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Investigate the Corrosion Inhibitive Ability of Caffeine for CT3 Steel in 1M HCl Solution by EIS Technique

Truong Thi Thao[1,*], Dinh Thi Kim Dung[2]

[1]*Faculty of Chemistry, Thai Nguyen University of Science, Thai Nguyen University*
[2]*Department of Natural Sciences, Hoa Lu University*

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Abstract: Corrosion inhibition of mild carbon steel, CT3 in hydrochloric acid by caffeine (with different concentrations, from 0.01g/l to 3.00g/l) was investigated at room temperatures using weight loss and electrochemical impedance spectroscopy (EIS) technique. Experiment result under two methods has good coincidence and shows that: as the concentration of caffeine increases, the inhibition efficiency increases. Caffeine is found to be an excellent inhibitor for steel alloys with an efficiency reaching 90 % at 3.00g/l of inhibitor concentration. When the trial period lasting up to 10 days, %IE decreased slightly but relatively stable.

Keywords: Caffeine, CT3 steel, corrosion inhibitor, adsorption.

1. Introduction

Among metals, CT3 steel, one type of mild carbon steel, is extensively investigated in corrosion studies because of its wide application in different corrosive environment. One of the important and practical methods of protecting steel from corrosion is to use inhibitors. Corrosion inhibitors are compounds that are commonly added in small quantities to an environment for preventing corrosion. Due to the increase of environmental awareness, research in corrosion prevention is oriented to the development of the so-called green compounds with good inhibition efficiency and with low risk of environmental pollution. 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 [1-3]. However, plant extracts are unstable, decomposed quickly over time. To overcome this drawback, we are looking for the pure substances which it has inhibiting corrosion capable in those extract. Caffeine is a natural organic substance existing in different parts of a great number of vegetables. Caffeine is effective, environmental friendly corrosion inhibitor [4-8]. Also, caffeine is biodegradable and environmentally benign with minimal health and safety concern. The aim of this paper is to study the corrosion inhibition behaviour of caffeine for CT3 steel in 1M HCl solution by weight loss method and electrochemical impedance spectroscopy (EIS) technique.

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[*] Corresponding author. Tel.: 84-915216469
Email: thao.truong671@gmail.com

2. Experimental

2.1. Preparation of the specimens

CT3 carbon steel (produced in Thai Nguyen) specimens were chosen from the same sheet with the following composition: 0.154%C; 0.636%Mn; 0.141%Si; 0.019%P; 0.044%S and Fe. The dimensions specimens of all samples for weight loss study are 5.0x8.0x0.2cm. With electrochemical studies, the surface area of metal surface was 0.785 cm^2 as fig.1.

Fig.1. Electrochemical specimens.

2.2. Corrosion measurements

2.2.1 Weight loss method

Weight loss experiments were carried out for a period of one day at room temperature in quiety conditions. Prior to each experiment, specimens were prepared for test and cleaned after testing following G1 ASTM standards 2000. Mass of specimens were determined by a analytical balances Startorius Ag Germany CP224S, and measured accurately sample size before immered in the test solution. Inhibition efficiency (IE) was calculated from the relationchip:

$$IE = 100(1-W_2/W_1)\ (\%) \qquad (1)$$

Where W_1 is the corrosion rate in the absence of inhibitor and W_2 is the corrosion rate in the presence of inhibitor. They were caculated from the equation:

$$W = (m_b - m_a)/t.S \qquad (2)$$

Where m_b and m_a is the mass of specimen before and after immered in the test solution one day (t = 1). S is the surface area of specimen.

2.3.2. Electrochemical impedance spectroscopy method

All experiments were done in unstirred and nondeaerated solutions at room temperature after immersion for 60 min in 1M solution with and without addition of inhibitor. 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. Electrochemical impedance spectroscopy (EIS) was obtained with a scan frequency range of 100 kHz to 5 mHz with amplitude of 10 mV. The inhibition efficiency has been calculated from the equation:

$$IE = 100(1-R_a/R_p) \qquad (3)$$

where R_a and R_p are the polarization resistance in absence and in presence of inhibitor, respectively.

3. Result and discussion

3.1. Effects of caffeine concentrations to inhibit corrosion ability

3.1.1 Weight loss method

The corrosion rates of CT3 steel when it is immersed in 1M HCl solution in the absence and the presence of various concentrations of caffeine, for a period of 1 day, by weight loss method are given in Table 1.

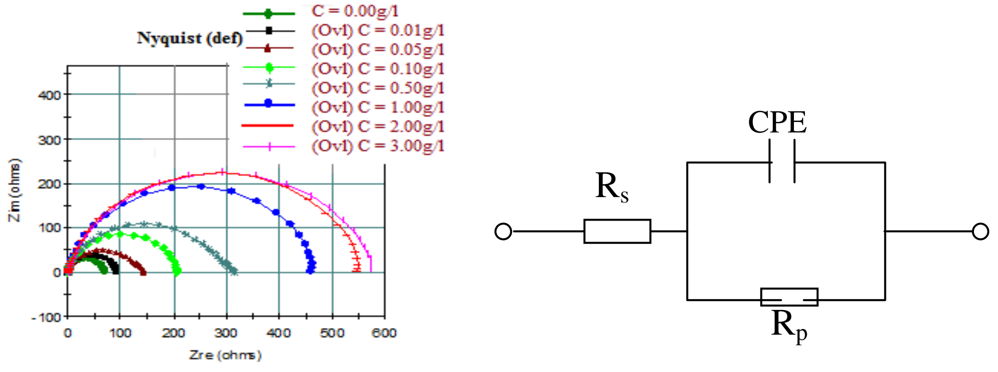
Table 1. Corrosion rates of CT3 steel immersed in 1M HCL solution for 1 day and inhibition efficiency of caffeine

$C_{caffeine}$(g/l)	0.00	0.01	0.05	0.10	0.50	1.00	2.00	3.00
S (cm^2)	58,3438	57,0492	56,2482	55,9998	56,0838	56,1758	55,9326	56,6104
m_b(g)	45,0657	44,8175	44,6105	43,9625	44,0044	44,5568	44,2840	44,5730
m_a (g)	43,3952	43,3257	43,2945	43,1627	43,5954	44,3573	44,1128	44,4696
$W_{corr}.10^2$ (g/cm^2.day)	2.86	2.61	2.34	1.43	0.73	0.36	0.31	0.18
IE (%)	-	8.97	18.29	50.12	74.53	87.60	89.31	93.62

It is observed that, as the concentration of caffeine increases from 0.01g/l to 3.00g/l, the inhibition efficiency increases gradually from 8.97% to 93.62%; It indicates that caffeine molecules are adsorbed on the CT3 steel surface restricting metal dissolution. (At higher concentration of caffeine, solution is not stable and inhibition efficiency decreases).

3.1.2. EIS studies

The EIS for CT3 steel in 1M HCl solution in the absence and in the presence of various concentrations of caffeine are given in Figure 2.



a b

Fig. 2. EIS (a) and Equivalent circuits used for fitting the measured impedance spectra (b) for CT3 steel in 1M HCl solution in the absence and in the presence of caffeine.

From Fig. 2a we see: spectrum obtained consists only one compression semicircle. Equivalent circuits used for fitting the measured impedance spectra are given in figure 2b.

As shown in Fig. 2b, the caffeine inhibitor does not affect the solution resistance (R_s). From the comparison of the simulation and experimental data of the CT3 steel corrosion with the presence of caffeine, the most accurate equivalent circuit model for all the semicircles in the Nyquist plots is $R_s(C[R_p])$. Instead of the pure capacitance (C), a constant phase element (CPE, denoted as Q in the circuit) is introduced in the simulation process to obtained good agreement between simulated and experimental data[3,4]. The impedance (Z) of the CPE is defined as:

$$Z_{CPE} = 1/Q.(j\omega)^{-n} \qquad (4)$$

With Q is value of CPE, j is the imaginary unit, ω is the angular frequency; n is the compression ratio is used to evaluate the degree of surface heterogeneity. Depends value n that

CPE can perform resistance value (n = 0, Q = 1/R), capacitance C (n = 1, Q = C), inductance (n = -1, Q = 1/L) or Warburg element (n = 0.5). In particular, n =1, calculate the capacitance double layer capacitance C_{dl}. In fact, when n ~ 1, the CPE characteristic for double layer capacitance commonly used in corrosion systems or adsorption systems. Double layer capacitance values are calculated from the formula)

$$C_{dl} = Q\ (\omega_{max})^{n-1} \qquad (5)$$

With ω_{max} is the angular frequency in virtual impedance value reaches the maximum value.

The value calculated from the EIS spectrum and equivalent circuist are given in Table 2.

Table 2. The typical of CT3 steel corrosion process in 1M HCl with and without the presence of diferent caffeine concentrations from EIS spectrum

C(g/l)	$R_P(\Omega.cm^2)$	$Q(\mu F/cm^2)$	n	$C_{dl}(\mu F/cm^2)$	H(%)
0.00	71.13	239.28	0.823	99.44	
0.01	54.42	260.34	0.861	128.13	-
0.05	91.15	175.04	0.844	80.23	21.96
0.10	132.88	170.39	0.734	52.91	46.47
0.50	206.59	134.86	0.816	51.92	65.57
1.00	296.42	147.04	0.731	48.28	76.00
2.00	425.51	108.34	0.815	47.65	83.28
3.00	559.04	97.38	0.806	46.42	87.28

Tab.2 shows that:

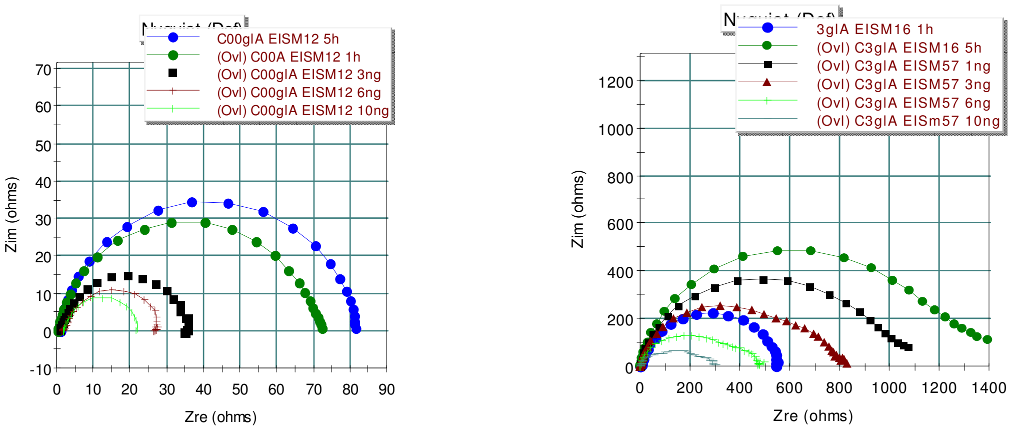
At caffeine concentrations is small, effective corrosion protection is low, even concentration of 0,01g/l also increases corrosion. The more of the concentration of caffeine increased, the more of R_P increased, effective protection significantly increased, especial from 0.05g/l to 1.00g/j; when concentration is higher than 1.00g/l, R_P slowly decreased. These results are quite consistent with the results obtained from the weight loss method.

The surface of the electrode in corrosive solutiom format a double layer which is indeal capacitor. In corrosive solution without and with small caffeine concentration (less than and equal 0.05g/l), n is higher demonstrate that: the surface is corroded sharply, surfaces become porous due to corrosion product and caffeine adsorption are uneven, unstability; Q and C_{dl} at caffeine concentrations 0.05g/l are quite large. When the concentration of caffeine greater than 0.10g/l, the compression ratio n, Q and C_{dl} are fall prove double layer formed up thicker, the conductivity decreases, the contact of the corrosive solution and metal surfaces reduced and corrosion limits. The reduction in capacitance value C_{dl} when the concentration of caffeine increased can be inferred from the reduced dielectric constant region and/or an increase in the thickness of the double layer, suggesting that the adsorption on the surface boundary steel/solution dependent on caffeine concentration. The decrease C_{dl} when the concentration of caffeine increased demonstrate the gradual replacement of water molecules on the surface of steel by molecules adsorbed caffeine reduces Fe solubility in aqueous solution.

Caffeine has two aromatic and contains three N atoms in the aromatic, two O atoms linked ketone form, so the density of electrons on caffeine quite large, may occur physical adsorption onto steel caffeine.

3.2. Effect of immersion time

CT3 steel electrodes are immersed in a solution of 1M HCl with and without caffeine 3.00g/l and measured EIS from 1 hour to 10 days. The EIS Nyquist was given in fig.3.



a)

b)

Fig. 3. EIS for CT3 steel in 1M HCl solution in the absence
(a) and in the presence (b) of 3.00g/l caffeine at different times.

Fig.3 indicated:

The EIS Nyquist of ST38 steel in 1M HCl from 1h to 10 days only have a quite ideal semicircle. This is consistent with the fact that the corrosion process of CT3 steeel in 1M HCl occurs strongly and increases gradually over time, the corrosion products difuse fast enough to the solution that it does not exist a layer of corrosion products on the electrode surface. In the trials time is from 1 hour to 5 hours, impedance increased, but when the trial time lasting more than one day, the impedance decreases. In generally, the corrosion increase over time. It may be explained that, initial, the corrosion of CT3 steel in 1M HCl solution should be points, after that, points gradually developed into the holes and destruction increased.

EIS for CT3 steel in 1M HCl solution in the presence of 3.00g/l caffeine (b) shows: The polarization resistance (Rp) increased approximately 8 to 15 times than it is in solution which absence of caffeine. It proved the caffeine maintain effective corrosion inhibition for 10 days. Simultaneously, the shape of EIS changed also: semicircle is compressed strongly and the trial time was longer than one day, it had form of two overlapping semicircular; The first semicircular characterize adsorption layer of caffeine, the second semicircular characterize the corrosion process occurring under the adsorption layer. It mean that the caffeine absorption is unevenly on the surface of steel, not enough to form the shielding layer after 5 hours. At time of 1 day, adsorption layer formed stable on the surface, the solution diffuse through adsorption layer slowly and the second semicircular of corrosion process is clearer.

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 90% at concentration of caffeine 3.00g/l. Mechanism of corosion inhibition is adsorption. IE (5) of caffeine 3.00 g/l maintained relatively steady within 10 days.

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Khảo sát khả năng ức chế ăn mòn thép CT3 trong dung dịch HCl 1M của caffeine bằng phương pháp tổng trở

Trương Thị Thảo[1], Đinh Thị Kim Dung[2]

[1]*Khoa Hóa học, Trường Đại học Khoa học, Đại học Thái Nguyên*
[2]*Khoa Khoa học Tự nhiên, Đại học Hoa Lư, Ninh Bình*

Tóm tắt: Caffeine là một hợp chất có nhiều trong chè, cà phê. Một số nghiên cứu đã cho thấy caffeine có khả năng ức chế ăn mòn cho Ni, đồng, thép không gỉ [4,5,6,7]. Nghiên cứu này tiếp tục đánh giá khả năng ức chế ăn mòn thép CT3 sản xuất tại Thái Nguyên của caffeine theo phương pháp hụt khối và phương pháp tổng trở. Hai phương pháp đều cho thấy tốc độ ăn mòn giảm khi nồng độ caffeine trong dung dịch nghiên cứu tăng lên, ở nồng độ caffeine 3,00g/l, hiệu quả ức chế ăn mòn đạt tới xấp xỉ 90%. Hiệu quả bảo vệ duy trì khá ổn định khi thời gian thử nghiệm kéo dài tới 10 ngày. Phân tích các kết quả đo tổng trở còn góp phần khẳng định, cơ chế ức chế ăn mòn thép CT3 của caffeine trong dung dịch HCl 1M là cơ chế hấp phụ.

Từ khóa: Caffeine, thép CT3, ức chế ăn mòn, hấp phụ.