Natural honey as corrosion inhibitor for metals and alloys. II. C-steel in high saline water

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Abstract

The inhibitive action of natural honey on the corrosion of C-steel, which used in manufacturer of petroleum pipelines, in high saline water was evaluated. The inhibition efficiency was calculated using weight loss measurements and potentiostatic polarization technique. It was found that, natural honey exhibited a very good performance as inhibitor for steel corrosion in high saline water. The inhibition efficiency increases with an increase in natural honey concentration. After some time, the inhibition efficiency decreased due to the growth of fungi in the medium. The adsorption of natural honey on the C-steel was found to follow the Langmuir adsorption isotherm. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Natural honey; Corrosion; Inhibition; Steel

1. Introduction

Carbon steel is frequently used in manufacturer the pipe lines for usage in petroleum industries. Many corrosion problems arise in these pipe lines due to the aggressiveness of the liquids which carried by them. These liquids may be petroleum containing water and sulfur, high saline formation water or sea water. However, all kinds of water passed through these lines contain very high chloride

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concentrations and considerable amount of sulfate anions. For this reason, the injection of corrosion inhibitors through different sites of pipes is very important.

Inhibition of C-steel corrosion in aqueous solutions by organic [1–4] and inorganic [5–8] compounds as well as synergetic inhibition [9–11] was extensively studied. In the previous work [12], natural honey was successfully used as a cheap and safe corrosion inhibitor for copper corrosion in aqueous solution. The present work is the second in a series aimed to evaluation the inhibitive action of natural honey on the corrosion of some metals and alloys, with slightly approach to its inhibition mechanism. In the present work a trial is made to use natural honey as corrosion inhibitor for carbon steel in high saline water. Weight loss and potentiostatic polarization techniques were used to evaluation the inhibition efficiency of the inhibitor.

2. Experimental method

C-steel of type A-106 is used in the manufacturer of petroleum production lines used in the fields of (Qarun) Petroleum Company, Egypt. Coupons of steel with surface area of 1.0 cm$^2$ were used for weight loss measurements. For potentiostatic studies, a cylindrical rod embedded in araldite with exposed surface area of 0.6 cm$^2$, was used. The electrodes were polished with different grades of emery papers, degreased with acetone and rinsed by distilled water.

The composition of natural honey was given else where [12]. In Egypt, there are three types of natural honey according to type of the flower from which the bees exclude the nectar. These types are; citrus, trefoil and cotton flowers. The chemical composition of the natural honey differs slightly from type to type. However, before the start in the first part of this series, we have tried the three types of honey in the same experiments and comparable results were obtained. The rest of the works were carried out using trefoil flower honey.

The test solution is formation water obtained from the oil field (lower Baharya) which related to (Qarun) petroleum company. The formation water has a pH value of 5.47 and contains the anions listed in Table 1.

Weight loss measurements were carried out as described elsewhere [13]. Potentiostatic polarization studies were carried out using EG&G model 173 potentiostat/Galvanostat. Three-compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. Polarized atomic absorption spectroscopy (Z-6001) was used for determination of iron in the test solutions.

<table>
<thead>
<tr>
<th>Cl$^-$</th>
<th>Br$^-$</th>
<th>SO$_4^{2-}$</th>
<th>HCO$_3^-$</th>
<th>NO$_3^-$</th>
<th>PO$_4^{3-}$</th>
<th>Org. acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>129,200</td>
<td>1336</td>
<td>522</td>
<td>82.8</td>
<td>&lt; 10</td>
<td>&lt; 20</td>
<td>&lt; 60</td>
</tr>
</tbody>
</table>
3. Experimental results and discussion

3.1. Weight loss measurements

The values of inhibition efficiencies obtained from weight loss measurements for steel A106 corrosion in the test solution containing different concentrations of natural honey are listed in Table 2. Table 2 includes also the values of a parameter, \( \theta \) which represent the part of the surface covered by inhibitor molecules. The equations used to calculate the values of inhibition efficiency (p%) and the parameter (\( \theta \)) have been mentioned in the previous work [12]. Inspection of Table 2, reveals that natural honey gives a very good inhibitive action towards the corrosion of C-steel A106 in high saline water. The inhibition efficiency increases with an increase in natural honey concentration.

This behavior could be attributed to the increase of the surface area covered by the adsorbed molecules of honey with the increase of its concentration. Most of the compounds contained in natural honey can be easily adsorbed on the corroded metal giving rise to such inhibition. It is hard to decide which of these components is responsible for this inhibition. It may be one component, more or even all of them acting in synergism. The study of the inhibition mechanism requires extended studies e.g. work on every component contained in natural honey separately and measurements of too many parameters using different analysis techniques. Such study is beyond the scope of the present work and needs a solitary work.

On the other hand, the inhibition efficiency falls down with an increase in the exposure time as observed previously for copper corrosion in 0.5 M NaCl solution [12]. It was reported that the loss of inhibition efficiency is due to the growth of fungi in the medium [12]. However, the loss of inhibition efficiency in the present work is much lesser than that observed in case of copper corrosion in 0.5 M NaCl solution. This observation may be attributed to the presence of NaCl concentration much higher than that used in the previous work. This high concentration of NaCl may retard the growth of fungi. The visual observation supports this idea, since no fungi colonies could be recognized in the medium by naked eye even after five days.

Table 2
Inhibition efficiencies of different concentrations of natural honey for steel corrosion in high saline water

<table>
<thead>
<tr>
<th>Honey (ppm)</th>
<th>Inhibition efficiency (p%)</th>
<th>( \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>100</td>
<td>82.46</td>
<td>75.01</td>
</tr>
<tr>
<td>200</td>
<td>90.42</td>
<td>86.36</td>
</tr>
<tr>
<td>300</td>
<td>90.86</td>
<td>87.80</td>
</tr>
<tr>
<td>400</td>
<td>91.23</td>
<td>87.84</td>
</tr>
</tbody>
</table>
Fig. 1. Relationship between inhibitor concentration ($C$) and $C/\theta$. 
Fig. 2. Potentiostatic polarization of C-steel in high saline water devoid and containing different concentrations of inhibitor. f = free solution, h = inhibited solution, a = anodic, c = cathodic and the numbers are concentrations of honey in ppm.
The values of surface coverage ($\theta$) have been obtained from weight loss measurements for various concentrations of natural honey and presented in Table 2. The plot of $C/\theta$ versus honey concentration ($C$) showed a linear correlation of slope close to unity (Fig. 1). This behaviour suggests that the adsorption of natural honey on steel/chloride interface obeys Langmuir's adsorption isotherm. The Langmuir's isotherm involves the assumption of no interaction between the adsorbed species on the electrode surface [14].

3.2. Potentiostatic technique

The anodic and cathodic polarization curves of steel A106 in high saline water devoid and containing increasing concentrations of natural honey are traced and represented in Fig. 2. Inspection of Fig. 2 reveals that there is a difference of about 25 mV between the start potentials of anodic and cathodic branches of the free solution. However, this slight variation in the equilibrium potential does not affect the main features of the polarization curves.

Further inspection of Fig. 2 reveals an overpotential increase followed by decrease (peak-like A) appears at current density of about 90 $\mu$A in presence of the inhibitor. The overpotential value of this peak-like increases slightly with an increase in the inhibitor concentration. After the end of this peak-like, the values of overpotentials become lower than those recorded in the case of free solution. Table 3 contains the concentrations of iron in the test solutions after the electrode had been held polarized for 15 minutes at current density values corresponding to the peak-like A and after it. Table 3 shows that, the concentration of iron, at the peak-like current, is higher in presence of inhibitor than that in free solution. On the other hand, after the end of peak-like, iron has a lower value in presence of inhibitor. This behaviour suggests that the peak-like A is corresponding to dissolution of iron electrode followed by an adsorption of natural honey molecules at the electrode surface. This adsorption results in decrease in the rate of anodic dissolution of the electrode. The anodic dissolution of C-steel in the presence of natural honey has indicated that the adsorbed inhibitor participates in the reaction, probably in the form of complex.

Because the presence of these peaks-like in the anodic branch it was very hard to use it in the calculation of corrosion rate precisely. Instead, the corrosion current density was calculated by extrapolation of the cathodic Tafel line to intercept the equilibrium potential of the system. The electrochemical parameters

<table>
<thead>
<tr>
<th>Table 3</th>
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<tbody>
<tr>
<td>Concentration of iron (ppm) in the test solutions in presence and absence of inhibitor at different current densities, as obtained from atomic absorption</td>
</tr>
<tr>
<td>Free solution &amp; Inhibited solution</td>
</tr>
<tr>
<td>90 $\mu$A &amp; 400 $\mu$A &amp; 90 $\mu$A &amp; 400 $\mu$A</td>
</tr>
<tr>
<td>Iron (ppm) &amp; 3.5 &amp; 13.5 &amp; 6.57 &amp; 11.24</td>
</tr>
</tbody>
</table>
calculated from the polarization curves are represented in Table 4. Inspection of Table 4 reveals that, the corrosion potential shifts to the noble direction as the inhibitor concentration is increased. It is of interest to note that the natural honey has high inhibition efficiency toward steel corrosion in high saline water. The value of inhibition efficiency increases with an increase in natural honey concentration. The inhibition efficiencies calculated using potentiostatic technique are comparable with those obtained by weight loss measurements.

Table 4 shows also that, there is almost no change in the values of anodic Tafel constant ($\beta_a$) in absence and presence of natural honey. On the other hand, there is a considerable change in the values of the cathodic Tafel constant ($\beta_c$) in presence of natural honey. This result suggests that, the presence of natural honey may change the mechanism of cathodic reaction and did not affect the anodic dissolution mechanism.

4. Conclusions

1. Natural honey acts as an inhibitor for the corrosion of C-steel A 106. It can be used in petroleum fields to reduce the corrosion rate of steel pipelines.
2. The effect of fungi on the inhibition efficiency of natural honey is markedly decreased in high saline water.
3. Natural honey starts its inhibition action in presence of dissolved iron cations.
4. The adsorption of natural honey on the steel surface in high saline solution obeys Langmuir’s adsorption isotherm.

References