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Electrochemical Behavior of Jasmine Tea Extract as Corrosion Inhibitor for Carbon Steel in Hydrochloric Acid Solution

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The extract of jasmine tea was studied as corrosion inhibitor for carbon steel in 1 mol L^{-1} HCl solution by electrochemical method, scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). Inhibition efficiency for carbon steel in HCl solution increases with inhibitor concentration and temperature. Adsorption behavior of the extract obeys Langmuir adsorption isotherm. Polarization curves results indicate that this extract is a mixed type inhibitor. SEM and XPS reveal that the extract adsorbs on metal surface and forms a protective layer.

Keywords: corrosion inhibitor, EIS, XPS, carbon steel, acid solution

1. INTRODUCTION

Acid solutions are universally applied in industry, especially in acid pickling, acid descaling, oil well acidizing and so on [1, 2]. However, in such highly corrosion environments, metals are suffered serious corrosion attack. Adding corrosion inhibitor is one of the most effective and economic measures to alleviate the corrosion of metals. Many of commercial corrosion inhibitors had been exploited to prevent corrosion of metals in acidic solution, including organic and inorganic chemicals. More practically, mixtures of corrosion inhibitors are more commonly used in industry. Although most of the corrosion inhibitors exhibit excellent inhibition performance, it still has many deficiencies like expensive in raw materials, complicated in processing and more or less toxic to the environment [3].

Especially the latter one, the toxicity of corrosion inhibitors becomes more and more important in practical applications.

Historically, natural plants were firstly utilized as corrosion inhibitors for quite a long time. It encountered troubles of lacking of enough raw materials, expensive in economy and insufficiency in inhibition efficiency. Later on, more and more chemicals form factories were applied as corrosion inhibitors. Inorganic inhibitors, like chromate, nitrate, arsenate, molybdate, etc. were widely used in history for their relative low cost and highly effective. Organic corrosion inhibitors, which often contain groups of N, O, S and P, have been popular till now. Most of the present corrosion inhibitors have environmental problems more or less, no matter in inhibitor itself or in the production process.

Nowadays, corrosion inhibitors have attracted great attention again. The most important reason lies in the environmental friendly of the natural inhibitors [4]. Although extensive substituting of the present industrial products is not practical in quite a long time, the natural corrosion inhibitor, in no doubt, is a main trend in research and application of the future. Many researchers had proved that some natural plants are very useful as corrosion inhibitors. Natural plant resources have been investigated as natural corrosion inhibitors, such as Garlic peel, Musa paradisica peel, Gingko biloba fruit, Ginkgo leaves, Jasminum nudiflorum Lindl. Leaves, Henna, Jamun, Aloe vera, Neolamarckia cadamba, Silybum marianum, Aloe plant and Wwatermelon rind [3, 5–15].

Jasmine tea, the famous traditional scented tea in china, is popular in food industry and our daily consumption. It is reported [16] that the jasmine tea acts as a source of natural polyphenol antioxidants which mainly contain (-) epicatechin (EC), (-) epicatechin gallate (ECG), (-) epigallocatechin (EGC) and (-) epigallocatechin gallate (EGCG) [17] and other natural compounds, such as tea catechins, caffeine, theophylline, theobromine, etc [18]. In the structures of these compounds, they contain O, N atoms and aromatic ring, which could be the useful structure of typical corrosion inhibitor. Besides, it is a common sense in our daily life that the tea stain often occurs on the surface of cups and it is hard to be washed off. It implies that some ingredients in the tea may have excellent adsorbing ability. Therefore, the jasmine tea has the potential to be an excellent corrosion inhibitor.

In our present work, the extract of Jasmine tea was studied as corrosion inhibitor for carbon steel in HCl solution via electrochemical impedance spectroscopy (EIS), polarization curves, scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). Effects of concentration and temperature on corrosion density and inhibition efficiency were discussed. Additionally, the inhibition mechanism of Jasmine tea extract was discussed as well.

2. EXPERIMENTAL

2.1 Preparation of corrosion inhibitor

The leaf of Jasmine tea was used as the raw material of the corrosion inhibitor (Commercial Jasmine tea produced by Tenfu’s Tea Corporation, China). The Jasmine tea leaves were crushed into powder by machine. The jasmine tea extract was prepared from 15 g of the tea powder with 50 mL 1 mol L^{-1} HCl solution by magnetic stirring at room temperature for 5 h. After filtration, the extracts were preserved in a refrigerator. The residue was dried in an oven at 333.15 K for one day, and weighed the residue to calculate the concentration of the tea extract.

2.2 Electrochemical experiments

Q235 carbon steel, with the element of C=0.02%, Mn=1.22%, Si=0.30%, S=0.026% and P=0.015%, was used for the experiments. The samples of 40 mm×13 mm×2 mm were abraded with a range of emery paper (grade 320, 500, 1000 and 2000 in turn). After washed with deionized water and ethanol, the samples were dried by a cold drier. Then they were exposed with a surface area of 1 cm^2 and the rest of the surface was covered by epoxy resin. The traditional three-electrode cell was adopted to evaluate the corrosion inhibition of jasmine tea extract. A KCl-saturated calomel electrode worked as reference electrode and a platinum foil as counter electrode.

All electrochemical experiments were tested by electrochemical workstation (Ivium Stat). In all electrochemical experiments, the first step was measuring the open circuit potential (OCP) for 1 h to reach the stable OCP. Electrochemical impedance spectra (EIS) were tested in the frequency range of 100 kHz–0.01 Hz with 10 mV alternating-current (AC) amplitude around the open circuit potential after measured OCP for 1 h. The impedance data were analyzed by *ZSimpWin* software. Potentiodynamic polarization curves (PC) were recorded after OCP and EIS measurements. The anodic and cathodic polarization curves were measured at the range of potential from -300 mV to +300 mV (vs. OCP) at scan rate of 0.5 mV s^{-1}. The corresponding parameters were fitted and obtained by linear polarization resistance (the LPR method). The following relations were used to calculate the inhibition efficiency from EIS and PC, respectively.

$$\eta\% = \frac{R\mathrm{ct}_{\mathrm{inh}} - R\mathrm{ct}_0}{R\mathrm{ct}_{\mathrm{inh}}} \times 100\% \qquad (1)$$

$$\eta\% = \frac{I\mathrm{corr}_0 - I\mathrm{corr}_{\mathrm{inh}}}{I\mathrm{corr}_0} \times 100\% \qquad (2)$$

where R_{ct0} and I_{corr0} are charge transfer resistance and corrosion density without extract in the corrosion solution, respectively. $R\mathrm{ct}_{\mathrm{inh}}$ and $I\mathrm{corr}_{\mathrm{inh}}$ are charge transfer resistance and corrosion density with extract in the corrosive medium, respectively.

2.3 X-ray photoelectron spectroscopy (XPS)

The sample with size of 40×13×2 mm was abraded with a series of emery papers grade 320, 500, 1000 and 2000, washed by water, ethanol and dried by a blow drier, then sample was immersed in 1 mol L^{-1} HCl solution with 1.00 g L^{-1} jasmine tea extract for 4 h at 293.15 K, last it was carefully taken out the samples, washed by water and ethanol in turn. The samples were dried after the above steps. The samples were tested in ESCALAB 250 spectrometer (ThermoFisher Scientific USA) with the monochromatized Al-Kα X-ray source (150 W). XPS PEAK 41 software was used to analyze the experiment data.

2.4 Fourier transform infrared spectrophotometer (FT-IR)

FT-IR was used to characterize jasmine tea extract. Jasmine tea extract was prepared by KBr disk method and test in FT-IR (Nicolet Instrument Corporation, Madison, WI). The measured wavelength was from 4000 cm^{-1} to 400 cm^{-1}.

2.5 Scanning electron microscope (SEM)

The carbon steel samples for SEM were prepared as the steps of electrochemical measurements. After dried by a cold drier, the samples were immersed in the solution with and without 1.00 g L^{-1} jasmine tea extract at 293.15 K for 4 h, then the samples were carefully took out and washed by water and ethanol, last the samples were dried by a cold drier. After finishing the above steps, the sheets were tested by SEM (EVO MA15, ZEISS).

3. RESULTS AND DISCUSSION

3.1 OCP measurement

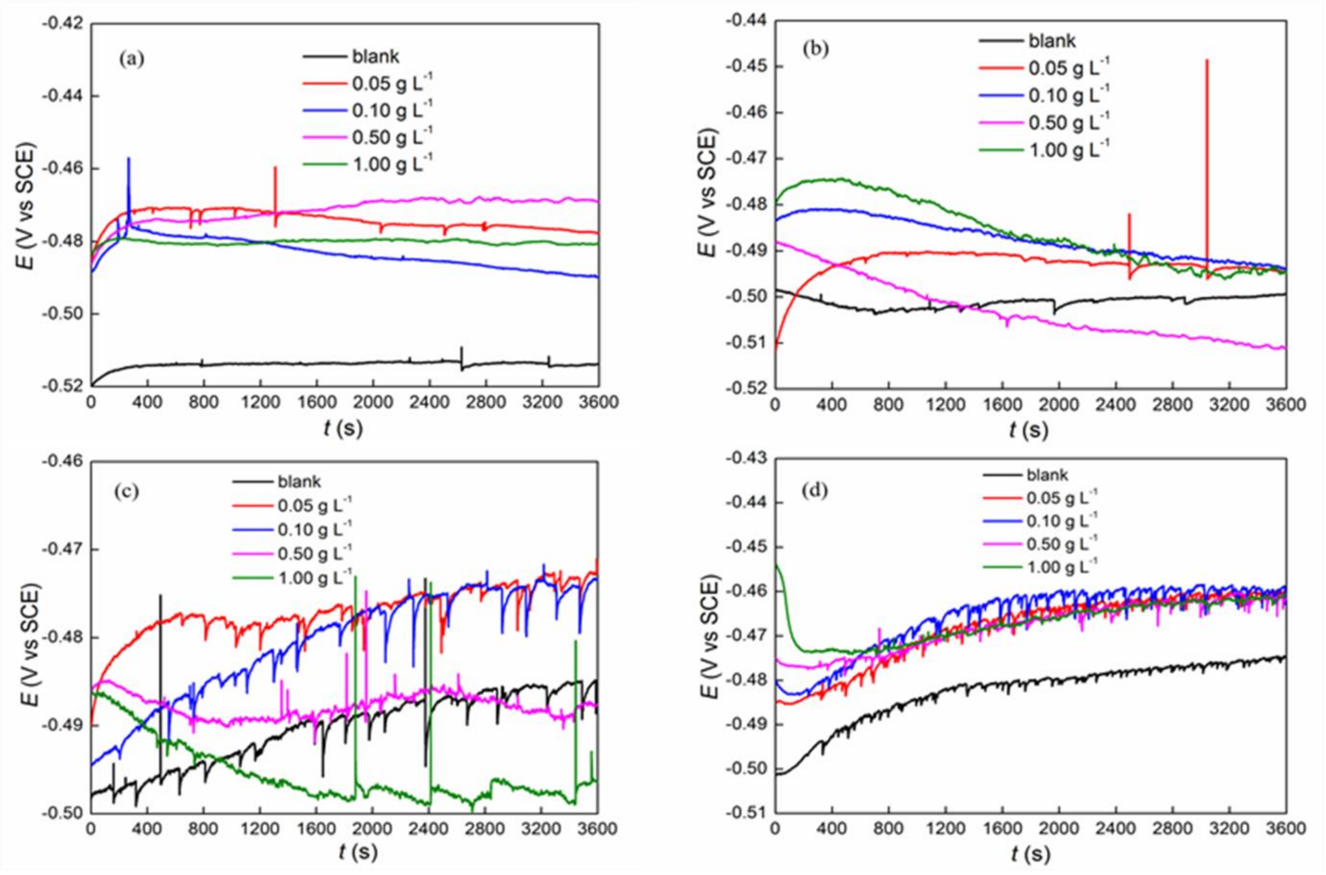

Figure 1. OCP plots for carbon steel in 1 mol L^{-1} HCl in the absence and presence of different concentrations of Jasmine tea extract at different temperatures: (a) 293.15 K, (b) 313.15 K, (c) 333.15 K, (d) 353.15 K.

Fig. 1 shows the OCP plots of carbon steel in 1 mol L^{-1} HCl solution in the presence of different concentration of jasmine tea extract at different temperatures. The OCP variations behave differently with temperatures and concentrations of corrosion inhibitor. It is shown that in solution without inhibitor, OCP moves positively with immersion time at almost all temperatures. Sudden fluctuation exists in all temperatures especially in higher ones of 333.15 K and 353.15 K. The emergence of sudden fluctuation can be attributed to the breakdown of oxide film or corrosion product formed on the surface of carbon steel [19]. A relatively stable OCP state is established with immersion time prolonged. That is because of the relatively stable rates of corrosion process and forming of oxides at interface [20].

The presence of extract inhibitor has remarkable influence on OCP variation. At 293.15 K, the presence of inhibitor results in sharply shifting of OCP towards positive direction. However, in higher temperatures, such behavior is not quite apparent. At 333.15 K, the OCP fluctuations are very intense at all concentrations. In the presence of 0.05 g L^{-1} and 0.10 g L^{-1} of inhibitor, OCP moves positively with time, which is similar with the blank. While, in the presence of 0.50 g $L^{-1}$and 1.00 g L^{-1} of inhibitor, OCP increases slightly and then decreases towards negative direction sharply. At 353.15 K, during the first stage of immersion the OCP varies with the increase of concentration. The maximum original OCP value occurs at -0.454 V with 1.00 g L^{-1} of inhibitor. All the OCP variations at 353.15 K exhibit fast declining after started immersion then slowly increasing and relatively stabilizing with time.

All the phenomena happened in the presence of inhibitor are due to opposite processes existed at the metal/solution interface [20]. On the one hand, the inhibitor forms a protective film on metal surface, which leads to the OCP value shifting to positive direction, on the other hand, the metal is corroded in the medium, which results in decreasing of potential. It is also noticed that, in most circumstances, the value of OCP in the presence of Jasmine tea extract shifts towards more positive potential in comparison with blank solution, which can be explained as the effective adsorption of inhibitor molecules on the metal surface [21].

3.2 Polarization curves

Fig. 2 shows the polarization curves for carbon steel in the absence and presence of different concentrations of Jasmine tea extract at different temperatures. It is noticeable that both cathodic and anodic current densities decrease with the presence of inhibitor by comparing with the curves in blank solution at all studied temperatures, which suggests that the addition of extract inhibitor can influence on cathodic and anodic reaction at the same time. It is also shown from the shape of curves that the corrosion of carbon steel in HCl behaves as active corrosion. The polarization curves contain region of Stern and Geary (linear polarization), weak polarization and linear polarization region. A series of electrochemical parameters, including corrosion density (I_{corr}), corrosion potential (E_{corr}), Tafel constants of cathodic (bc), constants of anodic (ba) and inhibition efficiency, are included and presented in Table 1. According to Table 1, it is obviously that the values of I_{corr} decrease observably in the presence of extract as well as decrease on increasing of extract concentration, indicating that the inhibitor molecules adsorbed on the metal surface to inhibit the dissolution of active sites [22].

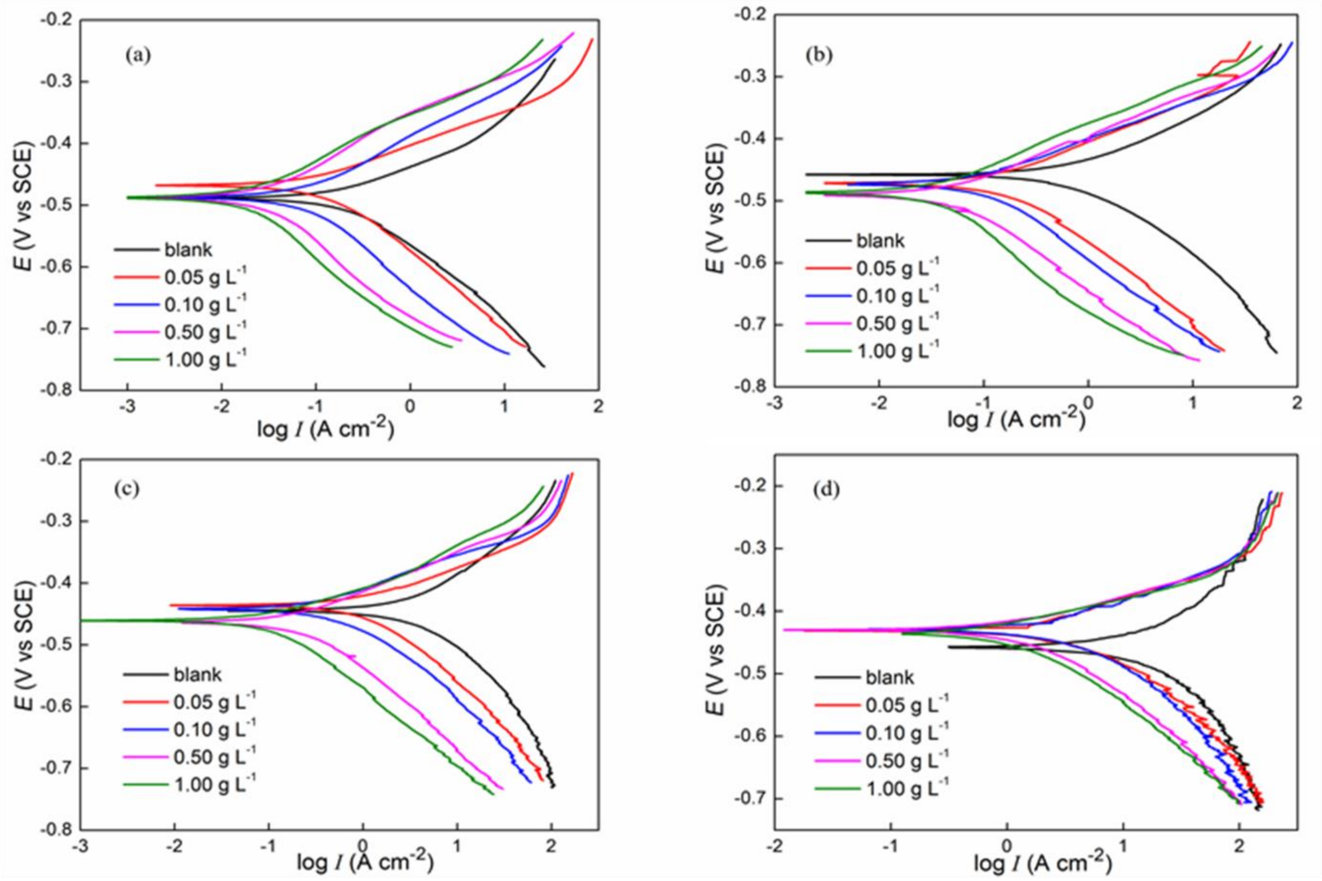

Figure 2. Polarization curves plots for carbon steel in 1 mol L^{-1} HCl in the absence and presence of different concentrations of Jasmine tea extract at different temperatures: (a) 293.15 K, (b) 313.15 K, (c) 333.15 K, (d) 353.15 K.

By comparison with blank solution, the displacement of E_{corr} is less than 85 mV in the presence of extract, which suggests that this extract acts as a mixed inhibitor [23, 24]. It can be seen from Table 1 that inhibition efficiency increases with rising of extract concentration at all temperatures, indicating that the extract inhibitor influences the corrosion of metal via adsorbing on the surface of carbon steel [25]. Moreover, it also can be observed that the inhibition efficiency presents a slight change with increase of temperature in the same concentration of extract, which suggests that this extract can strongly adsorb on the metal surface to alleviate the corrosion of carbon steel in HCl solution.

The effect of temperature on the corrosion of carbon steel in HCl solution has been studied in the temperature range from 293.15 K to 353.15 K in the presence of different concentrations of extract. Polarization measurements were used to obtain the activation parameters. The corresponding polarization results are shown in Table 1. The influence of temperature can be explained by Arrhenius equation [26, 27]:

$$I_{corr} = k \exp\left(-\frac{E_a}{RT}\right) \qquad (3)$$

where I_{corr} is corrosion density, E_{a} is the activation energy and k represents the pre-exponential factor. The plots of ln I_{corr} vs 1000/T for carbon steel in 1 mol L^{-1} HCl in the presence of different concentration of extract are shown in Fig. 3. The values of the activation energy are calculated from the straight line slopes and presented in Table 2. It can be seen that E_{a} in the absence of extract (68.7 kJ mol^{-1}) is much higher than those in the presence of different concentrations of Jasmine tea extract. The higher activation energy can be ascribed to the chemisorption happened at the interface. The opposite one is physical adsorption [26, 28, 29]. Therefore, the decrease of activation energy in the presence of inhibitor indicates that there is a chemical adsorption between Jasmine tea extract and carbon steel surface.

Table 1. Electrochemical parameters of carbon steel in 1 M HCl without and with different concentrations of Jasmine tea extract at different temperatures

C ($\text{g}\cdot\text{L}^{-1}$)	T (K)	Ecorr (mV)	ba ($\text{mV}\cdot\text{dec}^{-1}$)	-bc ($\text{mV}\cdot\text{dec}^{-1}$)	Icorr ($\mu\text{A cm}^{-2}$)	η (%)
blank	293.15	-487.7	29	46	276.6	-
0.05		-466.8	28	43	161.6	41.6
0.10		-487.4	44	67	150.5	45.6
0.50		-487.8	50	78	66.4	76.0
1.00		-488.1	59	95	60.3	78.2
blank	313.15	-458.5	34	44	967.3	-
0.05		-460.9	31	48	188.6	80.5
0.10		-471.8	33	55	164.7	83.0
0.50		-490.2	37	55	89.8	90.7
1.00		-486.7	39	67	65.5	93.2
blank	333.15	-444.2	54	56	5745	-
0.05		-436.0	26	50	1424	75.2
0.10		-441.2	29	38	585.3	89.8
0.50		463.4	28	39	270.3	95.3
1.00		-459.1	22	49	150.1	97.4
blank	353.15	-457.0	79	93	32390	-
0.05		-430.1	37	39	3751	88.4
0.10		-428.5	30	42	3598	89.0
0.50		-429.3	25	50	1891	94.2
1.00		-433.0	22	43	1272	96.1

Besides, the Arrhenius equation also can be expressed as follows [28]:

$$I\text{corr} = \frac{RT}{Nh}\exp(\Delta S\text{a}/R)\exp(-\Delta H\text{a}/RT) \qquad (4)$$

where N is Avogadro constant, h represents Plank’s constant, ΔSa and ΔHa are the apparent entropy and enthalpy of activation, respectively. The plots of ln I_{corr}/T vs 1000/T for carbon steel in 1 mol L^{-1} HCl in the absence and presence of different concentration of extract are shown in Fig. 4. Values of ΔSa and ΔHa can be obtained by the intercept and slope of straight lines and shown in Table 2.

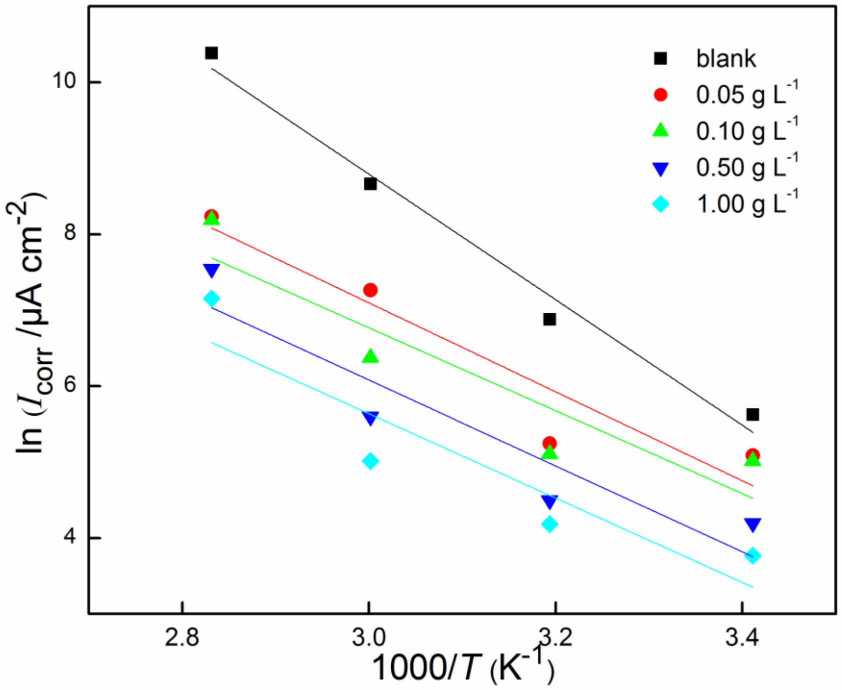

Figure 3. Arrhenius plots for carbon steel in 1 mol L^{-1} HCl with different concentrations of Jasmine tea extract

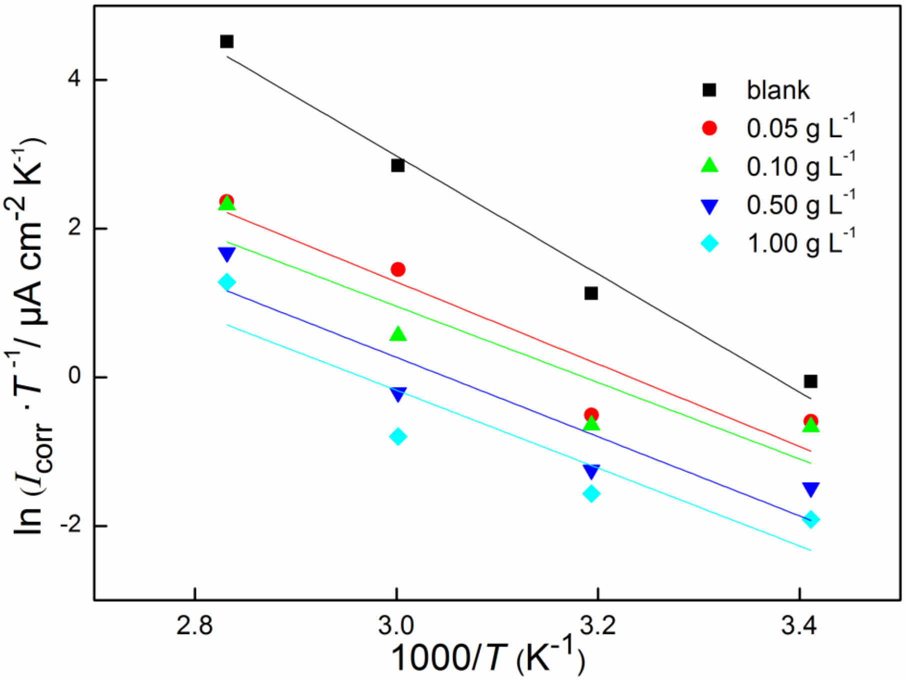

Figure 4. The plots ln I_{corr}/T vs 1000/T for carbon steel in 1 mol L^{-1} HCl with different concentrations of Jasmine tea extract

Table 2. Activation energies, enthalpy and entropy of adsorption for Jasmine tea extract at different concentrations

C (g L^{-1})	Ea (kJ mol^{-1})	ΔHa (kJ mol^{-1})	ΔSa (J mol^{-1} K^{-1})
blank	68.7	66.1	-25.4
0.05	47.2	46.1	-48.7
0.10	45.4	42.7	-61.4
0.50	47.0	44.3	-62.4
1.00	46.2	43.5	-68.4

It can be seen from Table 2 that all values of ΔHa are positive no matter in the absence or presence of extract, which indicates that the dissolution of metal in acid solution is an endothermic process. It is also noticed that the value of ΔHa in the presence of extract is lower than the one in the absence of extract. This result can be explained that the dissolution of metal was prevented owing to the inhibitor adsorbed on metal surface to form a protective film. The entropy ΔSa increases more negative in the presence of extract, indicating that the corrosive medium become more ordered by the forming of activated complex from reactants [28, 29].

3.3 Electrochemical impedance spectroscopy (EIS)

Fig. 5 shows the EIS behavior, including Nyquist and Bode plots, of carbon steel in 1 M HCl solution in the absence and presence of different concentrations of Jasmine tea extract. It is observed that the Nyquist plots display one capacitive loop in both blank solution and low concentration of extract at all studied temperatures, which means one time constant at such conditions. The diameter of semicircle markedly increases with the concentration of extract in comparison to blank solution, suggesting that the addition of extract can effectively onfluence the corrosion of carbon steel in HCl solution. The diameter of semicircle decreases with temperature at the same concentration of extract. Moreover, the shape of semicircle is not a perfect semicircle but a depressed one, which is ascribed to the inhomogeneity of working electrode [23].

The equivalent circuit as shown in Fig. 6 (a) was applied to fit the experimental results in blank solution and low concentrations of extract at all studied temperatures [30]. R_s and R_t are the solution resistance and charge transfer resistance. *CPE*, constant phase element, includes the double capacitance (C_{dl}) and the depression coefficient. Only one capacitive loop displayed indicates a relative simple corrosion process at interface.

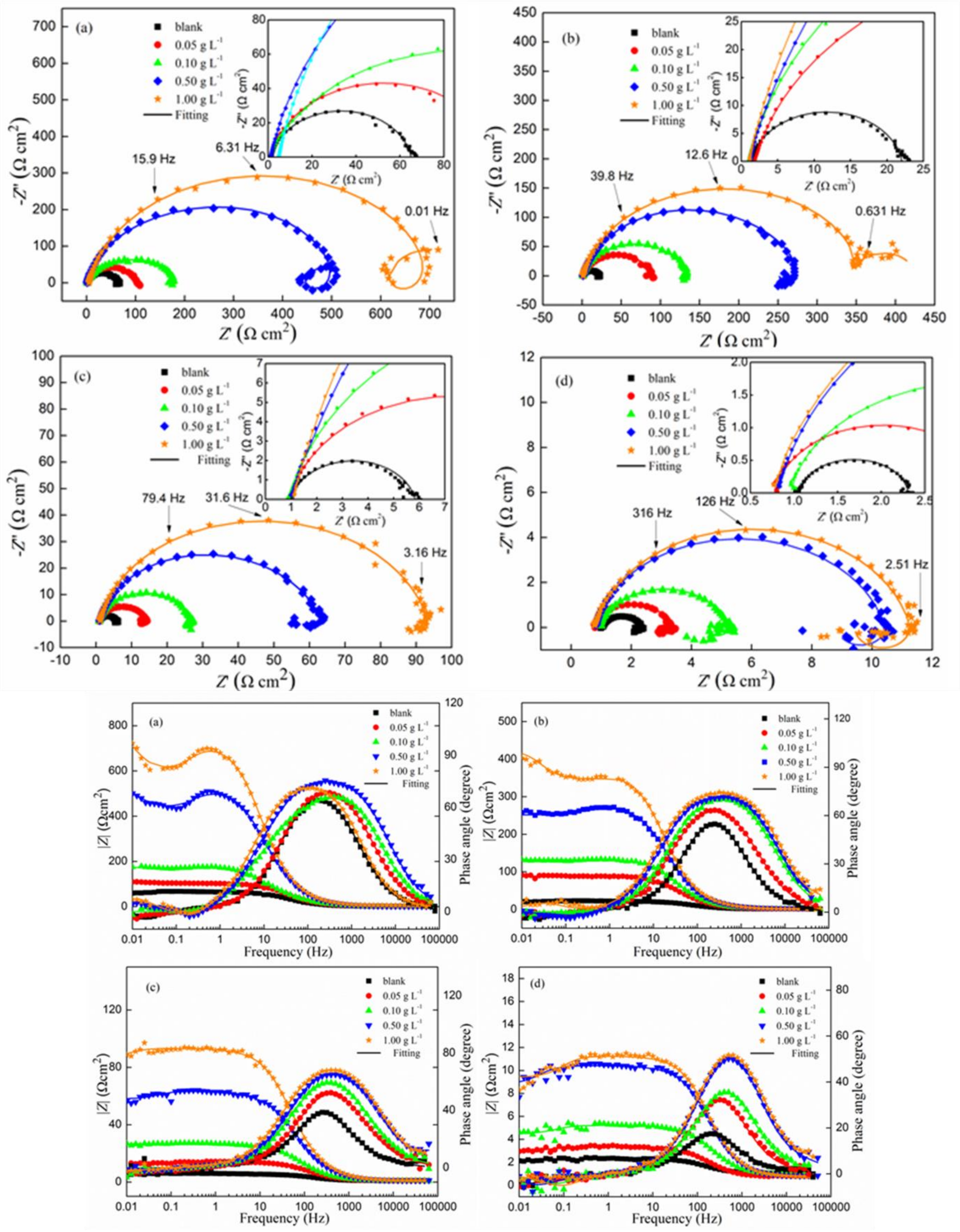

Figure 5. Nyquist and Bode plots for carbon steel in 1 mol L^{-1} HCl in the absence and presence of different concentrations of Jasmine tea extract at different temperatures: (a) 293.15 K, (b) 313.15 K, (c) 333.15 K, (d) 353.15 K.

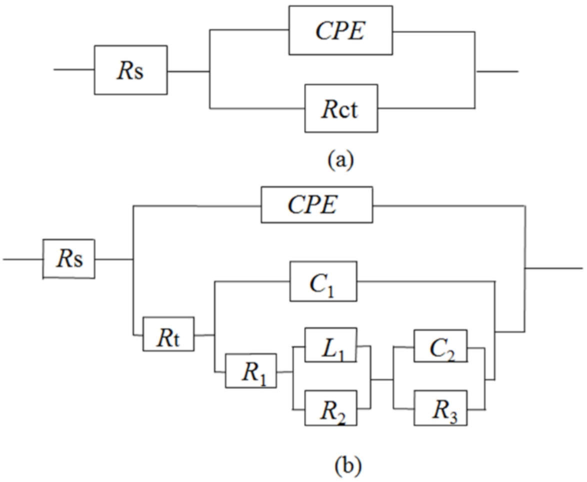

Figure 6. Equivalent circuits to fit EIS results: (a) fit EIS results in blank and low concentration of extract, (b) fit EIS results in the high concentration of extract.

Table 3. EIS parameters for carbon steel in 1 M HCl in the absence and presence of different concentrations jasmine tea extract at different temperatures

C (g·L^{-1})	T (K)	Rs (Ωcm^2)	CPE (10^6 s^n Ω^{-1} cm^{-2})	C_{dl} (μF/ cm^2)	n	L (μHcm^2)	R_{ct}/R_p (Ωcm^2)	η (%)	X^2
blank	293.15	1.6	178	106.5	0.90	-	63.5	----	0.00092
0.05		1.3	115	67.8	0.89	-	102.5	38.1	0.00218
0.10		1.2	102	59.3	0.88	2.7	177.0	64.1	0.00050
0.50		1.2	542	36.7	0.90	45.5	597.4	89.4	0.02130
1.00		4.7	548	29.7	0.83	75.7	1068.3	94.1	0.00104
blank	313.15	1.4	265	151.9	0.90	-	20.6	-	0.00162
0.05		0.7	135	69.6	0.87	-	87.6	76.4	0.00058
0.10		1.0	95.9	53.7	0.88	-	131.6	84.3	0.00054
0.50		1.2	60.1	37.0	0.89	21.2	277.0	92.6	0.01990
1.00		1.0	60.1	29.0	0.83	2.6	441.7	95.3	0.02200
blank	333.15	1.0	764	344.8	0.88	-	4.9	-	0.00237
0.05		0.9	308	142.9	0.88	-	12.9	62.5	0.00300
0.10		0.9	240	116.2	0.87	-	25.9	81.3	0.00192
0.50		0.6	163	19.2	0.82	18.2	63.2	92.3	0.00105
1.00		0.9	97.1	32.9	0.81	88.1	92.6	94.8	0.01070
blank	353.15	1.0	1150	481.1	0.88	3.0	1.3	-	0.00162
0.05		0.8	1110	203.4	0.88	1.2	2.6	50.2	0.00266
0.10		0.9	608	120.1	0.87	1.7	4.3	70.0	0.00509
0.50		0.8	304	97.5	0.68	8.5	9.7	86.6	0.00280
1.00		0.7	257	71.7	0.81	3.1	10.6	87.8	0.00156

The equivalent circuit of Fig. 6 (b) was used to fit the EIS results in the presence of high concentration of extract [31]. $C1$ and $C2$ are capacitance, L is inductance, R_1, R_2 and R_3 are resistances which are in relation with two capacitance loops and inductance loop in the full range of frequency. The Nyquist plots in the presence of high concentrations of extract display an inductance at low frequency. The emergence of inductance at low frequency can be owing to the dissolution of corrosion product or inhibitor film. This change implies that the addition of high concentrations of extract in solution results in the emergence of other time constants. There exist four time constants, as is shown in equivalent circuit of Fig. 6 (b), which indicates a complicated process in the presence of high concentrations of corrosion inhibitor.

In equivalent circuit of Fig. 6 (b), the R_p was obtained by following equation:

$$R_p=R_t+R_1+R_2+R_3 \qquad (5)$$

All EIS parameters, R_s, R_{ct}, n and double layer capacitance (C_{dl}), are listed in Table 3. The values of C_{dl} were obtained from the Hsu and Mansfeld formula [32, 33]:

$$C_{dl}=(Y_0R^{1-n})^{1/n} \qquad (6)$$

In the Eq. (6), Y_0 is the magnitude of the CPE ($\Omega^{-1}S^n\ cm^{-2}$), R represents the charge transfer resistance (R_{ct}) or polarization resistance (R_p), n is an exponent to decide the CPE belongs to the detail electronics. It is obviously that the charge transfer resistance or polarization resistance increase with the extract concentration at all studied temperatures. It is also obtained that the charge transfer resistance or polarization resistance decreases with the rise of temperatures in the same concentration of extract. The inhibition efficiency displays the opposite tendency. Besides, the values of C_{dl} decrease with increasing of Jasmine tea extract concentration at different temperatures. The double layer of capacitance can be calculated by Helmholtz model [26, 34]:

$$C_{dl}=\frac{\varepsilon\varepsilon_0}{d}A \qquad (7)$$

where A is the area of electrode surface. ε and ε_0 are permittivity of local and vacuum. d stands for the thickness of protective layer. In Eq. (7), A and ε_0 are constants. The decrease of C_{dl} is owing to the increase of d or decrease of ε. The increase of protective layer (d) is attributed to the adsorption of extract on metal surface. The maximum inhibition efficiency reaches 87.8% in the concentration of extract 1.00 g L^{-1} even if at 353.15 K. EIS results indicate that the Jasmine tea extract exhibits excellent inhibition on the corrosion of carbon steel in HCl solution.

3.4 Adsorption isotherm of Jasmine tea extract at carbon steel surface

The adsorption isotherms are usually involved in the inhibition mechanism of inhibitors [35]. Adsorption isotherms can also provide useful information concerning with interaction between corrosion inhibitor and the metal surface. The adsorption isotherms of Langmuir, Frumkin and Temkin are commonly applied to fit and explain the adsorption process [36]. In our present study, it is found that Langmuir adsorption isotherm can fit the adsorption process best. Langmuir adsorption isotherm can be expressed by the following equation [21, 22]:

$$\frac{C_{inh}}{\theta}=\frac{1}{K_{ads}}+C_{inh} \qquad (6)$$

where θ represents surface coverage, which can be obtained by (η/100). C_{inh} and K_{ads} are inhibitor concentration and the adsorption equilibrium constant, respectively. The plot of C_{inh}/θ vs C_{inh} is shown in Fig. 7. The linear association coefficient is, in the range of 0.9973 to 0.9999, very close to 1, which implies that the adsorption of Jasmine tea extract on the metal surface can be interpreted by Langmuir adsorption isotherm.

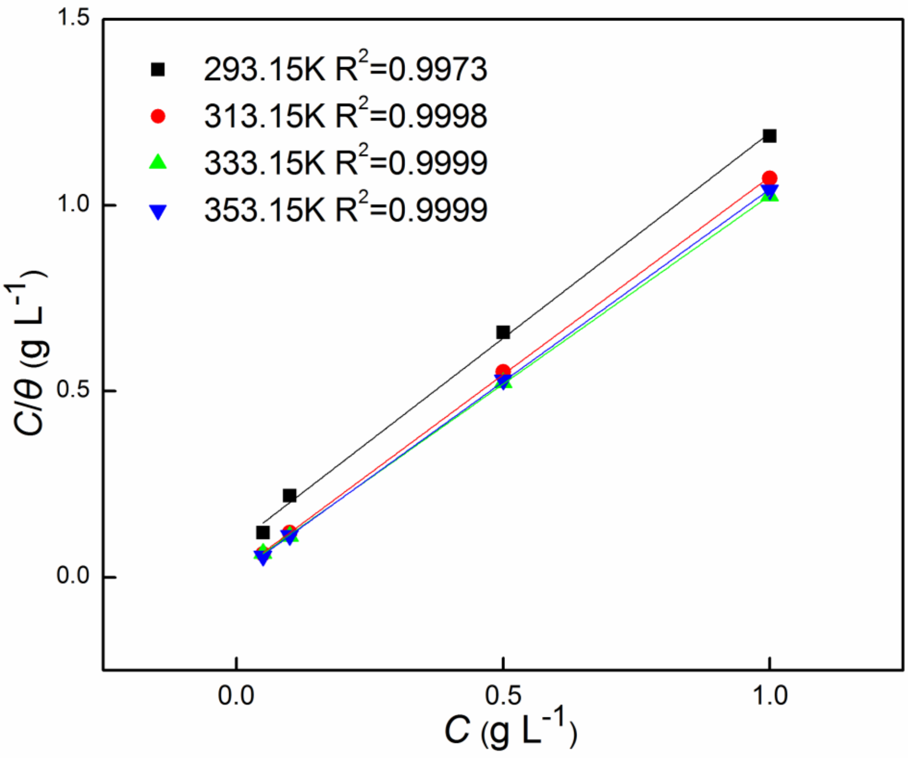

Figure 7. Langmuir adsorption plots for carbon steel in 1 mol L^{-1} HCl at different temperatures.

To obtain the type of adsorption between inhibitor and metal surface, it is necessary to acquire the standard free energy of adsorption (ΔG_{ads}^0). The standard free energy can be calculated as follows [37]:

$$\Delta G_{\text{ads}}^{0} = -RT \ln(55.5K_{ads}) \quad (8)$$

where 55.5 is the molar concentration of water, R and T are the universal gas constant and the absolute temperature, respectively. The values of ΔG_{ads}^0 at different conditions are listed in Table 4. The negative value of ΔG_{ads}^0 implies that the adsorption of extract on the metal surface is a spontaneous process [35]. It can be seen that the values of ΔG_{ads}^0 increase with temperature, suggesting that the stronger interaction between Jasmine tea extract and carbon steel surface happened at higher temperature [38]. The values of ΔG_{ads}^0 are in the range from -20 kJ mol^{-1} to -40 kJ mol^{-1}, indicating that the type of adsorption process belongs to mixed type adsorption (including physisorption and chemisorption) [39].

Table 4. Values of ΔG_{ads}^{0} for carbon steel in 1 M HCl at different temperatures

Temperature (K)	ΔG_{ads}^{0} (kJ mol^{-1})
293.15	-15.6
313.15	-21.7
333.15	-23.3
353.15	-25.9

3.6 XPS analysis

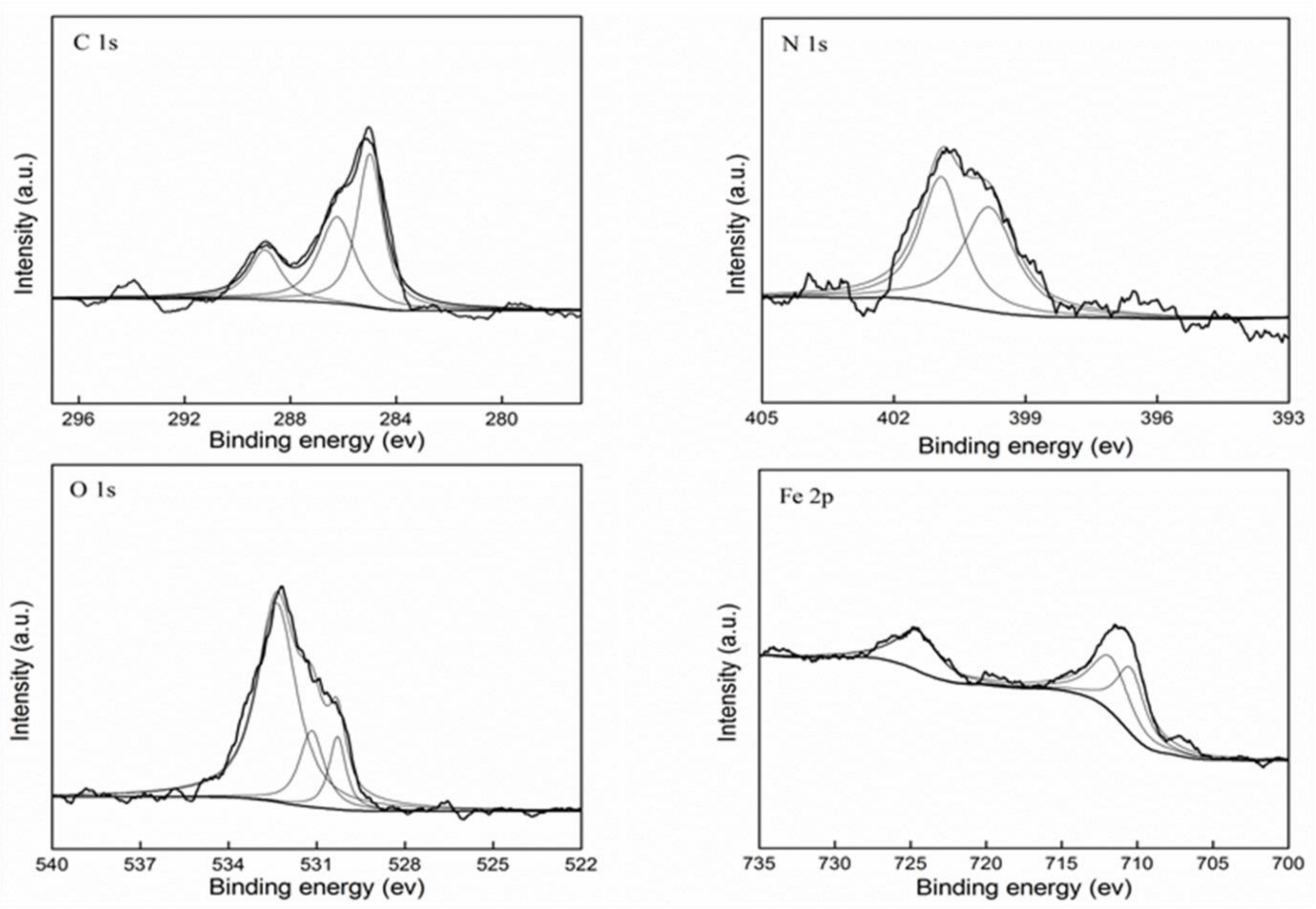

Figure 8. The XPS deconvoluted profile for C 1s, N 1s, O 1s and Fe 2p for carbon steel in 1 mol L^{-1} HCl with 1.00 g L^{-1} Jasmine tea extract at 293.15 K.

Fig. 8 shows the XPS deconvoluted profile for C 1s, N 1s, O 1s and Fe 2p of carbon steel after immersed for 4 h in 1 mol L^{-1} HCl with 1.00 g L^{-1} Jasmine tea extract at 293.15 K. It demonstrates that the C 1s was deconvoluted into three peaks at 285 eV, 285.6 eV and 288.9 eV, these three peaks at different binding energy represent different groups or components. The peaks at 285 eV and 285.6 eV are ascribed to C-C, C=C, C-H aromatic bonds, C-O and C-N, other peak at 288.9 eV represents C=O [23, 40]. The O 1s spectrum can be deconvoluted into three peaks. One peak at 530.1 eV stands for O^{2-} and combined with Fe^{2+} or Fe^{3+} to form Fe_3O_4 or Fe_2O_3 oxides, other peak at 531.7 eV represents OH^{-}

which can be easily react with FeO to obtain hydrous iron oxides (FeOOH) [23], the rest of peak at 532 eV can be owing to O-C-O bond [2]. The N 1s spectrum can be interpreted as two peaks. One peak at binding energy of 400.1 eV can be ascribed to NH_2 and =N-, another peak at binding energy 401.2 eV is attributed to $=N^{+}H$ [41, 42]. The Fe 2p spectrum shows three peaks at different binding energy. These peaks at 711 eV, 712.5 eV and 724.3 eV are owing to FeO, Fe_2O_3, FeOOH and Fe^{3+} compound, respectively [40]. The XPS results indicate that the compound film is formed on metal surface, which contains iron oxide/hydroxide and the molecules of extract. These components provide a protective film which can effectively isolate the corrosion medium and reduce the corrosion of carbon steel in HCl solution.

3.7 FT-IR result

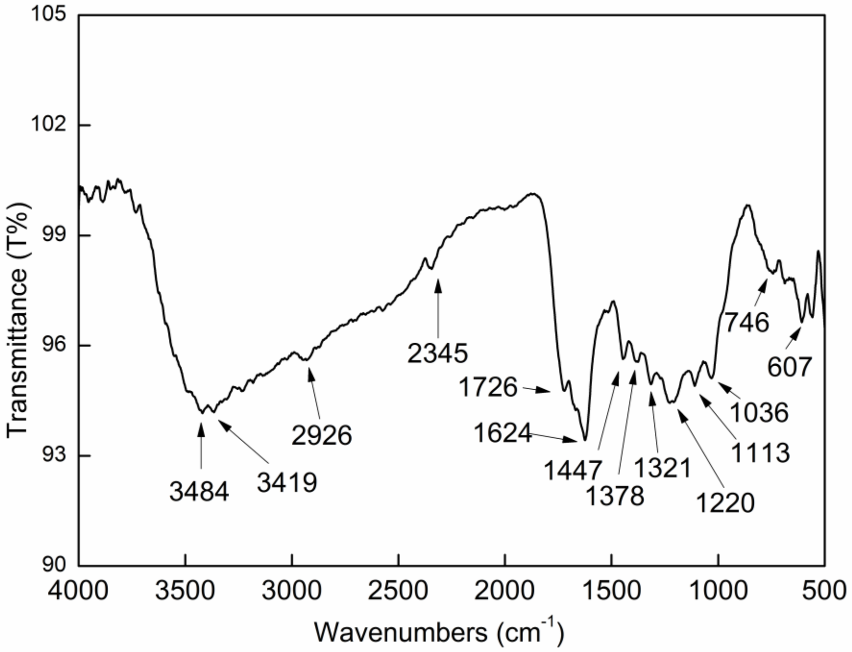

Figure 9. FT-IR result of Jasmine tea extract

Fig. 9 shows the FT-IR result of Jasmine tea extract. A wide absorb peak at 3484 and 3419 cm^{-1} is owing to –OH or N–H stretching vibration. The wavenumbers at 2345 cm^{-1} can be attributed to N–H stretching vibration. The peaks at 1378 and 1321 cm^{-1} are assigned to O-H and C-N stretching vibration, respectively. The absorb peaks around 1726 and 1321 cm^{-1} are related to C=O and C-O stretching vibration. The rest peaks for extract are ascribed to the C-H group and aromatic. FT-IR result shows Jasmine tea extract contains –OH, N–H, C-N, C=O, C-O etc. functional group and aromatic, this result suggests that the extract has the potential of acting as corrosion inhibitor.

3.8 Observation on surface morphologies by SEM

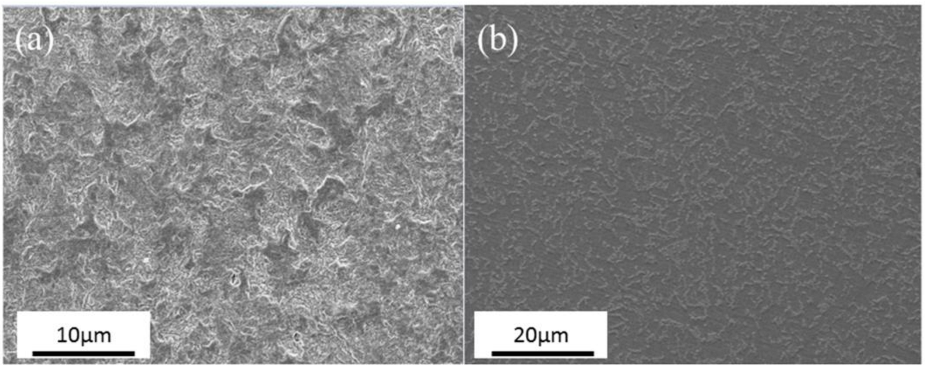

Figure 10. SEM images of carbon steel after immersion in 1 mol L^{-1} HCl at 293.15 K (a) in the absence of Jasmine tea extract, (b) in the presence of 1.00 g L^{-1} Jasmine tea extract.

Fig. 10 demonstrates the surface morphologies of carbon steel immersed in 1 mol L^{-1} HCl without and with 1.00 g L^{-1} Jasmine tea extract at 293.15 K. It is clearly that the surface of carbon steel in 1 mol L^{-1} HCl without inhibitor appears serious corrosion attack with irregular microtopography. On the contrary, the sample surface in the presence of Jasmine tea extract is smooth and only slightly corroded (Fig. 10b). This is attributed to the adsorption of inhibitor molecules on metal surface. Inhibition effects of jasmine extract provide protection to carbon steel. The adsorption leads to effective isolation of the metal from corrosive medium and alleviating of the corrosion of carbon steel in HCl solution [29, 35].

3.9 Inhibition mechanism of Jasmine tea extract at carbon steel surface

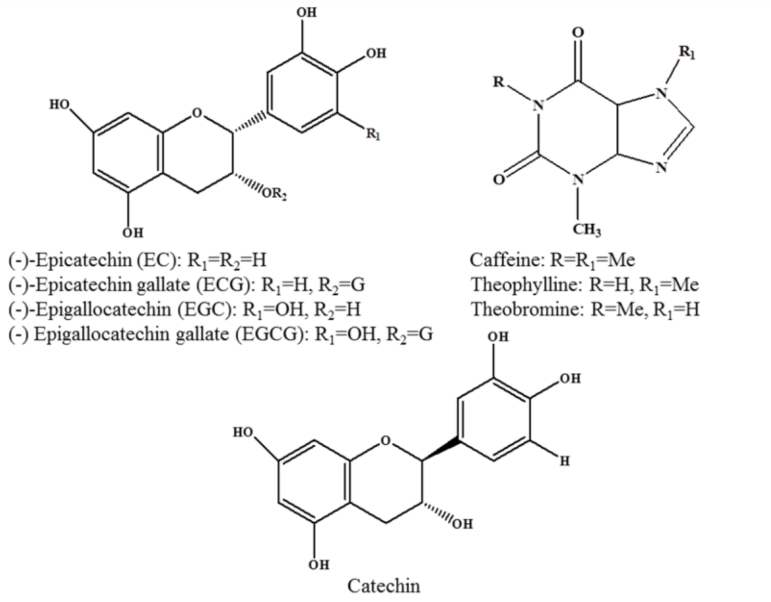

Figure 11. Chemical structures of mainly components in Jasmine tea

The inhibition behavior of Jasmine tea extract can be owing to the adsorption of organic compounds of extract on carbon steel surface. The major constituents of Jasmine tea contain (-) epicatechin (EC), (-) epicatechin gallate (ECG), (-) epigallocatechin (EGC)， (-) epigallocatechin gallate (EGCG), catechin, caffeine, theophylline and theobromine, etc [17, 18]. The structures of these constituents are shown in Fig. 11. It can be seen from Fig. 11 that the chemical structures of these compounds include -OH, C=O, C=N, C-O, N-heterocyclic and aromatic ring, which accord the structures of typical corrosion inhibitors. It is noticeable that in the chemical structures of these compounds, such as O, N atoms and aromatic ring, can provide lone pair electrons. It is well-known that the iron exists the vacant orbitals ‘‘d’’. The adsorption of jasmine tea extract on the carbon steel surface via donor–acceptor interactions between long pair electrons of O, N, aromatic ring and the vacant orbitals ‘‘d’’ of iron. Therefore, it is reasonable to infer that these compounds in extract exhibit excellent inhibition ability. XPS results illustrate that the protective layer contains the above function groups as well. According to the above results, the inhibition mechanism of Jasmine tea extract can be owing to the adsorption of extract on metal surface and forming a compact protective layer.

4. CONCLUSIONS

(1) The extract of Jasmine tea displayed excellent inhibition effects for carbon steel in 1 mol L^{-1} HCl. Inhibition efficiency increased with the rise of extract concentration and temperature.

(2) Polarization curves revealed that the Jasmine tea extract was a mixed inhibitor.

(3) EIS results showed that polarization resistance increased with inhibitor concentration but decreased with temperature.

(4) The adsorption process belonged to mixed type adsorption. Adsorption of Jasmine tea extract obeyed Langmuir adsorption isotherm.

(5) SEM results demonstrated that the surface of carbon steel was smooth and slightly corroded in the presence of extract. XPS analysis revealed that the compound protective layer contained iron oxide/hydroxide and inhibitor molecules.

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