Adsorption and corrosion inhibition characteristics of two medicinal molecules

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ABSTRACT

The corrosion inhibition characteristics of two medicinal molecules phenylalanine and rutin on mild steel in 1.0M Hydrochloric acid were evaluated using gravimetric method. Corrosion inhibition efficiency of 83.78 and 90.40% was obtained respectively after seven days. However, phenylalanine showed weak accumulative higher corrosion inhibition efficiency. The presence of both molecules in the corrosive environment reduced the corrosion rate constant and increased the material half-life. Thermodynamic data calculated suggests a spontaneous adsorption of the molecules on the mild steel's surface.

INTRODUCTION

The challenge posed by metallic corrosion is as old as civilization. There have been several approaches to corrosion mitigation. However, some of these approaches are deleterious to humans and the environment. Hence the quest for convenient, safe, cheap and sustainable corrosion mitigation measures are of importance. The injection of corrosion inhibitors into corrosive environment is most suited for certain industrial process environments as well as in the formulation of self-healing surface coatings. While selecting corrosion inhibitor for specific corrosive environments, convenience as well the above novel objectives should be considered. The application of corrosion inhibitor to an industrial process should not necessarily cause process disruption because the mechanism of inhibition is such that it can function side by side with some of the processes (Nyongbela and Johanssen, 2014; McNealy, et al., 2009). This is so mostly because corrosion and corrosion inhibition are both surface phenomenon.

Corrosion inhibitors function either by adsorption on the metallic surface, (thereby blocking the corrosion active sites itself or with its reaction product/s); by altering the corrosive environment to be less corrosive; and by inhibiting one or more steps in the corrosion reaction mechanism (Bockris and Swinkels, 1964; Oguzie, 2004; Oguzie, 2005). There are different corrosion inhibition behaviours and efficiencies for different corrosion inhibitors. These have been attributed to their different chemical structures and corrosive environments with consequent different corrosion inhibition reaction mechanism (Popova et al., 2003; Raja et al., 2008; Abdel-Gaber et al., 2008). It therefore follows that different corrosion inhibitors are suited for different purposes and application environments (Bill et al., 2004; Chauhan, and Gunasekaran, 2007). Hence,
there is need to compare the corrosion inhibition characteristics and efficiencies of different corrosion inhibitors.

Literature reports that corrosion inhibitors adsorption to a metallic substrate is usually through their structural polar ends (Durnie, 1999; Kern, and Landolt, 2001, Hamza et al., 2013). It has been reported that most pharmaceutical compounds exhibit similar chemical characteristics as some corrosion inhibitors because of similarities in their chemical structures (Karthik, and Sundaravadivelu, 2013). This paper reports a comparative study between two pharma-active compounds:-Phenylalanine (PH-A) and Rutin ; 2-(3,4-dihydroxy)-3-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranosyloxy]-4H-chromen-4-one (RT-N). Both compounds are constituted with aromatic ring with hetero-atoms on which there is available lone pair of electrons. These enhance the polarity of the compounds and strengthen its bond with vacant valence orbital on the metallic surface atoms.

The compounds Phenylalanine (PH-A) and Rutin (RT-N) were extracted from Pigeon pea and orange mesocarp respectively in the department of Pharmacy University of Port Harcourt.

Gravimetric experiment

The weighed test coupons were fully immersed in six 250 ml beakers, each containing about 200 ml 1 M Hydrochloric acid (HCl) with different serial concentration of test additives, $1.0 \times 10^{-2}$ to $1.0 \times 10^{-6}$ M (PH-A and RT-N). Glass hooks were used to suspend the pre-polished coupons into the beaker. The corrosion reaction temperature was maintained using thermo stated water baths at 303, 313 and 333 K for each additive in each set of experiment. This test method has been previously reported (Khalid and Sisodia, 2011; Sangeetha et al., 2011.). The coupons for 303 K experiment were retrieved after 24 hours and 4 hours for the 313 and 333 K experiments, washed with the aid of brittle brush inside water to remove corrosion products, degreased in absolute ethanol, dried in acetone and kept to air dry to a constant weight. The experiments were conducted in triplicates to ensure reproducibility. The mean weight between the initial weight and weight after immersion (final weight) was recorded as the weight loss for each test. The experiments were allowed to run between seven days to four hours for 303 to 333 K respectively except for instances the corrosion cell fluid dried up.

RESULTS AND DISCUSSION

Weight loss, corrosion rate and corrosion inhibition efficiency

The weight loss pattern of mild steel in HCl environment was studied with and without various concentrations of PH-A and RT-N. The results are presented in Figures 1 to 6. Figures 1 and 2 shows the variation of weight loss with time at 303 K for the corrosion of Mild steel in 1 M HCl environment with and without various concentrations of phenylalanine and rutin. Both figures showed an increase in the rate of weight loss of mild steel in HCl with time. However the presence of PH-A and RT-N reduced the rate of weight loss with time. The rate of weight loss is inversely related to increase in concentration of the additives. This can be attributed to the corrosion inhibition potentials of the additives (Oguzie, 2004; Obot et al., 2012). Rutin reduced the rate of weight loss of mild steel in hydrochloric acid more than Phenylalanine at 0.01 M concentration. This may be attributed to the bigger molecular size with more adsorption sites of Rutin molecules compared to Phenylalanine, thereby, blocking more corrosion active sites on mild steel surface.
**Fig. 1:** Variation of weight loss with time at 303 K for the corrosion of Mild steel in 1.0 M HCl environment with and without various concentrations of Phenylalanine.

**Fig. 2:** Variation of weight loss with time at 303 K for the corrosion of Mild steel in 1.0 M HCl environment with and without various concentrations of Rutin.

**Fig. 3:** Variation of weight loss with time at 313 K for the corrosion of Mild steel in 1.0 M HCl environment with and without various concentrations of Phenylalanine.

**Fig. 4:** Variation of weight loss with time at 313 K for the corrosion of Mild steel in 1 M HCl environment with and without various concentrations of Rutin.

**Fig. 5:** Variation of weight loss with time at 333 K for the corrosion of Mild steel in 1.0 M HCl environment with and without various concentrations of Phenylalanine.

**Fig. 6:** Variation of weight loss with time at 333 K for the corrosion of Mild steel in 1.0 M HCl environment with and without various concentrations of Rutin.
Fig. 7: Variation of corrosion inhibition efficiency with time at 303 K for the corrosion of Mild steel in 1 M HCl environment with and without various concentrations of Phenylalanine.

Fig. 8: Variation of corrosion inhibition efficiency with time at 303 K for the corrosion of Mild steel in 1 M HCl environment with and without various concentrations of Rutin.

Fig. 9: Variation of corrosion inhibition efficiency with time at 313 K for the corrosion of Mild steel in 1 M HCl environment with and without various concentrations of Phenylalanine.

Fig. 10: Variation of corrosion inhibition efficiency with time at 313 K for the corrosion of Mild steel in 1.0 M HCl environment with and without various concentrations of Phenylalanine.

Fig. 11: Variation of corrosion inhibition efficiency with time at 333 K for the corrosion of Mild steel in 1.0 M HCl environment with and without various concentrations of Phenylalanine.

Fig. 12: Variation of corrosion inhibition efficiency with time at 333 K for the corrosion of Mild steel in 1 M HCl environment with and without various concentrations of Rutin.
Fig. 13: Comparison of corrosion inhibition efficiency of Phenylalanine and Rutin at various concentrations for the corrosion of mild steel in 1.0 M HCl environment.

Fig. 14: Variation of corrosion rate (mm/Yr) of PH-A with time at 303 K for the corrosion of Mild steel in 1 M HCl environment.

Fig. 15: Variation of corrosion rate (mm/Yr) of RT-N with time at 303 K for the corrosion of Mild steel in 1 M HCl environment.

Fig. 16: Variation of corrosion rate (mm/Yr) of PH-A with time at 313 K for the corrosion of Mild steel in 1 M HCl environment.

Fig. 17: Variation of corrosion rate (mm/Yr) of RT-N with time at 313 K for the corrosion of Mild steel in 1 M HCl environment.

Fig. 18: Variation of corrosion rate (mm/Yr) of PH-A with time at 333 K for the corrosion of Mild steel in 1 M HCl environment.
Figures 3 to 6 shows the variations of weight loss with time at 313 to 333 K for the corrosion of Mild steel in 1.0 M HCl environment with and without various concentrations of Phenylalanine and Rutin. The pattern of weight loss was similar to the pattern at 303 K. However there is a direct relationship between weight loss and increase in temperature. These patterns of weight loss have also been reported by several researchers (Lebrini et al., 2013; Ashassi-Sorkhabi, and Seifzadehi., 2006; Obot et al., 2012).

Worthy of note is that the experimental variations in concentration of the additives did not result in appreciable variations in weight loss at lower temperature. This further emphasizes the huge effect of temperature on the corrosion mechanism.

The corrosion inhibition efficiency of PH-A and RT-N were calculated from the relation shown in Eq. 1.

$$\text{IE}\% = \left(1 - \frac{\text{CR}_{\text{inh}}}{\text{CR}_{\text{blank}}} \right) \times 100$$  

(1)

Where, CR_{inh} and CR_{blank} represent either the weight loss or corrosion rates in inhibited and uninhibited solutions, respectively.

Table 1: Elemental composition of test mild steel coupon

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>S</th>
<th>P</th>
<th>Si</th>
<th>Mn</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>0.26</td>
<td>0.028</td>
<td>0.006</td>
<td>0.23</td>
<td>1.51</td>
<td>0.02</td>
<td>Balance</td>
</tr>
<tr>
<td>(wt %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Calculated values of Gibbs free energy of adsorption and average surface coverage for corrosion inhibition of mild steel by CAC and CYC in pipeline Hydrochloric acid

<table>
<thead>
<tr>
<th>Conc. (g/L)</th>
<th>$\Delta G_{ad}$ (PH-A)</th>
<th>$\Delta G_{ad}$ (RUT-N)</th>
<th>$\theta$ (PH-A)</th>
<th>$\theta$ (RUT-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000001</td>
<td>-45.64</td>
<td>-42.73</td>
<td>0.65</td>
<td>0.50</td>
</tr>
<tr>
<td>0.00001</td>
<td>-40.06</td>
<td>-39.35</td>
<td>0.67</td>
<td>0.51</td>
</tr>
<tr>
<td>0.001</td>
<td>-34.44</td>
<td>-34.07</td>
<td>0.69</td>
<td>0.52</td>
</tr>
<tr>
<td>0.01</td>
<td>-29.57</td>
<td>-28.83</td>
<td>0.70</td>
<td>0.55</td>
</tr>
<tr>
<td>0.1</td>
<td>-45.64</td>
<td>-23.63</td>
<td>0.72</td>
<td>0.62</td>
</tr>
</tbody>
</table>

The results obtained were plotted against time and concentration and presented in Figures 7 to 13. Figures 7 and 8 presents the variation of corrosion inhibition efficiency with time at 303 K for the corrosion of Mild steel in 1.0 M HCl environment with and without various concentrations of Phenylalanine and Rutin. The plots show an increase in corrosion inhibition efficiency with time and concentration. This behaviour has been attributed to the ability of an inhibitor to inhibit the corrosion of metal in a corrosive environment (Huang et al., 2013; Ita and Edem, 2000, Ita et al., 1994). Figures 9 to 12 shows the variation of corrosion inhibition efficiency with time at 313 K to 333 K for the corrosion of Mild steel in 1.0 M HCl environment with and without various concentrations of Phenylalanine and Rutin. The results show a decrease in the corrosion inhibition efficiency with increase in temperature. It has been proposed that most organic corrosion inhibitors inhibit corrosion by the adsorption of their molecules on the metal surface. However, depending on the mechanism of adsorption some inhibitors get desorbed with rise in temperature. Our research group has earlier explained that optimal corrosion inhibition efficiency is attained at optimal interaction between corrosion inhibitor molecules and atoms at metallic surface (Ngobiri et al., 2015). Figure 13 shows a comparison of corrosion inhibition efficiency of various concentrations Phenylalanine and Rutin for the corrosion of mild steel in 1.0 M HCl environment. Both additives showed an increase in corrosion inhibition efficiency with increase in additive concentration. Rutin showed higher corrosion inhibition efficiency of 90.40 % at 0.01 M after day 7, than Phenylalanine which showed an efficiency of 83.78 % under same condition. Phenylalanine however comparatively showed accumulative higher corrosion inhibition efficiency because Rutin initially exhibited lower corrosion inhibition efficiencies. The incidence where a heavier molecule takes time to attain higher inhibition efficiency has earlier been attributed to stearic hindrance (Ngobiri et al., 2015).

The corrosion rate (CR) for the corrosion of mild steel in acidic environment with various concentrations of PH-A and RT-N were calculated from the weight loss data using Equation 2 and the results obtained was plotted as a...
**Fig. 19:** Variation of corrosion rate (mm/Yr) of RT-N with time at 333 K for the corrosion of Mild steel in 1 M HCl environment.

**Fig. 20:** Comparison of corrosion rate constant at 303 K for PH-A and RT-N at various concentrations for the corrosion of mild steel in 1 M HCl environment.

**Fig. 21:** Comparison of corrosion rate constant at 313 K for PH-A and RT-N at various concentrations for the corrosion of mild steel in 1.0 M HCl environment.

**Fig. 22:** Comparison of corrosion rate constant at 333 K for PH-A and RT-N at various concentrations for the corrosion of mild steel in 1.0 M HCl environment.

**Fig. 23:** Comparison of material half-life of mild steel at 303 K for PH-A and RT-N at various concentrations for the corrosion of mild steel in 1.0 M HCl environment.

**Fig. 24:** Comparison of material half-life of mild steel at 313 K for PH-A and RT-N at various concentrations for the corrosion of mild steel in 1.0 M HCl environment.
function of time and additive concentration and presented in Figures 14 to 22.

\[ CR_{\text{mm per year}} = 87.6 \frac{\Delta w}{DAT} \]  

(2)

\( \Delta w \) is the weight loss, \( D \) the density of steel \((\text{g/cm}^3)\), \( A \) the area of the coupon in \((\text{cm}^2)\) and exposure time \((\text{h})\). Steel is predominantly iron, therefore the density of iron can be applied.

Figures 14 and 15 shows the variation of corrosion rate \((\text{mm/Yr})\) of Phenylalanine and Rutin with time at 303 K for the corrosion of mild steel in 1.0 M HCl environment. From the results the corrosion rate decreased generally with time and additive concentration. Figures 16 to 19 show the variation of corrosion rate \((\text{mm/Yr})\) of Phenylalanine and Rutin with time at 313 to 333 K for the corrosion of Mild steel in 1.0 M HCl environment. The decrease of corrosion rate with time was less pronounced with rise in temperature. This still emphasizes the significant effect of temperature on the corrosion and inhibition process. The corrosion rate varied directly with rise in corrosion reaction temperature. Rutin comparatively showed earlier higher corrosion rates with time. This may be attributed to the rate at which molecules settle and get adsorbed at the steel surface which is related to its molecular size and weight.

The corrosion rate constant \((K)\) and material half-life \((t_{1/2})\) for the corrosion of mild steel in Hydrochloric acid with and without various concentrations of PH-A and RUT-N were calculated from the weight loss data as follows:

\[ K = \frac{2.303}{t} \log \frac{w_i}{w_f} \]  

(3)

While the half-life \(t_{1/2}\) was calculated from \(K\):

\[ t_{1/2} = \frac{0.693}{k} \]  

(4)

Where, \(w_i\) and \(w_f\) are initial and final weight respectively. The plots of \(K\) versus concentration \(C\) (Figures 20 to 22) and \(t_{1/2}\) versus \(C\) (Figure 23 to 26) shows that \(K\) varied inversely with concentration of PH-A and RUT-N, while the material half-life varied directly with concentration. Therefore, the corrosion rate constant \(K\) is the inverse of the material half-life \((t_{1/2})\) (Ngobiri et al., 2013). The \(t_{1/2}\) of the mild steel in HCl was higher in the inhibited cells compared to the uninhibited cells and increased generally with increase in inhibitor concentration, while the corrosion rate constant was higher in the uninhibited cells compared to the inhibited cells and decreased generally with inhibitor concentration. This implies that the introduction of PH-A and RUT-N hinders the tendency of the steel specimen to undergo corrosion reaction in the acidic environment. This also confirms the corrosion inhibiting effect of the additives. The higher \(t_{1/2}\) of mild steel in HCl environment with PH-A comparatively could be related to its superior inhibition efficiency in the short term, while RUT-N gave the highest \(t_{1/2}\) in the long term. Therefore it is recommended for prolonged application more than PH-A.

**Adsorption**

Corrosion inhibitors have been reported to mitigate corrosion by adsorption on metallic substrate (Shanmugam et al., 2013; Abiola et al., 2004, Ebenso et al., 2004.). The mode of adsorption has helped corrosion expert to gain insight into mechanism of inhibition. The mode of adsorption is dependent on physio-chemical characteristics of the corrosion inhibitor, the corrosive environment and metallic substrate. The physio-chemical characteristics also determine the ability of the inhibitor molecules to achieve
higher surface coverage (θ) which consequently determines the corrosion inhibition efficiency. Hence the need to determine the inhibitor surface coverage and inhibitor mode of adsorption. The mode of inhibitor adsorption can be obtained more accurately with electrochemical impedance spectroscopy (EIS). However, if potentiometer for EIS studies is not available, adsorption isotherm is of value in mechanism elucidation. The graph of C/θ versus concentration C for both PH-A and RUT-N was approximately linear, confirming the fit of the adsorption pattern of the additives to the Langmuir adsorption isotherm. This suggests that both additives inhibited the corrosion of mild steel in acidic environment by adsorption on to the metallic surface as shown in Figure 26.

In this study two physio-chemical parameters surface coverage θ and Gibbs free energy of adsorption ΔG_{ads} were calculated using equations 5 and 6. The results obtained are presented in table 2.

\[
\theta = \frac{IE\%}{100} \tag{5}
\]

Where, IE% is the corrosion inhibition efficiency.

\[
\Delta G_{ads} = -2.303RT \ln \left( \frac{55.48}{Co(1-\theta)^n} \right) \tag{6}
\]

Where, Co is the concentration of inhibitor in the bulk of the solution; n is the size factor (9 for flat adsorption on the surface and 3 in the perpendicular direction to the surface). The negative values of ΔG_{ads} (Table 2) suggest spontaneous adsorption of PH-A and RUT-N molecules on the mild steel surface in hydrochloric acid. The higher negative values of ΔG_{ads} also suggest the nature of adsorption bond is more chemical than physical in character. (Atkins and Paula, 2002).

CONCLUSIONS

The corrosion of mild steel in hydrochloric acid was inhibited by Phenylalanine and rutin. Rutin inhibited the corrosion process better for long term, while phenylalanine inhibited corrosion better in the short term. The corrosion inhibition mechanism was preceded via a spontaneous adsorption process.

REFERENCES


Lebrini, M., Robert, F., Ross, C., 2013. Adsorption properties and inhibition of C$_{30}$ steel corrosion in hydrochloric


