

Short Communication

Study on the Synergistic Effect of Iodide Ion with the Extract of *Artemisia Halodendron* on the Corrosion Inhibition

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The synergistic inhibition effect of iodide ion with the extracts of *Artemisia Halodendron* was studied by electrochemical potentiodynamic polarization methods. It was found that the inhibition efficiency increased with increasing the iodide ion concentration when fixed the concentration of the extract. But increased first and decreased then with increasing concentration of the extract when fixed the iodide ion concentration. The synergism parameters were evaluated from the inhibition efficiency values. SEM and EDX study confirmed the corrosion inhibition of the extract and iodide ion on the mild steel surface in HCl solution.

Keywords: Plant extract, Corrosion, Green inhibitor, Acid solution

1. INTRODUCTION

The inhibitors are commonly used for protecting iron against corrosion in acidic media[1]. Unfortunately, most of corrosion inhibitors have a high risk for environment and human beings[2-4]. Plant extracts have become a more important corrosion inhibitor as their low toxicity, rich availability and simple preparation[5]. According to the literature[6], it presents most of the recent contributions made to the application of plant extracts as corrosion inhibitors for steel in acid solution, such as oak-bark[7], Aloe[8], Punica[9], *Mansoa alliacea*[10], Cannabis[11], *Neolamarckia cadamba*[12]. It is clear from these studies that the inhibitory properties of plant extracts are usually attributed to their complex organic substances such as carbohydrates, alkaloids, amino acids and tannins. These organic compounds contain N, S, O atoms and polar functional groups as conjugated double bonds or aromatic rings as the main adsorption centers[13].

In recent years, a great of force to improve the inhibition effect and decrease the cost, synergism is viewed as an effective way. Among these work, synergistic inhibition effect between

halide ions and plant extract inhibitors in acidic solution has been summarised[14]. Obviously, the researches reveal that the improvement of the inhibitive force. As the coexist of halide ions and plant extract chemicals, synergistic inhibition effect happened. In most case, the contribution of halide ions to the synergistic effect was in the order of: $\text{Cl}^- < \text{Br}^- < \text{I}^-$. I^- , the largest size (216 pm) among Cl^- , Br^- , I^- , has the highest synergistic effect due to its dimension and polarizability.

Recently, we presented the electrochemical experimental evidence demonstrating that *Artemisia Halodendron* leaves extract (AHLE) works as a good corrosion inhibitor on mild steel in 1M HCl solution.[15] In that scenario: (i) fourier transform infrared spectroscopy (FT-IR) study had suggested that AHLE contains abundant oxygen and nitrogen atom functional group such as C-O, O-H, N-H, C-N, etc., and aromatic ring; (ii) polarization studies showed that AHLE works as a mixed-type inhibitor in hydrochloric acid system; (iii) Nyquist plots integrated polarization curves revealed that AHLE make an increasing corrosion inhibition efficiency performance with increased concentration, as well as obeys Langmuir adsorption isotherm.

In the present work, we provide an expansion of earlier study and report the synergistic inhibition effect between AHLE and I^- on the corrosion of mild steel in 1 M HCl solution by electrochemical polarization techniques. The ensuing corrosion inhibition efficiency analysis affords *synergism parameters* (S) which enables comparisons of the synergy effect between AHLE and I^- . Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) studies were employed to detection the surface of the mild steel with and without inhibition intervention, to obtain further information of AHLE and I^- corrosion effect on the mild steel in 1 M HCl solution.

2. EXPERIMENTAL METHOD

2.1 Preparation of plant extract

Accurately weighed 5g dried plant *Artemisia Halodendron* leaves. The leaves were immersed in deionization water solution (500ml). The aqueous solution was refluxed for 5 h and then, filtered, concentrated the solution to 100ml. Use this concentrated solution ($5 \times 10^4 \text{ mg L}^{-1}$) as original solution, the different concentration plant extract solutions were prepared by dilution method, e. g, to configure the concentration of 50 mg L^{-1} inhibitor solution, the original solution can be diluted 1000 times to obtain the solution of the desired concentration. Other concentrations of the inhibitor solution only need to carry out by different dilutions times.

2.2 Electrochemical tests

Electrochemical experimental apparatus and methods refer to the literature[5]. A commercialized three-electrode cell consisting of mild steel working electrode with an exposed area in 0.785 cm^2 , a platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. All potential in this work were referred to the SCE. Before measurement, the working

electrode was immersed in test solution at open circuit potential (OCP) for 30 min to attain a stable state.

The potential sweep rate for potentiodynamic polarization curves was 1 mV s^{-1} . Corrosion current density (i_{corr}) was determined from the intercept of extrapolated cathodic and anodic Tafel lines at the corrosion potential (E_{corr}). The inhibition efficiency η_p (%) was calculated as the following equation:

$$\eta_p = \frac{i_{\text{corr}} - i'_{\text{corr}}}{i_{\text{corr}}} \times 100\%$$

Where i'_{corr} and i_{corr} are the corrosion current density values of mild steel in the absence and presence of inhibitors, respectively.

2.3 Scanning electron microscope

The surface morphologies of the samples were examined by scanning electron microscope (SEM, QUANTA200 plus VANTAGE EDX).

3. RESULTS AND DISCUSSION

3.1 Polarization curves for synergistic inhibition of AHLE and Γ

At 30°C , the potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of various concentration of AHLE and Γ are shown in Fig. 1. The electrochemical corrosion parameters of corrosion potential E_{corr} (mV, vs. SCE), cathodic and anodic Tafel slopes β_c and β_a (mV dec^{-1}), the corrosion current density i_{corr} (mA cm^{-2}) and inhibition efficiency η_p (%) are given in Table 1. Meanwhile, based on potentiodynamic polarization measurement, the inhibition efficiency was calculated by the equation mentioned in section 2.2.

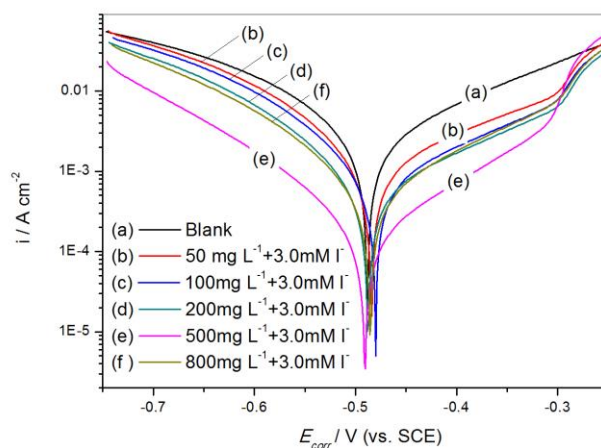


Figure 1. Polarization curves for the mixture of AHLE and fixed 3.0 mM concentration of Γ in 1 M HCl at 30°C . (Scan rate was 1 mV s^{-1})

As shown in Fig. 1 and Table 1, for the presence of AHLE and 3.0 mM Γ mixture, both the anodic and cathodic curves shift to lower current densities, accompanied by the emergence of lower values of current densities, which indicate that inhibitor can reduce the mild steel anodic dissolution and retard the hydrogen ions reduction. The inhibition effect enhances with the increase of AHLE concentration up to the 500 mg L⁻¹, resulting from the adsorption of inhibitors on the mild steel electrode surface. When the concentration reached by 800 mg L⁻¹, the inhibition effect slowing down again, probably because of the saturation on the surface of mild steel electrode [15].

Averaged electrochemical parameters and corrosion inhibition efficiency (η_p) from duplicated runs appear in Table 1, where they are compared to the data of AHLE in the same situation without binding Γ [15]. Obviously, with the addition of iodine, the corrosion efficiency has been improved compared to the same AHLE concentration absence of iodine. The addition of AHLE/ Γ complexes have not conspicuously impact the corrosion potential (E_{corr}), which indicates that AHLE/ Γ complexes can be summed up as mixed corrosion inhibitors [16,8].

Table 1 Polarization parameters for the corrosion of AHLE and 3.0 mM Γ in 1.0 M HCl containing inhibitors at 30°C.

Solutions	E_{corr} (vs SCE/ V)	i_{corr} (mA cm ⁻²)	β_a (mV dec ⁻¹)	β_c (mV dec ⁻¹)	η_p (%)	S
Blank	-0.488	2.789	165.9	-146.0	-	-
50 mg L ⁻¹	-0.470	1.419	103.9	-114.1	49.1 ^a	-
100 mg L ⁻¹	-0.481	1.143	133.8	-131.6	59.0 ^a	-
200 mg L ⁻¹	-0.485	0.870	120.1	-120.9	68.8 ^a	-
500 mg L ⁻¹	-0.492	0.582	130.9	-119.7	79.1 ^a	-
800 mg L ⁻¹	-0.483	0.393	96.7	-114.9	85.9 ^a	-
50 mg L ⁻¹ +3mM Γ	-0.484	1.415	187.7	-123.4	49.3	0.950
100 mg L ⁻¹ +3mM Γ	-0.480	0.956	173.5	-116.7	65.7	1.594
200 mg L ⁻¹ +3mM Γ	-0.488	0.723	173.6	-116.3	74.1	2.057
500 mg L ⁻¹ +3mM Γ	-0.490	0.193	130.6	-112.7	93.1	8.985
800 mg L ⁻¹ +3mM Γ	-0.486	0.633	154.3	-116.3	77.3	1.735

^a The data is from ref. [7]

The Tafel slopes of b_c and b_a change upon addition of AHLE/ Γ complexes, one possible mechanism is the adsorption of the inhibitors on mild steel surface through the electron pair of heteroatoms (S and O) [10,12], and electron binding effect accompanied by Γ , which blocks the mild

steel surface and reduces the corrosive attraction of mild steel in HCl media [17]. Apparently, the corrosion current density is much smaller in the presence of inhibitors comparing with that in the absence of inhibitor.

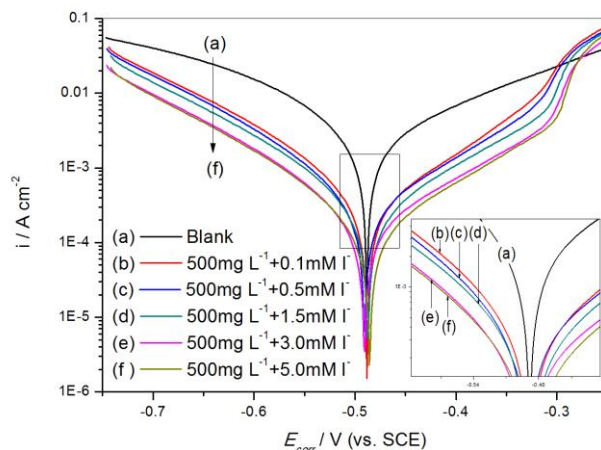


Figure 2. Polarization curves for the mixture of fixed 500 mg L⁻¹ concentration of AHLE and I⁻ in 1 M HCl at 30°C. (Scan rate was 1 mV s⁻¹)

Table 2 Polarization parameters for the corrosion of 500 mg L⁻¹ AHLE and different concentration I⁻ in 1.0 M HCl containing inhibitors at 30°C

Solutions	E_{corr} (vs SCE/ V)	i_{corr} (mA cm ⁻²)	β_a (mV dec ⁻¹)	β_c (mV dec ⁻¹)	η_p (%)	S
0.1mM I ⁻	-0.486	1.907	114.5	-121.9	31.6	-
0.5mM I ⁻	-0.485	1.626	107.1	-116.2	41.7	-
1.5mM I ⁻	-0.483	1.484	115.6	-115.7	46.8	-
3mM I ⁻	-0.484	1.338	96.8	-110.1	52.0	-
5mM I ⁻	-0.483	0.443	89.5	-105.4	84.1	-
500 mg L ⁻¹ +0.1mM I ⁻	-0.488	0.358	120.0	-113.6	87.1	3.487
500 mg L ⁻¹ +0.5mM I ⁻	-0.490	0.339	121.8	-111.1	87.8	3.604
500 mg L ⁻¹ +1.5mM I ⁻	-0.488	0.291	126.1	-116.3	89.6	4.529
500 mg L ⁻¹ +3mM I ⁻	-0.490	0.193	130.6	-112.7	93.1	8.985
500 mg L ⁻¹ +5mM I ⁻	-0.486	0.162	126.5	-110.9	94.2	5.344

Correspondingly, the inhibition efficiency increases with the inhibitors concentration, due to the increase of the blocked fraction of the mild steel electrode surface by adsorption. The inhibition efficiency of 500 mg L⁻¹ AHLE with 3 mM I⁻ complex reaches 93.1%, by contrast 79.1% of individual

500 mg L⁻¹ AHLE, which indicates that the AHLE/I complex acts as a better inhibitor than AHLE alone[15].

For corrosion inhibition synergistic effect study, another attractive investigation in this case is the influence of the concentration of iodine, in other words, affect of the iodine ion amount impelled us to examine the potentiodynamic polarization curves in 1 M HCl at various concentrations of I⁻ and fixed concentration of AHLE. The corresponding results are shown in Fig.2, and resulting data values appear in Table 2.

With the increasing of the I⁻ concentration from 0.1 mM to 5.0 mM, both the anodic and cathodic curves shift to lower current densities, which similar to the action of AHLE concentration shift. As shown in Table. 2, the concentration effect of I⁻ was generally not very significant, and the variety of inhibition efficiency was little with increase of the concentration of I⁻ from 0.1 mM to 1.5 mM I⁻ combine with 500 mg L⁻¹ AHLE. However, as the concentration of I⁻ reaches 3.0 mM, the inhibition efficiency was large improved relatively. It is worth noting that there is little difference between 3.0 mM I⁻ and 5.0 mM I⁻, cf. vignette in Fig.2, that is to say with the increase of the I⁻ concentration, the influence of inhibition gets weaker.

It can be seen from Table 2, the inhibition efficiency increased with the increasing of the concentration of I⁻. Our previous study found that as the concentration increases, the inhibition efficiency was also improved [15], it will be very interesting to explore whether similar effect will happen to combination of the AHLE and I⁻. It is well known that iodide ions are prone to synergistic with other compounds[14]. In order to further determine whether synergism is being carried out, it is necessary to calculate the cooperative parameter (S) [18, 19], which was used to describe the combination of amine and halide ion inhibition behavior. In general, for the interaction of inhibitors A and B, the synergistic parameter (S) is defined as follows[20]:

$$S = \frac{1 - \eta_A - \eta_B + \eta_A \eta_B}{1 - \eta_{A+B}}$$

Where η_A and η_B represent the inhibition efficiency obtained through inhibitor A and B acting alone respectively, and η_{A+B} represents the inhibition efficiency experimentally observed for the recombination of A and B, where the concentrations of A and B are same as in the corresponding individual situations.

When compound A or B exists at a known rate and when they do not interact with each other, at this point such expression can be used to compare the theoretical expected corrosion rate. Numerator is the theoretically expected rate, and the denominator is the experimentally rate in the presence of the inhibitor complex. Therefore, under the situation of inhibitors A and B have no effect on each other and are independently adsorbed at the metal / solution interface, $S = 1$, the inhibition act of independence, otherwise, if $S > 1$, indicating the existence of synergies effects or antagonistic effects if $S < 1$ [21, 22].

Table 1 and Table 2 show that all of S values are higher than 1 and more than unity, which reveals the existence of the synergistic effect between AHLE and I⁻. As shown in Table 1 and Table 2 that 500 mg L⁻¹ AHLE + 3.0 mM I⁻ has the highest S value, and this is in line with the result of experimental corrosion inhibition efficiency.

3.2 SEM and EDX analysis

SEM images are shown in Fig. 3 for (a) polished mild steel surface before immersion test, (b) corroded surface of mild steel obtained after 24 h dip in 1 M HCl, (c) 500 mg L⁻¹ AHLE in 1 M HCl, (d) 500 mg L⁻¹ AHLE + 3.0 mM KI in 1 M HCl. As shown in Fig. 3 a, in addition to the presence of subtle polishing scratches, the surface has no obvious defects, such as pits and cracks. In the presence of an uninhibited 1M HCl solution, damaged and non-uniform surfaces were observed due to the severe corrosion of the mild steel in the acid solution in Fig. 3 b. When corrosion inhibitors AHLE was present, the surface heterogeneity corrosion is greatly reduced in Fig. 3 c, which is further reduced in the presence of AHLE + I⁻ in Fig. 3 d.

Carefully examinations of the surface SEM image in the Fig. 3, there are huge differences between the presence and/or absence of corrosion inhibitors, e.g. Fig. 3 b reveals deep cavities that was strongly damaged by acid corrosion. In the case of addition of complex AHLE + KI, the mild steel sample has a better morphology and a smooth surface compared to the surface immersed in the 500 mg L⁻¹ AHLE solutions with little or no dent.

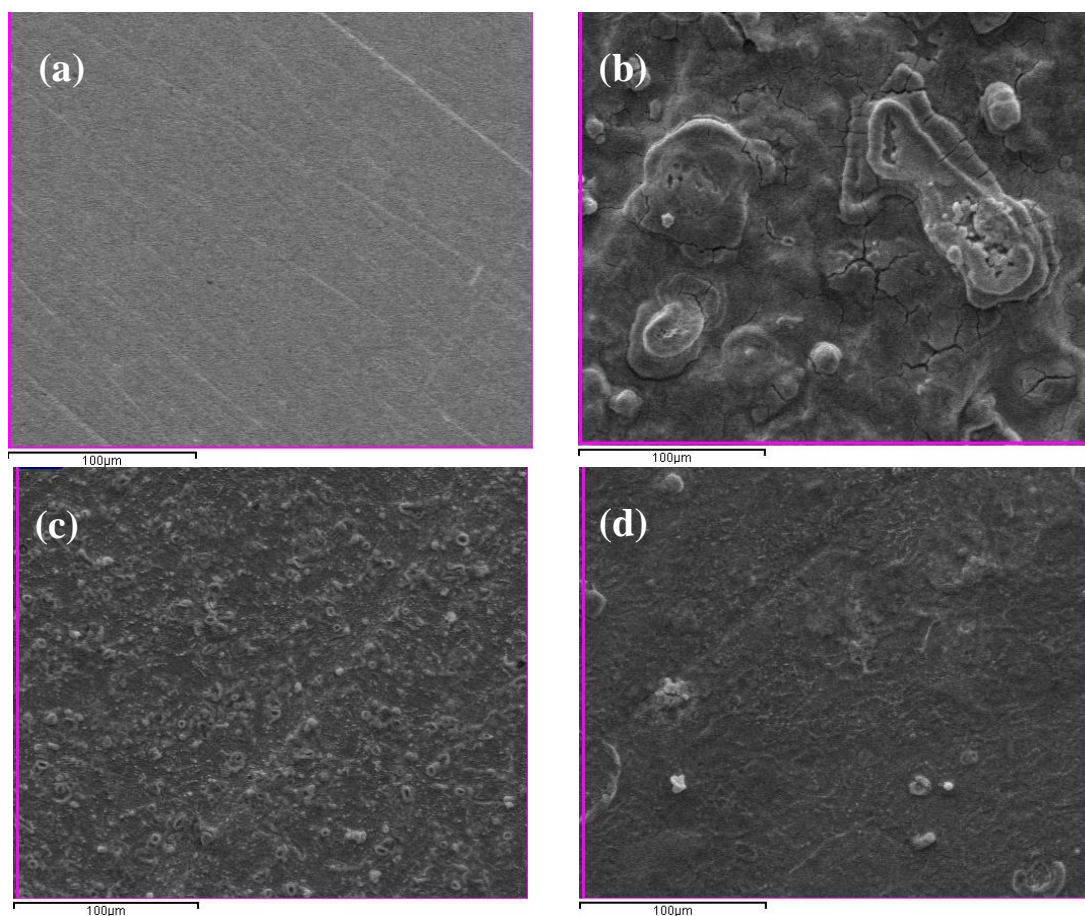


Figure 3. SEM photomicrographs of the surface of mild steel (a) blank; (b) uninhibited acid; (c) 500 mg L⁻¹ AHLE; (d) 500 mg L⁻¹ AHLE + 3.0 mM KI for 24 h at 30°C

This indicates that the combination of AHLE and KI effectively hinders the iron surface dissolution, which greatly reduces the severity of corrosion and exhibits good corrosion resistance.

When mild steel samples immersed in 1 M HCl containing AHLE and KI, the less damage effect may be due to the co-adsorption of I⁻ ions to specific surface of the mild steel[23], which is interpretation with the AHLE molecules.

EDX analysis confirms the synergistic effect between AHLE and I⁻. cf. Fig 4. The polished mild steel surface only exist iron (Fig. 4a), and carbon, oxygen and iron were detected in the film formed after 24 h dip in 1 M HCl (Fig. 4b). When inhibitor AHLE was added, nitrogen and sulfur elements were detected from the corrosive surface, as well as carbon, oxygen and iron (Fig. 4c). The nitrogen and sulfur elements are from the extract of AHLE, which was also to be verified through IR examination [15]. In last situation, 500 mg L⁻¹ AHLE + 3.0 mM I⁻ in 1 M HCl, it is unsurprised to find the additional element of iodine (Fig. 4d) compare to Fig. 4c. However, there is an interesting phenomenon of the detection of chlorine element in Fig. 4d, which reveals the existence of chlorine in mild steel corrosive surface and/or film formed in 500 mg L⁻¹ AHLE + 3.0 mM I⁻ 1 M HCl solution. We may pay more attention to the investigation of the effect of chloride ions in the process of protecting the mild steel in acid solution, and these works will be performed in our future studies.

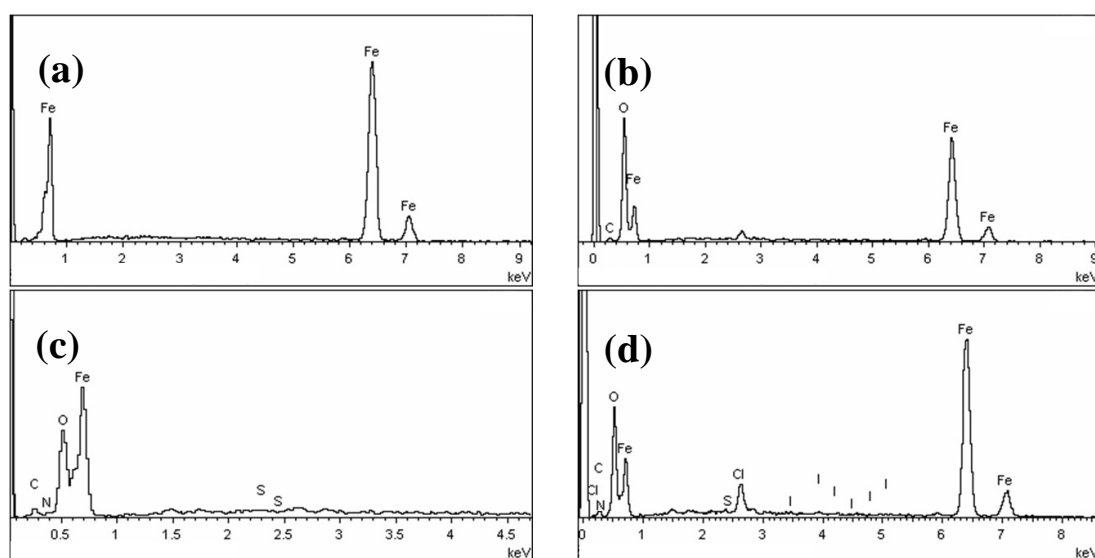


Figure 4. EDX of the surface of mild steel (a) blank; (b) uninhibited acid; (c) 500 mg L⁻¹ AHLE; (d) 500 mg L⁻¹ AHLE + 3.0 mM KI for 24 h at 30°C

4. CONCLUSION

Artemisia halodendron leaves extract (AHLE) acts as an environmentally friendly inhibitor for the corrosion of the mild steel in 1 M HCl solution have been studied, while the addition of I⁻ increases the inhibitory performance to a greater extent. The synergistic effect between AHLE and I⁻ was discussed, and the The synergistic parameter (S) well confirmed the experimental conclusion. SEM and EDX studies show that the presence of synergistic effects greatly reduces the corrosion of the mild steel in acid solution, and AHLE and I⁻ play a protective role might by specific co-adsorption.

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