Synergistic inhibitor effect of cetylpyridinium chloride and other halides on the corrosion of mild steel in 0.5 M \( \text{H}_2\text{SO}_4 \)

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A R T I C L E   I N F O

Article history:
Received 26 August 2012
Accepted 26 September 2012
Available online 4 October 2012

Keywords:
A. Mild steel
B. Polarization
C. Acid corrosion
C. Acid inhibition

A B S T R A C T

The synergistic inhibitory action of cetylpyridinium chloride (CPC) and different halides on the corrosion of mild steel in 0.5 M \( \text{H}_2\text{SO}_4 \) has been investigated using electrochemical methods and scanning electron microscopy (SEM). Experimental results showed that the protection efficiency \( (P_{\text{icor}}) \) of CPC improved in the presence of the different halides with different extents. Chemisorption was proposed from the trend of \( P_{\text{icor}} \) and the values of \( \Delta G_{\text{ads}} \). The synergism parameter is found to be greater than unity indicating that the enhanced \( P_{\text{icor}} \) caused by the addition of the halides to the CPC is due to a co-operative adsorption of both species.

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1. Introduction

Iron-containing alloys are used in different applications and they are susceptible to corrosion due to their thermodynamic instability especially in aggressive media. Organic inhibitors represent an important category of the well known methods for metals protection against acid corrosion. For instance, surfactants is a wide spread class of organic inhibitors that have been used for achieving such protection. Surfactants exert their inhibition action via the adsorption on the metal surface; the polar or ionic group (hydrophilic head) attaches to the metal surface and its tail (hydrophobic part) exposed to the solution. Ionic and non-ionic surfactants have been reported to be potent corrosion inhibitors for metals like copper, aluminum and mild steel [1,2].

On the other hand, synergistic effect demonstrates the increase in the effectiveness of a corrosion inhibitor in the presence of a secondary species. Recently, several studies have been reported to explain the role of synergism on the mechanism of corrosion inhibition of steel in \( \text{H}_2\text{SO}_4 \) medium [3–8]. This synergism has been reported to be due to the increased surface coverage as a result of ion–pair interactions between an organic cation and the halide anion. Halide ions present in an inhibiting solution firstly adsorbs on the corroding surface by creating oriented dipoles and thus it facilitates the adsorption of inhibitor cations on the dipoles [4]. In literature it has been reported that the synergism order in presence of different halides is \( \text{I}^- > \text{Br}^- > \text{Cl}^- \) [9,10]. However, in few cases the reverse order, i.e., \( \text{I}^- < \text{Br}^- < \text{Cl}^- \), has been also reported [8]. Saleh et al. [11–13] reported that hexadecyl pyridinium halide shows high inhibition efficiency for the corrosion of low carbon steel in 1.0 M \( \text{H}_2\text{SO}_4 \). In general, cationic surfactants are known of its toxicity and carcinogenicity in addition to their high cost, and hence it is of prime interest to use lower concentration of such inhibitors via using synergism with some ions which are known of its low costs and eco-friendly characteristics such as halides. Halide ions specially \( \text{Cl}^- \) can either accelerate or inhibit the steel corrosion. It has long been known that \( \text{Cl}^- \) initiates the pitting corrosion of steel. Also, the synergism between the \( \text{Cl}^- \) ions (or halides) and organic inhibitors (specially quaternary ammonium salts) is well documented. The issue is, the synergism can be achieved at some lower concentrations of the halides. However, the targeted protection is the protection in the presence of both the halide ion and the organic inhibitor in solution. At some higher concentration limits, the halide ions (specially \( \text{Cl}^- \)) began to have adverse effects and corrosion initiated. Halide ions have synergistic effects at some lower concentrations depending on the experimental conditions. In the present work, the synergistic inhibition between CPC and different halide ions in 0.5 M sulfuric acid is investigated by electrochemical methods, scanning electron microscopy (SEM). The interaction of halide ions with the CPC molecule and its synergism towards the inhibition of acid corrosion of mild steel is discussed.

2. Experimental

Mild steel sample has the following composition (wt.%): 0.07% C, 0.29% Mn, 0.07% Si, 0.012% S, 0.021% P and the remainder iron.

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0010-938X/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.corsci.2012.09.040
Cetylpyridinium chloride (CPC) and sodium halides were obtained from Aldrich and used as received. The solution of 0.5 M H₂SO₄ was prepared by dilution of AR grade 96% H₂SO₄. Stock solutions of surfactant and halides were prepared in 0.5 M H₂SO₄ and the desired concentrations were obtained by appropriate dilution.

Electrochemical measurements were carried out in a conventional three-electrode cell with a platinum counter electrode (CE) and a Hg/HgSO₄(1.0 M) SO₄²⁻ [E = 0.674 V (NHE)] coupled to a fine Luggin capillary as the reference electrode (RE). In order to minimize the ohmic contribution, the Luggin capillary was kept close enough to the working electrode (WE). The latter was fitted into a glass tube of proper internal diameter by using epoxy resins. The WE surface area of 0.5 cm² was abraded with emery paper (grade 320–500–800–1200) on test face, rinsed with distilled water, degreased with acetone, and dried with a cold air stream. Before measurements the electrode was immersed in the test solution at open circuit potential (OCP) for 15 min at 25 °C or until the steady state is obtained. All electrochemical measurements were carried out using an EG&G Princeton Applied Research (model 273A) potentiostat/galvanostat controlled by m352 electrochemical analysis software. The potentiodynamic polarization measurement was conducted starting from a cathodic potential (with respect to open circuit potential (OCP)) to anodic potential with scan rate of 2 mV/s. Current densities were calculated on the basis of the apparent geometrical surface area of the electrode. The measurements were repeated to test the reproducibility of the results, and quite acceptable reproducibility was obtained. Surface morphology of mild steel and protective film were examined by Scanning Electron Microscopy (FEI Quanta 3D 200i).

3. Results and discussion

3.1. Open circuit potential

The variation of the open circuit potential (OCP) of mild steel was followed as a function of time as shown in Fig. 1 in non-stirred 0.5 M H₂SO₄ solutions. Curve 1 is for the blank (0.5 M H₂SO₄) and curve 2 is for 10⁻⁵ M CPC (in 0.5 M H₂SO₄). Curves 3–5 are for 10⁻³ M CPC (in 0.5 M H₂SO₄) + 0.1 M halide ions (NaCl (curve 3), NaBr (curve 4) and NaI (curve 5)). In the blank 0.5 M H₂SO₄ (curve 1), the OCP shifted to more positive values, indicating the initial dissolution process of the air formed oxide film and the attack on the bare metal [14,15]. A steady potential was readily attained, corresponding to the free corrosion potential E_cor of the metal [16]. While the addition of 10⁻⁵ M CPC (curve 2) or 0.1 M Cl⁻ (curve 3) drifts the steady state E_cor to negative values, the addition of 0.1 M Br⁻ (curve 4) or I⁻ (curve 5) drifts E_cor to more positive values. However, the general shape of the OCP-time curves does not change. According to Riggs [17], the classification of a compound as an anodic or cathodic type inhibitor is feasible when the OCP displacement is at least ±85 mV in relation to that one measured for the blank solution. However, from Fig. 1, the shift in E_cor on adding the CPC is less than 30 mV revealing that the CPC acts both the anodic dissolution of iron and the hydrogen evolution reaction. By adding NaCl to the CPC (curves 3) the same trend as that in the presence of the CPC only is obtained. When NaBr (curve 4) and NaI (curve 5) are added, the steady state is obtained quickly and the shift in E_cor is less than in absence of NaCl indicating that CPC/NaBr and CPC/NaI systems more inhibiting systems than CPC/NaCl systems. The results clearly indicate that the shifting to noble direction of potential is in the order I⁻ > Br⁻ > Cl⁻.

3.2. Polarization studies

Fig. 2 shows the polarization curves for mild steel in 0.5 M H₂SO₄ in the absence and presence of various concentrations of CPC. It is clear that the presence of CPC causes a marked decrease in the corrosion rate i.e., it bodily shifts both the cathodic and anodic curves to lower currents but with different extents. According to the discussion of Fig. 1, CPC acts mainly as mixed-type inhibitor with little more effect on the cathodic reaction. As the concentration of CPC increases, the current for the hydrogen evolution reaction (HER) decreases at a specific potential. Table 1 lists important corrosion parameters such as the free corrosion potential (E_cor), corrosion current density (i_cor), slope of the cathodic branch (β_c) and slope of the anodic branch (β_a). The cathodic Tafel slope (β_c) for mild steel in the absence and presence of inhibitor does not change significantly indicating that the CPC does not change the mechanism of the HER, and the corrosion is rather inhibited by blocking of the iron surface by simple adsorption process.

It is noteworthy to mention that the difference in the shifts in the polarization curves at [CPC] of 7 × 10⁻⁵ M (curve 5) and 2 × 10⁻⁴ M (curve 6) is small. This could be attributed to that the latter concentrations are close to the critical micelle concentration (CMC) of the CPC surfactant (CMC = 8 × 10⁻⁴ M at 30 °C[11,18]). At this high concentration the CPC surfactant tends to form micelles instead of further adsorption on the iron surface.

The anodic branches reveal three regions, mainly region I, II and III, which represent the inhibited, flat and uninhibited regions,
respectively. During region I, the surfactant shows inhibition action without any sign of desorption (inhibition region). At the start of region II and at a potential dependent of CPC concentration the anodic curves begin to flatten (current increases) as a sign to the start of desorption of CPC from the iron surface (flat region) [19]. In region III strong desorption of the CPC molecules take place where the adsorption ability.

In region III strong desorption of the CPC molecules take place and eventually the anodic branches in the presence of CPC approaches that in the absence of the inhibitor i.e., region III is uninhibited region [20].

Fig. 3 shows the polarization curves for mild steel in 0.5 M H2SO4 (curve 1), containing 0.10 M halide (curve 2), 10⁻⁵ M CPC (curve 3) and both (0.1 M halide + 10⁻⁵ M CPC) (curves 4). Panel A, B and C show the case of Cl⁻, Br⁻ and I⁻, respectively. It is clear that the mild steel corrosion is slightly inhibited in the presence of either a small concentration of CPC (10⁻⁵ M curves 3) or halides (0.10 M curves 2). In the presence of both species (curves 4), however, both anodic and cathodic branches are dramatically shifted to lower currents. In the presence of halide ions only (curves 2) causes a slight decrease in the corrosion rate i.e., slight shifts in both anodic and cathodic currents. This could be ascribed to adsorption of halide over the corroded surface [21]. In other words, both cathodic and anodic reactions of mild steel are slowly retarded by halides. In the presence of iodide only (panel C, curve 2) the inhibition is significant. Generally, the adsorbability of anions is related to the degree of hydration. The less hydrated ion is preferentially adsorbed on the metal surface. The ease of adsorption (greater protection efficiency) shown in the case of the iodide ions may be due to its less degree of hydration. The protective effect of halide ions is found to be in the same order as that of adsorption ability.

It is clear from Fig. 3 that both flat (region II) and uninhibited (region III) regions which appeared in polarization curves of CPC only (Fig. 2) disappeared by adding halide ions as shown in curves 4 in Fig. 3A–C. This indicates that the halide ion improves the protective action of CPC, especially at higher anodic potentials, by retarding both the anodic dissolution and cathodic hydrogen evolution, and the mixture (CPC + halide) acts as a mixed type inhibitor.

### 3.3. Protection efficiency

Polarization curves of mild steel were collected (data are not shown here) in 0.5 M H2SO4 at different concentrations of the halide ions in presence of fixed [CPC]. Those polarization curves were used to determine the protection efficiency as shown in Fig. 4. The figure demonstrates the dependence of the protection efficiency, \( P_{icor} \), on the concentration of the halide. Panels A, B and C show \( P_{icor} \) at [CPC] = 7 × 10⁻⁶, 10⁻⁵ and 2 × 10⁻⁵ M, respectively. The protection efficiency, \( P_{icor} \), is given by:

\[
P_{icor} = \left(1 - \frac{i_{cor2}}{i_{cor1}}\right) \times 100
\]

where \( i_{cor2} \) and \( i_{cor1} \) are corrosion current densities in the presence and absence of the inhibitor, respectively. Using data in Table 1 of

### Table 1

<table>
<thead>
<tr>
<th>(CPC)/M</th>
<th>( E_{corr}/V ) (Hg/Hg2SO4)</th>
<th>( i_{corr}/mA cm^{-2} )</th>
<th>( \beta_{a}/V ) (decade)⁻¹</th>
<th>( \beta_{c}/V ) (decade)⁻¹</th>
<th>( P_{icor} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-0.233</td>
<td>0.969</td>
<td>0.219</td>
<td>-0.183</td>
<td></td>
</tr>
<tr>
<td>7 × 10⁻⁵</td>
<td>-0.926</td>
<td>0.854</td>
<td>0.194</td>
<td>-0.181</td>
<td>119.9</td>
</tr>
<tr>
<td>1 × 10⁻⁵</td>
<td>-0.926</td>
<td>0.571</td>
<td>0.221</td>
<td>-0.155</td>
<td>41.1</td>
</tr>
<tr>
<td>2 × 10⁻⁵</td>
<td>-0.926</td>
<td>0.330</td>
<td>0.224</td>
<td>-0.162</td>
<td>65.9</td>
</tr>
<tr>
<td>7 × 10⁻⁵</td>
<td>-0.914</td>
<td>0.159</td>
<td>0.208</td>
<td>-0.153</td>
<td>83.5</td>
</tr>
<tr>
<td>2 × 10⁻⁴</td>
<td>-0.905</td>
<td>0.085</td>
<td>0.208</td>
<td>-0.149</td>
<td>91.2</td>
</tr>
</tbody>
</table>

Fig. 3. Polarization curves for mild steel in (1) 0.5 M H2SO4 (blank), (2) 0.1 M halide, (3) 10⁻⁵ M CPC and (4) 10⁻⁵ M CPC + 0.1 M of halide; panel (A) for NaCl, panel (B) for NaBr and panel (C) for NaI. \( i_{corr} \), the values of \( P_{icor} \) in presence of CPC only (halide-free solution) is 11.9, 41.1 and 65.9% at CPC concentration of 7 × 10⁻⁶, 1 × 10⁻⁵ and 2 × 10⁻⁵ M, respectively.

Inspection of Fig. 4 reveals several interesting features;

1. The inhibition efficiency increases with the increase in the halide concentration reaching a constant value around 99%, i.e., almost complete suppression of corrosion. In the presence of the lowest concentration of the CPC (7 × 10⁻⁶ M) (panel A),
the largest increase in the protection efficiency was obtained upon addition of the different halides. For instance, $P_{\text{cor}}$ increases from 11.9% in the presence of only CPC to 83.6% in the presence of $(7 \times 10^{-6} \text{ M CPC} + 0.10 \text{ M Cl}^-)$. For the Cl$^-$, when its concentration increases above this concentration (0.1 M) the protection efficiency decreases especially at lower CPC concentrations.

2. The increase in $P_{\text{cor}}$ at higher concentrations of the CPC (panels B and C) is not as much as at the low concentration of the CPC (panel A). This is attributed to the fact that considerable high protection efficiencies were obtained in the presence of such high concentrations of the CPC (see Table 1).

3. Generally at the same concentration of CPC the $P_{\text{cor}}$ in the presence of similar concentrations of the halide decreases in the order: $I^- > Br^- > Cl^-$. Note that the $P_{\text{cor}}$ in presence of CPC alone (i.e., halide-free solution) is 11.9, 41.1 and 65.9% in $7 \times 10^{-6}$, $1 \times 10^{-5}$ and $2 \times 10^{-5} \text{ M CPC}$, respectively (see Table 1). This means that the [Cl$^-$] is equal to the same values of the [CPC] (assuming 100% dissociation). Accordingly, this Cl$^-$ ion coming from the CPC molecules will be added to the intentionally added halide concentrations. However, inspection of the values of $P_{\text{cor}}$ in Fig. 4, in case of Br$^-$ and I$^-$ added to CPC, we can see that the $P_{\text{cor}}$ values are much higher than in the case of using CPC alone. In case of the Cl$^-$ the start of the increase in $P_{\text{cor}}$ is when the added [Cl$^-$] is higher than that coming from the dissociation of the CPC itself. Wang [22] have reported that the addition of halide salt to sulphuric acid solution containing organic compound as 1,4-bis (1-chlorobenzyl-benzimidazolyl)-butane causes a synergistic or cooperative effect which inhibits iron corrosion. Halide ions have been shown to inhibit the corrosion of some metals in strong acids and this effect depends on the ionic size and charge, the electrostatic field set up by the negative charge of the anion on the adsorption site and the nature and concentration of the halide ion. From the observed trend of increase in the protective action in the order $I^- > Br^- > Cl^-$, it is likely that the radii and the electronegativity of the halide ions has a profound influence on the adsorption process. Electronegativity increases from $I^-$ to Cl$^-$ ($I^- = 2.5, Br^- = 2.8, Cl^- = 3.0$) while atomic radius decreases from $I^-$ to Cl$^-$ ($I^- = 135 \text{ pm}, Br^- = 114 \text{ pm}, Cl^- = 90 \text{ pm}$) [21]. The iodide ion is more predisposed to adsorption than the bromide and chloride ions. Stabilization of the adsorbed halide ions by means of interaction with the CPC leads to greater surface coverage $\theta$ and thereby greater protection efficiency.

By adding a large concentration of NaCl, $P_{\text{cor}}$ decreases. This might be due to the formation of a soluble complex between Cl$^-$ ions and the iron, which lead to an increase in the corrosion current. This phenomenon disappears at higher CPC concentration ($2 \times 10^{-5} \text{ M}$) as shown in Fig. 4C.

3.4. Synergism

Inhibiting effect of organic inhibitors depends mainly on their adsorption behavior on the metal surface, which depends on the molecular structure of the organic compounds, surface charge density and the potential of zero charge of the metal. It is likely that the adsorption of a cationic surfactant is enhanced by increasing the negative charge density on the metal surface. Thus the pre-adsorption of a halide could enhance the adsorption of the cationic surfactant due to ion–pair interactions between the CPC molecules and the halide ions, resulting in what is the so-called inhibition synergism. In this part, the effect of halide concentration on the inhibition efficiency of CPC is studied. This interaction can be quantized by a parameter called synergism parameter ($S_0$) [23,24] which is defined as,

$$S_0 = \frac{1 - \theta_{1+2}}{1 - \theta_{1+2}}$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$, $\theta_1$ and $\theta_2$ are the degrees of surface coverage in presence of the halide ion and the CPC, respectively.
and $\theta_{e+2}$ is the degree of surface coverage in the presence of both species. Note that the degree of surface coverage, $S_h$, was determined from the polarization data ($\theta = P_{cor}/100$). $S_h$ approaches unity when no interaction takes place between the inhibitor molecules and the halide ion. At $S_h > 1$, a synergistic effect is obtained as a result of a co-operative adsorption. In case of $S_h < 1$, antagonistic behavior prevails due to a competitive adsorption [9]. Fig. 5 shows the effects of the halides ion concentration on $S_h$ estimated in the presence of 0.5 M H$_2$SO$_4$ solution containing 10$^{-3}$ M CPC. The $S_h$ values are found to be higher than unity, suggesting the synergistic action of halide ion with the CPC. The above results reveal that CPC can act as an effective inhibitor in 0.5 M H$_2$SO$_4$ solution even at low concentration in the presence of halide ions. In the present case $E_{cor}$ equals −512 mV vs. SCE of iron and in view of the fact that the potential of zero charge for iron in H$_2$SO$_4$ -550 mV vs. SCE [25]. It is concluded that the iron surface is positively charged. Since the halide anions adsorb specifically on the iron surface, they create an excess negative charge exposed to the solution and favor more adsorption of the surfactant cation [26,27]. Further, the electrostatic influence on the inhibitor adsorption is followed by chemisorption of the surfactant on the iron surface giving rise to a protective effect in the halide-containing solution [28]. The synergism parameter, $S_h$ increases with the halide concentrations until it reaches a maximum value after which it decreases. This may be due to the following reasons:

(a) Adsorption of the CPC molecules on the metal surface via the nitrogen atom might compete with the halide ion leading to lesser synergistic effect at higher concentrations of the halide ion [4]. This appears at halide ion concentrations $>0.10$ M. Also, the halide ions may desorb or form soluble product with the iron surface and thus $S_h$ (for all halides) and $P_{cor}$ (for Cl$^-$) decreases when the concentration of the halide increases above certain values (in our case [halide] $>0.1$ M) [29].

(b) The obtained $S_h$ is in the order Cl$^-$ < I$^-$ < Br$^-$. Although the highest $P_{cor}$ obtained in the case of iodide with CPC, the highest $S_h$ is obtained in the case of bromide. This is due to that the inhibition efficiency in the presence of iodide alone Fig. 3 (panel C) is relatively high, compared with the bromide. While some literatures [30,31] showed order of $S_h$ as Cl$^-$ < Br$^-$ < I$^-$, others [6] reported different orders that depends on the nature of the metal surface and solution composition.

### 3.5. Adsorption isotherms

Adsorption isotherms can provide the basic information on the interaction between the inhibitor and the mild steel surface. Attempts were made to fit experimental data to various isotherms including Frumkin, Langmuir, Temkin, Freundlich, Bockris–Swinkels, and Flory–Huggins isotherms. It has been found that the experimental results in this study for CPC alone fit with Bockris–Swinkels [11] but both CPC (halide-free) and CPC/halide systems fit with Temkin adsorption isotherm. It is preferable to use one adsorption isotherm (Temkin isotherm in our case) for better comparison between different systems. Temkin isotherm is given by Eq. (3); [32–35]:

$$\exp(-2a\theta) = KC$$

where $\theta$ is the degree of surface coverage, $C$ is the inhibitor concentration, $a$ is the molecular interaction parameter and $K$ is the equilibrium constant of the adsorption process. Plots of $\theta$ against log [halide] are depicted in Fig. 6 at 10$^{-3}$ M CPC. The inset shows the plot for CPC only. The validity of Temkin’s isotherm favors the assumption of chemisorption mode between the inhibitor molecules and the iron surface [36]. That is to say the unshared electron pairs in nitrogen atom and/or pi electron of pyridinium ring of CPC could interact with the d-orbitals of the iron to form a protective chemisorbed film. The adsorption and thermodynamic parameters deduced from the above plots are listed in Table 2. It can be deduced that there is a repulsion force in the compact adsorption layer since $a > 0$. The values of $a$ in all CPC/halide systems are negative indicating that repulsion exists in the adsorption layer. It is generally known that $K$ denotes the strength between the adsorbate and adsorbent. Large values of $K$ imply more efficient adsorption and hence better protection efficiency. The standard adsorption free energy ($\Delta G_{ads}^0$) was estimated using the following equation [37,38]:

$$\Delta G_{ads}^0 = -RT \ln (K)$$

![Fig. 5. Effect of halide ions concentration on the synergism parameter $S_h$ obtained in the presence of 10$^{-3}$ M CPC.](image)

![Fig. 6. Temkin adsorption isotherm for CPC (Inset) and CPC + halide ions.](image)

<table>
<thead>
<tr>
<th>System</th>
<th>$a$</th>
<th>$K$/L mol$^{-1}$</th>
<th>$R^2$</th>
<th>$\Delta G_{ads}^0$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPC</td>
<td>−4.10</td>
<td>3.56 × 10$^6$</td>
<td>0.9942</td>
<td>47.34</td>
</tr>
<tr>
<td>10$^{-3}$ M CPC + NaCl</td>
<td>−11.73</td>
<td>6.80 × 10$^{10}$</td>
<td>0.9967</td>
<td>−71.76</td>
</tr>
<tr>
<td>10$^{-3}$ M CPC + NaBr</td>
<td>−12.99</td>
<td>1.09 × 10$^{12}$</td>
<td>0.9994</td>
<td>−78.66</td>
</tr>
<tr>
<td>10$^{-3}$ M CPC + NaI</td>
<td>−15.77</td>
<td>4.54 × 10$^{14}$</td>
<td>0.9946</td>
<td>−93.60</td>
</tr>
</tbody>
</table>
The $\Delta G_{\text{ads}}^0$ values (see Table 2) are more negative than 40 kJ/mol, which means that both physical adsorption and chemical adsorption would take place. Inspection of Table 2 reveals that $K$ and $\Delta G_{\text{ads}}^0$ values are in the order;

$$\text{CPC/Cl}^- > \text{CPC/Br}^- > \text{CPC/I}^- > \text{CPC}$$

Generally, values of $\Delta G_{\text{ads}}^0$ up to 20 kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than 40 kJ/mol involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorption) [39,40]. The above values of $\Delta G_{\text{ads}}^0$ are consistent with the results of the protection efficiency.

$\Delta G_{\text{ads}}^0 = \frac{1}{55.5} \exp \left( -\frac{\Delta G_{\text{ads}}^0}{RT} \right)$ (4)

3.6. SEM analysis

SEM images are shown in Fig. 7 for mild steel taken after 30 min immersion in (a) 0.5 M H$_2$SO$_4$, (b) 0.10 M NaCl, (c) $10^{-5}$ M CPC, (d) $10^{-3}$ M CPC + 0.10 M NaCl.

Close examinations of SEM image taken in the absence of the inhibitor reveals that the specimen surface was strongly damaged with deep cavities (Fig. 7a). In presence of combined CPC + NaCl (Fig. 7d), the steel specimen has a better morphology and smooth surface compared with that of the surface immersed in either NaCl or CPC solutions (Fig. 7b and c, respectively) with few small notches. This indicates that the combined use of CPC and NaCl hinders the dissolution of iron and thereby reduces the rate of corrosion, and it reveals good protection against corrosion. The less damage of mild steel surface when dipped in 0.5 M H$_2$SO$_4$ containing CPC and NaCl (Fig. 7d) might be due to the specific adsorption of Cl$^-$ ions on the mild steel which facilitates the adsorption of CPC molecules.

4. Conclusions

(a) Protection efficiency obtained in the presence of CPC with the coexistence of halides decreases in the order: $\text{I}^- > \text{Br}^- > \text{Cl}^-$, which seems to indicate that the radii and the electronegativity of the halide ions play a significant role in the adsorption process.

(b) The values of $S_h$ (synergistic parameter) are greater than unity showing the corrosion inhibition brought about by CPC in combination with the halides is synergistic in nature and co-operative adsorption between halides and CPC prevails over competitive adsorption.

(c) CPC adsorption is chemical in nature as revealed from the $\Delta G_{\text{ads}}^0$ values for CPC/halide ions systems which are larger than CPC alone showing that a CPC/halide system is strongly adsorbed than CPC alone. The efficient inhibition in the case of the combined use of CPC and halides, consistently with SEM images.

References
