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Aqueous extract of propolis as corrosion inhibitor for carbon steel in aqueous solutions

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The inhibition efficiency of aqueous extract of propolis on the corrosion of carbon steel in 35 ppm aluminum sulfate and 10 ppm chloride solution was investigated by weight loss and electrochemical measurements. The corrosion rate of carbon steel and the inhibition efficiency of the propolis were calculated. The results obtained showed that propolis could serve as an effective inhibitor for the corrosion of carbon steel in aqueous media. Inhibition was found to increase with increasing concentration of the extract. The inhibitive action of propolis is discussed on the basis of adsorption of stable complex at the carbon steel surface. Theoretical fitting of different isotherms, Langmuir was tested to clarify the nature of adsorption. Potentiodynamic polarization curves revealed that this extract acts as a mixed type inhibitor and the inhibition efficiency of up to 92% can be obtained.

Key words: Corrosion inhibition, propolis extract, carbon steel, 35 ppm aluminum sulfate and 10 ppm chloride solution.

INTRODUCTION

Carbon steel is widely used in industries due to its good mechanical property. Carbon steel has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions. The investigation of corrosion of carbon steel is always a subject of high theoretical as well as practical interest. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. One way of protecting steel from corrosion is to use corrosion inhibitors. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The recent trend is towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in different media (Arora et al., 2007; Al-Sehaibani, 2000; Chaieb et al., 2005; Chaieb et al., 2004; Chauhan and Gunasekaran 2007; El-Etre et al., 2005; Olusegun et al., 2004; Orubite et al., 2004; Rehan, 2003; Saratha et al., 2003a,b; 2007; Sheyreese et al., 2005; Smita and Mehta, 1999; Akshay and Swami 2011; Lakshmi et al., 2012; Baban and Milind, 2011; Yadav et al., 2012; Senhaji et al., 2013; Belkhaouda et al., 2013a,b,c; Sennhji et al., 2013; Afia et al., 2012; Senhaji et al., 2013).

Honey bee products especially propolis which we considered in this study constitutes several organic compounds which have corrosion inhibiting abilities. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the chemical composition of propolis which depends largely upon the plant source available to bees at the site of collection (Bankova, 2005; Saratha and Priya (2007a, b)

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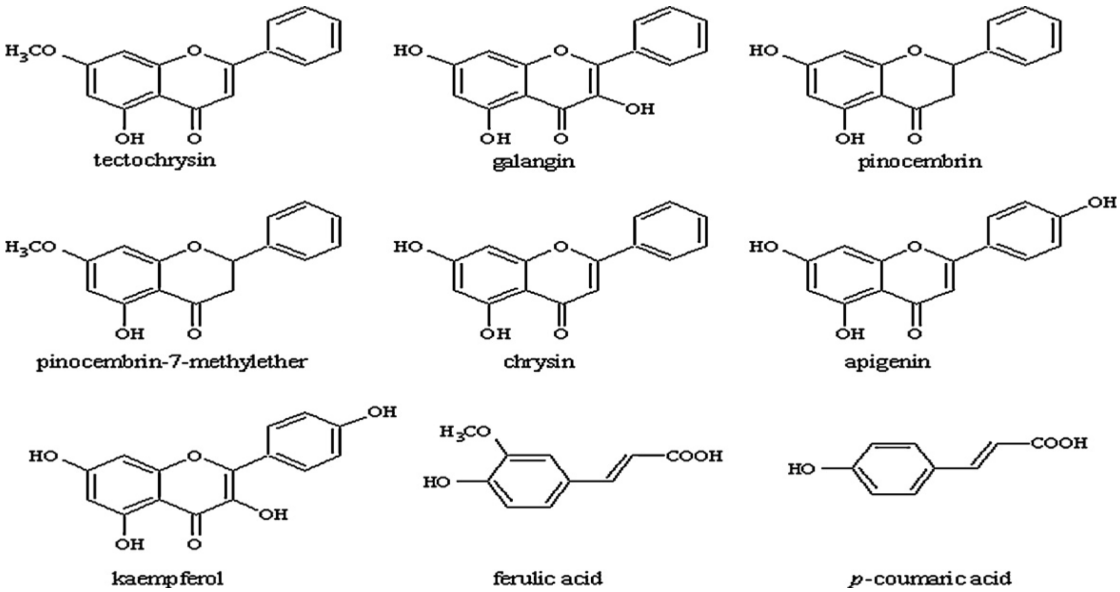

Scheme 1. Structural formulas of flavonoids and phenolic acids present in propolis samples.

The composition of propolis varies with the plant species used as raw materials, but is approximately 50% resin, 30% wax, 5% pollen, 10% aromatic oils, and 5% other organic residues (Cirasino et al., 1987; Monti et al., 1983).

The aim of the present work is to find a naturally occurring cheap and environmentally safe substance that could be used for inhibiting the corrosion of carbon steel. The use of natural product will establish, simultaneously, the economic and environmental goals.

MATERIALS AND METHODS

The chemical composition (weight %) of the carbon steel used in these tests was 0.200 C, 0.350 Mn, 0.024 P, 0.003 Si and Fe was the rest. The carbon steel specimens were cut into different coupons, each of dimensions, 20 × 18 × 1 mm. They were abraded with different grades of emery papers in the normal way starting from coarser to finer, followed by degreasing with acetone and finally washing with bi-distilled water, just before use. The weight loss was determined by weighting the cleaned samples before and after hanging the sample into 100 ml of corrosive solution in the absence and presence of various concentrations of the extract. After the time elapsed the coupons were washed with bi-distilled water and ethanol. For the electrochemical tests, carbon steel with dimension of 1 × 1 cm^2, welded with copper wire for electrical connection and was mounted in epoxy resin, to expose geometrical surface areas of 1 cm^2. Prior to these measurements, the exposed surface was pretreated in the same manner as for weight loss experiments. All reagents (NaCl, Al_2 $(SO4)_3$) used as corrosive medium were from Analar grade and bi-distilled water was used for their preparation.

Preparation of aqueous extract of propolis samples

Propolis samples were collected from Daqahlia province (delta Nile) of Egypt and were then kept and dried in the dark until processing. Extraction was carried out as described previously Gulion (2005). For water extraction, 25 g of air-dried propolis was ground into a fine powder in a blender and mixed with 400 ml boiling water by magnetic stirrer for 15 min. Then the aqueous extract was filtered over cheese-cloth and Whatman paper No. 1, respectively. The filtrates were frozen at - 84°C in ultra-low temperature Freezer.

Daqahlia propolis was a typical poplar propolis but it contained two new caffeate esters and two new triterpenoids (Faten and Ahmed 2002). Brown propolis is the most common, used and studied propolis worldwide (Cuesta et al., 2007; Fonseca et al., 2011), the Polyphenols content in brown propolis equal 34.4 ± 1.7% and the major components are Pinocembrin, caffeic acid, phenyl ester, quercetin and galangi are shown in Scheme 1.

The corrosive media

Stock solutions of 100 ppm NaCl were prepared by dissolving 0.1 g of NaCl in 1000 ml of bi-distilled. Stock solutions of 1000 ppm aluminum sulfate were prepared by dissolving 1 g of aluminum sulfate in 1000 ml bi-distilled water. The required concentrations were obtained by dilution. The parameters used for the present study are: (1) Time: 3 – 21 h, (2) Concentration of the inhibitor: 100, 200, 300, 400, 500, 600 ppm, (3) Temperatures: (303 - 333 ± 2 K). From the change in weight of specimens, the inhibition protection (% P) was calculated using Equation (1):

$$\%P=100[1–W_2/W_1] \quad (1)$$

Where W_2 and W_1 are the weight losses (mg cm^{-2}) in presence and absence of the extract, respectively.

Potentiodynamic polarization measurement

The electrochemical experiments were carried out in a three-electrode electrochemical cylindrical Pyrex glass cell with a platinum counter electrode and saturated calomel electrode (SCE)

Table 1. Variation of propolis concentrations with percentage inhibition and corrosion rate at 30°C.

S/No	Inhibitor concentration (ppm)	Corrosion Rate (mg cm^{-2} min^{-1})	Protection efficiency (% P)
1	---------	0.00114	------
2	100	0.00011	90.28
3	200	0.00009	92.22
4	300	0.00007	94.17
5	400	0.00005	96.09
6	500	0.00003	97.57
7	600	0.00001	99.03

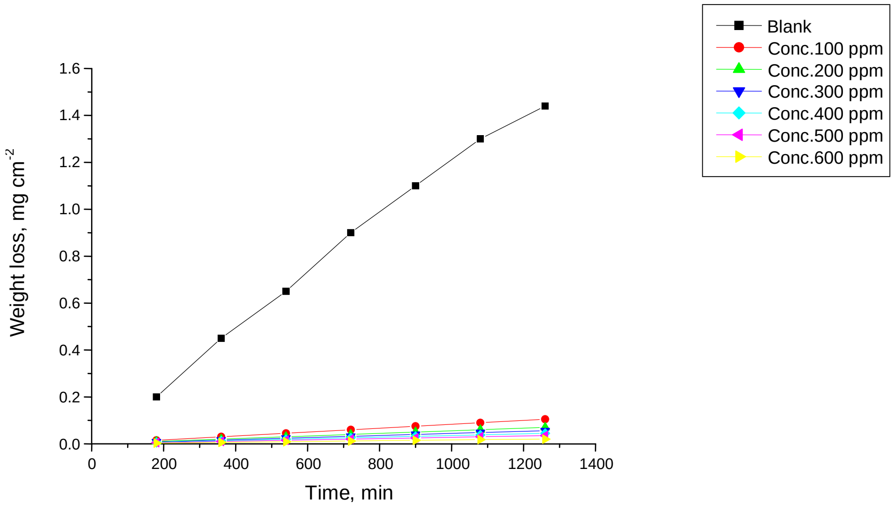

Figure 1. Variation of the weight loss with the concentration of propolis at 30°C.

as reference. The working electrode had the form of a square cut from carbon steel sheet (1 cm^2). The exposed area was treated as before. A constant quantity of the test solution (100 ml) was taken in the polarization cell. A time interval of about 30 min was given for the system to attain a steady state and the open circuit potential (OCP) was noted. Both cathodic and anodic polarization curves were recorded potentiodynamically by changing the electrode potential between ±350 mV from open OCP at the scan rate of 1 mV s^{-1}. protection efficiency and degree of surface coverage (θ) was calculated from the electrochemical measurements by the following Equation (2):

$$\%P=\theta x100=[(i_{corr(free)}-i_{corr(inh)})/i_{corr(free)}x100 \qquad (2)$$

Where, $i_{corr(free)}$ is corrosion current without inhibitor, $i_{corr(inh)}$ is corrosion current with inhibitor. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were calculated by extrapolation of anodic and cathodic Tafel slopes.

Impedance measurements

The electrochemical impedance spectroscopy measurements were performed over a frequency range between 10 kHz to 100 mHz at an amplitude of 10 mV and the impedance diagrams were given in Nyquist representations. In the represented electrical equivalent circuit (Figure 2), R_s is the solution resistance, R_{ct} is the charge transfer resistance and C_{dl} is the double layer capacitance. The protection efficiency was calculated from the charge transfer resistance (R_{ct}) values using the following Equation (3):

$$\%P=[(R'_{ct}-R_{ct})/R'_{ct}]\times100 \qquad (3)$$

Where Rct and R'ct are charge transfer resistances.

All electrochemical experiments were carried out using Gamry PCI 300/4 Potentiostat/ Galvanostat/ Zra analyzer, DC 105 corrosion software, EIS 300 Electrochemical impedance software, EFM 140 Electrochemical frequency modulation software and Echem Analyst 5.21 for results plotting, graphing, data fitting and calculating.

RESULTS AND DISCUSSION

Weight loss measurements

The inhibitor was tested for six different concentrations and their corresponding corrosion rate and % protection efficiency data at 30°C are presented in Table 1. Figure 1 represents the weight loss-time curves in absence and

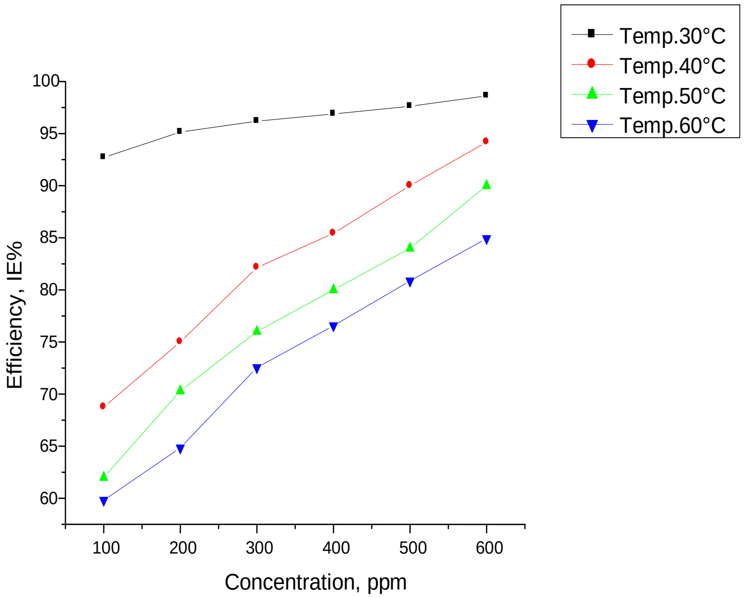

Figure 2. Variation of % protection efficiency with concentrations of propolis at different temperatures.

Table 2. Protection efficiency (% P) at different concentration of propolis for the corrosion of carbon steel after 21 hours immersion in 35 ppm aluminum sulfate and 10 ppm chloride solution at different temperatures

Temperature (°C)	**(% P)**					
	100 ppm	**200 ppm**	**300 ppm**	**400 ppm**	**500 ppm**	**600 ppm**
30	92.71	95.14	96.11	96.88	97.57	99.03
40	68.75	75.00	82.14	85.42	90.00	96.07
50	62.00	70.29	76.00	80.00	84.00	90.00
60	59.78	64.83	72.54	76.56	80.86	85.02

presence of different concentrations of propolis extract. The curves obtained shows that the weight loss of carbon steel in presence of inhibitor is lower than free inhibitor and decreases with increasing inhibitors concentrations (Bentiss et al., 2002). This means that this extract acts as inhibitor for carbon steel in 35 ppm aluminum sulfate and 10 ppm chloride solution. The addition of extract increases the % P, irrespective of the time of immersion. This may be due to the adsorption of phytochemical constituents of the extract on the metal surface. The % P reaches 99.03% at a concentration of 600 ppm.

The effect of temperature on the % P of the inhibitor was determined by weight loss method at different concentrations and at different temperatures (30-60 ± 2°C) for a fixed immersion time of 21 h was shown in Figure 2 and Table 2. The data in Table 2 and curves of Figure 2, revealed that the inhibition efficiency decreased by increasing the temperature, due to desorption of adsorbed inhibitor components on carbon steel surface. This indicates that these extract components are physically adsorbed on the metal surface.

Thermodynamic parameters

The apparent activation energy (E^*_a) of metal corrosion in acid media can be calculated from the Arrhenius equation (Zhang and Hua 2010).

$$\ln k = (E^*_a)/RT + A \qquad (4)$$

Where k is the corrosion rate, (E^*_a) is the apparent activation energy for the corrosion of carbon steel, R is the universal gas constant, A is Arrhenius pre exponential factor and T is the absolute temperature. The values obtained from the slope of the log k vs 1/T plot (Figure 3) are given in Table 3. The relationship between the temperature dependence of inhibition efficiency of an inhibitor and the activation energy found in its presence was given as follows (Dehri, 2006):

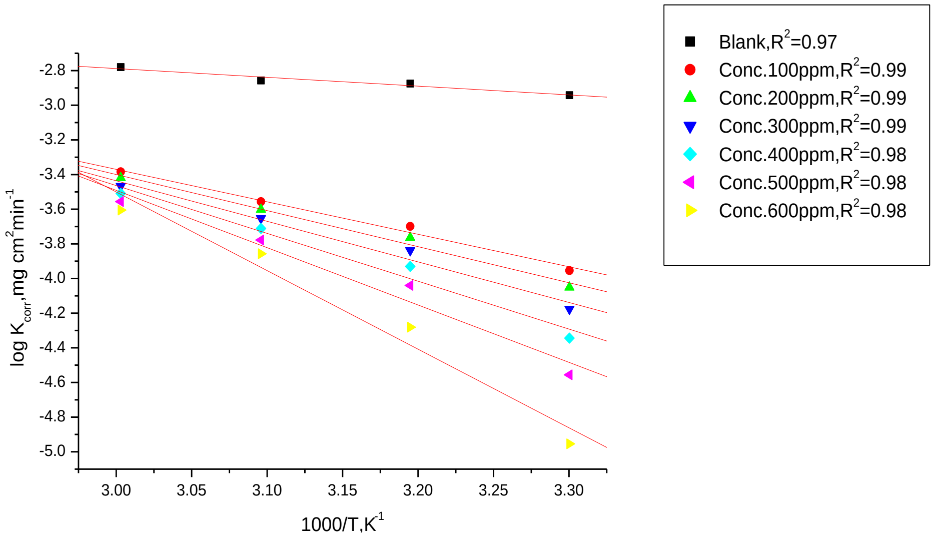

Figure 3. Arrhenius plots of carbon steel in 35 ppm aluminum sulfate and 10 ppm chloride solution and in presence of different concentrations of propolis.

Table 3. Thermodynamic parameters for carbon steel corrosion in 35 ppm aluminum sulfate and 10 ppm chloride solution with different concentrations of propolis

Conc., ppm	**E^*_a kJ mol^{-1}**	**ΔH^* kJ mol^{-1}**	**$-\Delta S^*$ J mol K^{-1}**
Blank	10.21	7.12	277.68
100	35.80	33.87	208.20
200	40.21	36.94	200.09
300	44.03	40.19	190.20
400	51.69	47.84	170.69
500	63.18	59.33	134.33
600	86.16	88.03	50.12

(i) Inhibitors whose protection efficiency decreases with temperature increase. The value of activation energy (E^*_a) found is greater than that in the uninhibited solution.
(ii) Inhibitors whose protection efficiency does not change with temperature variation. The value of activation energy (E^*_a) does not change with the presence or absence of inhibitors.
(iii) Inhibitors whose protection efficiency increases with temperature increase. The value of activation energy (E^*_a) found is less than that in the uninhibited solution. The higher value of activation energy (E^*_a) in the presence of inhibitor than in its absence is attributed to its physical adsorption and its chemisorptions (Obot et al., 2009), while pronounced in the opposite case (Olusegun et al., 2004). In the present study the lower value of for mild steel in an inhibitor's presence, compared to that in its absence, indicates the formation of chemisorbed mono layer. The decrease in activation energy of corrosion at higher levels of inhibition arises from a shift of the net corrosion reaction from that on the uncovered part on the metal surface to the covered one. An alternative form of Arrhenius equation is the transition state equation (Cruz et al., 2004) which is given as:

$$k=(RT/Nh)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \quad (5)$$

Where h is the Planck's constant, N is the Avogadro's number, ΔS^* is the entropy of activation, and ΔH^* is the enthalpy of activation. A plot of log (k/T) vs 1/T gave a straight line (Figure 4) with a slope of ($-\Delta H^*/2.303R$) and an intercept of [log(R/Nh) + ($\Delta S^*/R$)], from which the values of ΔH^* and ΔS^* were calculated and listed in Table 3. The positive values of ΔH^* for corrosion of mild steel in the presence and absence of the inhibitor reflect the endothermic nature of metal dissolution process. The negative increment in ΔS^* with increase in the concentration of the inhibitor reveals that decrease in randomness takes place on going from reactant to the activated complex (Quraishi et al., 2007). This reflects the formation of an ordered stable film of inhibitor on mild

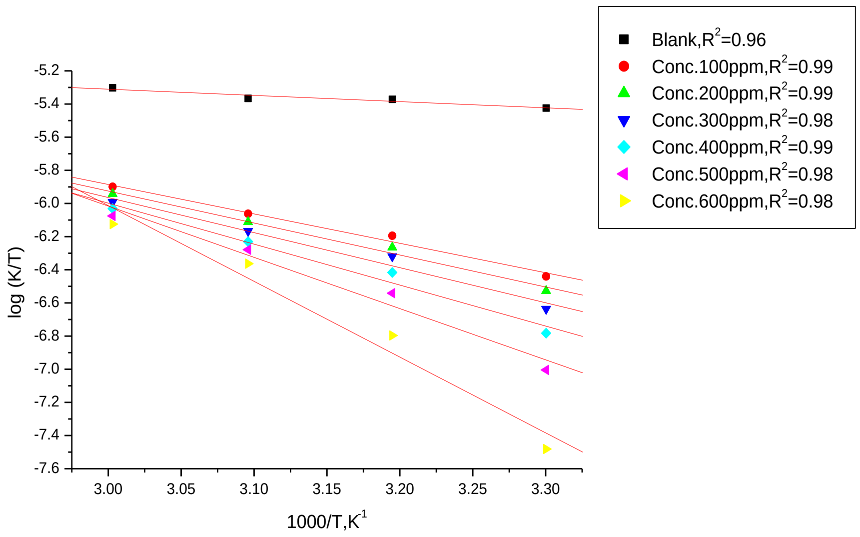

Figure 4. Transition state plots of carbon steel in 35 ppm aluminum sulfate and 10 ppm chloride solution and in presence of different concentrations of propolis.

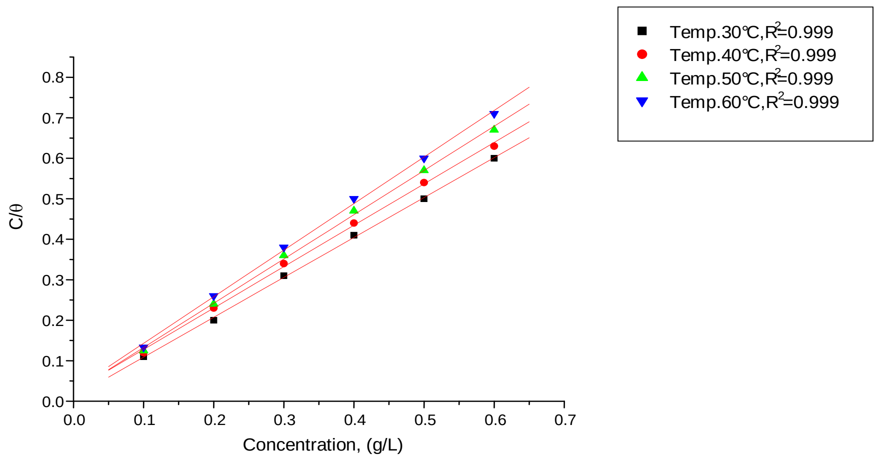

Figure 5. Langmuir adsorption isotherm for the inhibition of corrosion of carbon steel by propolis in 35 ppm aluminum sulfate and 10 ppm chloride solution at different temperatures.

steel surface (Bentiss et al., 2005).

Adsorption isotherms

Adsorption isotherm values are important to explain the mechanism of corrosion inhibition of organo-electrochemical reactions. The most frequently used isotherm include: Langmuir, Frumkin, Hill de Boer, Parsons, Temkin, Flory-Huggins, Dhar-Flory-Huggins, Bockris-Swinkels and recently formulated thermodynamic / kinetic model of El-Awady and Ahmed (1985), Kamis (1990), El-Rehim et al. (1999) and Cafferty and Leidheiser (1979). Adsorption of the organic molecules occurs as the interaction energy between the molecules and the metal surface is higher than between the H_2O molecule and the metal surface. Langmuir isotherm was tested for its suitability to the experimental data. Langmuir isotherm is given by Equation (6):

$$C/\theta=1/K_{ads}+C \qquad (6)$$

Where θ is the degree of surface coverage, C the molar inhibitor concentration in the bulk solution and Kads is the equilibrium constant of the process of adsorption. Though the plot of C/ θ versus C was linear (Figure 5), so the

Table 4. Adsorption parameters for carbon steel corrosion in the absence and presence of various temperatures.

Temperature (K)	log K_{ads}	$-\Delta G^{\circ}_{ads}$ kJ mol^{-1}	$-\Delta H^{\circ}$ kJ mol^{-1}	$-\Delta S^{\circ}$J mol^{-1}K^{-1}
303	2.0	22.0	31.2	0.03
313	1.7	20.6	31.2	0.03
323	1.6	20.6	31.2	0.03
333	1.5	20.6	31.2	0.03

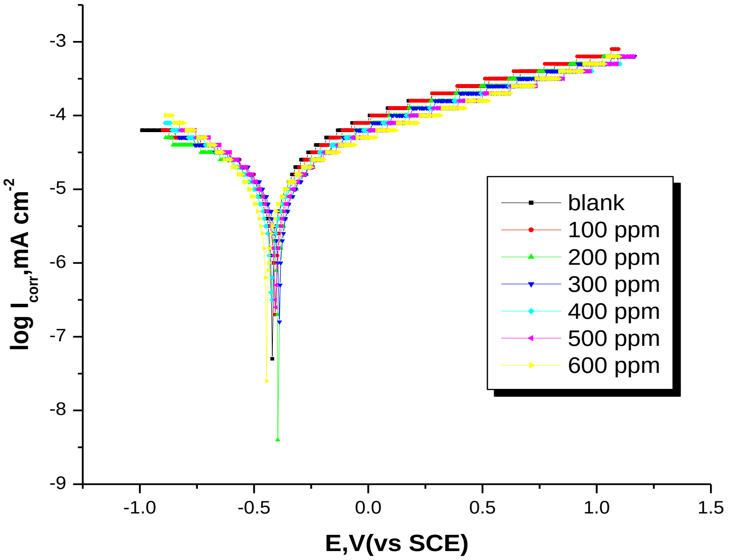

Figure 6. Potentiodynamic polarization curves for the dissolution of carbon steel in 35 ppm aluminum sulfate and 10 ppm chloride solution in the absence and presence of different concentrations of propolis at 30°C.

most frequently used isotherm is Langmuir. The regression values (R^2) are greater than 0.99 as shown in Table 4. The data obtained in Table 4 for the propolis extract fits well in Langmuir adsorption isotherms. Since it obeys Langmuir adsorption isotherm, it implies monolayer adsorption of inhibitor. As the slope values of Langmuir adsorption isotherm are slightly deviate from the value of unity. The deviation of the slopes from unity can be attributed to the molecular interaction among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation. Langmuir isotherm assumes that:

(i) The metal surface has a fixed number of adsorption sites and each site holds one adsorbate
(ii) ΔG°ads is the same for all sites and it is independent of degree of surface coverage (Table 4) and
(iii) The adsorbates do not interact with one another, that is, there is no effective interaction of the adsorbates on ΔG°ads. In the present study the extract component molecules are adsorbed on the corroding site of metal surface thus reduces the number of active sites involved in corrosion, which can be represented in the Equation (7):

$$Fe(H_2O)_2 + inhibitor \rightarrow Fe(inhibitor)_2 + 2H_2O \qquad (7)$$

The adsorption of the inhibitor on the metal surface leads to high degree of surface coverage and hence shows better inhibitive property.

Polarization measurements

Figure 6 illustrates the polarization curves of carbon steel in solutions containing different concentrations of extract at 30°C. The presence of extract shifts both anodic and cathodic branches to the lower values of corrosion current densities and thus causes a remarkable decrease in the corrosion rate, showing the inhibition tendency of

Table 5. The corrosion parameters for carbon steel in 35 ppm aluminum sulfate and 10 ppm chloride solution with propolis from polarization measurements.

Concentration, ppm	**i_{corr}, µA cm^{-2}**	**-E_{corr}, mV vs SCE**	**β_a, mV dec^{-1}**	**β_c, mV dec^{-1}**	**CR mm y^{-1}**	**θ**	**% P**
Blank	149	420	205	88	1.74	-----	**-----**
100	60	406	178	88	0.70	0.600	60
200	51	396	169	158	0.59	0.660	66
300	43	390	155	122	0.50	0.710	71
400	34	424	125	108	0.40	0.770	77
500	22	405	120	97	0.26	0.850	85
600	12	445	103	61	0.14	0.920	92

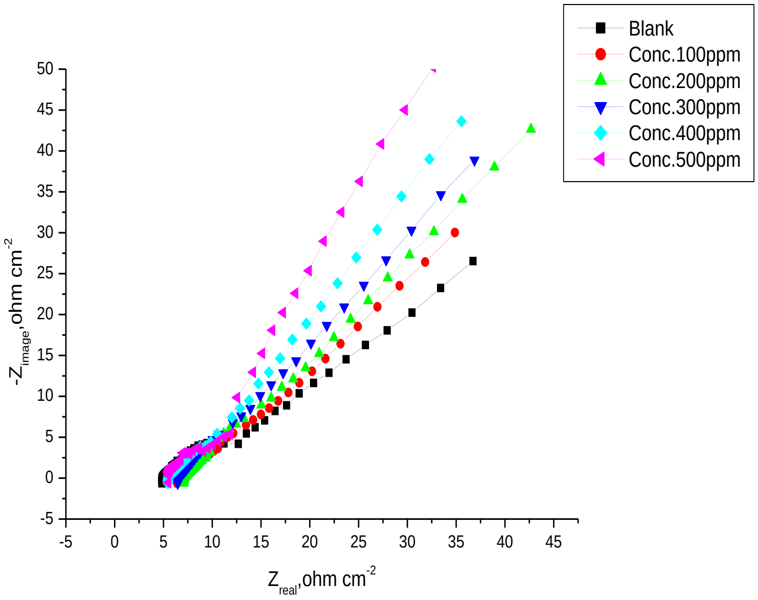

Figure 7. Nyquist plots for carbon steel in 35 ppm aluminum sulfate and 10 ppm chloride solution containing different concentrations of propolis at 30°C.

the extract. The various electrochemical parameters calculated from Tafel plot are given in Table 5. The lower corrosion current density (i_{corr}) values in the presence of extract without causing significant changes in corrosion potential (E_{corr}) (- 445 to - 420 mV) suggests that the extract is mixed type inhibitor (that is, inhibit both anodic and cathodic reactions) and are adsorbed on the surface thereby blocking the corrosion reaction centers. Since b_a is greater than b_c suggesting that the extract is under mixed control but its effect on the anodic polarization is more pronounced than on the cathodic polarization.

Impedance measurements

Impedance diagram (Nyquist plot) obtained for carbon steel in the presence of various concentrations of the propolis extract is depicted in Figure 7. The linear features observed at lower frequencies were attributed to diffusion-limited electron transfer. The electrochemical impedance parameters (R_{ct} and C_{dl}) were established from the Nyquist plots and are given in Table 6. Values of R_s and charge transfer resistance (R_{ct}**)** increase with increasing extract concentration. This is attributed to high resistance shown by the adsorbed extract components at the metal – solution interface. Similarly, the decrease in double layer capacitance (C_{dl}**)** is attributed to increase in thickness of electrical double layer due to adsorption of extract components. The charge transfer resistance, R_{ct} and double layer capacitance (C_{dl}**)** is much higher than those in free acid. It is inferred that the extract molecules gradually replace the water molecules by adsorption at

Table 6. The corrosion parameters for carbon steel in 35 ppm aluminum sulfate and 10 ppm chloride solution with Propolis from impedance measurements.

Concentration, ppm	R_{ct}, Ω cm^2	R_s, Ω	C_{dl}, × 10^{-2}, F cm^{-2}	θ	% P
Blank	5.6	5.35	47.0	_	_
100	22.4	5.57	11.1	0.749	74.9
200	49.0	5.71	7.2	0.886	88.6
300	75.9	6.49	0.9	0.926	92.6
400	127.6	6.60	0.3	0.956	95.6
500	159.9	7.15	0.1	0.996	99.6

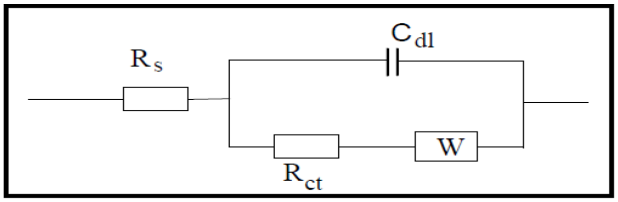

Figure 8. The equivalent circuit model used to fit the experimental results for blank and propolis, equivalent circuit with mixed kinetic and charge transfer control.

the metal/solution interface, which leads to the formation of a protective film on the carbon steel surface and thus decreases the extent of the dissolution reaction (Bentiss et al., 2000). Moreover, the increase of extract concentration leads to the increase of R_{ct} and % P values. The % P obtained from EIS measurements are close to those deduced from polarization method. The equivalent circuit depicted in Figure 8 is employed to analyze the impedance spectra for propolis.

Mechanism of inhibition

Literature survey revealed the presence of following principle constituents in the leaves extract of propolis extract (Faten and Ahmed 2002; Cuesta et al., 2007; Fonseca 2011). The probable mechanism can be explained on the basis of adsorption process and the structure of the constituents present in the propolis extract. The anodic inhibition may be due to the adsorption of principle phytochemical constituents present in the extract through oxygen atoms/or ring oxygen atom in Flavonoids and Phenolic acids and /or oxygen atoms of –OH group in Kaempferol, Tectochrysin and others and forms a protective coating on the metal surface, thus prevents the contact between the metal and corrosive acid. The protonated species of the principle constituents may compete with H^+ ion reduction and may control the cathodic reaction.

Conclusions

The following conclusions were made from the following studies:

1. The corrosion rate of carbon steel in surface water decreases with increase in concentration of propolis.
2. The inhibition efficiency increases with respect to the concentration of the inhibitor and decreases with rise in temperature from 30 to 60°C.
3. The maximum inhibition efficiency of propolis is found to be 99.03% at 600 ppm of inhibitor from mass loss studies at 30°C.
4. The decrease in the energy of activation values indicates that the addition of propolis metal dissolution and also indicates that decrease in the adsorption of the inhibitor on carbon steel surface with increase in temperature.
5. The negative values of $\Delta G°_{ads}$ indicates that the propolis is physicochemical adsorbed and spontaneous adsorption of inhibitors on the surface of carbon steel.
6. The higher value of heat of adsorption also showed that the inhibition efficiency decrease with rise in temperature.
7. The low negative enthalpy value of adsorption is evident that the propolis was strongly adsorbed on the carbon steel was probably chemisorptions.
8. The adsorption of propolis on carbon steel surface from the acid solution followed Langmuir adsorption isotherm.
9. The results of polarization study showed that the formulation function as a mixed type inhibitor, more predominantly controls the anodic reactions.
10. The AC impedance spectral studies revealed the formation of a film with higher resistance than that of blank solution.

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