

A study on the corrosive inhibition ability of CT3 steel in 1 M HCl solution by caffeine and some characteristics of the inhibition process

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Received 2 June 2016; Accepted for publication 19 December 2016

Abstract

Caffeine was isolated from dry green tea leaves and used as corrosion inhibitor. The aim of this paper is to study the corrosion inhibition behavior of caffeine with its different concentrations (from 0.01 g/L to 3.00 g/L) for CT3 steel in 1M HCl solution by the curve polarization measurements and surface examination studies. Experiment result showed that: as the concentration of caffeine increases, the inhibition efficiency increases; %IE max is approximately 83.27% at concentration of caffeine 3.00 g/L. The experimental data from all measurements was found to fit well with the Langmuir caffeine adsorption isotherm. Calculated values of free energy of adsorption ΔG_{ads} are -14.71 kJ/mol. It shown that, the adsorption is spontaneous and consistent with the mechanism of physical adsorption. It showed that, the adsorption is spontaneous and consistent with the mechanism of physical adsorption. As temperature increase from 298 to 318 K, the inhibition efficiency is relatively stable: decrease slightly from 83.27 % down 78.50 %. Calculated values of the heat of adsorption ΔH_{ads} are ranged from -6.38 kJ/mol to -19.89 kJ/mol, indicating that the adsorption of caffeine on the surface of CT3 steel is exothermic. The increasing of activation energy in corrosion process which presents caffeine 3.00 g/L compared to absent caffeine proved that caffeine have corrosion occurred more difficult.

Keywords. Caffeine, corrosion inhibitor, adsorption.

1. INTRODUCTION

Using plant extracts as green corrosion inhibitors is a trend that is being tested extensively in both of Vietnam and many parts of the world in recent years [1-11]. However, one of the drawbacks of the plant extracts is that they are unstable. They are decomposed quickly over time and lose inhibition corrosion property. To overcome this drawback, we are looking for the pure substances which have inhibiting corrosion capability in those extract. Based on some our studies and some research of other authors in the world [1-4, 8], we have realized that, extracts of plants such as green tea, tobacco, coffee,... have shown good inhibitory property. These extracts contain caffeine. So that, caffeine was isolated from dry green tea leaves and used as corrosion inhibitor [12-14]. The present work (i) evaluates the inhibition efficiency of caffeine concentration in controlling corrosion of CT38 steel in 1M HCl acid solution, (ii) examines the inhibition efficiency of 3.00 g/L caffeine at different temperatures, (iii) observes microscopic surface by SEM method.

2. EXPERIMENTAL

2.1 Caffeine Extraction

Leaves of Green tea were collected in Thai Nguyen City. The clean air-dried leaves were grounded and entered to 100 ml heatproof cup. The lime water was pouring flooded more than 3 cm, heated to boiling, then simmer for 150 minutes. Filtering out by the pulp, the solution is neutralized by instillation 5 M HCl and then is extracted three times with chloroform. The chloroform solution was dried by anhydrous sodium sulphate then chased solvent by rotary vacuum. The final product is used to prepare solutions with its different concentrations in 1 M HCl solution.

2.2 Preparation of the specimens

The working electrode was made from CT3 carbon steel (produced in Thai Nguyen, composition: 0.154%C; 0.636%Mn; 0.141%Si; 0.019%P; 0.044%S and Fe). Prior to each measurement, the electrode surface was mechanically treated by grinding and polishing with different grades of emery paper, degreased in

ethanol and rinsed in twice distilled water. The exposed geometric area was 0.785 cm^2 . A new electrode surface was used for each run.

2.3. Method

2.3.1. Electrochemical measurements

All experiments were done in unstirred and nondeaeerated solutions at room temperature after immersion for 60 min in 1 M solution with and without addition of inhibitor. Corrosion tests were performed electrochemically at room temperature ($\sim 25^\circ\text{C}$). Electrochemical measurements were performed using a potentiostat manufactured by PAR (Model PARSTAT 4000, Princeton Applied Research, USA) at Institute of Materials, Vietnam academy of Science and Technology. The test specimens were placed in a glass corrosion cell, which was filled with fresh electrolyte. A silver/silver chloride electrode and a piece of stainless steel with large area were employed as pseudo-reference and counter electrode, respectively.

The linear polarization study was carried out from -20 to $+20 \text{ mV}$ versus corrosion potential (E_{corr}) at a scan rate of 0.1 mV.s^{-1} to determine the polarization resistance (R_p). Tafel curves were obtained by changing the electrode potential automatically from -250 to $+250 \text{ mV}$ versus corrosion potential (E_{corr}) at a scan rate of 3 mV.s^{-1} . The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}). The inhibition efficiency has been calculated from the equation:

$$IE = \frac{v_0 - v_t}{v_0} \cdot 100\% \quad (2)$$

Where v_0 and v_t are the corrosion rate of CT3 steel in absence and in presence of inhibitor in working solution, respectively.

2.3.2. Surface examination study

The surface morphology after 60 minutes immersion in the test solution was analyzed by scanning electron microscopy (SEM) and EDS, using Quanta 3D scanning electron microscope (model AL99/D8229) at Institute of Materials, Vietnam Academy of Science and Technology.

2.3.3. Some thermodynamic parameters of adsorption and corrosion process

The Langmuir adsorption isotherm applied to investigate the adsorption mechanism [9-11] is:

$$\theta = \frac{KC}{1+KC} \quad (3)$$

$$\text{or } \frac{C}{\theta} = C + \frac{1}{K} \quad (4)$$

Where C is the inhibitor concentration in the electrolyte, K is the equilibrium constant of the adsorption process, θ is the degree of surface coverage ($\theta = IE(\%) / 100$).

The standard free energy of adsorption is calculated according to the following equation [10, 11]:

$$\Delta G^0 = -2.303RT\log(55.5 \times K) \quad (5)$$

Where R is the molar gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution expressed in molar.

Values of the heat of adsorption are calculated according to equation [9-11]:

$$\Delta H_{\text{ads}} = 2.303Rx \frac{T_1 x T_2}{T_2 - T_1} \left[\log \frac{\theta_2}{1 - \theta_2} - \log \frac{\theta_1}{1 - \theta_1} \right] \quad (6)$$

Where ΔH_{ads} is entanpi of adsorption (kJ/mol); T_1, T_2 are test temperatures, respectively; θ_1 and θ_2 are the degree of surface coverage of the inhibitor at corresponding temperature.

Activation energy of corrosion process (E^* , kJ/mol) is calculated according to the equation Arrhenius [9]:

$$v = A \cdot C \cdot e^{-E^*/RT} \quad (7)$$

$$\text{or } \log v = -E^*/RT + \log(A \cdot C) \quad (8)$$

Where: C = reactant concentration.

3. RESULTS AND DISCUSSION

3.1. Effects of caffeine concentrations to inhibit corrosion ability

3.1.1. Polarization measurements

Polarization curves measurements for mild steel are shown in figure 1. The calculation of the corrosion rate and inhibition efficiency is given in table 1.

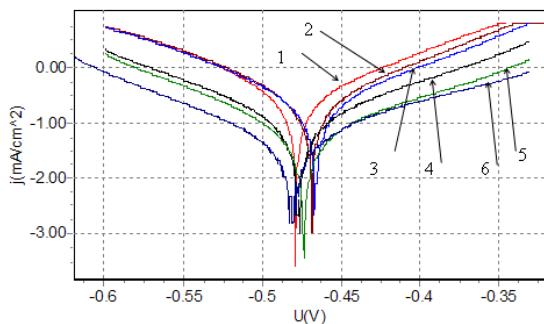


Figure 1: Polarization curves in absence and presence of different concentrations of caffeine in 1 M HCl solution
 1 – 0.00 g/L; 2 – 0.01 g/L; 3 – 0.05 g/L
 4 – 0.50 g/L; 5 – 2.00 g/L; 6 – 3.00 g/L

Table 1: The corrosion rate of CT3 steel in 1M HCl solution and inhibition efficiency of caffeine by polarization curves measurements

C _{affeine} (g/L)	E _{corr} (V)	R(Ω)	v×10 (mm/year)	H%
0.00	-0.466	77.71	8.76	
0.01	-0.472	84.10	8.01	7.60
0.05	-0.469	91.12	7.40	14.72
0.10	-0.474	135.59	4.94	42.69
0.50	-0.470	246.96	2.81	68.53
1.00	-0.477	354.65	1.91	78.09
2.00	-0.462	391.27	1.73	80.14
3.00	-0.467	464.49	1.44	83.54

Figure 1 and table 1 show that the presence of caffeine reduces the corrosion rate, v_{corr} (v). The decrease in v_{corr} values is due to the decrease of the aggressive acid attacking on the mild steel surface, attributed to the adsorption of inhibitor molecule. Furthermore:

- The anodic current density decreased as the concentration of caffeine increase from 0.01 g/L to 3.00 g/L but when its concentrations is less than or equal to 0.05 g/L, cathode current density did not change compared to the curve in the background, when the concentration of caffeine increased from 0.10 g/L to 3.00 g/L, the current density decreased rapidly.

- The corrosion potential E_{corr} shifted to the positive side when caffeine concentrations increase from 0.01 g/L to 0.05 g/L but after that, when caffeine concentrations increase from 0.10 g/L to 3.00 g/L, E_{corr} ascending gradually translated into the negative again.

Thus, at low concentrations (≤ 0.05 g/L), caffeine expressed as anodic inhibitors, at concentrations > 0.05 g/L, caffeine acts as an

inhibitor mixture. It means that, the inhibitors were adsorbed on the mild steel surface, which prevented the metal dissolution reaction and thus controlling the corrosion process.

The results obtained are in good agreement with those obtained from the weight loss measurements.

3.1.2 Surface examination study

The SEM photomicrography and analysis EDS steel surface which were soaked in 1M HCl solution in the absence and presence 3.00 g/L caffeine after 60 minutes immersion have been done. Results shown in figure 2 and table 2.

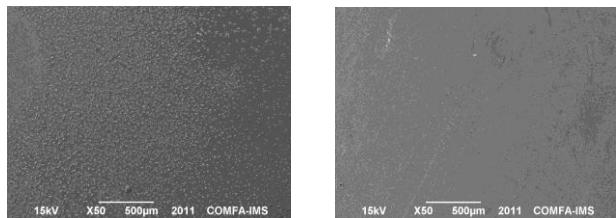


Figure 2: SEM micrographs of CT3 steel in without and with 3.00 g/L caffeine

Table 2: EDS analysis CT3 steel surfaces after immersion in corrosive solution 60 minutes

Atom	Fe	O	Cl	C	Other
Blank	86.26	10.6	0.75	1.9	0.49
Inhibitor	97.91	0.39	0.18	1.41	0.11

We can easily see that: CT3 steel surface immersion in HCl solution without caffeine has the thick corrosion centers density, corrosion points are large and corrosion products are pushed to the surface while sample soaking in the 1 M HCl with 3.00 g/L caffeine has the center density corrosion significantly reduced.

This result was also confirmed that in 1 M HCl and caffeine presence 3.00 g/L the CT3 steel corrosion has been significantly limited compared with a solution without caffeine.

3.2. Effects of temperature to inhibit corrosion ability of caffeine for CT3 steel in 1 M HCl solution

To examine the effect of temperature to corrosion and ability of caffeine to inhibit corrosion for CT3 steel, the work electrodes were measured for the polarization resistance and polarization curve in corrosive solution with and without 3.00 g/L caffeine at 25 °C, 35 °C and 45 °C. The corrosion rate calculated from polarization measurement is

given in table 3.

Table 3: The typical parameters of CT3 steel corrosion process in 1 M HCl solution with and without 3.00 g/L caffeine at different temperatures

Solution	E_{corr} (V)	R_p (Ω)	V (mm/year)	H%
Blank 25 °C	-0.466	77.71	0.876	
Blank 35 °C	-0.473	48.23	1.411	
Blank 45 °C	-0.463	26.51	2.568	
inhibitor 25 °C	-0.467	464.49	0.144	83.27
inhibitor 35 °C	-0.467	241.78	0.282	82.36
inhibitor 45 °C	-0.477	123.23	0.552	78.52

As the temperature rises. For the solution with or without caffeine. the polarization resistance of corrosion process is reduced so the corrosion rate increases. However. the protective effect of caffeine 3.00 g/L at different temperatures relatively stable. temperatures rising but the protective effect decreases dramatically.

3.3. Some characteristics of corrosive inhibition and corrosion process

3.3.1. Mechanism of corrosive inhibition process

The result of 3.1 can showed that the values of surface coverage increases, the corrosion rate decreases with the rise in inhibitor concentration as a result of more inhibitor molecules adsorption on the steel surface.

Now assuming that the adsorption of caffeine belongs to monolayer adsorption and the lateral interaction between the inhibitor molecules is ignored. By plotting values of C/θ versus C (table 1) following equation (4), straight line graphs were obtained (Fig. 3) which proves that Langmuir adsorption isotherm is obeyed over the range of studied concentrations.

The degree of linearity of Langmuir adsorption isotherm as measured by values of R^2 is nearly equal to 1 which indicates that the assumption and the deduction were correct. In other words, the adsorption of caffeine on steel surface in 1 mol.L⁻¹ HCl solution is well described by the Langmuir adsorption isotherm [9-11]. The considerable deviation of the slopes from unity shows that the isotherm cannot be strictly applied. This deviation is attributable to interaction between adsorbate species on the metal surface. A modified Langmuir adsorption isotherm [9, 10] could be applied to this phenomenon, which is given by the corrected

equation:

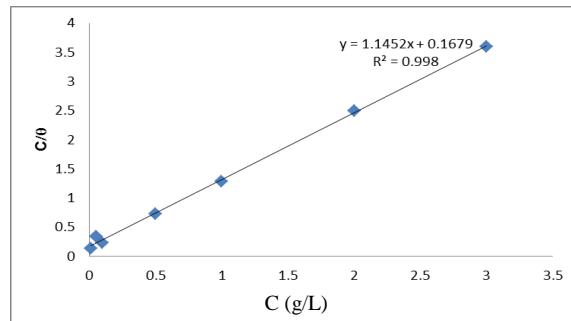


Figure 3: Langmuir isotherm for the adsorption of caffeine on the surface of CT3 steel in 1 M HCl

$$\frac{C}{\theta} = nC + \frac{n}{K} \quad (9)$$

The equilibrium constant and the standard free energy of adsorption process calculated from equation (5) are: $K = 6.82$ and $\Delta G^\circ = -14.71$ kJ/mol. The negative values of ΔG° suggest that the adsorption of caffeine onto steel surface is spontaneous. Furthermore, the obtained values of ΔG_{ads}° indicate that adsorption of caffeine occurs via physical adsorption mechanism [7, 8].

Values of ΔH_{ads} were calculated according to equation (6) are ranged from -6.38 kJ/mol to -19.89 kJ/mol, indicating that the adsorption of caffeine on the surface of CT38 steel is exothermic. This is another indication that the adsorption process is essentially physical adsorption.

3.3.2. The activation energy of corrosive process

We construct a graph showing the relationship between the log and $1/T$ (equation (8)) according to the data in table 3.

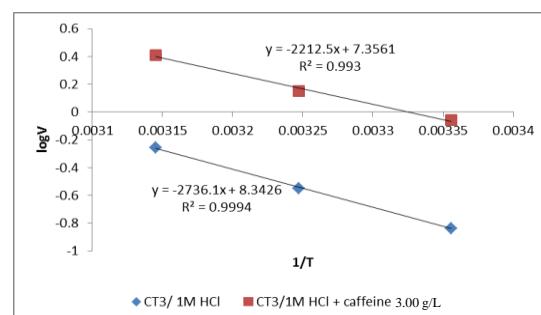


Figure 4: Arrhenius equation for the corrosion of CT3 steel in 1M HCl solution with and without caffeine 3.00 g/L

Empirical equations have high correlation coefficients ($R^2 \sim 1$) demonstrating that the corrosion obeys Arrhenius equation.

Following the equation (8) calculated the activation energy of CT3 steel corrosion in 1 M HCl with and without caffeine 3.00 g/L is:

$$E^*(\text{CT3/1M HCl}) = 42.1486 \text{ kJ;}$$

$$E^*(\text{CT3/1M HCl + caffeine 3.00 g/L}) = 52.5781 \text{ kJ.}$$

The value activation energy increases when present caffeine in solution proved corrosion occurs more difficult, requiring higher energy. It is due to caffeine adsorbed onto the surface so H^+ ion and/or dissolve O_2 attack the steel surface more difficult, or absorption that leads to change surface potential and electrode reactions occur more difficult.

4. CONCLUSIONS

- Caffeine has corrosion inhibition ability for CT3 steel in 1M HCl solution. Inhibition efficiency increases with the rise in caffeine concentration, Inhibition efficiency max is approximately 83 % at concentration of caffeine 3.00 g/L.

- As temperature increases from 298 to 318 K, the inhibition efficiency is relatively stable: decreases slightly from 83.27 % down 78.5 %.

- Mechanism of corrosion inhibition is physical adsorption, obeys the Langmuir adsorption isotherm. The adsorption of caffeine onto steel surface is spontaneous and exothermic.

- Calculated The activation energy of CT3 steel corrosion in 1 M HCl with and without 3.00 g/L caffeine was calculated. This value proved caffeine inhibits corrosion process.

Those results indicate that caffeine is a very good corrosion inhibitor for CT3 steel in 1 M HCl solution. It also open up the great possibility of practical application because caffeine is quite cheap, easy to obtain and safe for environment and human.

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