events in a corrosion process. Two nominally identical working electrodes (WEs) are connected via a zero-resistance ammeter (ZRA) monitoring the coupling current between the electrodes. Although EN studies tend to include both current and potential signals, to keep the measuring and data evaluation system as simple as possible this study concentrated on current signals only.

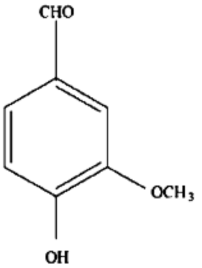

Fig. 1. Molecular structure of vanillin.

While the EN measurement is simple the understanding of the information included in the EN signals, i.e. the EN analysis, remains difficult. Wavelet transform (WT) is a mathematical tool that has gained popularity for EN analysis [19-24]. Using WT, the different EN components contributing to the original signal can be characterized. Each component, called crystal, is defined by a set of wavelet coefficients which contain information about the timescale characteristic of the associated corrosion event. Table 1 shows the timescale range of the case in which J=7 and f_s=4 Hz.

Table 1. The timescale range of different crystals for J=7 and f_s=4 Hz

Crystal name	d1	d2	d3	d4	d5	d6	d7
Timescale range/s	0.25-0.5	0.5-1	1-2	2-4	4-8	8-16	16-32

The inverse wavelet transform can produce partial signals of the original signal. Each partial signal is a signal which resembles the fluctuations of the original signal at a particular timescale range. The standard deviation of partial signal (SDPS) can indicate the variations in the intensity of the partial signal about its mean, which could be an indication of the intensity of electrochemical activity on the surface of the electrodes within a particular timescale range [24]. The plot of the SDPS versus their corresponding crystal name is called SDPS plot. Such a plot provides mechanistic information about physical processes: the position of the maximum in the SDPS plot indicates the dominant process in certain corrosion events and its change can reflect the behavior of the dominant corrosion process. For a more detailed discussion on wavelet transform and SDPS plot, one can refer to an earlier paper [24].

In this paper the use of vanillin as environment-friendly corrosion inhibitor of carbon steel in 1.0 M hydrochloric acid solution have been studied by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) methods. Furthermore, this paper employs EN technique under open circuit conditions for the quantitative evaluation of corrosion inhibition by using the SDPS plots from wavelet analysis of EN data.

EXPERIMENTAL

The employed working electrodes with surface area of 100 mm^2 were prepared from carbon steel with the chemical composition (wt%) of: C (0.15), Mn (0.73), Si (0.72) and Fe (balance). Potentiodynamic polarization, EIS and EN measurements have been used to study the corrosion behavior of carbon steel in 1.0 M hydrochloric acid solution without and with doping with vanillin at concentrations of 1.0, 1.5, 2.0, 2.5 and 3.0 mM. Vanillin with purity of 99.0% and the analytical grade 37% HCl was obtained from Merck.

Before performing experiments, the specimens were connected to a copper wire at one end sealed using resin, with the other end that exposed as the WEs surface. Then the working surface was polished by wet abrasive papers through 600-2500-grade, washed with distilled water, degreased with ethanol, finally dried in air.

Potentiodynamic polarization, EIS and EN experiments were conducted using Autolab 302N potentiostat with Nova 1.6 software. This equipment allows resolutions of 0.76 μV for voltage signals and 10 nA for current signals. Potentiodynamic polarization and EIS measurements were conducted in a conventional three-electrode cell. A platinum rod was used as the counter and a saturated (KCl) Ag/AgCl electrode as reference electrode. To obtain the stabilized open circuit potential (OCP), the samples were immersed 30 min in the solution before EIS and potentiodynamic polarization measurements. Polarization curves were recorded at a scan rate of 1 mV/s and Nova software was used for determination of corrosion current densities and Polarization parameters. A sinusoidal potential perturbation of 10 mV versus OCP was used in the EIS measurements and a frequency range from 10 mHz to 100 kHz was employed and Nyquist plots of the impedance data were analyzed with Nova software.

Two WEs were facing each other vertically at a distance of about 2 cm in the EN experiments. The EN records were collected 30 min after immersion time and during 15 min. Two nominally identical WEs with surface areas of 100 mm^2 were used. The entire cell was placed inside a Faraday cage to limit external electromagnetic interference. The sampling frequency for the electrochemical noise data was 4 Hz. The surfaces of alloy were observed in a CamScan MV2300 scanning electron microscope (SEM). Noise data were analyzed with wavelet technique using the orthogonal Daubechies wavelets of the fourth order (db4). The necessary calculations for construction of the SDPS plots were performed using Matlab software. Standard errors of the slopes and intercepts were calculated using LINSET function in the Excel spreadsheet program.

RESULTS AND DISCUSSION

Potentiodynamic polarization

Fig. 2 shows the potentiodynamic polarization curves of carbon steel in 1.0 M hydrochloric acid in the absence and presence of vanillin. The relevant parameter values are listed in Table 2 (corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic Tafel slope (b_a) and cathodic Tafel slope (b_c)). It is clear that corrosion current density decreases as the concentration of inhibitor goes up. Addition of vanillin to acid media affects both cathodic and anodic branches of the potentiodynamic polarization curves; therefore, vanillin behaves as mixed inhibitor. However, small potential shifts in the positive direction in the presence of inhibitor indicate that the effect of vanillin on the anodic reaction is more observable than on the cathodic reaction.

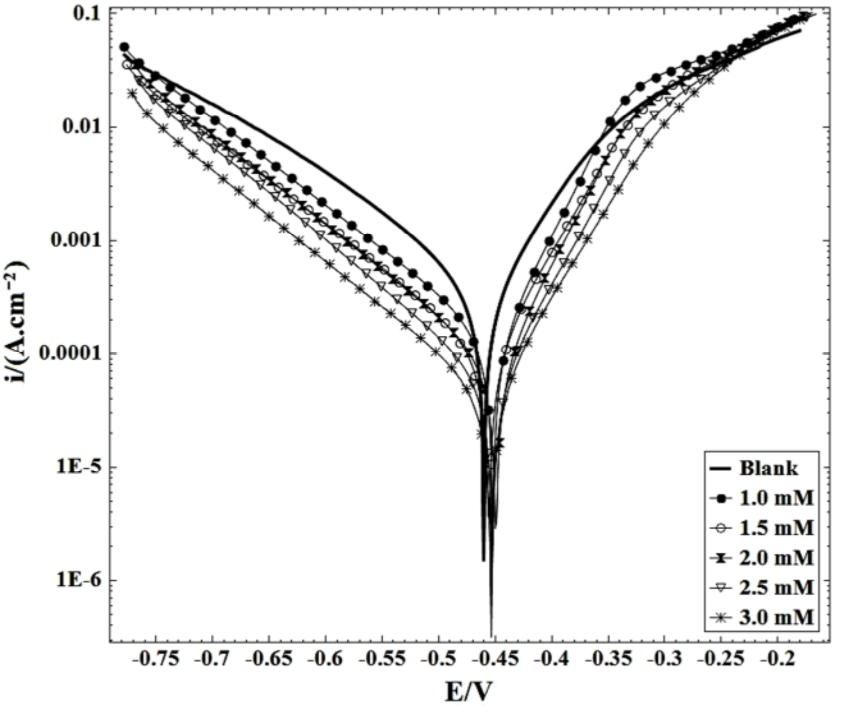

Fig. 2. Polarization curves in 1.0 M hydrochloric acid solution in the absence and presence of different concentrations of vanillin at 25°C.

Table 2. Corrosion parameters obtained from polarization curves of mild steel in 1.0 M hydrochloric acid solution in the absence and presence of various concentrations of vanillin

C /mM	i_{corr}/μA.cm^{-2}	-E_{corr}/mV	β_a/mV.decade^{-1}	β_c/mV.decade^{-1}	IE_P(%)
0	771	461	182	103	-
1.0	191	452	135	61	75
1.5	131	456	137	64	83
2.0	106	450	129	59	86
2.5	74	453	128	61	90
3.0	43	454	124	62	94

Table 2 presents values of the corrosion inhibition efficiency (IE) for which the expression in this case is:

$$IE\% = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100 \qquad (1)$$

where i_{corr} and i'_{corr} are corrosion current densities in the uninhibited and inhibited cases, respectively. The IE values shows that this inhibition is more pronounced with increasing inhibitor concentration.

To calculate the surface coverage, θ, it was assumed that the inhibition efficiency is due mainly to the blocking effect of the adsorbed species and hence θ=IE(%)/100 [25]. Here, an attempt was made to test the Langmuir, Temkin, Frumkin and Flory-Huggins isotherms having the following relationships:

$$\frac{C}{\theta} = C + \frac{1}{K} \qquad \text{(Langmuir)} \qquad (2)$$

$$\theta = \frac{1}{a}(\ln C + \ln K) \qquad \text{(Temkin)} \qquad (3)$$

$$\ln\left(\frac{\theta}{C(1-\theta)}\right) = \ln K + a\theta \qquad \text{(Frumkin)} \qquad (4)$$

$$\log\left(\frac{\theta}{C}\right) = \log(xK) + x\log(1-\theta) \qquad \text{(Flory-Huggins)} \qquad (5)$$

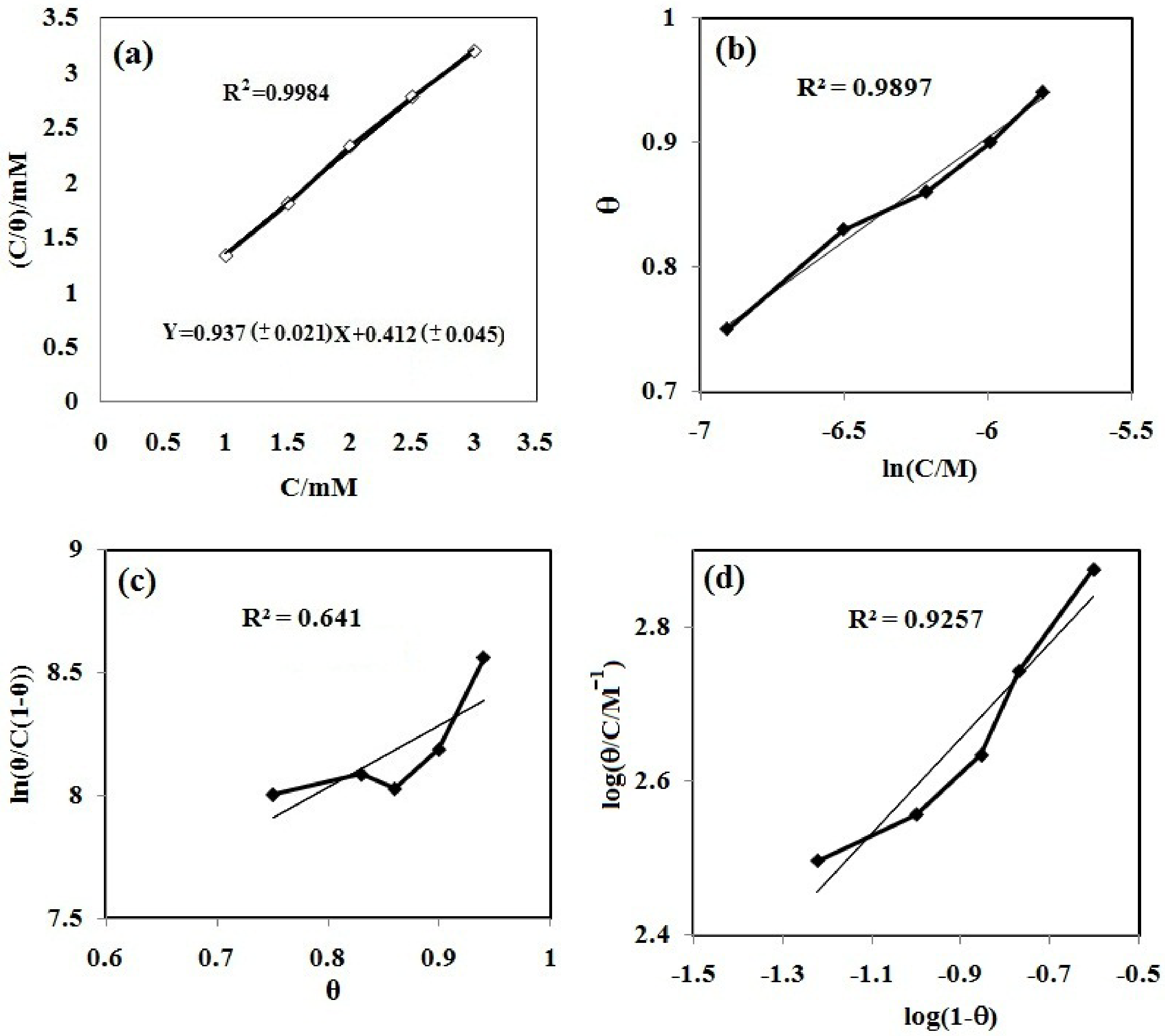

Fig. 3. Adsorption isotherms of vanillin by using surface coverage values calculated by Tafel polarization results (a) Langmuir (b) Temkin (c) Frumkin and (d) Flory-Huggins.

where θ is the surface coverage, C is the inhibitor concentration, K is the adsorption equilibrium constant, x is the size ratio and *a* is the molecular interaction constant, a constant expressing the interaction between adsorbed and adsorbing molecules.

The Langmuir adsorption isotherm was found to fit well with the experimental data (Fig. 3). Straight line were obtained when C/θ were plotted against C (Fig. 3). The correlation coefficient is close to 1.0, confirming that the adsorption of vanillin obeys the Langmuir isotherm. This isotherm is based on the assumption that all the adsorption sites are equivalent and that the particle binding occurs independently from the nearby sites being occupied or unoccupied.

Electrochemical impedance spectroscopy

Nyquist presentations of EIS for carbon steel in 1.0 M hydrochloric acid in the absence and presence of various concentrations of vanillin are shown in Fig. 4. Increasing the concentration of vanillin caused the values of charge transfer resistance to shift to elevated amounts. Table 3 lists impedance parameters in the absence and presence of different concentrations of vanillin.

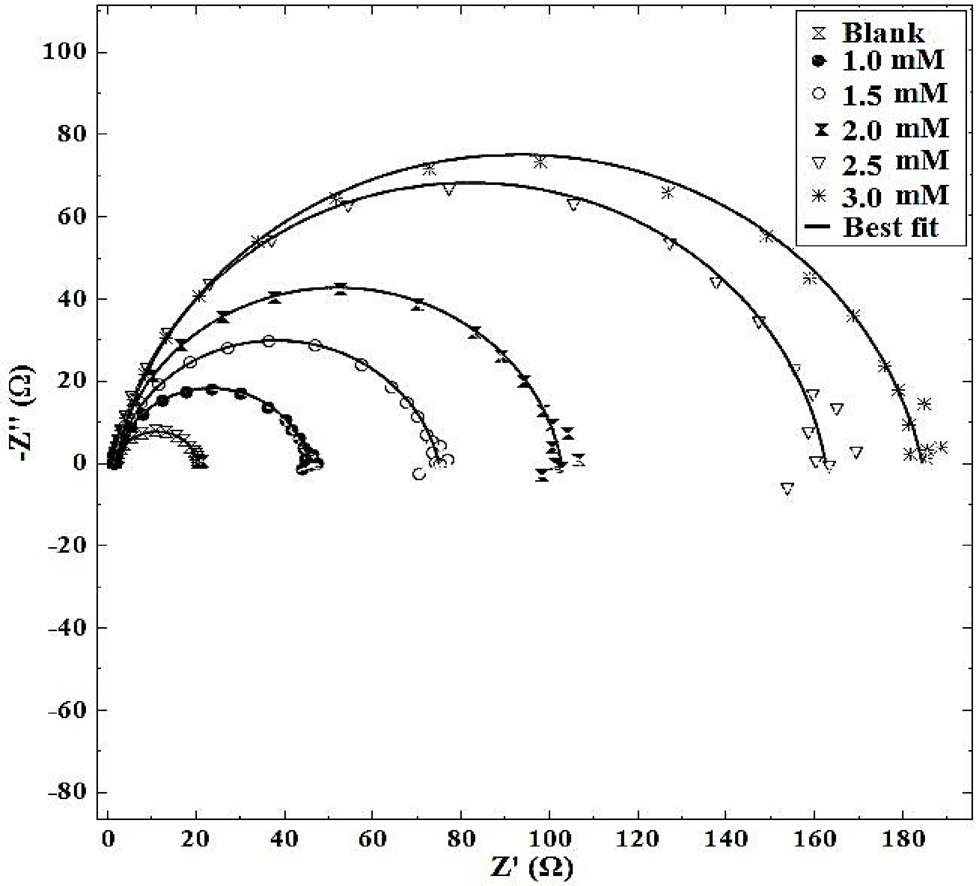

Fig. 4. (a) Nyquist plots for mild steel in 1.0 M hydrochloric acid solution in the absence and presence of different concentrations of vanillin at 25°C.

Table 3. Impedance parameters and the corresponding inhibition efficiency values for mild steel in 1.0 M hydrochloric acid solution containing different concentrations of vanillin at 25 ^{0}C

C /mM	R_s/Ω.cm^2	R_{ct}/Ω.cm^2	n	10^6 Y/F.cm^{-2}	IE_{EIS}(%)
0	1.7	19	0.831	264	-
1.0	1.1	44	0.886	194	57
1.5	1.2	74	0.874	133	74
2.0	1.1	102	0.895	114	81
2.5	1.2	161	0.897	77	88
3.0	1.2	183	0.877	65	90

Fig. 5 shows the electrical equivalent circuit employed to analyze the impedance plots. In this figure, R_s is the solution resistance and R_{ct} is the charge transfer resistance. The impedance of the constant phase element (CPE) is defined as follows [26]:

$$Z_{CPE} = \frac{1}{Y_0\left(jw\right)^n} \qquad (6)$$

where Y_0 is a proportional factor, j equals $\sqrt{-1}$, w is the angular frequency and n is the phase shift. For $n=0$, Z_{CPE} represents a resistance with $R = Y_0^{-1}$, for $n=1$ a capacitance with $C = Y_0$, for $n=0.5$ a Warburg element and for $n=-1$ an inductive with $L = Y_0^{-1}$ [27]. Because it was observed (Table 3) that the phase shift was closely near 1, the CPE obeys the capacitive behavior.

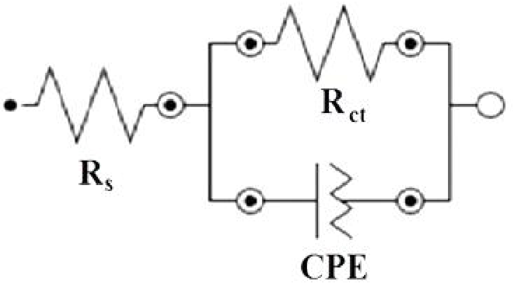

Fig. 5. The equivalent circuit used to fit the experimental data.

As it can be seen from Table 3 the R_{ct} values increased with the increasing the concentration of vanillin. On the other hand, the values of C_{dl} decreased with an increase in vanillin concentration. This situation was the result of an increase the surface coverage by vanillin. The thickness of the protective layer, d_{org}, was related to C_{dl} by the following equation [28]:

$$d_{org} = \varepsilon_0 \varepsilon_r / C_{dl} \qquad (7)$$

where ε_0 is the vacuum dielectric constant and ε_r is the relative dielectric constant. This decrease in the C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggested that the vanillin molecules function by adsorption at the metal/solution interface. Thus, the change in C_{dl} values was caused by the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface and thus decreasing the extent of the metal dissolution.

Inhibition efficiencies in Table 3 were calculated through the following expression:

$$IE\% = \frac{R_{ct}^{'} - R_{ct}}{R_{ct}^{'}} \times 100 \qquad (8)$$

where R_{ct} and $R_{ct}^{'}$ represent the charge transfer resistance, before and after addition of the inhibitor to the corrosion media, respectively. Comparison with the data in Table 2 learns that satisfactory agreement is found with the inhibition efficiencies as obtained through potentiodynamic polarization measurements. Plots of the data for each isotherm showed the EIS data are agreed with the Langmuir isotherm (Fig. 6).

Electrochemical noise

The EN signals corresponding to two nominally identical WEs with 100 mm^2 surface area in the absence and presence of vanillin have been measured during 15 min starting at 30 min after immersion time (Fig. 7). The last 1000 data points of EN signals have been chosen to be analyzed by wavelet transform and the SDPS plots of them were obtained as shown in Fig. 8.

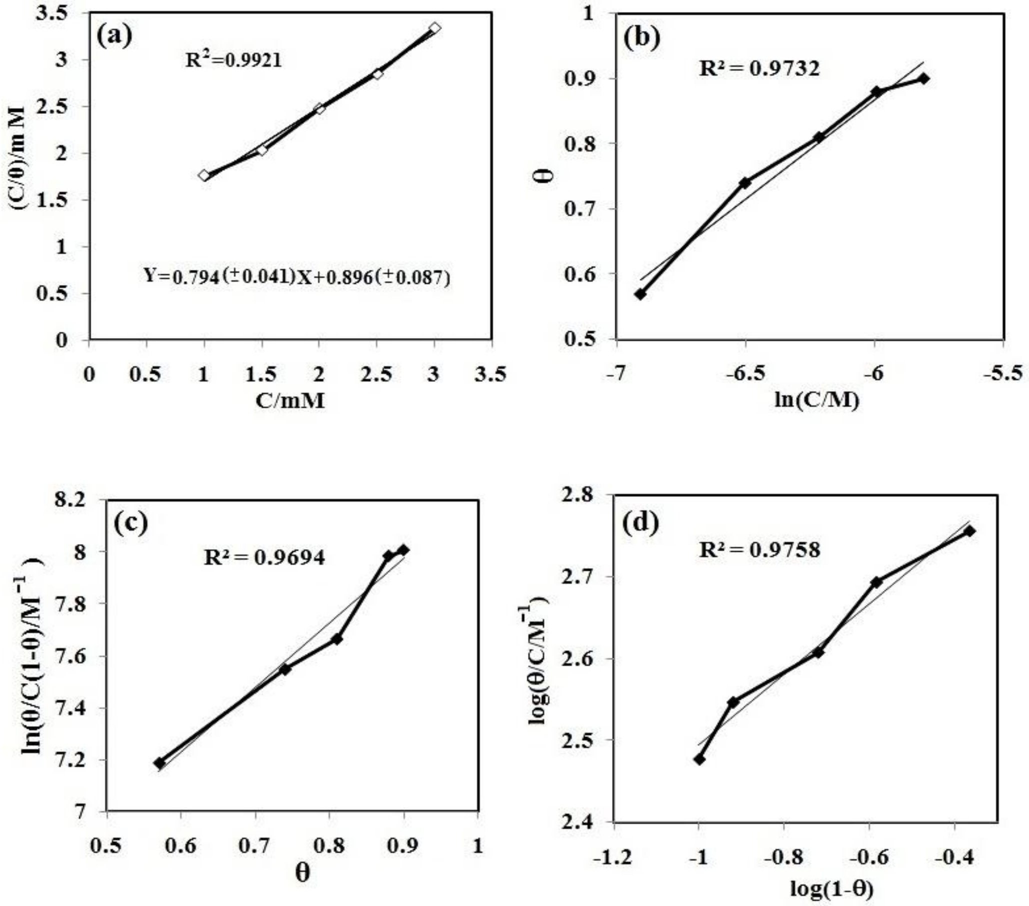

Fig. 6. Adsorption isotherms of vanillin by using surface coverage values calculated by EIS results (a) Langmuir (b) Temkin (c) Frumkin and (d) Flory-Huggins.

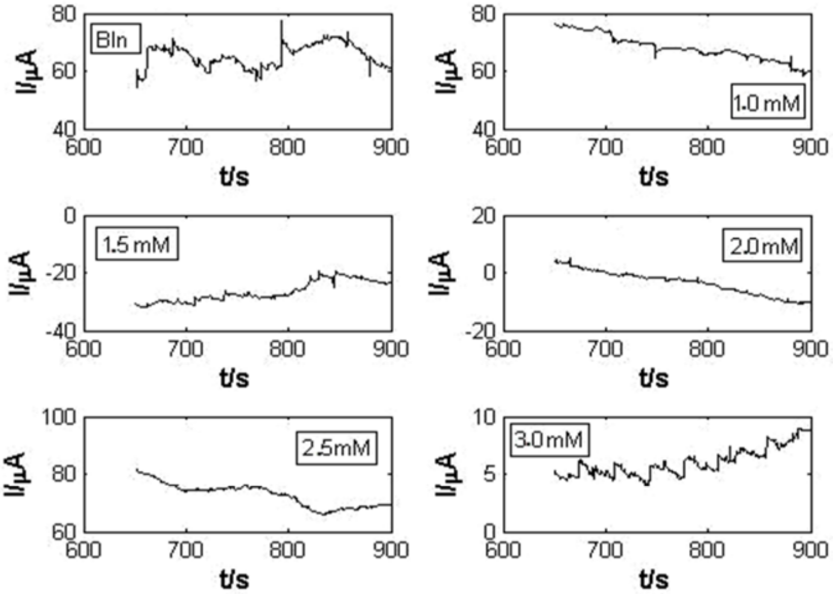

Fig. 7. EN current records of mild steel in 1.0 M hydrochloric acid solution in the absence and presence of different concentrations of vanillin during 15 min starting at 30 min after immersion **time.**

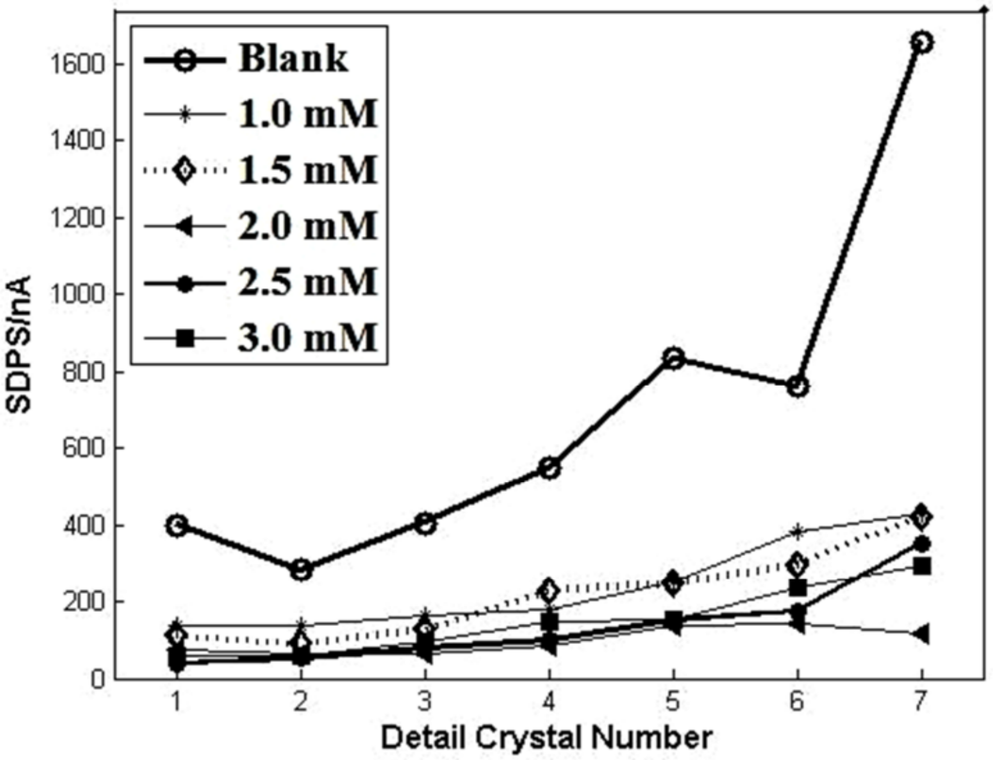

Fig. 8. SDPS plot of the last 1000 data points of EN signals in Fig. 7.

It is suitable to use the SDPS plots for calculation of the amount of noise charges at a particular timescale range. The maximum peak in SDPS plots corresponds to predominant transients in the original EN signal [24]. The predominant transients can be attributed to metastable pits. The development of a pit causes a quantity of electric charge to flow in the circuit which can be estimated by the following equation [29]:

$$Q = i_{\max} . \tau_{\max} \tag{9}$$

where $i_{\max}$ is the SDPS value at the maximum peak crystal (d_{max}) and $\tau_{\max}$ is the average time width of d_{max} crystal. Then it seems suitable to define the corrosion inhibition efficiency as follows:

$$IE_{EN}(\%) = \frac{Q - Q'}{Q} \times 100 \tag{10}$$

where Q and Q' are the noise charges in the uninhibited and inhibited cases, respectively.

It is evident from the SDPS plot of Signal Blank (Fig. 8) that the maximum is located at d5 crystal with the SDPS value of 836 nA ($i_{\max}$). According to Table 1, the average time width of crystal d5 is equal to 6 s. The values of the parameters derived from all of the SDPS plots in Fig. 8 have been summarized in Table 4 (d_{max}, τ_{max} and i_{max}). Table 4 further presents the values of Q and the inhibition efficiencies. Comparison with data in Tables 2 and 3 reveals that reasonable agreement is found with the IE values as obtained through potentiodynamic polarization and EIS measurements. Attempts were made to fit θ values to various isotherms and the Langmuir isotherm presents the best fit (Fig. 9).

Table 4. Noise parameters and the corresponding inhibition efficiency values for mild steel in 1.0 M hydrochloric acid solution containing different concentrations of vanillin at 25 ^{0}C

C /mM	d_{max}	τ_{max}/s	i_{max}/nA	Q/nCoul	IE_{EN}(%)
0	d5	6	836	5016	-
1.0	d5	6	255	1530	69
1.5	d5	6	249	1494	70
2.0	d5	6	135	810	84
2.5	d5	6	128	768	85
3.0	d4	3	150	450	91

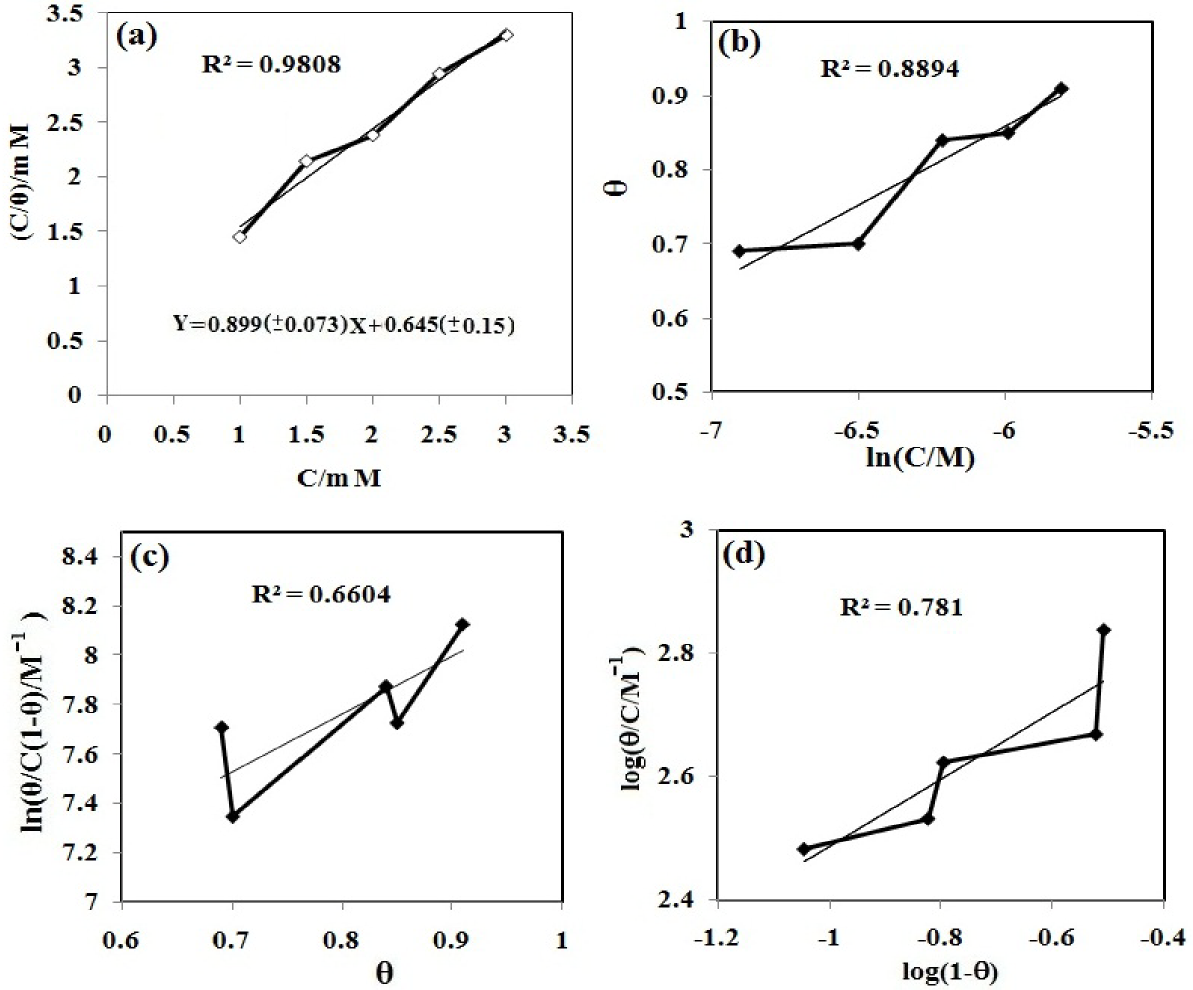

Fig. 9. Adsorption isotherms of vanillin by using surface coverage values calculated by EN results (a) Langmuir (b) Temkin (c) Frumkin and (d) Flory-Huggins.

Effect of temperature and thermodynamic parameters

In order to evaluate the adsorption of inhibitor and to calculate activation energy and thermodynamic parameters of the corrosion process of carbon steel in acidic media, potentiodynamic polarization measurements were performed in the temperature range of 25–55 ^{0}C in the absence and presence of various concentrations of vanillin solutions. The polarization curves in the absence and presence of 3.0 mM vanillin are illustrated in Fig. 10. The corrosion parameter values at different concentrations and temperatures are listed in Table 5. The results obtained from polarization curves show an increase in current density and decrease in IE% with increasing temperature. Generally, the decrease in the inhibition efficiency with increase in temperature may be explained by the fact that the time lag between the process of adsorption and desorption of inhibitor molecules over the metal surface is becoming shorter with increase in temperature [30]. Hence, the metal surface remains exposed to the acid environment for a longer period thereby increasing the rate of corrosion with increase in temperature and therefore IE% falls at elevated temperatures.

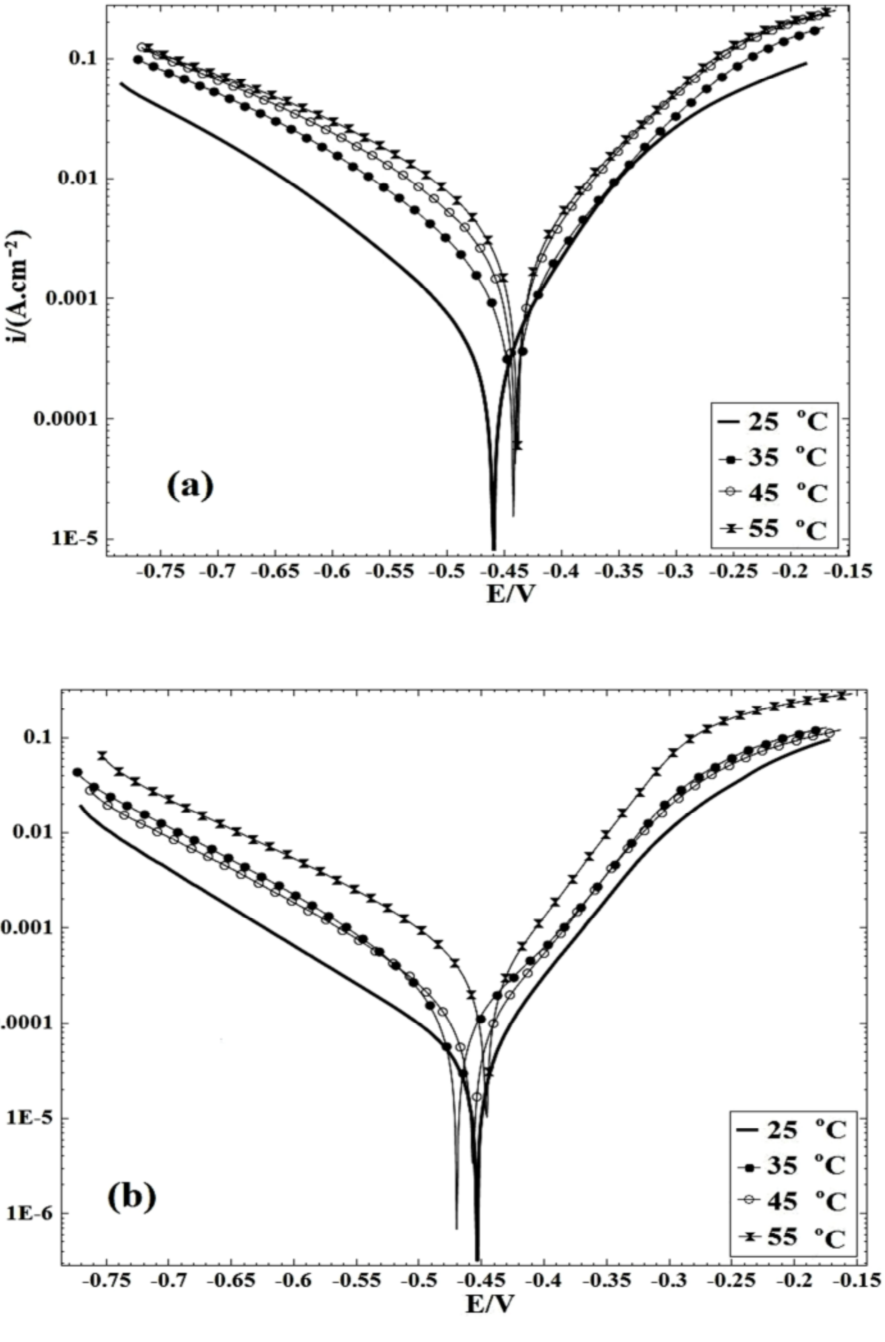

Fig. 10. Effect of temperature on the polarization curves in 1.0 M hydrochloric acid solution (a) without vanillin and (b) in the presence of 3.0 mM of vanillin.

The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation [28]:

$$i_{corr} = A\exp\left(\frac{-E_a}{RT}\right) \qquad (11)$$

where i_{corr} is corrosion current, A is a constant, E_a the activation energy of the metal dissolution reaction, R is the gas constant and T is the absolute temperature. The E_a values can be determined from the slopes of Arrhenius plots [ln i_{corr} versus 1/T (Fig. 11)]. Calculated activation energies for the corrosion process in the absence and presence of 3.0 mM vanillin are given in Table 6. A decrease in inhibition efficiency with rise in temperature with analogous increase in corrosion activation energy in the presence of 3.0 mM inhibitor compared to its absence is frequently interpreted as being suggestive of formation of an adsorption film of physical nature.

Table 5. Effect of temperature on the corrosion parameters of mild steel in 1.0 M hydrochloric acid solution containing vanillin

T/°C	C/mM	i_{corr}/μA.cm^{-2}	IE%	θ	T/°C	C/mM	i_{corr}/μA.cm^{-2}	IE%	θ
25	0	771	-	-	**45**	0	2463	-	-
	1.0	191	75	0.75		1.0	887	64	0.64
	1.5	131	83	0.83		1.5	740	70	0.70
	2.0	106	86	0.86		2.0	499	80	0.80
	2.5	74	90	0.90		2.5	464	81	0.81
	3.0	43	94	0.94		3.0	237	90	0.90
35	0	1387	-	-	**55**	0	4179	-	-
	1.0	344	75	0.75		1.0	1793	57	0.57
	1.5	328	76	0.76		1.5	1482	64	0.64
	2.0	204	85	0.85		2.0	1017	76	0.76
	2.5	154	89	0.89		2.5	962	77	0.77
	3.0	107	92	0.92		3.0	674	84	0.84

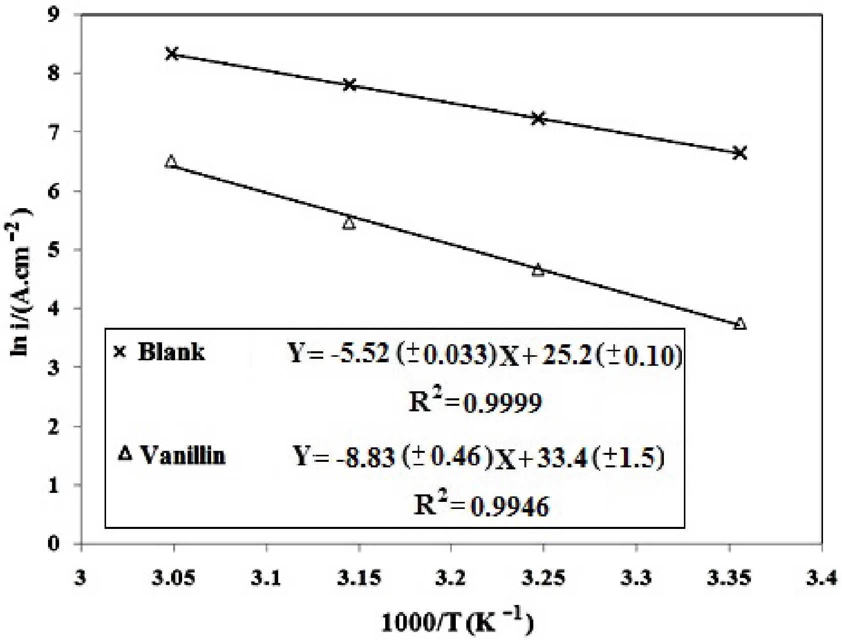

Fig. 11. Arrhenius plots for mild steel in 1.0 M hydrochloric acid solution in the absence and presence of 3.0 mM vanillin.

The Langmuir adsorption isotherm may be expressed by following equation [31]:

$$\ln\left(\frac{\theta}{1-\theta}\right) = \ln A + \ln C - \frac{\Delta H_{ads}}{RT} \qquad (12)$$

where θ is surface coverage, A is independent constant, C is concentration, R is gas constant, T is absolute temperature, and ΔH_{ads} is enthalpy of adsorption. The plot of ln(θ/(1-θ)) versus 1/T at constant additive concentration is shown in Fig. 12. The slope of the linear curves is equal to $-\Delta H_{ads}/R$ from which the average enthalpy of adsorption was calculated and its value is given in Table 6. The negative values of ΔH_{ads} reflect the exothermic behavior of inhibitor on the carbon surface. In an exothermic process, physisorption is distinguished form chemisorption by considering the absolute value of adsorption enthalpy. Typically, the absolute enthalpy of a physisorption process is lower than 41.86 kJ.mol^{-1} while the absolute enthalpy of a chemisorptions process approaches 100 kJ.mol^{-1} [32]. In the present study, the absolute values of enthalpy are smaller than the common physical adsorption heat, emphasizing that physical adsorption take place.

Table 6. Activation and thermodynamic parameters of adsorption obtained by potentiodynamic polarization measurements for mild steel in 1.0 M hydrochloric acid solution in the absence and presence of 3.0 mM of vanillin

	E_a (kJ.mol^{-1})	K (M^{-1})	ΔG_{ads} (kJ.mol^{-1})	ΔH_{ads} (kJ.mol^{-1})	ΔS_{ads} (J.K^{-1}. mol^{-1})
Blank	45.9	-	-	-	-
Vanillin	73.4	2425	-29.3	-28.5	2.7

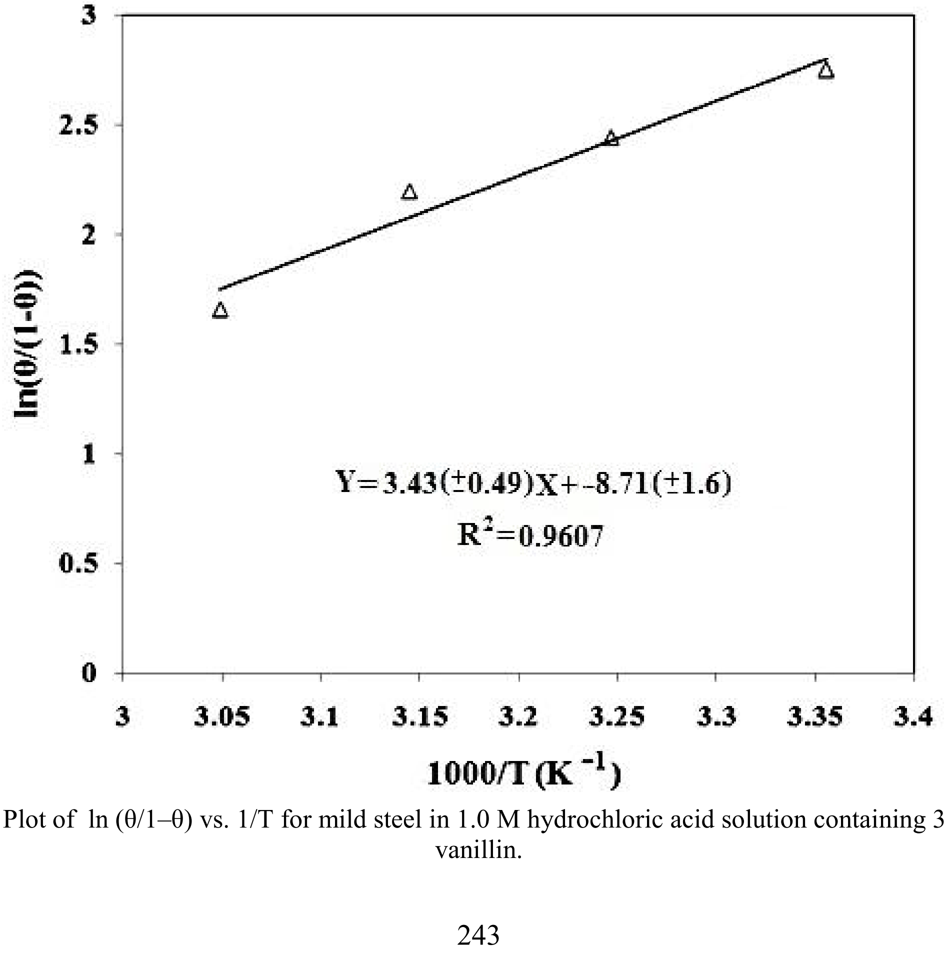

Fig. 12. Plot of ln (θ/1–θ) vs. 1/T for mild steel in 1.0 M hydrochloric acid solution containing 3.0 mM of vanillin.

The value of adsorption equilibrium constant, K_{ads}, is calculated from the reciprocal of the intercept of isotherm line (Fig. 3). The free energy of the adsorption of inhibitor on carbon steel surface can be evaluated with the following equation;

$$\Delta G_{ads} = -RT\ln(55.5K_{ads}) \qquad (13)$$

where 55.5 is the molar concentration of water in the solution expressed in M ($mol.L^{-1}$), R the gas constant ($8.314\ J\ K^{-1}.mol^{-1}$) and T the absolute temperature (K). The values of K_{ads} and ΔG_{ads} derived from Langmuir adsorption isotherms of Tafel polarization measurements (Fig. 3) are given in Table 6. Table 7 summarizes K_{ads} and ΔG_{ads} values obtained through Tafel polarisation, electrochemical impedance and electrochemical noise measurements. Satisfactory agreement is found between the different methods.

Table 7. The values of K_{ads} and ΔG_{ads} corresponding to polarization, EIS and EN data in 1.0 M hydrochloric acid solution

Tafel		EIS		EN	
K_{ads} (M^{-1})	ΔG_{ads} ($kJ.mol^{-1}$)	K_{ads} (M^{-1})	ΔG_{ads} ($kJ.mol^{-1}$)	K_{ads} (M^{-1})	ΔG_{ads} ($kJ.mol^{-1}$)
2425	-29.3	1116	-27.3	1550	-28.2

The value of the ΔG_{ads} of -40 kJ mol^{-1} is usually accepted as a threshold value between chemisorption and physisorption [33]. Therefore, the obtained values of the adsorption free energy, ΔG_{ads}, once again are indicative of physical adsorption.

Vanillin is an aromatic aldehyde containing carbonyl, methoxy and hydroxyl groups arranged around the aromatic ring (Fig. 1). Thus, the adsorption of vanillin on the surface of carbon steel may take place through all these functional groups. The simultaneous adsorption of the three functional groups forces the vanillin molecule to be horizontally oriented at the surface of alloy [10]. As the inhibitor concentration increases the area of the alloy surface covered by the inhibitor molecule also increases, leading to an increase in the IE.

SEM observations

SEM images were obtained from carbon steel surface after specimen immersion in 1.0 M hydrochloric acid solution in the absence and in the presence of 3.0 mM vanillin for 1 h at room temperature. Fig. 13a shows the SEM image of steel after immersion in blank solution which reveals a severe damage on surface due to metal pitting. Fig. 13b presents the steel surface protected after adding 3.0 mM of inhibitor, it is observed that the surface damage has diminished in comparison to the blank solution.

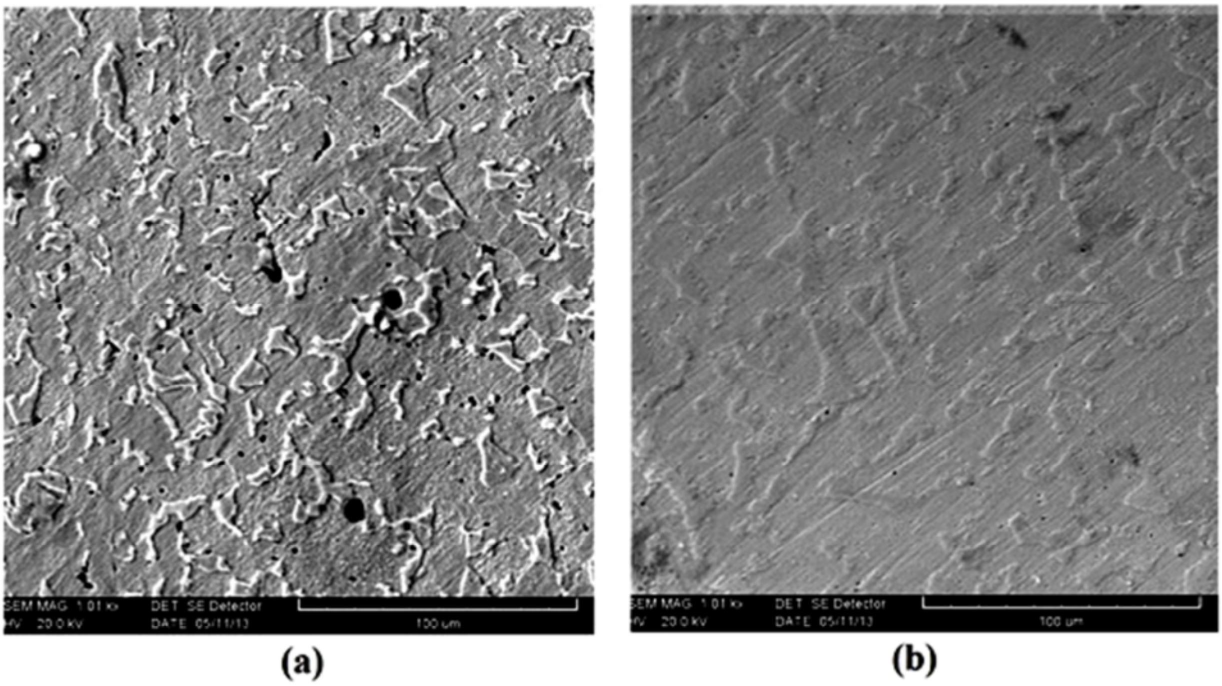

Fig. 13. SEM images of mild steel after immersion in 1.0 M hydrochloric acid for 1 h (a) in the absence of vanillin and (b) in the presence of 3.0 mM vanillin.

CONCLUSIONS

Results obtained from potentiodynamic polarization, EIS and EN measurements demonstrated that the adsorption of vanillin on carbon steel in 1.0 M hydrochloric acid followed the Langmuir isotherm. The calculated values of free energy and enthalpy adsorption indicated that the adsorption of vanillin on carbon steel is physical in nature.

The effect of temperature on the rate of corrosion in the absence and presence of vanillin was also studied and the thermodynamic parameters were computed.

According to calculation of the amount of noise charges by using the SDPS plots at the particular timescale rang it is possible to obtain the inhibition efficiency of an inhibitor. The IE and ΔG_{ads} values obtained from EN data of vanillin show a reasonable agreement with those obtained from potentiodynamic polarization and EIS measurements.

REFERENCES

[1] G. Gece, Corros. Sci., 53 (2011) 3873.
[2] P.B. Raja and M.G. Sethuraman, Mater. Lett., 62 (2008) 113.
[3] K.C. Emregul and M. Hayvali, Mater. Chem. Phys., 83 (2004) 209.
[4] K.C. Emregul and M. Hayvali, Corros. Sci., 48 (2006) 797.
[5] N.A. Negm, N.G. Kandile, I.A. Aiad and M.A. Mohammad, Colloid Surface A, 391 (2011) 224.
[6] X. Li, S. Deng and H. Fu, Prog. Org. Coat., 67 (2010) 420.
[7] N.A. Negm, N.G. Kandile, E.A. Badr and M.A. Mohammed, Corros. Sci., 65 (2012) 94.
[8] R. Rosliza, A. Nora'aini and W.B.W. Nik, J. Appl. Electrochem., 40 (2010)

833.
[9] A.Y. El-Etre, Corros. Sci., 43 (2001) 1031.
[10] X. Li, S. Deng, H. Fu, G. Mu and N. Zhao, Appl. Surf. Sci., 254 (2008) 5574.
[11] X. Li, S. Deng, G. Mu and Q. Qu, Mater. Lett., 61 (2007) 2514.
[12] X. Li, S. Deng, H. Fu and G. Mu, Corros. Sci., 50 (2008) 3599.
[13] N.J. Walton, M.J. Mayer and A. Narbad, Phytochemistry, 63 (2003) 505.
[14] Y. Tan, Sensor Actuat. B-Chem., 139 (2009) 688.
[15] R. A. Cottis, Corrosion, 57 (2001) 265.
[16] G. Schmitt, K. Moeller and P. Plagemann, Mater. Corros., 55 (2004) 742.
[17] G. Schmitt, Mater. Corros., 58 (2007) 924.
[18] S. Ritter, T. Dorsch and R. Kilian, Mater. Corros., 55 (2004) 781.
[19] A. Aballe, M. Bethencourt, F.J. Botana and M. Marcos, Electrochim. Acta, 44 (1999) 4805.
[20] A. Aballe, M. Bethencourt, F.J. Botana and M. Marcos, Electrochem. Commun. , 1 (1999) 266.
[21] M.T. Smith and D.D. Macdonald, Corrosion, 65 (2009) 438.
[22] S. R. Allahkaram and M. Khodayari, Anti-Corros. Method. M., 55 (2008) 250.
[23] Z. Dong, X. Guo, J. Zheng and L. Xu, Electrochem. Commun., 3 (2001) 561.
[24] M. Shahidi, S.M.A. Hosseini and A.H. Jafari, Electrochim. Acta, 56 (2011) 9986.
[25] G. Achary, Y. A. Naik, S. V. Kumar, T.V. Venkatesha and B.S. Sherigara, Appl. Surf. Sci., 254 (2008) 5569.
[26] M. G. Hosseini, M. Ehteshamzadeh and T. Shahrabi, Electrochim. Acta, 52 (2007) 3680.
[27] D. A. Lopez, S. N. Simison and S.R.d. Sanchez, Electrochim. Acta, 48 (2003) 845.
[28] F. Bentiss, M. Lebrini and M. Lagrenee, Corros. Sci., 47 (2005) 2915.
[29] M. Shahidi, H. Tajabadipour, H.G. Hakemi and M.R. Gholamhosseinzadeh, Int. J. Electrochem. Sci., 8 (2013) 11734.
[30] E.A. Noor, Corros. Sci., 47 (2005) 33.
[31] H. Ashassi-Sorkhabi, B. Shaabani and D. Seifzadeh, Appl. Surf. Sci., 239 (2005) 154.
[32] S. Martinez and I. Stern, Appl. Surf. Sci., 199 (2002) 83.
[33] Q.B. Zhang and Y.X. Hua, Electrochim. Acta, 54 (2009) 1881.