VNU Journal of Science: Natural Sciences and Technology, Vol. 33, No. 3 (2017) 105-111

Study the Corrosion Inhibition of Mix of Caffeine and 1.0 g/l Iodide for CT3 Steel in 1 M HCl Solution by Electrochemical Methods

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Received 05 April 2017
Revised 30 May 2017; Accepted 28 June 2017

Abstract: Corrosion inhibition of mild carbon steel, CT3, in 1.0 M HCl solution by iodide (with different concentrations, from 0.1g/l to 1.0g/l), mix of caffeine and 1.0 g/l iodide was investigated by electrochemical methods and micro surface observations (SEM). Experiment result showed that: (1) the inhibition efficiency increaseed with increased of iodide concentration; iodide acted as a mix – type inhibitor but inhibits anodic reaction was predominant. (2) Mix of 1.0 g/l iodide and caffeine acted as a typical mix – type inhibitor. The current densities of both of anodic and cathode declined when concentration of caffeine was 1.0 g/l or more, inhibition efficiency max was approximately 96% at concentration of 5.0 g/l caffeine, the inhibition efficiency maintained relatively stable within 5 days.

Keywords: Mix of iodide and caffeine, CT3 steel, corrosion inhibitor.

1. Introduction

Carbon steel is the most commonly used material in industrial applications such as industrial cleaning and processing of oil wells. Corrosion is a serious problem in modern industry for almost of metals. The use of inhibitors is one of the best ways to protect metals against corrosion caused by acid solutions such acid pickling and acid descaling. Corrosion inhibitors are compounds that are commonly added in small quantities to work solution of metals and it reduces the speed of metal dissolution. So the researchers have interest in using alternatives to toxic chemical inhibitors and the search for non-toxic natural inhibitors to reduce corrosion of metals. The majority of inhibitors used in industry in acid corrosion are organic compounds consisted of nitrogen, oxygen and sulfur atoms. Inhibitors that contain double or triple bonds take an important part in facilitating the adsorption of these compounds onto metal surfaces as well, since a bond can be formed between the electron pair and/or the π-electron cloud of the donor atoms and the metal surface, there by reducing corrosive attack in acidic media. We have done some research using caffeine as corrosion inhibitors [1-2]. Other authors have also reported that caffeine can inhibit metal corrosion [3-5]. However, the active ingredient is expensive and the inhibitory capacity is not high enough, is only about 70% to 80%.

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https://doi.org/10.25073/2588-1140/vnunst.4315

Kali iodide used to be a good inhibitor for a long time [6]. A series of reports highlighted the synergistic effect of iodide ions on the corrosion inhibition of aluminium/mild steel in acidic [7-11]. Synergism has become one of the most important effects in inhibition processes and serves as the basis for all modern corrosion inhibitor formulations. For the purpose of increasing the effectiveness of caffeine, we studied the corrosion inhibition behaviour of mixture of caffeine and kali iodide for CT3 steel in 1M HCl solution by electrochemical methods.

2. Experimental

2.1 Materials and sample preparation

CT3 carbon steel (produced in Thai Nguyen) specimens were chosen from the same sheet of the following composition: C(0.154 wt%); Mn(0.636 wt%); Si(0.141 wt%); P(0.019 wt%); S(0.044 wt%) and Fe. The dimensions specimens of all sample for weight loss study are 5.0x8.0x0.2cm. With electrochemical studies, the surface area of metal surface was 0.785 cm^2. The CT3 steel specimen surface was abraded with abrasive papers starting from 320 to 2000 grit size. The samples were rinsed with distilled water and dried in air, then followed by acetone degreasing. The KI, HCl were supplied by Merck, caffeine was extracted from leaves of Thai Nguyen green tea. In each experiment, a freshly prepared solution was used.

2.2. Electrochemical measurements

The electrochemical measurements were performed on 0.785 cm^2 of the mild steel panels exposed to a 1.0 M HCl solutions containing various concentrations of inhibitor at 25◦C with 30 min of immersion without de-aeration of the solution. Electrochemical measurements were carried out employing an Autolab instrument model PGSTAT302N. Prior to implementing the test, it is mandatory to reach a steady state of potential; therefore, the electrode was immersed in the test solution for 30 min at open circuit potential to attain steady state condition. To perform EIS and polarization measurements, a conventional three electrode cell was used, with the mild steel specimen as the working electrode, A silver/silver chloride electrode and a piece of stainless steel with large area were employed as reference and counter electrode, respectively. All data analysis was performed using NOVA 1.8 software.. Corrosion tests were performed electrochemically at room temperature (~ 25^oC).

The linear polarization study was carried out from −20 to +20 mV of OCP at a scan rate of 0.1 $mV.s^{-1}$ to determine the polarization resistance (R_p).

Impedance spectra were plotted at open circuit potential (OCP) within the frequency domain of 10 kHz to 5 mHz by applying 10 mV sine wave AC voltage. The inhibition efficiency has been calculated from the equation:

$$IE = 100(1-R_a/R_p) \qquad (2)$$

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

Tafel curves were obtained by changing the electrode potential automatically from −250 to +250 mV of OCP 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}).

2.3 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).

3. Result and discussion

3.1 Effects of iodide concentrations on inhibit corrosion ability

The potentiodynamic polarization curve of CT3 steel in 1.0 M HCl solution in the absence and presence of different concentrations of kali iodide was shown in Fig. 1.

Several features can be inferred from the plots. Regardless of the concentration of iodide in the acidic solution, a significant drop in both cathodic and anodic current densities occurred, indicating that the compound might affect both cathodic and anodic reactions. Moreover, the shift in the corrosion potential (E_{corr}) towards more positive values corresponds to the dominant anodic inhibition of the inhibitor [12]. The displacement of corrosion potential in the presence of the inhibitor was less than 50 mV, which consequently suggested a mixed-type inhibitor [13]. Since addition of the inhibitor to the acid solution had no significant effect on the slope of cathodic branch, the drop in cathodic current densities could be a reflection of the fact that adsorption of the inhibitor molecules did not modify the hydrogen evolution mechanism [14]. Contrary to the cathodic branch, a considerable effect of the inhibitor could be observed on the shape and the slope of the anodic branch, which may be associated with the displacement of the iron dissolution mechanism while blocking anodic sites [13]. The anodic polarization curves also showed linear Tafel behavior throughout a wide range of current and potential.

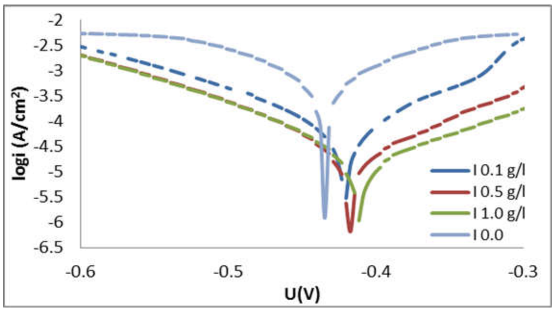
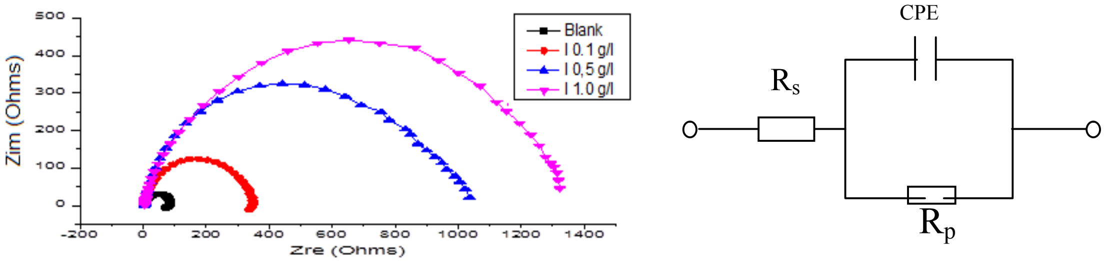


Fig. 1. Polarization curves of CT3 steel immers for 30 minutes in 1.0 M HCl solution containing different concentrations of kali iodide at room temperature.

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



a b

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

From Fig. 2a we see: Despite the similar appearance of the semicircles, the plots did not conform to a perfect semicircle. The deviation from an ideal semicircle is assumed to be attributed to inhomogeneity and roughness of the surface [4,8]. Equivalent circuits used for fitting the measured impedance spectra are given in figure 1b.

In the evaluation of Nyquist plots, the charge transfer resistance is commonly considered as a difference in real impedance at lower and higher frequencies. It is important to note that charge transfer resistance (R_{ct}) is the resistance between the metal and oxidizer on metal surfaces. So that, the contribution of all metal/solution interface resistances including charge transfer resistance (R_{ct}), accumulation resistance (R_a), and diffusion layer resistance (R_d) must be taken into account in R_P [13]. From Fig. 4, the Nyquist plot of mild steel showed a depressed semicircle and only one time constant which indicated that the corrosion of CT3 steel in 1.0 M HCl solution is dominated by a charge transfer process [1]. So, the adsorption of iodide on mild steel in 1.0 M HCl solution leads to a structural modification in the double layer. In this study, the difference at lower and higher frequencies was considered as polarization resistance (Rp). Therefore, continuous expansion of the loops could reveal an ascending trend of resistance as the inhibitor's concentration increased. Fig. 2b depicts the proposed equivalent circuit to simulate the impedance data, where R_s, R_p and CPE represent the solution resistance, the polarization resistance and the constant phase element.The use of CPE instead of double layer capacitance (C_{dl}) could be linked to a more accurate fit in the case of deviation from an ideal capacitor as a result of different physical phenomena like surface roughness, inhibitor adsorption, porous layer formation, etc. This parameter is composed of Y_0 and n, which are the magnitude and exponent of CPE, respectively. The parameter n has a value range of 0-1; it approaches unity for a more homogenous surface, which could be a reflection of an ideal capacitor (n=1) [1,4,7,11,13]. The elements extracted from EIS are presented in Table 1.

Table 1. The Electrochemical parameters obtained from the EIS plots for CT3 steel in 1.0 M HCl in the absence and presence of diferent concentrations of kali iodide

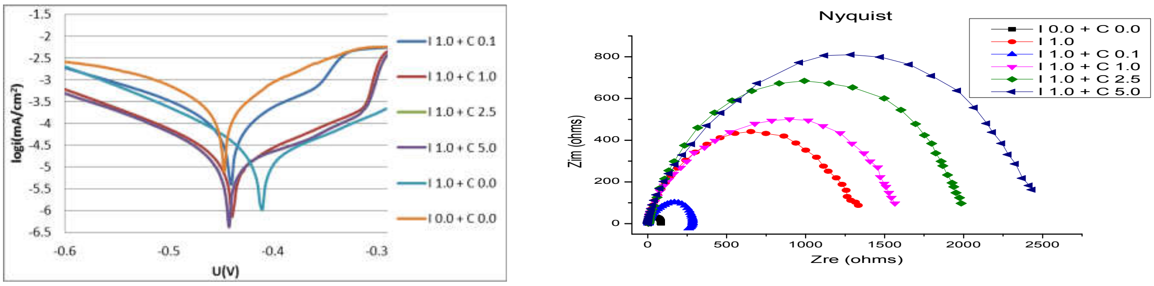
C(g/l)	R_s(Ω.cm^2)	R_P(Ω.cm^2)	Q(μF/cm^2)	n	C_{dl}(μF/cm^2)	H(%)
0.0	6.07	85.61	704.66	0.736	179.78	
0.1	4.91	335.11	245.74	0.713	60.35	75.91
0.5	4.82	1046.27	226.64	0.622	53.79	92.36
1.0	4.92	1333.52	208.39	0.661	52.40	94.01

It is clear from Table 2 that the inhibitor provided excellent corrosion protection to mild steel exposed to an HCl solution even at a low concentration, indicating the blocking active sites at the metal/solution interface. Moreover, the EIS data showed that an increasing concentration resulted in lower capacitance (C_{dl}). According to the OBot [7], a drop in the local electric constant and/or an increase in the thickness of the electrical double – layer may be the reasons for the decrease in the C_{dl}. This behavior was likely associated with the gradual replacement of water molecules by iodide on the surface, leading to a reduction in the number of active sites needed for the corrosion reaction [7,9]. As previously mentioned, taking into account the n values, inhibitor adsorption and metal dissolution can be discussed as the two main processes during corrosion. Therefore, the suppressed n value in the case of uninhibited solution could confirm the inferences relating to a more homogenous surface in the presence of inhibitor [1].

3.2. The corrosion inhibitive ability for CT3 steel in 1.0 M HCl solution of mix of caffeine and iodua

Although the inhibition efficiency of kali iodide is very good, but it is very unstable and quickly oxidized to I_2 due to the effect of sunlight and dissolved oxygen, therefor the inhibition efficiency will decrease rapidly. To increase the inhibitory activity of iodide at a lower concentration and the duration of action, we investigated using mix of iodide with caffeine - which was extracted from Thai Nguyen green tea - as a corrosion inhibitor for CT3 steel in solution HCl 1M. The polarization curve and the Nyquist plots of CT3 steel in 1.0 M HCl solution in the absence and presence of mix of 1.0 g/l iodide and caffeine were shown in Fig. 3.

Fig.3a indicated that: comparing the polarization curve of CT3 steel in 1.0 M HCl solution (blank) with that of the solution when added the mixture of caffeine and iodide: the current density of cathode and anodic branch of system were decreased. At low concentration of caffeine (0.1 g/l), the slope and the current density of both of anodic and cathode increased compare with that of the solution when added only 1.0 g/l iodide but from the caffeine's concentration is from 1.0 g/l to 5.0 g/l, the current densities of both of anodic and cathode declined. The mixture acted as a mixed-type inhibitor.

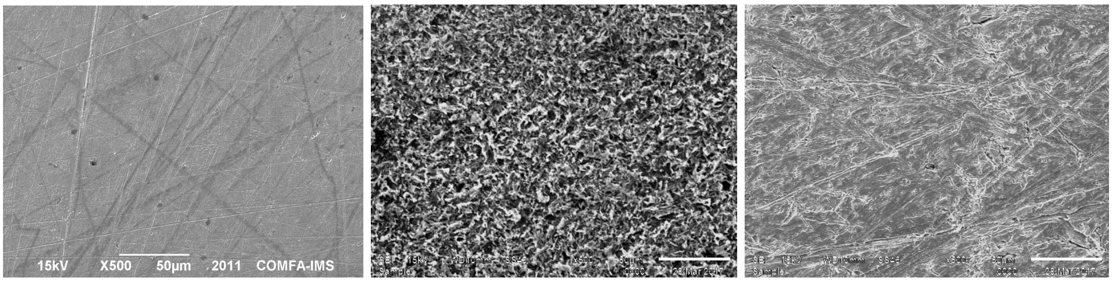


a b

Fig. 3. The polarization curve (a) and the Nyquist plots (b) of CT3 steel immers for 30 minutes in 1.0 M HCl solution containing different concentrations of iodide and caffeine.

Fig.3b also showed the same results: the present of mix of 1.0 g/l iodide and 0,1 g/l caffeine in 1.0 M HCl solution made R_p of system decreased compared to R_p of system in 1.0 M HCl solution which was added 1.0 g/l iodide but still greater than R_P of CT3 steel in 1.0 M HCl solution. When the caffeine's concentration increased from 1.0 to 5.0 g/l, R_P of system was greater than R_P of CT3 steel in background solution present 1.0 g/l iodide. Maximum R_p of system achieved and caffeine 5.0 g/l (inhibition efficiency is 96.5 %;).

This result is perfectly consistent with the SEM image of the CT3 steel surface before and after being immersed in the research solution (Fig. 4).



a b c

Fig. 4. SEM micrographs of CT3 steel before immersing in inhibitive solution (a) and after immersing 60 min in 1.0 M HCl solution without inhibitor (b), with 1.0 g/l iodide and 5.0 g/l caffeine at room temperature.

More ever, Fig. 5 show the effect of changing immersion time (0 to 5 days) at 25°C on the corrosive inhibition efficiency of mixture of of 5.0g/l caffeine and 1.0 g/l iodide for CT3 steel in 1.0 M HCl: In the trials time was from 30 min to 1 hour and to 5 hours, impedance increased slightly: from R_P ~2250 Ω.cm^2 at 30 min to R_P ~ 2620 Ω.cm^2(h ~ 96.72 %) at 60 min and to 5 hours (R_P ~2650 Ω.cm^2); and then slightly decreases when the trial time lasting to 1 day and 5 days (R_P ~2250 Ω.cm^2 at 5 days) The shape of EIS also varied negligibly. It proved that the mixture could maintain effective corrosion inhibition for 5 days.

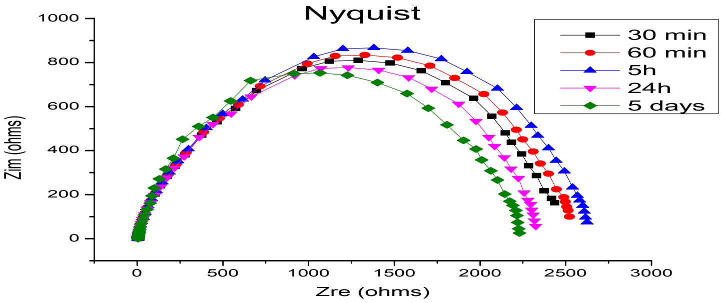


Fig. 5. EIS for CT3 steel in 1M HCl solution in the presence (b) of 1.0 g/l iodide and 5.0 g/l caffeine at different times.

4. Conclusions

Iodide is a good inhibitor for the corrosion of CT3 steel in 1.0 M HCl solution, but the solution is unstable due to the influence of sunlight and dissolved oxygen. The combination of iodide with caffeine not only increased the efficiency of corrosion inhibition but also maintained the stability of the working solution. Inhibition efficiency max was approximately 96% at concentration of mix of 1.0 g/l iodide and 5.0 g/l caffeine (increase rapidly compared with using only caffeine [1,2]). The mechanism and the inhibition efficiency maintained relatively steady within 5 days.

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Nghiên cứu sự ức chế ăn mòn thép CT3 trong dung dịch HCl 1M của hỗn hợp caffeine và iotua bằng phương pháp điện hóa

Trương Thị Thảo

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Tóm tắt: Sự ức chế ăn mòn của ion iotua, hỗn hợp iotua và caffeine đối với quá trình ăn mòn thép CT3 trong dung dịch HCl 1M đã được nghiên cứu bằng các phương pháp điện hóa và phương pháp quan sát bề mặt vi mô (SEM). Kết quả thực nghiệm cho thấy: (1): Ion iotua có khả năng ức chế tốt ngay cả ở nồng độ thấp, khi nồng độ tăng khả năng ức chế ăn mòn tăng. Ion iotua hoạt động như một chất ức chế hỗn hợp, làm thay đổi cơ chế của phản ứng anot. (2) Hỗn hợp iotua 1.0 g/l và caffeine với các nồng độ khác nhau cũng hoạt động như một chất ức chế hỗn hợp, đặc biệt khi nồng độ caffeine từ 1.0 g/l trở lên. Hiệu quả ức chế ăn mòn cao nhất đạt tới khoảng 96% khi dùng hỗn hợp với hàm lượng caffeine 5.0 g/l, hiệu quả ức chế duy trì khá ổn định theo thời gian.

Từ khóa: Iotua, hỗn hợp iotua - caffeine, thép CT3, ức chế ăn mòn.