



Osmanthus Fragan Leaves Extract as Corrosion Inhibitor for Carbon Steel in Hydrochloric Acid Solution

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The aqueous extract of osmanthus fragran leaves was evaluated as a corrosion inhibitor for carbon steel in 1M hydrochloric acid using electrochemical polarization and electrochemical impedance spectroscopy techniques. The extract was found to reduce the corrosion rate of carbon steel. The inhibition efficiency increased with increasing the extract concentration to exceed 90 % at 0.2040 g/L at 298 K. The inhibition efficiency was temperature independent within 288-318 K. The extract acted as a mixed inhibitor and did not modify the apparent activation energy of the corrosion process of carbon steel. The adsorption of the extract components on the carbon steel surface belonged to the physical adsorption, which followed Langmuir adsorption isotherm.

Key Words: Corrosion, Inhibition, Carbon steel, Osmanthus fragran leaves extract.

INTRODUCTION

Carbon steel, as one of the most important and widely used alloys in industries, frequently incurs corrosion problems when it contacts with acid solutions such as hydrochloric acid and sulfuric acid during acid pickling and cleaning processes¹. The use of inhibitors is one of the most practical methods for protection of carbon steel against corrosion in acidic media²⁻⁴.

In the past decades, the synthetic compounds with high inhibition efficiencies play a great role in inhibiting the carbon steel corrosion. However, most of them are expensive and highly toxic to both human beings and environment⁵⁻⁷. The plant extracts emerge out as effective inhibitors of corrosion in recent days due to their low cost, high biodegradability, easy availability and non-toxic nature. It was reported that the extracts of zenthoxylum alatum⁸, occimum viridis⁹, nypa fruticans¹⁰, phyllanthus amarus¹¹, artemisia pallens¹², dacryodis edulis¹³, henna¹⁴, coconut shell¹⁵, centella asiatica¹⁶, were good corrosion inhibitors for carbon steel corrosion in aggressive acid solutions. However, developing more effective new green inhibitors is still urgent and has great significance for industrial applications.

The present work aims at evaluating the aqueous extract of the osmanthus fragran leaves as corrosion inhibitor for carbon steel in hydrochloric acid. Osmanthus fragran is one of the most popular gardening plants in China, whose flowers are expansively used to produce high-grade essence, special

drugs and aromatic teas. However, osmanthus fragran leaves are rare utilized and hence wasted. Exploiting the utility of osmanthus fragran leaves is helpful to expand their industrial applications and to develop new green inhibitors.

In this paper, the electrochemical polarization and electrochemical impedance spectroscopy (EIS) techniques were employed to investigate the inhibition efficiency of the extract of the osmanthus fragran leaves. The effect of temperature was also studied.

EXPERIMENTAL

Q235 carbon steel (0.17 % C, 0.46 % Mn, 0.26 % Si, 0.017 % S, 0.0047 % P, the remainder is Fe) was used. The aggressive solution (1M HCl) was prepared by dilution of analytical grade 37 % HCl with distilled water.

Fresh osmanthus fragran leaves were collected around the campus of Chongqing University in P. R. China. The aqueous osmanthus fragran leaves extract (OFLE) was prepared in the following way: 600 g fresh osmanthus fragran leaves were finely shredded and then heated in 3.6 L boiled distilled water for 1 h. The mixture was filtered and the clear liquid was concentrated, dried in an oven to gain the brown solid and then ground to obtain the extract powder, whose weight was 8.1576 g. The extract powder was added to the aggressive solution (1M HCl) to prepare the test solutions with the desired OFLE concentration.

Electrochemical measurements were carried out on a CHI660C electrochemical workstation (Shanghai Chenhua Instruments Inc.). The electrochemical cell consisted of a conventional three-electrode configuration with the platinum sheet as the counter electrode and the saturated calomel electrode (SCE) as the reference electrode. The working electrode was cut from a Q235 carbon steel rod with cross-section area of 1 cm² and embedded in epoxy resin holders. Before each experiment, the surface of the working electrode was mechanically polished with 200, 600, 800# grit emery papers to a plane mirror finish, then degreased ultrasonically in absolute ethanol for 3 min, rinsed with distilled water and dried in air.

The EIS and polarization measurements were conducted after immersion of the working electrode in the testing solution for 1 h to stabilize the open circuit potential (OCP). The electrochemical impedance spectra were measured at open circuit potential with 5 mV AC amplitude over a frequency range of 10 mHz-100 kHz. The polarization measurements were carried out from -0.30 V (*vs.* OCP) to +0.30 V (*vs.* OCP) at a sweep rate of 0.5 mV/s. The temperature was controlled by thermostatic water bath.

RESULTS AND DISCUSSION

Effect of osmanthus fragran leaves extract (OFLE) concentration: Fig. 1 shows the polarization curves of carbon steel in 1M HCl in the presence and absence of OFLE at 298 K after 1 h of immersion. The inhibition efficiency (IE %) can be calculated by the relation:

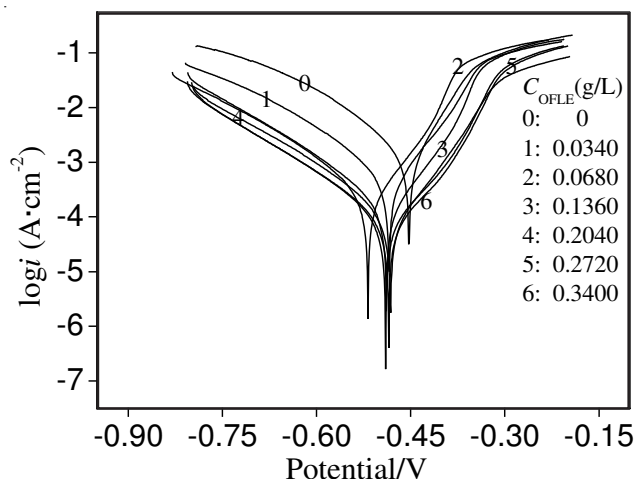


Fig. 1. Polarization curves of carbon steel in 1M HCl with different concentrations of osmanthus fragran leaves extract after 1h of immersion at 298 K

$$IE (\%) = 100 \times \left(1 - \frac{I_{\text{corr}}}{I_{\text{corr}}^0} \right)$$

where I_{corr}^0 and I_{corr} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of cathodic Tafel lines to corrosion potential. Table-1 lists the values of corrosion potential (E_{corr}), cathodic and anodic Tafel slope (b_c , b_a), corrosion current (I_{corr}) and inhibition efficiency (IE %). It is clear that the I_{corr} value decreases from 1383.6 $\mu\text{A}/\text{cm}^2$ to 103.3 $\mu\text{A}/\text{cm}^2$ with 0.2040 g/L OFLE and the inhibition efficiency reaches 92.54 %, which indicates that OFLE is a very effective inhibitor for carbon steel in 1M HCl solution. The parallel cathodic polarization curves in Fig. 1 suggest that the hydrogen evolution is activation-controlled and the reduction mechanism is not affected by the presence of OFLE^{17,18}. The anodic current decreases in the presence of OFLE compared to its absence, which implies that OFLE can also suppress the anodic dissolution of carbon steel. Generally, an inhibitor can be classified as cathodic or anodic type if the shift of corrosion potential is more than 85 mV with respect to that in the inhibitor absence¹⁷⁻²². From Fig. 1 and Table-1, E_{corr} decreases less than 85 mV in the presence of OFLE compared to its absence, which infers that OFLE acts as a mixed-type inhibitor. From the above results, it can be deduced that the OFLE molecules might take part in the adsorption on the surface of carbon steel and hence decrease the surface area for corrosion while do not affect the mechanism of either the anodic carbon steel dissolution or the cathodic hydrogen evolution reaction.

The corrosion behaviours of carbon steel in 1M HCl solutions with various concentrations of OFLE are also investigated by EIS method at E_{corr} at 298 K after 1 h of immersion. The impedance diagrams are given in the Nyquist representation (Fig. 2). The existence of single semicircle shows that the single charge transfer process during carbon steel dissolution is unaffected by the presence of the OFLE molecules. The deviation of semicircles from perfect circular shape is often referred to the frequency dispersion of interfacial impedance. This anomalous behaviour is usually attributed to the inhomogeneity of the metal surface arising from surface roughness or interfacial phenomena^{23,24}. Therefore, it is necessary to consider the distributed capacitance through a constant phase element (CPE) instead of a pure capacitor in EIS fitting.

The equivalent circuit depicted in Fig. 3 is used to fit the EIS data, where R_s represents the solution resistance, R_i denotes the charge-transfer resistance and CPE represents the interfacial capacitance. The impedance of the CPE is expressed as:

TABLE-1
POLARIZATION PARAMETERS FOR THE CORROSION OF CARBON STEEL IN 1M HCl WITH DIFFERENT CONCENTRATIONS OF OFLE AFTER 1 h OF IMMERSION AT 298 K

C_{OFLE} (g/L)	E_{corr} (mV <i>vs.</i> SCE)	b_c (mV dec^{-1})	b_a (mV dec^{-1})	I_{corr} ($\mu\text{A cm}^{-2}$)	IE (%)
0	-453	119	70	1383.6	-
0.0340	-484	123	62	503.5	63.62
0.0680	-518	120	56	248.9	82.02
0.1360	-489	118	58	152.1	89.01
0.2040	-482	122	62	103.3	92.54
0.2720	-490	124	68	86.3	93.76
0.3400	-485	125	64	81.5	94.11

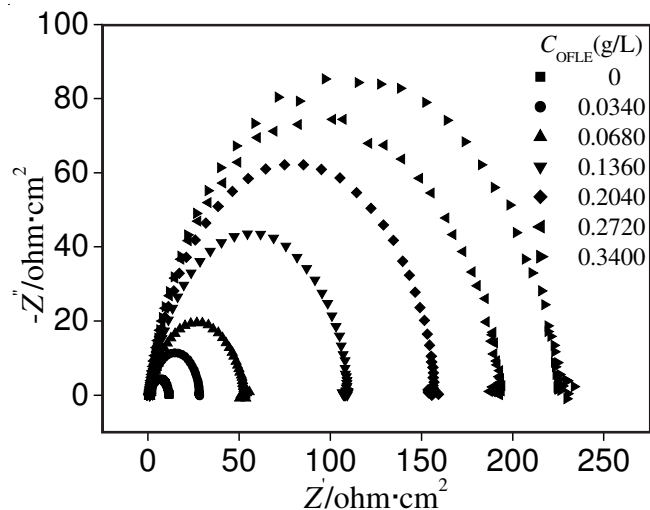


Fig. 2. Nyquist diagrams of carbon steel in 1M HCl with different concentrations of OFLE after 1 h of immersion at 298 K

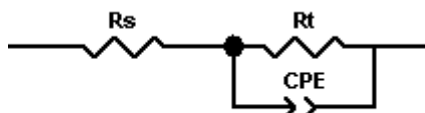


Fig. 3. Equivalent circuit for carbon steel in 1M HCl solution

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (2)$$

where Y_0 is the magnitude of the CPE, ω is the angular frequency at which Z_i reaches its maximum values and n is the deviation parameter of the CPE: $-1 \leq n \leq 1$. The values of the interfacial capacitance C_{dl} can be calculated from CPE parameter values Y_0 and n using the expression²⁵:

$$C_{dl} = \frac{Y_0 \omega^{n-1}}{\sin\left(\frac{n\pi}{2}\right)} \quad (3)$$

The inhibition efficiency (IE %) based on the charge-transfer resistance is calculated by:

$$IE (\%) = 100 \times \left(1 - \frac{R_t}{R_t'}\right) \quad (4)$$

where R_t' and R_t are the charge-transfer resistance values with and without inhibitor, respectively. The values of the parameters such as R_s , R_t , Y_0 , n through EIS fitting as well as the derived parameters C_{dl} and IE % are listed in Table-2.

It is seen that the C_{dl} values are brought down to the minimum in the presence of OFLE. The decrease of C_{dl} suggests that OFLE functions by adsorption at the carbon steel surface. It is inferred that the OFLE molecules gradually replace the water molecules by adsorption at 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 reaction²⁶. It is also noted that addition of OFLE increases the R_t values and the corrosion inhibition efficiency. A good agreement is observed between the electrochemical polarization method and EIS.

Adsorption isotherm of osmanthus fragran leaves extract: Generally, the inhibition mechanism of plant extract inhibitors may be explained on the basis of their adsorption behaviour. The variation of surface coverage θ against the inhibitor concentration c indicates the nature of adsorption⁶, where θ can be defined by $IE \% / 100$ ²⁷. Several adsorption isotherms, such as Langmuir (c/θ vs. c), Frumkin (θ vs. c) and Temkin (θ vs. $\log c$), are commonly used to characterize the inhibitor performance. In this work, the relation between c/θ and c obeys a linear function (Fig. 4), which indicates that the Langmuir adsorption isotherm best explains the experimental results for OFLE at 298 K:

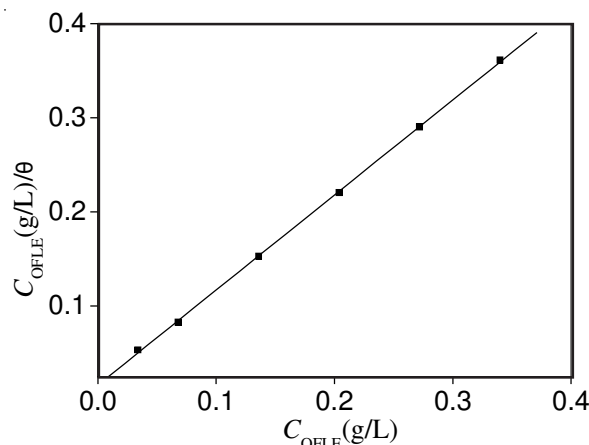


Fig. 4. Adsorption isotherm of OFLE on carbon steel surface

$$\frac{c}{\theta} = \frac{1}{K} + c$$

and
$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G^\theta}{RT}\right) \quad (5)$$

where c is the OFLE concentration, θ is the surface coverage, K is the equilibrium constant of the adsorption reaction and ΔG^θ is the standard free energy of adsorption.

TABLE-2 IMPEDANCE PARAMETERS FOR CORROSION OF STEEL IN ACID AT VARIOUS CONCENTRATIONS OF OFLE AT 298 K						
C_{OFLE} (g/L)	R_s (Ω cm ²)	R_t (Ω cm ²)	CPE-T/ $Y_0 \times 10^6$ (Ω^{-1} cm ² s ⁿ)	n	C_{dl} (μ F cm ⁻²)	IE (%)
0	1.21	10.44	601.78	0.88	312.77	-
0.0340	1.10	28.05	520.23	0.84	239.44	62.78
0.0680	0.88	52.44	317.61	0.81	122.18	80.09
0.1360	1.01	110.90	155.01	0.84	73.60	90.59
0.2040	1.09	155.60	94.47	0.87	53.01	93.29
0.2720	0.91	189.81	90.23	0.87	50.51	94.50
0.3400	0.99	220.60	71.17	0.88	39.50	95.27

The values obtained are $K = 62.00 \text{ L/g}$ and $\Delta G^0 = -20.18 \text{ kJ/mol}$. The negative ΔG^0 indicates that OFLE is spontaneously adsorbed on the carbon steel surface. Generally, $\Delta G^0 > -40 \text{ kJ/mol}$ is interpreted by the physical adsorption while $\Delta G^0 < -40 \text{ kJ/mol}$ is regarded as the chemisorptions phenomenon⁶. The value of ΔG^0 obtained in this work suggests that the adsorption of OFLE on the carbon steel surface belongs to the physical adsorption.

Effect of temperature: The effect of temperature on the corrosion rate of carbon steel in 1M HCl without and with OFLE (at the concentration of 0.2720 g/L) has been studied within the temperature range of 298-348 K by the electrochemical polarization method. The parameters, I_{corr}^0 , I_{corr} and IE % that derived from the polarization curves are summarized in Table-3. The corrosion current densities, I_{corr}^0 and I_{corr} , increase with the rise of the temperature. IE % is almost constant with the temperature changes.

Temperature (K)	I_{corr}^0 ($\mu\text{A cm}^{-2}$)	I_{corr} ($\mu\text{A cm}^{-2}$)	IE (%)
288	719.4	36.1	94.98
298	1383.6	86.3	93.76
308	5821.0	352.4	93.95
318	14621.7	729.5	95.01

The apparent activation energy for carbon steel in uninhibited and inhibited solutions can be determined by the relations:

$$\ln I_{\text{corr}}^0 = \frac{-E_a^0}{RT} + B$$

and

$$\ln I_{\text{corr}} = \frac{-E_a}{RT} + B \quad (6)$$

where E_a^0 and E_a are the apparent activation energy without and with OFLE, respectively. T represents the temperature. B is the pre-exponential factor and R is the gas constant.

The apparent activation energy calculated from the Arrhenius plots (Fig. 5) are 79.55 kJ/mol and 79.46 kJ/mol for carbon steel in 1M HCl without and with OFLE, respectively. Clearly, the presence of OFLE does not modify the values of apparent activation energy, which is similar to the cases of Limonene and Rosmarinus of ficinalis oil as corrosion inhibitors for steel in acid solutions^{6,28}. Radovici has classified the inhibitors into three groups according to the temperature effects, among which the second-group inhibitors are those that IE % does not change with temperature variation and the apparent activation energy does not change with the presence or absence of the inhibitor²⁹. The corrosion inhibition of these inhibitors is ascribed to their physical adsorption on metal surface^{29,30}. Hence, it is inferred that the adsorption of OFLE on carbon steel surface belongs to the physical (electrostatic) adsorption, which is consistent with the deduction from the adsorption energy ΔG^0 .

As well known, a plant extract is usually a mixture that contains many compounds. Therefore, it is difficult to obtain the exact chemical structure of OFLE. However, the functional groups, e.g., carboxyl, hydroxyl, aromatic hydrocarbon, amino,

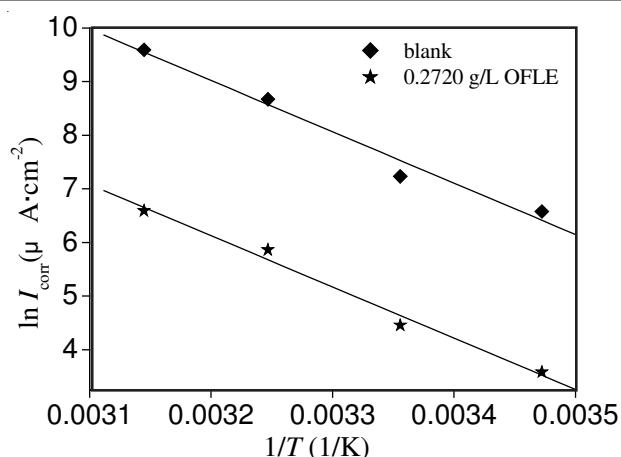


Fig. 5. Arrhenius plots of the corrosion rates for carbon steel in 1M HCl without and with OFLE

have been identified by GC (gas chromatography), TLC (thin layer chromatography) and IR (infrared spectrum) techniques³¹. The molecules containing the above functional groups can easily adsorb on the metal surface, which might be responsible for the high inhibition efficiency of OFLE for carbon steel.

Conclusion

Osmanthus fragran leaves extract (OFLE) was first evaluated as the corrosion inhibitor for carbon steel in hydrochloric acid in the present work. The following principal points can be summarized: OFLE is a very efficient mixed inhibitor for the corrosion of carbon steel in 1M HCl solution. The inhibition efficiency of OFLE exceeds 90 % at 0.2040 g/L at 298 K. The inhibition efficiency of OFLE increases with the concentration increase and is temperature independent within 288-318 K. The adsorption of OFLE on the carbon steel surface belongs to the physical adsorption, which obeys Langmuir adsorption isotherm model. The apparent activation energy of the corrosion process of carbon steel is not affected in the presence of OFLE.

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