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Unexpected mixed valence iron(II, III) μ₃-oxo furfuryl complex with wheel motif isolated when preparing iron(II) arene complexes

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A series of new compounds including 2-{{[(4-(propoan-yl)benzyl]Oxy)methyl}tetrahydrofuran ligand were tested in order to link auxiliary and labile ligands to iron arene complexes. The given reaction of benzyletherfurane ligand with Fe (II) sources resulted to the isolation of unexpected mixed valence μ₃-oxo-Fe₆⁵Fe³⁺ compound, which has been fully characterized by x-ray crystallography. The resulting complex differs from the similar compound known in the literature.

Key words: Mixed valence complex, heptanuclear Fe(II,III), wheel motif structure, dangling spatial orientation of furfuryl ligand, 2-{{[(4-(propoan-yl)benzyl]Oxy)methyl}tetrahydrofuran, single crystal.

INTRODUCTION

Stoechiometrical and functional organometallic materials based on molecular building blocks represent an increasingly important area of research in contemporary materials applied chemistry. Due to their constitutional order, such compounds have always attracted much attention in a variety of applications. These applications include electrochemical sensors (Balzani et al., 2006; Daniel et al., 2003a, 2004), redox catalysts (Kim et al., 2003), and molecular Batteries (Astruc et al., 2002; Nlate et al., 2000). In some occasion they act as dendrimers (Balzani et al., 2006; Daniel et al., 2003a; Daniel et al., 2003b). Also, their properties can be modulated by the size and nature of external branching groups (Oshio et al., 2003, 2009). On the other hand, the use of iron clusters as models for biological systems such as the iron-storage protein ferritin has been also exploited as well as their use as nanoscale magnetic particles, the so-called Single Molecule Magnets SMMs (Oshio et al., 2003, 2009).

Actually, few mixed-valence species containing {Fe⁵⁺(μ-Oxo),Fe³⁺}n⁺ core have been described (Day et al., 2008). Labat et al. (2005) made use of the tridentate ligand amino-methylpropene-1,2-diolato (O,O,N) to prepare the corresponding discrete μ₁-2-amino-2-methylpropane-1,3-diolato)hexachloroheptairon(II,III)acetonitrile dissolvate monohydrate complex, [Fe⁶⁺Fe⁵⁺(C₄H₉NO₂)₆Cl₈]-2CH₃CN·H₂O. Similar compound [Fe⁶⁺Fe⁵⁺(bmsae)]₆(μ₃-}
OMe)_6]Cl_2.3H_2O, where bmsae = 5-bromo-3-methoxysalicylidelamineoethanol has been also reported by Oshio et al. (2003, 2009) (Figure 2). The magnetic susceptibility in this complex shows the predominant of antiferromagnetic interactions. An attempt to synthesize Fe(II) like tweezers complexes by reacting new 2-[[[4-(propyl-2-yl)benzyl]Oxy]methyl]tetrahydrofuran ligand 4 with Fe(II) sources, was possible to isolate an unexpected heptanuclear Fe^II^Fe^III^ mixed µ_3-oxo complex (Figure 1), this is similar to the one reported by Gaele et al. (2005) and Oshio et al. (2003, 2009) as probably a minor by-product from the crystallization of arene complex. The structure of this compound was fully characterized by x-ray analysis.

**EXPERIMENTALS**

**Reagents and apparatus**

Reactions were generally performed under argon or dry nitrogen atmosphere. Most of the chemical reagents were purchased from Fluka, Merck, Acros or Strem, and used without further purification. Tetrahydrofuran, dichloromethane, toluene and diethyl ether were dried, under argon atmosphere, through activated Alox columns (Mafua, 2006). Thin-layer chromatography analysis (TLC) were performed using aluminium sheets coated with silica gel 60 F-254 (0.2 mm) (Merck). The product were revealed with UV-light (254 nm) or by spraying the TLC with either KMNO_4_ solution or a HNO_3/KSCN combination. Column chromatographic purifications were performed with Merck 230-400 mesh silica gel or Macherey-Nagel silicagel 60 (0.063-0.2 mm (70-230 mesh ASTM)). NMR
spectra were recorded either on a Bruker Avance DRX-500 (1H: 500 MHz and 13C: 125 MHz), on a Bruker DPX-360 (1H: 360 MHz and 13C: 91 MHz) or on a Varian Gemini 200 (1H: 200 MHz and 13C: 50 MHz). Chemical shifts are given in ppm relative to tetramethylsilane (TMS) or the residual proton signal of the deuterated solvent employed. The NMR signals were assigned using APT, HETCOR and COSY techniques. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 40 diode array spectrophotometer. The Infrared (IR) was acquired on FTIR Unicam Mattson 5000 spectrometer. Mass spectra were recorded either on a Vacuum Generators Micromass VG 70/70E (FAB ionisation) or on a Bruker 4.7T BioApex II FT/ICR mass spectrometer (EI). Analysis of volatile compounds were carried out on a Thermoquest Finnigan Voyager GC-MS Trace GC 2000 series equipped with a Zebron ZB1 capillary column (30m L x 0.25 mm ID x 0.25 µm df, 100% methyl polysiloxane). The X-ray analysis was carried out at the University of Neuchâtel by Prof Helen Stoeckli-Evans, Dr Antonia Neels and Dr Gael Labat. The structures were solved by direct methods using the program SHELXS-97 and refined by full matrix least squares F2 with SHELXL-97. The figures were drawn with PLATON99 and Mercury 1.4.

**Figure 2.** Example of high spin heptanuclear mixed valence Fe(II, III) complex reported by Oshio et al. (2003).

FeCl$_2$ and 20 ml of THF under argon. The obtained suspension was heated to reflux for 8 h. Then the mixture was allowed to cool down to Room Temperature (RT) and the upper yellowish solution was filtered. After evaporation of solvent and drying under vacuum, 1.5 g (68% yield) of pale yellow solid was obtained. The isolated product is air sensitive, it turns red – brown if in contact with air. UV–Vis (THF, 200-800 nm): 335. IR (KBr film, 4000-400 cm$^{-1}$) : 1599s, 598 m. MS (ESI+) : m/z 433 (96), 371(70), 323(50), 279(50), 270(100) [M]$^+$.

1-(Bromomethy)-4-(propan-2-yl)benzene 7

To a solution of commercial available [4-(propan-2-yl)phenyl]methanol 8 (3.0 g, 20 mmol) in diethylether at 0°C was added dropwise tribromophosphine (5.4 g, 20 mmol), then the mixture was allowed to stir and then warmed to RT over 2 h period. After addition of a saturated aqueous solution of NaHCO$_3$ (50 ml), the mixture was extracted with diethylether (2 x 100 ml). The organic phase was washed with a saturated solution of NaCl (50 ml) and dried over MgSO$_4$. After evaporation of the solvent under vacuum, a yellowish oily product was obtained. A flash column chromatography (SiO$_2$, pentane/diethylether (1:1), $R_f = 0.92$), permitted the isolation of pure product 7 as a slightly yellow oil (2.9 g, 68%). $^1$H-NMR (360 MHz, CDCl$_3$): $\delta$7.32 (d, J = 7.7, 2H, HC(4)), 7.20 (d, J = 7.7, 2H, HC(3)), 2.90 (hept, J = 7.1, 1H, HC(6)), 4.49 (s, 2H, H$_2$C(1)), 1.24 (d, J = 7.1, 6H, H$_3$C(7)). $^{13}$C-NMR (91 MHz,
CDCl$_3$: $\delta$ 149.7 (C(5)), 135.6 (C(2)), 129.5 (C(3)), 127.3 (C(4)), 123.4 (C(1)), IR (NaCl film, 4000–400 cm$^{-1}$): 2960 s, 2871 w (sh), 1610 w, 1514 m, 1463 m, 1419 m, 1226 m, 1053 m, 837 m, 665 m, UV–Vis (THF, 200–800 nm): 235 MS (EI); m/z 212 [M$^+$].

2-[(4-(propano-2-yl)benzyl]Oxy)methyl]tetrahydrofuran 4

To a two-necked flask equipped with a bubbler was charged with 140 mg, (2.1 mmol) of NaH (60% in mineral oil washed three times with pentane and dried under vacuum), then a solution of tetrahydrofuran-2-yl-methanol (0.22 g, 2.1 mmol) in terahydrofuran (10 ml) was added dropwise over a period of 15 min. The solution was left to stir until gas evolution ceased followed by addition of KI (0.08 g, 0.5 mmol), benzyloxibromide 7 (0.5 g, 2.3 mmol) dissolved in 1 ml of THF over a period of 15 min. The reaction mixture was stirred overnight and then washed with 5 ml of water and saturated NaCl solution (5 ml). The aqueous phase was extracted three times with CH$_2$Cl$_2$ and the combined organic phases were washed with 20 ml of water then dried over MgSO$_4$. After evaporation of the solvent, the obtained yellow oil product was purified by flash column chromatography (diethylether/pentane (1:1); R$_f$ = 0.7 affording 0.5 g (92%) of 53 as a pale-yellow liquid. $^1$H-NMR (360 MHz, CD$_2$Cl$_2$): $\delta$ 7.23 (2H, J = 8.2, Hz(4)), 7.20 (2H, J = 8.2, Hz(5)), 4.48 (s, 2H, Hz(12)), 4.03–4.00 (m, 1H, Hz(10)), 3.85–3.79 (m, 1H, Hz(12)), 3.74–3.68 (m, 1H, Hz(12)), 3.44 (2H, J = 5.4, Hz(8)), 2.90 (sept, 1H, J = 6.8, Hz(2)), 1.98–1.80 (m, 3H, Hz(10, 11)), 1.65–1.57 (m, 1H, Hz(10)), 1.23 (2H, J = 6.8, Hz(11)), 1.15–1.05 (m, 1H, Hz(10)); $^{13}$C-NMR (91 MHz, CD$_2$Cl$_2$): $\delta$ 149.1 (C(3)), 136.9 (C(6), 128.6 (C(4)), 73.9 (C(8)), 73.8 (C(9)), 68.8 (C(7)), 34.7 (C(2)), 29.0 (C(11)), 26.5 (C(10)), 24.6 (C(1)), UV–Vis (THF, 200–800 nm): 220, 263. IR (NaCl film, 4000–400 cm$^{-1}$): 2960 s, 2875 b, 2868 m, 1462 w, 1088 m, 818 w. MS (EI): m/z 312 [M$^+$]; 191(14), 149(43), 133(100), 117(27), 71(46).

(bischloro) (2-[(4-(propano-2-yl)benzyl]Oxy)methyl]tetrahydrofuran) Iron(II) 5

A solution of FeCl$_3$ (0.11 g, 0.9 mmol) or FeCl$_3$(THF)$_2$ (0.25 g, 0.9 mmol) in 15 ml of THF under argon atmosphere was added to 2-[(4-(propano-2-yl)benzyl]Oxy)methyl]tetrahydrofuran 4 (0.1 g, 0.4 mmol) in 5 ml of THF. The reaction mixture was allowed to reflux over 8 h. Then after cooling the reaction at RT, yellow solution was filtered through Celite; the solvent was removed in vacuum resulting complex 5 (0.22 g, 60%) as a yellow oil. $^1$H-NMR (360 MHz, CD$_2$Cl$_2$): $\delta$ 7.24 – 7.18 (br m, 4H, Hz(4)), 4.89 (br, 1H, Hz(7, 9)), 4.30 (br, 1H, Hz(9, 7)), 2.95 (br, 1H, Hz(8, 12)), 2.20 (br m, 3H, Hz(8, 11, 12)), 1.27 (2H, J = 3.5, 6H, Hz(12)), $^{13}$C-NMR (91 MHz, CD$_2$Cl$_2$): $\delta$ 148.1 (C(4)), 138.2 (C(9)), 128 (C(5, 6)), 125.8 (C(7, 8)), 75.1 (C(12)), 72.2 (C(11)), 70 (C(15, 10)), 33.3 (C(3)), 29.2 (C(14)), 23.5 – 23.4 (C(1, 2, 13)). UV–Vis (THF, 230–800 nm): 369, 324, 281, 237. IR (NaCl film, 4000–400 cm$^{-1}$): 2960 s, 2930 s, 2875 s, 1601 m, 1461 m, 1364 w, 1042 m, 876 m, 820 m. MS (ES+): m/z 594(100) [M$^+$], 559 (9 - Cl$^-$), 491 (9 - 103), 432 [5 + THF$^-$], 360(70) [5$^+$], 270 [FeCl$_3$(THF)$_2$]$^+$.

RESULTS AND DISCUSSION

Recently, Raemy reported a possible existence of N$_2$Fe$^+$ (toluene) complex 2 resulting from the treatment of FeCl$_2$ in toluene under permanent nitrogen bubbling trough the reaction mixture (Raemy, 2003). This discovery is important since Fe-N$_2$ complexes play an important role in biological and industrial nitrogen derivatization (Delfino et al., 2010; Bothe et al., 2010). The UV-Vis spectrum of this material in toluene shows two maxima at 358 and 315 nm, respectively. This double band was taken as confirmation for the formation of the proposed compound. Additionally, when the UV-Vis spectrum was taken in THF, the peak of absorption at 358 nm was slightly shifted to a higher value of 363 nm. This bathochromic shift was assumed to be provoked by an exchange of the labile nitrogen ligand with a THF fragment 3 (Scheme 1).

All attempts to isolate these compounds failed and the use of NMR and MS experiments were unsuccessful; indeed the product decomposes during the measurements. It is important to note that when the reaction was carried out under continuous argon bubbling conditions, the UV-Vis spectra of obtained material show only singular weak absorption. Since the isolation and characterization of the presumed FeCl$_3$(THF)(toluene) compound 3 was not possible, it was of interest to develop a new type of ligand containing both strong and weak donor groups. The choice was directed to a bidentate ligand in which the tetrahydrofuran moiety was attached to the aryl group via an ether link resulting in the chelate- tweezer-like benzyletherfuran ligand 4 thus the aryl linkage would protect the dissociation of the weakly coordinated furan from the metal in complex 5 by the chelation effect (Scheme 2).

Furthermore, the hemilabile arm of such ligands will provides the capability to do reversible dissociation from the metal center. Such a dynamic behaviour will produce vacant coordination sites that allow complexation of substrates during the catalytic cycle. Simultaneously the strong donor moiety remains attached to the metal center. To our knowledge there is no report in literature concerning complexes of Fe(II) with both chelating aryl and dangling donor tetrahydrofuran groups.

Arene Fe(II) chloride complexes was found also to be excellent precatalysts for hydrogenation of olefins, oligo- and polymerization of acetylenes after activation with LiAlH$_4$, BuLi or DiBAH. However, this require the presence of an additional labile ligand such as ethylene (Figure 3), (Raemy, 2003).

Synthesis of 2-[(4-(propano-2-yl)benzyl]Oxy)methyl]tetrahydrofuran (4)

Compound 4 was prepared by reaction of 1-(Bromomethyl)-4-(propano-2-yl)benzene 7 with “in situ” deprotonated tetrahydrofuran-2-yl-methanol 6 in the presence of NaI (Scheme 3). Compound 4 was isolated as colourless oil in 92% yield. The structure of 4 was confirmed by $^1$H and $^{13}$C-NMR, and by GC-MS. We denote two UV–Vis absorption maxima in
Scheme 1. Nitrogen ligand exchange occurred in THF solvent (Raemy, 2003).

Scheme 2. Chelate benzyletherfuran ligand 4 and their complex with FeCl₂ 5.

Figure 3. Some allylaryl ligands developed by Raemy in his FeCl₂ complexation and hydrogenation study.


tetrahydrofuran at 220 and 263 nm. Unlike the starting materials 6 and 7, the infrared spectrum of compound 4 shows a new absorption band at 1088 cm⁻¹ which was attributed to the ether C-O-C stretching. The 1-(Bromomethyl)-4-(propan-2-yl)benzene 7 was easily prepared by treating [4-(propan-2-yl)phenyl]methanol 8 with PBr₃ in diethylether at RT, yielding 57% of colourless oil after purification on silica column chromatography (Scheme 4). The product was identified by ¹H- and ¹³C-NMR, infrared and GC-MS techniques.

Reaction of 2-((4-(propan-2-yl)benzyl)Oxy)methyl)tetrahydrofuran (4) with iron chloride sources

Reaction of 4 with FeCl₂ or FeCl₂(THF)₂ under argon in toluene or in THF at 70°C overnight give a yellow solution (Scheme 5). Filtration over Celite and evaporation of the solvent affords yellowish-green oil.

In the MS(ESI⁺) spectrum, the peak at m/z 594(100%) was attributed to complex 9 or 9a where FeCl₂ is linked with two ligands 4 via the aryl functions or the ether functions respectively. The peak at m/z 360 (40%) corresponds to the expected complex 5 or the ether complex 5a. We assumed that both complexes exist in solution as Fe(II) species. The cationic Fe(III) species observed in the mass spectrum are probably formed under the spragring conditions of electrospray ionisation, known to be oxidizing in the positive mode. The UV-Vis spectrum in THF shows three maxima at 364, 308 and 256 nm, respectively. These absorbances are in the same range of those observed by Raemy (Raemy, 2003) in his nitrogen-aryl or allylbenzylether Fe(II)chloride
complexes (Figure 3). The UV–Vis spectrum of the benzyletherfuran 4 is dominated by two absorptions in the UV region of the spectra (220 and 263 nm), which is characteristic for \( \pi-\pi^* \) transitions.

According to the reported studies of Lambert et al. (1999) on similar substituted iron–arene complexes and of Velusamy et al. (2003) on iron-Phenolate complexes, the absorbance in the range of 300-400 nm could be attributed to a metal to ligand charge transfer or ligand to metal charge transfer (MLCT or LMCT). In our case, the metal to ligand charge transfer (MLCT) is found at 364 nm and the position of this band demonstrates the high-spin state of complex 5. However, the values observed here are lower as those normally observed in others systems such as iron oxo- or amido-pyridine complexes, which usually display a MLCT band in the visible region (ca. 410 nm) in polar solvent such as tetrahydrofurane, methanol or acetonitrile (Bernal et al., 1995). Moreover, there is no \( d-d \) transition observed in the spectrum of 5. These transitions are reported to appear near the infrared region of the spectrum.

Compared to the free ligand, the absorptions in the infrared show slight shifts to the low frequencies for the C-O-C ether stretching at 1042 cm\(^{-1}\) instead of 1088 cm\(^{-1}\).
Figure 4. The $^1$H-NMR (500 MHz) spectrum of complex 5.

three new different absorption appear at 1601 (very strong), 920 and 820 cm$^{-1}$, respectively. The $^1$H-NMR spectrum of complex 5 is also typical for a high-spin ferrous compound and is difficult to be interpreted because of the absence of distinct signals (Figures 4 and 5).

However, the signals corresponding to the alkyl-protons are easily identifiable via the integration of the peaks situated at $\delta$1.3 and 3.0ppm respectively giving six and one protons attributed to the isopropyl moiety on the aromatic group (figure 5). The remained peaks, whose integrals do not correspond to the numbers of the protons, could be assigned to the benzyl and furfuryl protons.

In the $^{13}$C-NMR spectrum of 5 (Figure 6), it is interesting to note that only the expected peak located at $\delta$ 138.2 ppm and attributed to the carbon bearing benzylic linker can be identified, all the other aromatic peaks are only less influenced by the paramagnetism of the metal center, that is in contrast to the furfuryl carbon signals located between $\delta$ 64 to 76 ppm.

The previous observation can lead to formulate the hypothesis according to which in the complex 5 the aromatic ring is not complexed directly with the metal atom, the connection will be done somewhat via the oxygen atoms 9a. Consequently, only the carbon bearing benzyl linker, which is near to the complexed oxygen atom, is influenced by this paramagnetic effect of iron. Another direct consequence of this formulation is that the oxygen atom connected to the iron becomes very acidic and, could thus be stabilized by losing the aromatic moiety as isopropylbenzylalcohol compound, when some water traces exist in solution. This mechanism could explain the formation of surprising multinuclear iron complex 1 (Figure 1). Crystallization attempts in a mixture of toluene and dichloromethane allow the isolation of
Figure 5. The $^{13}$C-NMR (125 MHz) spectrum of 5.

Figure 6. The new heptanuclear Fe(II, III) tetrahydrofurane complex 1.
green hexagonal crystals. The X-ray analysis yields the unexpected oxo-polymetallic complex 1, probably as a result of decomposition of complex 5 or 9 via ether cleavage induced by Fe(III) impurities (Figures 6, 7 and 8).

The starting ligand 2-\{[4-(propoan-2-yl)benzyl]Oxy)methyl\}tetrahydrofurane 4 has lost the benzyl moiety, only the tetrahydrofuran-2-ylmethanolate part remains attached to the iron centers in 1. The tetrahydrofuran-2-ylmethanolate ligand has two possible coordination sites, namely the alkoxy and the cyclic oxygen. As per description of Labat and Oshio for similar compounds, the core can be regarded as a wheel with crystallographically imposed \(S_6\) symmetry, in which the central iron atom Fe1 is in distorted octahedral environment attached to six other iron atoms Fe2 through six hydroxyl ligands in a \(\mu_2\)-oxo mode. Furthermore, each external iron is hexacoordinated with one chloride atom, two other positions are occupied by hydroxyl groups and the two remaining sites are engaged with oxygen atoms of tetrahydrofuran-2-ylmethanolate molecules. Each of the six exocyclic oxygen atoms of the tetrahydrofuran-2-ylmethanolate moiety is shared by two peripheral iron atoms Fe2 in a \(\mu_2\)-oxo mode, while each cyclic oxygen atom complexes only one Fe2 center. Selected bond distances and angles are given in the Table 1 with Fe1—O1 bond lengths in the range of 2.095(2) to 2.176(1)Å, these values are comparable with those reported for similar compounds (Figures 2 and 3). The O—Fe1—O cis-angles are 80.23\(^{(10)}\)° and 100.69\(^{(10)}\)°, but the O—Fe1—O trans arrangement is 180°.

As shown in Figures 1 and 6, the six tetrahydrofuran-2-ylmethanolate rings are dangling oriented from each other to mitigate the steric interaction around the external iron atoms. Such steric hindrance may rationalize the facile cleavage of the oxo-bridge of original 2-\{[4-(propoan-2-yl)benzyl]Oxy)methyl\} tetrahydrofuran ligand with weak proton sources such as H\(_2\)O. The chloro

Figure 7. Cl---H(OH) interactions in 1 between the [FeCl\(_4\)]\(^-\) counteranions and the cationic core.
Figure 8. Crystal Packing of complex 1 viewed along the a axis (top). The compound crystallizes in monoclinic space group P21/n, with unit cell dimensions \(a = 14.1021(11) \text{ Å}, \ b = 13.1512(7) \text{ Å}, \ c = 16.8828(14) \text{ Å}, \alpha = 90^\circ, \beta = 93.87(9)^\circ, \gamma = 90^\circ, \) and \(Z = 2.\) The structure was refined to final \(R = 0.0404\) for 24345 data with \(I \geq 2.0\sigma(I).\)

Table 1. Selected bond distances and angles of complex 1.

<table>
<thead>
<tr>
<th>Bond distances / Å</th>
<th>Angles / °</th>
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<tr>
<td>Fe(1)-O(1)</td>
<td>2.105(2) Fe(2)-Cl(1)</td>
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<tr>
<td>Fe(1)-O(2)</td>
<td>2.103(2) Fe(5)-Cl(4)</td>
</tr>
<tr>
<td>Fe(1)-O(3)</td>
<td>2.095(2) Fe(5)-Cl(5)</td>
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<tr>
<td>Fe(2)-O(5)</td>
<td>2.009(3) O-H—Cl</td>
</tr>
<tr>
<td>O(1)-Fe(1)-O(1a)</td>
<td>180        O(3)-Fe(2)-O(4)</td>
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<tr>
<td>O(1a)-Fe(1)-O(2)</td>
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<td>O(1)-Fe(2)-O(3)</td>
<td>80.5(10)  Fe(4)-O(9)-Fe(2)</td>
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ligands are oriented orthogonal to the plane of the iron avoiding steric interactions with the tetrahydrofuran-2-ylmethanolate ligands.

The counter ion is clearly Fe(III) Fe—Cl distances in the range of 2.167 to 2.183Å and allows no other interpretation, which oblige to the oxo-heptametallic core double positive charge (+2). On the assumption that all μ-O ligands are hydroxyl groups and all tetrahydrofuran-2-yl-methanol are deprotonated alkoxy ligands, the seven iron centers mostly possess a Fe$_4$Fe$_6$ configuration.

Unfortunately, we were unable to obtain sufficient material for measurement such as Magnetic susceptibility or Mössbauer Spectroscopy. We performed MS (ESI+, FAB and MALDI) experiments in order to find out if there are hydrogen atoms on all the bridging μ-O ligands, the obtained spectra does not afford peaks in favour of an expected structure.

Conclusions

Assumptions about the ability of Fe(II) allyletheraryle bidentate complexes to carry out the catalytic hydrogenation and polymerization of olefins, guided us to successfully prepare new iron benzyletherfuran complex 5. Unfortunately, the complex failed to perform polymerization either with butadiene or with ethylene, under mild reaction conditions (RT, 2 bar for ethylene). However, we were able to isolate a new hepta-core iron complex resulting probably from the degradation of 5.

Conflict of Interest

The authors have not declared any conflict of interest.

ACKNOWLEDGEMENTS

We are thankful to Professor Helen Stoeckli-Evans from Benefri Crystallography Service, University of Neuchâtel, Switzerland for the support with X-Ray determination and analysis. Additional thanks goes to Professor Titus Jenny from Department of Chemistry at University of Fribourg, Switzerland. The Financial support from the Swiss National Science Foundation and the University of Fribourg is also gratefully acknowledged.

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Balzani V, Bandmann H, Ceroni P, Giansante C, Hahn U, Klärner F-
The inhibition of mild steel corrosion in 0.5 M sulphuric acid solution by ethanol extracts of Parinari polyandra as an eco-friendly inhibitor was studied at different temperatures by weight loss technique and linear polarization. The test plant extracts has a promising inhibitory action against corrosion of mild steel in the sulphuric acid media. The inhibition efficiencies increase with a corresponding increase in the concentration of the inhibitor. The adsorption of the inhibitor on mild steel surface is exothermic, spontaneous and is best described by Freundlich and Temkim adsorption models. Calculated values of activation energy, enthalpy of activation, entropy of activation, free energy of adsorption and the trend in the variation of inhibition efficiency with temperature, the mechanism of the process is by physical adsorption. Ethanol extract of Parinari polyandra is a good adsorption inhibitor for the corrosion of mild steel in sulphuric acid. Tafel polarization analyses indicate that the studied plant extract is a mixed type inhibitor.

**Key words:** Isotherm, polarization, adsorption, inhibitor, Parinari polyandra.

**INTRODUCTION**

Corrosion is the deterioration of materials by chemical interaction with their environment. The consequences of corrosion are many and its effects on the safe, reliable and efficient operation of equipment or structures are severe. Most corrosion inhibitors are synthetic chemicals that are expensive and hazardous to the environment (Okafor, 2007). Basically, attention is however shifting away from the use of synthetic organic compounds as metal corrosion inhibitors. This is because many of them have been found to be toxic to humans and the environment. In recent years, a lot of research efforts have gone into the search for non-toxic naturally occurring substances for use as metal corrosion inhibitors. In this regard, a number of amino acids (Fu et al., 2011; Eddy et al., 2010) as well as extracts from leaves, roots and stem barks of plant (biomass) and even fruits or fruit peels have been reported as effective inhibitors of metal corrosion (Oguzie, 2008; Rosliza and...
Wan Nik, 2010; Kumar et al., 2011; Oguzie, 2005; Ostovari et al., 2009; Satapathy et al., 2009; Ekanem et al., 2010; Oguzie et al., 2006; Umoren et al., 2009; Oguzie and Ebenso, 2005; Oguzie, 2007; Okafor et al., 2008; Ameh et al., 2012). The crucial property of the plant extracts is because they contain phytochemical compounds such as alkaloids, tannins, flavonoids, saponins, amino acids, ascorbic acid, phenolic acids, pigments, resins, triterpenoids, phlobatansins, anthraquinone, cardiac glycosides, with molecular electronic structures close to conventional corrosion inhibitors. Such plant extracts could thus serve as sources of non-toxic and inexpensive corrosion inhibiting additives. In spite of the large numbers of green corrosion investigated and tested, literature is scanty on the inhibitive properties of ethanol extract of *Parinari polyandra* for the corrosion of mild steel in sulphuric acid media. Therefore the objective of the study is to investigate the inhibitive properties of ethanol extract of *P. polyandra* leaves for the corrosion of mild steel in sulphuric acid.

**MATERIALS AND METHODS**

**Materials and sample preparation**

Materials used for the study were mild steel sheet of composition (wt %) Mn (0.6), P (0.36), C (0.15), and Si (0.03) and Fe (balance). The sheet was mechanically pressed cut into different coupons, each of dimension, 3 cm x 2 cm x 0.12 mm of thickness 0.12 mm”. Each coupon was polished with different size of emery paper grids (600 – 1200), and was later degreased by washing with ethanol, rinsed with acetone and air dried before they were preserved in a desiccator. All reagents used for the study were Anilar grade and double distilled water was used for their preparation.

**Plants extraction**

Samples of *P. polyandra* leaves were obtained from Zango – Shantu, Sabon Gari Local Government, Kaduna State Nigeria. The samples were later taken to Herbarium in Department of Biological sciences, Ahmadu Bello University Zaria Nigeria for identification and was assigned a batch number. The leaves were dried, ground, and soaked in a solution of ethanol for 48 h. After 48 h, the samples were filtered. The filtrates were further subjected to evaporation at 352 K in order to make it free of ethanol. The stock solutions of the extract so obtained were used in preparing different concentrations of the extract by dissolving 0.1, 0.2, 0.3, 0.4, and 0.5 g of the extract in 1L of 2.5 M H2SO4, respectively. For gravimetric analysis as well as linear polarization analysis, the concentration of H2SO4 used for the preparation of the inhibitor-acid solutions was 0.5 M (Eddy and Odoemelam, 2009).

**Chemical analysis**

Phytochemical analysis of the ethanol and aqueous extract of the sample was carried out according to the method reported elsewhere (Odiongeyi et al., 2009). Frothing and Na2CO3 tests were used for the identification of saponin, bromine water, ferric chloride tests were used for the identification of tannin while Leberman’s and Salkowski’s tests were used for the identification of cardiac glycosides while Dragendorf, Hagger, and Meyer reagent tests were used for the identification of alkaloid.

**Scanning electron microscopy (SEM)**

Morphological studies of the mild steel electrode surfaces exposed to uninhibited and inhibited 0.5 M H2SO4 solutions for seven days at 303 K were taken by using a Jeol JSM – 7500 F scanning electron microscope (Eddy and Ita, 2010) .

**Gravimetric analysis**

A previously weighed metal (mild steel) coupon was completely immersed in 250 ml of the test (in a close beaker). The beaker was inserted into a water bath maintained at a temperature of 303 K. After every 24 h, each sample was withdrawn from the test solution, washed in a solution containing 50% NaOH and 100 g/L of zinc dust. The washed steel coupon was rinsed in acetone and air dried before re-weighting. The difference in weight for a period of 168 h was taken as the total weight-loss. The effect of temperature on mild steel corrosion and corrosion inhibition was investigated by performing experiments in 0.5 M H2SO4 at 303, 313, 323 and 333 K for 3 h immersion period. All tests were run in triplicates and the data showed good reproducibility. From the weight loss results, the inhibition efficiency (%I) of the inhibitor, the degree of surface coverage (θ), and the corrosion rate of mild steel (CR) were calculated using the Equations (1), (2) and (3) respectively (Sethuraman and Raja, 2005).

\[ %I = 1 - \frac{W_1}{W_2} \times 100 \]  
\[ \theta = \frac{1 - W_1}{W_2} \]  
\[ CR (\text{g/m}^2 \cdot \text{h}) = \frac{\Delta W}{At} \]

Where \( W_1 \) and \( W_2 \) are the weight losses (g/L) of mild steel in the presence and absence of inhibitor (0.5 M H2SO4 solution, respectively, θ = the degree of surface coverage, A =area of specimen (cm²), and t = period of immersion (hours), \( \Delta W = W_2 - W_1 \) is the weight loss of mild steel after time, t.

**Electrochemical measurements**

Metal samples for electrochemical experiments were of dimensions 1.0 cm x 1.0 cm of thickness 0.12 mm. These were subsequently sealed with epoxy resin in such a way that only one square surface of area 1.0 cm² was left uncovered. The exposed surface was degreased in acetone, rinsed with distilled water and dried in warm air. Linear polarization studies were carried out in the potential range of 300 to 2000 mV at a scan rate of 0.333 mV s⁻¹ at room temperature of 303 K. Each test was run in triplicate to verify the reproducibility of the systems (Oguzie et al., 2010).

**RESULTS AND DISCUSSION**

**Phytochemical constituent**

Table 1 shows the phytochemical composition of ethanol extract of *P. polyandra*. The results obtained, indicate that saponin, tannin, anthraquinone, cardiac glycosides, flavanoid, terpene, andalkaloid are present in ethanol extract of *P. polyandra* hence the inhibition efficiency of ethanol extract of *P. polyandra* may be attributed to the
Table 1. Phytochemical composition of the ethanol extract of *P. polyandra*.

<table>
<thead>
<tr>
<th>Phytochemicals</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saponins</td>
<td>+</td>
</tr>
<tr>
<td>Tanins</td>
<td>+</td>
</tr>
<tr>
<td>Phlobatanins</td>
<td>---</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td>++</td>
</tr>
<tr>
<td>Cardiac glycoside</td>
<td>++</td>
</tr>
<tr>
<td>Flavanoid</td>
<td>++</td>
</tr>
<tr>
<td>Terpene</td>
<td>+++</td>
</tr>
<tr>
<td>Alkaloid</td>
<td>+++</td>
</tr>
</tbody>
</table>

+ present; ++ moderately present; +++ present in large amount; - absence or presence in negligible quantity.

**Figure 1.** Variation of weight loss of mild steel with time for the corrosion of mild steel in 0.5 M H$_2$SO$_4$ containing various concentration of *P. polyandra* at 303 K.

**Effect of ethanol extract of *P. polyandra* (PB)**

Figure 1 shows the variation of weight loss with time for the corrosion of mild steel in various concentrations of H$_2$SO$_4$. The figure indicates that the rate of corrosion of mild steel in sulphuric acid increases with increase in concentration. It is evident from the plot that weight losses of mild steel increases with increase in the concentration of H$_2$SO$_4$ and contact time. It is also important to note that weight loss of mild steel decreases with increasing concentration of ethanol extract of *P. polyandra* which indicates that ethanol extract of *P. polyandra* is an adsorption inhibitor for the corrosion of mild steel. It is also noted that as the temperature increases, the weight-loss were found to be more higher than at room temperature and was also found to decrease with increase in concentration of inhibitors similar to those obtained at 303 K. However, the inhibition efficiency of ethanol extract of *P. polyandra* decreases with increasing temperature. This also suggests that the adsorption of ethanol extract of *P. polyandra* on mild steel surface is consistent with the mechanism of physical adsorption. In order to sustain further, the inhibition efficiencies and corrosion rate was determined, the inhibition efficiencies of ethanol extract of *P. polyandra* and the corrosion rates of mild steel in H$_2$SO$_4$ in the absence and presence of ethanol extract of *P. polyandra* as an inhibitor. From the results obtained, it is evident that the corrosion rate of mild steel decreases with increasing concentrations of the extract while the inhibition efficiency increases with increasing phytochemical constituent of the extract.
Table 2. Corrosion rates (CR) of mild steel of ethanol extract of *P. polyandra*.

<table>
<thead>
<tr>
<th>Conc. (g/L)</th>
<th>333K CR (g h⁻¹ cm⁻²)</th>
<th>323K</th>
<th>313K</th>
<th>303K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>37.79</td>
<td>30.18</td>
<td>19.98</td>
<td>13.84</td>
</tr>
<tr>
<td>0.1</td>
<td>34.31</td>
<td>27.20</td>
<td>13.63</td>
<td>8.71</td>
</tr>
<tr>
<td>0.2</td>
<td>33.83</td>
<td>23.46</td>
<td>10.99</td>
<td>6.86</td>
</tr>
<tr>
<td>0.3</td>
<td>32.14</td>
<td>20.92</td>
<td>9.94</td>
<td>6.10</td>
</tr>
<tr>
<td>0.4</td>
<td>31.22</td>
<td>18.46</td>
<td>8.71</td>
<td>5.58</td>
</tr>
<tr>
<td>0.5</td>
<td>29.57</td>
<td>17.78</td>
<td>7.96</td>
<td>4.78</td>
</tr>
</tbody>
</table>

Table 3. Inhibition efficiencies (% I) of ethanol extract of *P. polyandra*.

<table>
<thead>
<tr>
<th>333K</th>
<th>323K</th>
<th>313K</th>
<th>303K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>09.88</td>
<td>31.77</td>
<td>37.09</td>
</tr>
<tr>
<td>1.59</td>
<td>22.28</td>
<td>45.01</td>
<td>50.46</td>
</tr>
<tr>
<td>4.78</td>
<td>30.70</td>
<td>50.26</td>
<td>55.92</td>
</tr>
<tr>
<td>5.39</td>
<td>38.83</td>
<td>56.43</td>
<td>59.65</td>
</tr>
<tr>
<td>8.61</td>
<td>41.08</td>
<td>60.18</td>
<td>65.47</td>
</tr>
</tbody>
</table>

concentration of the extract. This implies that ethanol extract of the inhibitor retarded the rate of corrosion of mild steel in H₂SO₄. From the calculated values of corrosion rate of mild steel and of the inhibition efficiency of the plant extracts (Tables 2 and 3), it can be seen that the inhibition efficiency of *P. polyandra* for mild steel in solutions of sulphuric acid increases with increase in the concentration of the inhibitor, but decreases with increasing temperature, indicating that *P. polyandra* is an adsorption inhibitor for the corrosion of mild steel in solutions of H₂SO₄ and that the adsorption of *P. polyandra* favours the mechanism of physical adsorption (Chetounani et al., 2004).

**Effect of temperature**

The effect of temperature on the corrosion of mild steel in the absence and presence of various concentration of *P. polyandra* was investigated using the Arrhenius state equation shown in Equations (4) and (5) (Lebrini et al., 2010).

\[ \log CR = \log A - \frac{E_a}{2.303RT} \]  

(4)

\[ \log \left( \frac{CR}{T} \right) = \left[ \log \left( \frac{R}{NAR} \right) + \frac{\Delta S_a}{2.303R} \right] - \frac{\Delta H_a}{2.303RT} \]  

(5)

Where CR is the corrosion rate of the metal, A is the Arrhenius or pre-exponential factor, Eₐ is the activation energy (that is, the minimum energy needed before the corrosion reaction of the metal can proceed), R is the universal gas constant and T is the temperature of the system, Nₐ is the Avogadro’s constant, ΔSₐ is the entropy of activation and ΔHₐ is the enthalpy of activation.

From Equation (4), plot of log CR versus reciprocal of absolute temperature, 1/T, as shown in Figure 2 gives a straight line with slope equal to -Eₐ/2.303R, from which the activation energy for the corrosion process can be calculated. From Equation (5), plot of log CR/T versus reciprocal of absolute temperature, 1/T, as shown in Figure 3 gives a straight line with slope equal to -ΔHₐ/2.303R and intercept of {log R/Nₐh + ΔSₐ/2.303R}, from which the enthalpy and entropy of activation for the corrosion process can be calculated. Values of Eₐ, ΔSₐ, and ΔHₐ are presented in Table 4. Figure 2 and 3 also show a linear relationship between the corrosion rate and the temperature of the environment.

Values of the extrapolated activation energy Eₐ were found to be greater where corrosion rates were inhibited than those obtained where there were no inhibition indicating that the ethanol extract of *P. polyandra* retarded the corrosion of mild steel in H₂SO₄. It is also found that the activation energy was lowered than the value of 80 kJmol⁻¹ required for chemical adsorption to take place, confirming that the adsorption of the ethanol extract of *P. polyandra* occur through the mechanism of physical adsorption (Sethuran and Raja, 2005). Table 3 shows the enthalpies of activation of the corrosion
Figure 2. Variation of logCR of mild steel with inverse temperature for the corrosion of mild.

Figure 3. Variation of logCR/T of mild steel with inverse temperature for the corrosion of mild steel in 0.5 M H$_2$SO$_4$ containing various concentration of inhibitor.

Table 4. Activation energy parameters for the dissolution of mild steel in H$_2$SO$_4$ in the absence and presence of different concentration of *P. polyandra*.

<table>
<thead>
<tr>
<th>Conc. (g/L)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\Delta H_a$ (kJ/mol)</th>
<th>$\Delta S_a$ (kJ/molK)</th>
<th>$(E_a-\Delta H_a)$ (kJ/mol)</th>
<th>$Q_{ads}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>28.80</td>
<td>26.15</td>
<td>-0.194</td>
<td>2.65</td>
<td>-229.48</td>
</tr>
<tr>
<td>0.1</td>
<td>40.52</td>
<td>37.87</td>
<td>-0.160</td>
<td>2.65</td>
<td>-115.81</td>
</tr>
<tr>
<td>0.2</td>
<td>46.64</td>
<td>44.00</td>
<td>-0.142</td>
<td>2.64</td>
<td>-90.30</td>
</tr>
<tr>
<td>0.3</td>
<td>48.60</td>
<td>45.95</td>
<td>-0.136</td>
<td>2.65</td>
<td>-91.04</td>
</tr>
<tr>
<td>0.4</td>
<td>50.64</td>
<td>48.00</td>
<td>-0.130</td>
<td>2.64</td>
<td>-83.94</td>
</tr>
<tr>
<td>0.5</td>
<td>54.17</td>
<td>51.52</td>
<td>-0.120</td>
<td>2.65</td>
<td>-83.94</td>
</tr>
</tbody>
</table>
process to be positive which reflect endothermic nature of dissolution process. Moreover, the average difference value of \( (E_a - \Delta H_a) \) is 2.6467 kJ/mol which is approximately equal to the average value of RT is 2.6438 kJ/mol. Therefore, the corrosion process is a unimolecular reaction as it is characterized by the equation given below:

\[
E_a - \Delta H_a = RT
\]  

The entropy of activation in the presence and absence of the inhibitor also has negative values which indicates that the activated complex in the rate determining step represents an association rather than dissociation, implying that a decrease in disordering took place on going from the reactant to the activated complex (Lebrini et al., 2011).

**Adsorption thermodynamic considerations**

The relationship between inhibition efficiency and the bulk concentration of the inhibitor at constant temperature, which is known as isotherm, gives an insight into the adsorption process. Several adsorption isotherms were attempted to fit surface coverage values to classical isotherms of Langmuir, Freundlich, Temkin, Flory-Huggins. The surface coverage (\( \theta \)) values for different concentrations of the inhibitor in 0.5 M H\(_2\)SO\(_4\) have been evaluated from the weight-loss data. The data were tested graphically to find a suitable adsorption isotherm. A plot of \( \log(C/\theta) \) against \( \log C \) (Figure 4) gave a straight line indicating that adsorption follows the Langmuir adsorption isotherm and a straight line was also obtained in the plot between \( \log \theta \) versus \( \log C \), this shows that the adsorption also obeys Freundlich adsorption isotherm (Figure 5). The weight-loss data obtained were also tested in other adsorption isotherm, among the entire adsorption isotherm tested, Freundlich was found to be the best fit. The heat of adsorption of ethanol extract of PB on mild steel was also calculated using the Equation (7) (Eddy et al., 2009a).

\[
Q_{ads} = 2.303R \left[ \log \left( \frac{\theta_2}{\theta_1} \right) - \log \left( \frac{\theta_1}{\theta_2} \right) \right] \left( \frac{T_2}{T_1} \right) \text{kJ/mol} - 1
\]  

Where \( \theta_1 \) and \( \theta_2 \) are the degrees of surface coverage of the inhibitor at the temperature, \( T_1 \) (303 K) and \( T_2 \) (333 K) respectively and \( R \) is the molar gas constant. Calculated values of \( Q_{ads} \) are presented Table 4. The values are negative and ranged from indicating that the adsorption of the ethanol extract of the inhibitor on mild steel surface is exergonic. The free energies for the adsorption of ethanol extract of *P. polyandra* were calculated using the Equation (8) (Eddy et al., 2008b).

\[
\Delta G_{ads}^0 = -2.303RT\log (55.5K_{ads})
\]  

Where \( R \) is the molar gas constant, \( T \) is the temperature in Kelvin, 55.5 is the molar concentration of water and \( K_{ads} = \theta/(1-\theta)[C] \).

Calculated values of \( \Delta G_{ads}^0 \) are also presented in Table 5, the values ranged from -9.67 to 13.58 kJmol\(^{-1}\) and tend to be more negative as concentration of the inhibitor increases. These indicate that the adsorption of ethanol extract of *P. polyandra* on mild steel surface is spontaneous and that the strength of the adsorption

![Figure 4. Langmuir isotherm for the adsorption of the inhibitor on mild steel surface in 0.5 M H\(_2\)SO\(_4\) solution at various temperature.](image-url)
increases with increase in concentration of the inhibitor. It is also significant to note that values of $\Delta G^o_{\text{ads}}$ greater than -40 kJmol$^{-1}$ are consistent with the transfer of electron from the inhibitor to the metal surface which represent a chemical adsorption whereas, values of $\Delta G^o_{\text{ads}}$ less than -40 kJmol$^{-1}$ signifies that the adsorption is a physical process. Therefore the adsorption of ethanol extract of *P. polyandra* on mild steel surface supports the mechanism of physical adsorption from the values of $\Delta G^o_{\text{ads}}$ obtained from this study.

**SEM surface analysis**

Surface morphology of the mild steel specimens in uninhibited and inhibited acid solutions was carried out by SEM after immersion in the test solutions after 7 days at 303 K. Figure 6 (a) and (b) shows the SEM images of the mild steel in the absence of inhibitor and presence of the inhibitor. A severely corroded surface morphology was observed after the immersion in the uninhibited system, due to the corrosive attack of the acid solution. Corrosion was relatively general with no evidence of localized attack. The corrosion product layer on the metal surface in uninhibited is clearly very loose and porous and would thus offer insignificant corrosion protection. With addition of *P. polyandra*, the corrosion damage is visibly reduced, there is slight evidence of the adsorbate presence on the metal surface.

**Linear polarization resistance**

Linear polarization experiment was taken to understand the effect of *P. polyandra* on both the cathodic and anodic dissolution of the mild steel. A typical polarization
curves for mild steel in 0.5 M H$_2$SO$_4$ in the absence and presence of *P. polyandra* is shown in Figure 7, and also parameters derived from the curves were also presented in Table 6. It can be observed that both cathodic and anodic reactions were suppressed with the addition of various concentration of *P. polyandra* which indicate that the inhibitor affected the cathodic as well as the anodic partial reactions, shifting the corrosion potential slightly towards more positive values, thus reducing the anodic and cathodic current densities and the corresponding corrosion current density. This indicates that the extracts functioned as a mixed-type inhibitor in the acid solution. From the value of the corrosion current densities in both the absence and presence of the inhibitor, the inhibition efficiencies were calculated using the equation given below:
Table 6. Polarization parameters for mild steel in 0.5 M H2SO4 in the presence and absence of P. polyandra.

<table>
<thead>
<tr>
<th>System</th>
<th>ECorr (mV vs SCE)</th>
<th>Icorr (µA/cm²)</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-1004.4</td>
<td>1642.0</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>-926.15</td>
<td>1069.8</td>
<td>34.85</td>
</tr>
<tr>
<td>0.2</td>
<td>-956.73</td>
<td>861.27</td>
<td>47.55</td>
</tr>
<tr>
<td>0.3</td>
<td>-1003.4</td>
<td>722.32</td>
<td>56.01</td>
</tr>
<tr>
<td>0.4</td>
<td>-932.84</td>
<td>480.84</td>
<td>70.71</td>
</tr>
<tr>
<td>0.5</td>
<td>-935.00</td>
<td>372.01</td>
<td>77.34</td>
</tr>
</tbody>
</table>

IE, % = \(\frac{1 - i_{inh}/i_{corr}}{i_{corr}}\) \times 100 \hspace{1cm} (9)

Where \(i_{inh}\) and \(i_{corr}\) are the corrosion current densities in the absence and presence of inhibitors.

Conclusion

From the study, we found that ethanol extract of \textit{P. polyandra} is an adsorption inhibitor for the corrosion of mild steel in sulphuric acid. The adsorption characteristics of the inhibitor favours the mechanism of charge transfer from the charged inhibitor’s molecule to the charged metal surface (Physical adsorption) and supported Freundlich adsorption model. Linear polarization results, indicate that the inhibitor is a mixed type inhibitor on the surface of mild steel.

Conflict of Interest

The authors have not declared any conflict of interest.

ACKNOWLEDGEMENTS

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A study of the morphology and optical properties of electro polished steel in the presence of Vitamin-C

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The studies of steel electrochemical polishing. Electropolishing (EP) in orthophosphoric acid were performed by potentiodynamic polarization. Electropolishing was conducted in solution containing Vitamin C. Addition of Vitamin C to electropolishing solution results in a lower limiting current. Vitamin C concentration influence on electropolishing process and surface texture (AFM, SEM) and UV-VIS-NIR Spectroscopy was established. The results show that by increasing Vitamin C concentration from $2 \times 10^{-5}$ to $5 \times 10^{-5}$ M, roughness and reflectance of steel specimens decrease/increase respectively. The opposite trend is seen when the concentration increases to $10 \times 10^{-5}$ M. The roughness of steel specimen before electropolishing is 236.7 nm and it will decrease to 140 nm by electropolishing in the presence of $5 \times 10^{-5}$ M Vitamin C. A similar trend is also seen in reflection. The SEM study confirms that low and moderate concentration of Vitamin C was effective to enhance levelling and brightness more than higher concentrations.

Key words: Steel, electropolishing, Vitamin C, scanning electron microscope (SEM), atomic force microscope (AFM), reflectance.

INTRODUCTION

Electropolishing (EP) is one of the anodic methods widely employed in the industry for the surface finishing of metals or alloys to obtain the fine surface brightness and stress-free surface (Rajurkr, 1992). The proposal of EP as an industrial surface finishing process is usually attributed to the work by Jacquet, who took a patent in 1930 (Figoux and Jacquet, 1930). However, the first recorded publication dealing with EP goes back even further (Hoar and Rothwell, 1964). The surface phenomena of EP are generally classified into two processes: anodic levelling and anodic brightening. Anodic levelling results from a difference in the dissolution rate between peaks and valleys on a rough metal/alloy surface depending on the current distribution or mass-transport conditions (Oniciu and Muresan, 1991; Wagner, 1954; Fitzgerald and McGeough, 1969; Fedkiw, 1980; Sautebin and Landolt, 1982; Clerc and Landolt, 1984; Clerc and Landolt, 1987; Matlosz and Landolt, 1989). It is usually associated with a decrease of roughness in the micrometer or larger range (Landolt, 1987) and can be achieved under the ohmic (primary current distribution), activation (secondary), and mass-transport (tertiary)-controlled metal dissolution reactions (Sautebin et al., 1980; Clerc et al., 1984).
Anodic brightening, on the other hand, is associated with the suppression of the influence of the metal microstructure on the dissolution rate. It can be achieved only under the conditions in which the metal dissolution is mass-transport-controlled and the formation of a precipitated salt layer at the electrode surface is possible. The presence of a salt layer can suppress the influence of crystallographic orientation and surface defects in the dissolution process (Sautetin et al., 1980; Clerc et al., 1984; Datta and Landolt, 1975; Datta and Landolt, 1980). This phenomenon will lead to microfinishing in the sub-micrometer scale and specular reflectivity of metals/alloys can be obtained. Accordingly, a fine electropolished surface of metals/alloys, which appears bright to the naked eye, generally results from an effective combination of levelling and brightening.

The use of an appropriate electrolyte and operating conditions in an EP process will produce smooth and bright surfaces that are free of defects, stress, and contamination. Gabe measured the anodic polarization curves of mild steel in phosphoric acid and phosphoric–sulfuric acid mixtures (Magaino et al., 1993; Gabe, 1973). Passivation was observed in these solutions and the passive current density was found to depend on the electrolyte composition. In addition, a phosphoric acid solution containing sulfuric acid gave a better surface finish than a pure phosphoric acid. Similar results were also obtained by Ponto et al. (1987) who studied the anodic behavior of steel in mixtures of phosphoric and sulfuric acids. Well-polished surfaces can be obtained at or above a limiting current density, which means that EP takes place in the trans passive region under mass-transport control.

The impedance study (Magaino et al., 1993) and the temperature effect on the appearance of metals/alloys through EP in the phosphoric–sulfuric acid system (Matlosz and Landolt, 1989; Datta and Vercruyssse, 1990) have also been done. Furthermore, addition of glycerol into this system was adopted (Datta and Romankiw, 1998; Datta et al., 1991). In this glycerol containing system, the limiting polishing current was found to depend slightly on the flow rate (Datta and Romankiw, 1998) and a concept for minimizing agitation of the electrolyte was proposed to eliminate the cost of pumping concentrated acids (Datta et al., 1991).

Based on these studies, several mechanisms have been proposed successively for the process of anodic dissolution: (i) salt film (dissolution products) mechanism (Landolt, 1987); (ii) acceptor mechanism (Landolt, 1987); (iii) preferential adsorption of shielding molecules (Yuzhakov et al., 1997; Bandyopadhyay et al., 1996); and (iv) formation of a solid oxide film of aluminum (Parkhutik and Shershulsky, 1992). Steel is an important category of materials due to their wide range of industrial applications. It is used in many industries due to its excellent mechanical properties. These are used in industries as pipelines for petroleum industries, storage tanks, reaction vessels and chemical batteries (Zhang et al., 2010).

The examination of steel dissolution in acid solutions by different type of organic compounds has been extensively studied (Shukla et al., 2008). Among them, very few are environmentally acceptable, such as natural products, that is, extracts of various parts of plants, pharmaceutically active compounds, that is, antibiotics, antibacterial, antioxidant etc. (Raja and Sethuraman, 2008; Shukla and Quraishi, 2009a, b; Shukla and Quraishi 2010a, b; Singh et al. 2011; Arslan et al., 2009; Eddy et al., 2010; Morad, 2008; Abdallah, 2002). In this study, an attempt is extended to reduce the roughness of the surface by reducing the etched pits and defects formed over the steel surface, consequently, the surface smoothness and brightness could be increased. Accordingly, the present work is aimed to study the effect of addition of Vitamin C (ascorbic acid) to orthophosphoric acid solutions used as electrolytes for EP of steel.

Ascorbic acid or Vitamin C is a common enzymatic cofactor in mammals used in the synthesis of collagen. Ascorbat is a powerful reducing agent capable of rapidly scavenging a number of reactive oxygen species (ROSs).

**EXPERIMENTAL DETAILS**

Electropolishing was performed on a rectangular steel sheet by an area of 10 × 5 cm covered with a Teflon coating with an exposed area of 5 cm × 1 cm. The test sheets were used directly without any pretreatment. The steel sheet [0.0257% S, 0.07% P, 0.4% Mn, 0.1% C and the rest iron] was immersed into the corner of a rectangular cell with the 100 mL EP solution, which was surrounded by an isothermally circulated water system (± 0.5°C) at different temperatures (20, 30, 40 and 50°C). The cathode, which was a rectangular steel sheet with an area of 5 × 10 cm, was also immersed in the solution and faced the test sheet. The EP solution was composed of 8M H₃PO₄ phosphoric acid (85%). The EP experiment was conducted by a direct current (dc) power supply. Ten concentrations of Vitamin C (ascorbic acid) with 8M H₃PO₄ are used, ranging from 1 × 10⁻³ to 10 × 10⁻⁶ M. Vitamin C (ascorbic acid) were Fluka products of pure quality (>97%). The polishing potentials generally reach a steady-state value after the current is applied for 200 s. After the EP treatment (under various conditions), the test sheet was rinsed in deionized water with a measured resistivity > 18 mΩ. The scanning electron microscope images were taken using (JEOL, JSM-5300, scanning microscope, OXFORD instrument). For this purpose the steel sheet anode was (1 × 1 cm). The average surface roughness factor (Ra) was measured at two points near the centers of the test sheet with an area of 75 × 75 μm² by an atomic force microscope (AP-0100 AUTOPROBE CP-Research, THERMOMICROSCOBES). The resolution is 256 × 256 lines, scan rate is 1 Hz and the AFM images were analyzed using proscan 1.8 software while the software used for image processing is IP2.1 A Shimadzu UV-3101 PC Spectrophotometer (UV-VIS-NIR) Scanning spectrophotometer was used to obtain reflection spectra of specimens in the range of 300 to 1500 nm.

The structure of Vitamin C (ascorbic acid) is given below:

```
\begin{align*}
\text{HO} & \quad \text{HO} \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{OH} & \quad \text{OH}
\end{align*}
```
RESULTS AND DISCUSSION

Different regions of electropolishing polarization curve

A typical polarization curve for an electropolishing system looks like Figure 1. Three major regions can be identified on the curve: etching, polishing and gas evolution regions. The etching region is characterized by an exponential increase in current until a certain voltage (Frankel, 2010).

It has been reported that sites such as grain boundaries and defects have different standard reversible potential than the metal surface and thus have a different value of overpotential, $\eta$, at a given overall applied potential, resulting in a different dissolution current (Bard and Faulkner, 2001). This results in crystallographic etching rather than polishing. The rate of transport of the anions to the surface also increases with voltage in the etching region. As further increase in voltage leads to a competition between the thickening viscous film and the increasing transport rate of anions to the surface. It becomes increasingly difficult for the anions to reach the surface because of the thickening viscous layer (Palmieri, 2003).

At plateau, the diffusion layer establishes a suitable thickness and further increase in voltage does not result in any increase in current. The current peak before the current density plateau is also explained on the basis of super-saturation of the contain electrolyte below the gas bubble resulting in etching. Depending on the system, the dissolution rate in the occluded area may be higher or lower than the remaining salt forming in the case of the salt film mechanism of Electropolishing. The film then equilibrates to the saturation level, resulting in a drop of the current density in the limiting current density value (Frankel, 2010).

The plateau region and the best electropolishing conditions are found in this region. The plateau is formed because of mass transport control. Increase in potential above plateau region results in oxygen evolution on the metal surface along with the metal dissolution. Electropolishing in this voltage regime result in the surface being rougher because oxygen bubbles formed may attach to the surface and cause occlusion of the surface at certain locations resulting in differing dissolution rates (Jacquet, 1935). The occluded area may be higher or lower surface. Pitting results if the rate is higher and a bump is formed if the rate is lower. In either case, a rough surface results if electropolishing is attempted in this potential region. It has also been reported that polishing can take place at potentials way above the plateau region. Palmieri et al. (2003) states that polishing occurs in this region because the rate of oxygen generation is so fast that oxygen bubbles leave the surface as soon as they are formed and hence do not get a chance to occlude the surface and cause pitting (Palmieri, 2003).

Electropolishing of steel in H$_3$PO$_4$ electrolyte with Vitamin C added

The anodic polarization curves for the steel anode that were electropolished in 8M H$_3$PO$_4$ electrolytes with the addition of Vitamin C of different concentrations are
shown in Figure 1. Clearly, a limiting current plateau could be found in each anodic polarization curve. An obvious decrease in the limiting current was detected when Vitamin C was added (Table 1). This suggests that the anodic polarization behavior of steel is very insightful to small concentrations of Vitamin C. If \( I_{L}^{\text{blank}} \) is the limiting current in absence of Vitamin C and \( I_{L}^{\text{Vitamin C}} \) is the presence of Vitamin C, then IE % can be calculated from Equation 1:

\[
IE\% = \frac{I_{L}^{\text{blank}} - I_{L}^{\text{Vitamin C}}}{I_{L}^{\text{blank}}} \times 100
\]

Vitamin C molecules may then combine with Fe\(^{2+}\) ions on the metal surface, forming metal-Vitamin C complexes. The resulting complex could either inhibit or catalyzed further metal dissolution, depending on its solubility (Okafor et al., 2008). From the results obtained in this present investigation, it follows that Vitamin C forms soluble complexes with the metal ions which retard the dissolution reaction.

Vitamin C has polycentric adsorption sites (including various O atoms). These characteristics would afford the compounds the abilities to adsorb on the metal/solution interface via, the electrostatic attraction between the charged metal and the charged inhibitor molecules, dipole-type interaction between unshared electron pairs in the compounds with the metal, \( \pi \) electrons-interaction with the metal, and a combination of all of the above (Abdel-Gaber et al., 2006; Schweinsberg et al., 1988).

The adsorption on the surface of the metal creates a barrier for mass and charge transfer leading to a decrease in the interaction between metal and acid environment. As a result, the dissolution rate of the metal is decreased. Vitamin C is heterocyclics in nature and contains O atoms in their structures. From the results of the dissolution process. It could be seen that the ascorbic acids have some inhibiting ability which is probable due to the adsorption of the heterocyclics on the surface of the metal (Okafor et al., 2013).

### Temperature effect

Potentiodynamic measurements were performed in the temperature range from 20 to 50°C in the absence and presence of different concentration of Vitamin C and the inhibition efficiencies was calculated and the relation between temperature and inhibition efficiencies was depicted in Figure 2. Inspection of Figure 2 reveals that, at lower concentration of Vitamin C as the temperature increase (20 to 40°C) an increase in the inhibition efficiencies (IE%) were clear, but at 50°C inhibition efficiencies (IE%) decreases due to desorption, at high concentration of Vitamin C as the temperature increase (20 to 40°C) a decrease in the inhibition efficiencies (IE%) were clear, but at 50°C inhibition efficiencies (IE%) increases.

### Activated parameters for the dissolution process

It was generally accepted that organic molecules inhibit the dissolution process by adsorption at the metal–solution interface and that the adsorption depends on the molecule's chemical composition, the temperature and the electrochemical potential of the metal/solution interface. Activated parameters for dissolution process play an important role in understanding the inhibitory mechanism, that is, in defining the spontaneity of the dissolution of the metal to dissolution products that can be formed in the environment to which the metal was exposed (Osman et al., 2003).

The dependence of the dissolution rate on temperature was expressed by the Arrhenius equation.

<table>
<thead>
<tr>
<th>Vitamin C Conc. (mol/l)</th>
<th>20°C</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
<th>Activated parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(I_{L}(A))</td>
<td>IE %</td>
<td>(I_{L}(A))</td>
<td>IE %</td>
<td>(I_{L}(A))</td>
</tr>
<tr>
<td>0.00</td>
<td>0.461</td>
<td>-</td>
<td>0.505</td>
<td>-</td>
<td>0.562</td>
</tr>
<tr>
<td>1.0E-05</td>
<td>0.432</td>
<td>6.29</td>
<td>0.461</td>
<td>8.71</td>
<td>0.502</td>
</tr>
<tr>
<td>2.0E-05</td>
<td>0.395</td>
<td>14.31</td>
<td>0.429</td>
<td>15.04</td>
<td>0.461</td>
</tr>
<tr>
<td>3.0E-05</td>
<td>0.365</td>
<td>20.82</td>
<td>0.392</td>
<td>22.38</td>
<td>0.431</td>
</tr>
<tr>
<td>4.0E-05</td>
<td>0.306</td>
<td>35.62</td>
<td>0.373</td>
<td>26.14</td>
<td>0.401</td>
</tr>
<tr>
<td>5.0E-05</td>
<td>0.282</td>
<td>38.83</td>
<td>0.342</td>
<td>32.28</td>
<td>0.381</td>
</tr>
<tr>
<td>6.0E-05</td>
<td>0.261</td>
<td>43.38</td>
<td>0.311</td>
<td>38.42</td>
<td>0.361</td>
</tr>
<tr>
<td>7.0E-05</td>
<td>0.24</td>
<td>47.94</td>
<td>0.291</td>
<td>42.38</td>
<td>0.342</td>
</tr>
<tr>
<td>8.0E-05</td>
<td>0.22</td>
<td>52.28</td>
<td>0.271</td>
<td>46.34</td>
<td>0.323</td>
</tr>
<tr>
<td>9.0E-05</td>
<td>0.201</td>
<td>56.4</td>
<td>0.253</td>
<td>49.9</td>
<td>0.29</td>
</tr>
<tr>
<td>10.0E-05</td>
<td>0.172</td>
<td>62.69</td>
<td>0.222</td>
<td>56.04</td>
<td>0.261</td>
</tr>
</tbody>
</table>
Figure 2. Variation of inhibition efficiency with Vitamin C concentration at different temperatures.

Figure 3. The Arrhenius plot of the dissolution process recorded for steel plate in 8M $\text{H}_3\text{PO}_4$ containing different concentrations of Vitamins C.

In $\ln I_L = \frac{-E_a}{RT} + \ln A$, where $A$ is the pre-exponential factor, which reflects the adsorption capacity of additives on the metal surface, $E_a$ is the activation energy of the metal dissolution reaction, $R$ is the gas constant and $T$ is the temperature.

Figure 3 shows the Arrhenius plots for the dissolution of
steel with and without Vitamin C. The results give rise to satisfactory straight lines with slopes of \((-E_a/R)\). From the results, we can draw a conclusion that the Ea in the presence of Vitamin C is lower than that in the absence of Vitamin C. Many researchers (Gomma, 1998; Ammar and el-Khorafi, 1973; Omar and Mokhtar, 2011; Avci, 2008) also reported the activation energy in the presence of additive molecules was lower than in the absence of them, where it was attributed to the chemical nature of interaction between additive molecules and the steel surface. Ammar and el-Khorafi (1973) proposed the lowering of activation energy by considering the kinetics of the dissolution process being diffusion controlled. Additionally, in the literature, the lower activation energy value of dissolution process in the presence of additive molecules (rather than the absence of additive molecules) also was attributed to its chemisorption, while it was found to be opposite in the case with physical adsorption (Omar and Mokhtar, 2011; Avci, 2008). In our case, the values of Ea were lower than that of free solution in the presence of Vitamin C, indicating that the chemisorption tendency is predominant in the presence of Vitamin C (Li et al., 2012). These results will be confirmed by the pre-exponential factor in the Arrhenius equation (A), for heterogeneous reaction is related to the number of active centers where the adsorbed additive molecules block an essential part of the active site, that is, those with the lowest Ea value, on the metal surface. On the other hand, these active centers have different energies, if energetic surface heterogeneity is assumed. There are two possibilities: in the first case \((E_{a, additives} > E_{a, free acid})\) where the values of A in case of additives are greater than that of blank. The additive molecules are adsorbed on the most active adsorption sites (having the lowest energy) and the dissolution process takes place predominantly in the active sites of higher energy. In the second case \((E_{a, additives} < E_{a, free acid})\) which observed in Vitamin C, the values of A in the presence of Vitamin C lower than in 8 M \(H_3PO_4\), that is, a smaller number of the more active sites remain uncovered which take part in the dissolution process (Amin et al., 2011).

This phenomenon is normally observed when the adsorbed molecules shield several sites on the electrode surface. The adsorbed additive molecules shield both the active and less active sites on the metal surface. Thus, some active sites (of lower Ea) are left, and they determine the value of the apparent activation energy of the dissolution process (Amin et al., 2011).

**Surface analysis**

Surface analysis includes three techniques:

i. Scanning electron microscope (SEM),
ii. Atomic force microscope (AFM),
iii. Reflectance.

**SEM analysis**

The surface of morphology before and after EP in the absence of additives and in the presence of different concentrations of Vitamin C was shown in Figure 4a-f. Raw sample (Figure 4a) looked uneven and appeared to have potholes. A large number of pits with large size and high depth distributed over the surface are seen. However, after EP in 8M \(H_3PO_4\), only a slight difference was observed more than raw material, where grain boundaries and the number of bits are still observed. The specimen surface was smooth to some extent, where levelling and brightening occur and some deep cavities were filled up (Figure 4b).

Figure 4c and d represent the SEM image of steel in the presence of \(2 \times 10^{-5}\) and \(5 \times 10^{-5}\) M Vitamin C. It shows a completely uniform, smooth and bright surface. Grain boundaries are completely diminished. The well polished surface may be due to increase in the adsorption ability of Vitamin C molecules, leading to filling up of all deep cavities.

By increasing Vitamin C to \(7 \times 10^{-5}\) (Figure 4e) M and \(10 \times 10^{-5}\) M (Figure 4f), smoothness and brightness are observed by visual observation. However, the SEM micrograph shows uniformity decreases where the surface appears not flat to some extent.

This may be explained as a result of the change of adsorption behavior of Vitamin C molecules on the surface of steel. At lower concentration \((2 \times 10^{-5}\) M, Figure 4c) and moderate concentration \((2 \times 10^{-5}\) M, Figure 4d) of Vitamin C, there is a compact surface coverage by Vitamin C particles including peaks and valleys which lead to uniform surface leveling. However, at higher concentration, the adsorbed layer became loose, where Vitamin C tends to repel each other, so we may conclude that the molecules of Vitamin C released from peaks which lead to localized difference in the dissolution rate of steel and lead to formation of small protrusions.

According to the results obtained, the addition of Vitamin C to the electrolytic solution improved the level of brightness and smoothness of the surface, the interpretation of that phenomenon may be attributed to:

i. Hydroxyl groups reduce the hydrogen embrittlement at the cathode surface,
ii. High viscosity reduces the electric conductivity and the aggressive attack of ions towards steel electrode,
iii. High densities of OH– groups reduce the random anodic dissolution of steel,
iv. Hydroxyl groups with negative charges reduce the evolution of oxygen adjacent to the surface of steel during EP treatment which may cause some defects and pitting over the surface,
v. Vitamin C containing high density of OH– groups increases the viscosity of the electrolytic solution, giving the advantage to retard the aggressive attack of ions and
the high dissolution of the working electrode (Awad et al., 2010).

**Atomic force microscope (AFM)**

Surface topography and roughness were characterized by AFM measurements. In order to highlight the effect of Vitamin C concentration on electropolishing, topography of a polished specimen is also compared. The two-dimensional AFM images of steel surface before and after EP without and with Vitamin C are shown Figure 5a-e. Figure 5(a) shows that the raw steel sample looked uneven and appeared to have potholes with a random hill like structure (Ra = 236.7 nm). The nonuniformity and non homogeneity is the general appearance of the specimen while after EP in 8M H$_3$PO$_4$, the surface becomes more flat and closely to some extent where the surface roughness decreases to 209.23 nm. It can be seen from Figure 5c and d that the micrograph of steel surface after electropolished in 8M H$_3$PO$_4$ containing $2 \times 10^{-5}$ M and $5 \times 10^{-5}$ M Vitamin C shows the main characteristic of uniform polishing. Steel surface appears flat, compact and homogenous. Random hills structure disappeared and replaced with uniform surface. On the other hand, Ra was decreased from 236.7 to 155 and
140 nm after addition $2 \times 10^{-5}$ M and $5 \times 10^{-5}$ M Vitamin C, respectively. This result suggests that Vitamin C molecules may adsorb on the sharp peaks and decrease the dissolution rate at peaks, leading to uniform dissolution rates between peaks and valleys and a brighter, cleaner appearance too. The shielding film of Vitamin C molecules is compact enough to extend its coverage on the whole surface so that the species will dissolve uniformly from the anode surface and a very smooth surface on the micrometer scale is obtained.

While in the presence of $10 \times 10^{-5}$ M Vitamin C, the AFM analysis revealed the non uniform, non homogenous surface, irregular random hill return to appear, potholes are represented in surface and additional roughening (Ra = 169.5 nm) as compared to the values obtained in the presence of lower concentration of Vitamin C. This behavior can be attributed to great molecular interaction between Vitamin C and the microstructure of the shielding film became loose. Hence, the difference in dissolution rates between shielded and less-shielded portions becomes obvious, resulting in a rough surface. From Table 2, it is clear that, the peak-valley ratio (R P-V) confirmed Ra, roughness values which have the same trend.

**Reflectance**

The UV-VIS-NIR Spectra of untreated specimen, the specimen that electropolished in 8M H$_3$PO$_4$ and the specimen that electropolished in 8M H$_3$PO$_4$ containing $2 \times 10^{-5}$, $5 \times 10^{-5}$, $10 \times 10^{-5}$ M Vitamin C (Figure 6). It is seen that the reflectance of electropolished specimens is affected by concentration of Vitamin C. It is observed that, by increasing Vitamin C concentration, the reflectance of the specimen will be enhanced and
Table 2. Measured roughness (Ra), Rq (RMS), Peak - valley ratio of steel samples.

<table>
<thead>
<tr>
<th>EP conditions</th>
<th>Peak - valley ratio (μm)</th>
<th>Ra (nm)</th>
<th>Rq (RMS) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before electropolishing</td>
<td>2.115</td>
<td>236.7</td>
<td>271.9</td>
</tr>
<tr>
<td>After electropolishing without additives</td>
<td>1.99</td>
<td>209.0</td>
<td>269.8</td>
</tr>
<tr>
<td>After EP + $2 \times 10^{-5}$ M Vitamin C</td>
<td>1.25</td>
<td>155.0</td>
<td>193.4</td>
</tr>
<tr>
<td>After EP + $5 \times 10^{-5}$ M Vitamin C</td>
<td>1.15</td>
<td>140.0</td>
<td>172.8</td>
</tr>
<tr>
<td>After EP + $10 \times 10^{-5}$ M Vitamin C</td>
<td>1.33</td>
<td>169.5</td>
<td>214.6</td>
</tr>
</tbody>
</table>

approached its maximum value in the presence of, $5 \times 10^{-5}$ M Vitamin C. When Vitamin C concentration exceed to $10 \times 10^{-5}$ M, the reflectance value decreases, which confirmed the result obtained from SEM images and roughness value. It is clear that Vitamin C is important for their effect on the formation of insulating layer on the anode. In 8M H$_3$PO$_4$ (blank), the thickness of insulating layer is low; so, the smoothness and brightness of the surface is very low even in comparison with the raw unpolished specimen. But in the presence of Vitamin C, the formation rate of the insulating layer and thickness is high and appreciate enough for producing a high reflectance for metal while at high concentration of Vitamin C ($10 \times 10^{-5}$ M), the faster formation of the insulating layer lead to deformation of the insulating layer and non uniform dissolution, consequently producing a rough surface and decrease the reflectance.

From the result of the surface morphology study (SEM, UV-VIS-NIR Spectra and AFM), the optimized parameters for electropolishing of steel in 8M H$_3$PO$_4$ in presence of Vitamin C. We can conclude that the optimum condition at 20°C is addition of low and moderate concentration of Vitamin C.

**Conclusion**

i. The enhancement of the surface morphology and topography was achieved by the addition of Vitamin C to the electrolytic solution,

ii. Improvement produced in EP by the studied Vitamin C was due to the adsorption of such molecules on the anode surface,

iii. According to SEM, UV-VIS-NIR Spectra and AFM, addition of lower and moderate concentration of Vitamin C to the electrolytic solution was highly effective to enhance surface quality,

iv. Vitamin C acts as a good inhibitor for the dissolution of steel in 8.0M H$_3$PO$_4$. The inhibition efficiency values increase with the Vitamin C concentration increase.
Conflict of Interest

The authors have not declared any conflict of interest.

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