Chemistry of
Metals and Alloys

Chem. Met. Alloys 7 (2014) 149-153
Ivan Franko National University of Lviv
www.chemetal-journal.org

Amodiaquine drug as a corrosion inhibitor for mild steel in 0.1M HCl solution

I.A. AKPAN[1]*, N.O. OFFIONG[1]

[1] *Corrosion and Materials Science Unit, Department of Chemistry, University of Uyo,*
P.M.B. 1017, Uyo, Akwa Ibom State, Nigeria
* *Corresponding author. E-mail: iaakpanchem2007@yahoo.com*

Received January 16, 2014; accepted December 24, 2014; available on-line September 1, 2015

The inhibition effect of an environmentally friendly and cost-effective drug, amodiaquine, on the corrosion of mild steel in an acidic medium was studied by the weight loss method at room temperature. The study revealed that the test drug has an inhibitory action on the corrosion of mild steel in the investigated medium. The inhibition efficiency was found to increase with increasing inhibitor concentration. Plots of the concentration of metal *versus* time indicate first-order kinetics for the inhibition process. It was also found that amodiaquine adsorbs according to a Langmuir's adsorption isotherm. Attempts were made to correlate the chemical structure and the inhibition mechanism.

Corrosion inhibitor / Mild steel / Amodiaquine drug / Weight loss method

1. Introduction

It is well known that a particular inhibitor, which ensures a very high efficiency for a particular metal in a specific medium, may not perform with the same efficiency for another metal in the same medium [1]. Therefore, efforts toward enhancing the resistance of metals constitute an on-going task [2].

Most corrosion inhibitors are very hazardous and expensive chemicals [3]. Recently, the attention of the researchers has been shifted to environmentally safe and cost-effective inhibitors, called "green inhibitors."

Several drugs are known to contain heteroatoms, π-electrons, rings and have high molecular weights, which all are indicators for good inhibitors. Some drugs have been proposed as alternative, eco-friendly, cost-effective corrosion inhibitors [4-10]

The main objective of the present work was to study the corrosion inhibition of mild steel in 0.1M HCl by amodiaquine drug, using the weight loss technique.

2. Experimental

Thus far, various techniques have been employed to monitor the corrosion of metals, *viz* the weight loss method, hydrogen evolution / gasometric methods, thermometric methods, theoretical and electrochemical methods, *etc.* [11-14]. The experimental model developed for this study was implemented using the weight loss method. The weight loss method of monitoring corrosion rate is useful because of its simple application and reliability.

2.1 Materials

The commercially available mild steel sheets (purity 98 %) of 0.10 cm thickness used in this study were obtained locally. The sheets were mechanically pressed and cut into 3 cm by 3 cm coupons with a small hole of about 5 mm diameter near the upper edge to help holding them with glass hooks. The coupons were polished and degreased with acetone, washed in double-distilled water and dried in a desiccator before use [15]. The corrosive medium used in this study was 0.1M HCl. It was prepared by appropriate dilution [16] of analytical grade HCl reagent with double-distilled water without further purification.

2.2 The inhibitor

The inhibitor used in this study was a drug with anti-malarial and anti-inflammatory activities, commonly called amodiaquine (AMQ). It is chemically designated as 4-[(7-chloroquinolin-4-yl)amino]-2-[(diethylamino)methyl]phenol. The molecular formula of amodiaquine is $C_{20}H_{22}ClN_3O$, with a molecular weight of 355.86 g/mol. Amodiaquine has the chemical structure shown in Fig. 1.

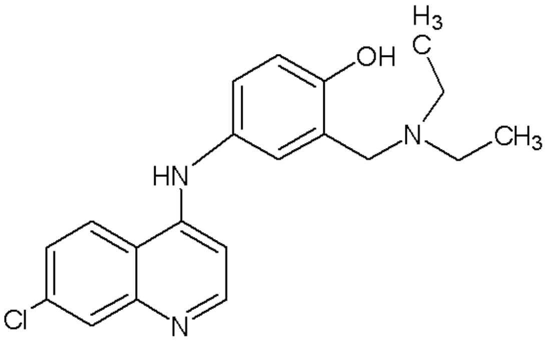

Fig. 1 Chemical structure of amodiaquine.

Tablets of amodiaquine were obtained from a local pharmacy and were used without further purification. Appropriate concentrations of the drug were prepared by dilution.

2.3 Weight loss measurements

In the weight loss experiments, five plastic containers were labeled from A to E, each containing 500 ml of HCl solution. The first beaker was reserved as blank, while each of the four remaining beakers contained the drug at different concentrations, all placed at room temperature (about 30°C). The metal coupons were immersed into the experimental solutions with the help of glass hooks and monitored daily (after 24 hours). The weights of the specimens were noted before immersion. After every immersion time of 24 hours, the specimens were removed, polished with emery paper, washed in double distilled water, degreased with acetone, dried in warm air, and re-weighed. From the initial and final weights of the specimens, the weight loss was calculated and the corrosion rate (in mp/y – millimeter penetration per year) was computed from the equation below [17]:

$$\text{Corrosion rate, } CR = \frac{534W}{DAt}, \qquad (1)$$

where W is the weight loss (g), D is the density of the specimen (7.85 g/cm^3), A is the surface area of the specimen (cm^2) and t is the immersion time (days).

The efficiency of the inhibitor was computed using the equation below [18]:

$$\text{Inhibition efficiency, \%} \quad IE = \frac{W_0 - W_1}{W_0} \times 100, \qquad (2)$$

where W_o is the weight loss without inhibitor and W_1 is the weight loss with inhibitor.

The degree of surface coverage (Θ) at different concentrations of the inhibitor was also computed from the weight loss measurements, using equation 3 [19]:

$$\theta = \frac{W_0 - W_1}{W_0}, \qquad (3)$$

where W_o is the weight loss without inhibitor and W_1 is the weight loss with inhibitor and

$$\frac{c}{\theta} = {}^{1}\!/_{\mathrm{k}} + C, \qquad (4)$$

where C is the concentration of the corrosion inhibitor, Θ is the degree of surface coverage and k is the adsorption equilibrium constant [20].

3. Results and discussion

3.1 Weight loss measurements

The acid corrosion of mild steel in the presence of different concentrations of amodiaquine drug as inhibitor was studied at room temperature by the weight loss method. The results obtained from the weight loss measurements are summarized in Table 1. The results indicate that introduction of amodiaquine into the corrosive medium caused a significant reduction in the corrosion rate of the steel. The corrosion inhibition efficiency increased, with increasing concentration of the drug. This may be due to larger surface coverage (Θ) by more inhibitor molecules.

The weight loss as a function of time (Fig. 2) shows that the weight loss increases with increasing time of exposure.

Table 1 Values of the inhibition efficiency, corrosion rate and surface coverage for corrosion of mild steel in 0.1M HCl with different concentrations of amodiaquine, obtained from weight loss measurements performed after 24 h.

Medium	Weight loss (g)	Inhibition efficiency (%)	Corrosion rate (mp/y)	Surface coverage
Blank (0.1M HCl)	0.28	–	0.0422	–
0.001M Amodiaquine	0.15	46.43	0.0226	0.4643
0.002M Amodiaquine	0.13	53.57	0.0200	0.5357
0.003M Amodiaquine	0.11	60.71	0.0166	0.6071
0.004M Amodiaquine	0.08	71.43	0.0121	0.7143

3.2 Kinetics of the corrosion inhibition process

Chemical kinetic treatment of the data was necessary in order to obtain information about the order of the reaction. If the concentration of the corroding metallic material is estimated in terms of weight loss per volume (g/l) of the corrodent, and later converted to molar concentration *via* a mass of metal-molar mass of iron relation, then the kinetics of the system may be deduced. Following the work of Sharma and Sharma [21], and as reported in our recent work [22], we assume that *a* mol/l is the initial concentration of the mild steel (Fe), and that after the time *t*, *x* mol/l of Fe has decomposed into corrosion products. Therefore, the remaining concentration of Fe at time *t* is *(a-x)* mol/l. If a plot of log(*a*-*x*), *i.e.* log[Fe] against *t* gives a straight line, then the reaction can be said to be a first-order reaction. Based on this, we calculated the concentration of reacted Fe from the weight loss measurements and obtained the graph shown in Fig. 3. The shape of the graph in Fig. 3 shows that the system under consideration follows first-order kinetics.

3.3 Adsorption isotherm

In corrosion inhibition studies, the action of the corrosion inhibitors is widely believed to include adsorption on the metal substrates. In order to find out the possible adsorption mode, the experimental data were tested against several adsorption isotherms. The degree of surface coverage (Θ) at different concentrations of the inhibitor was employed in this test.

Considering the Langmuir adsorption model, which is described by equation 4 [23,24], it was found that the experimental data plotted as C/Θ *versus* C

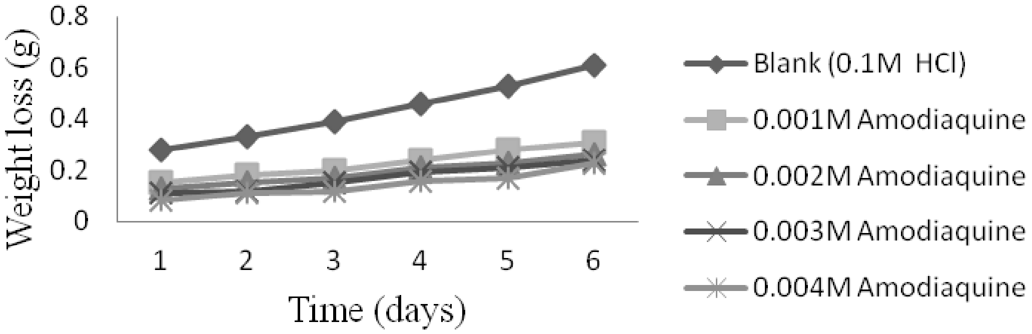

Fig. 2 Variation of weight loss with exposure time for mild steel corrosion in 0.1M HCl in the presence of different concentrations of amodiaquine.

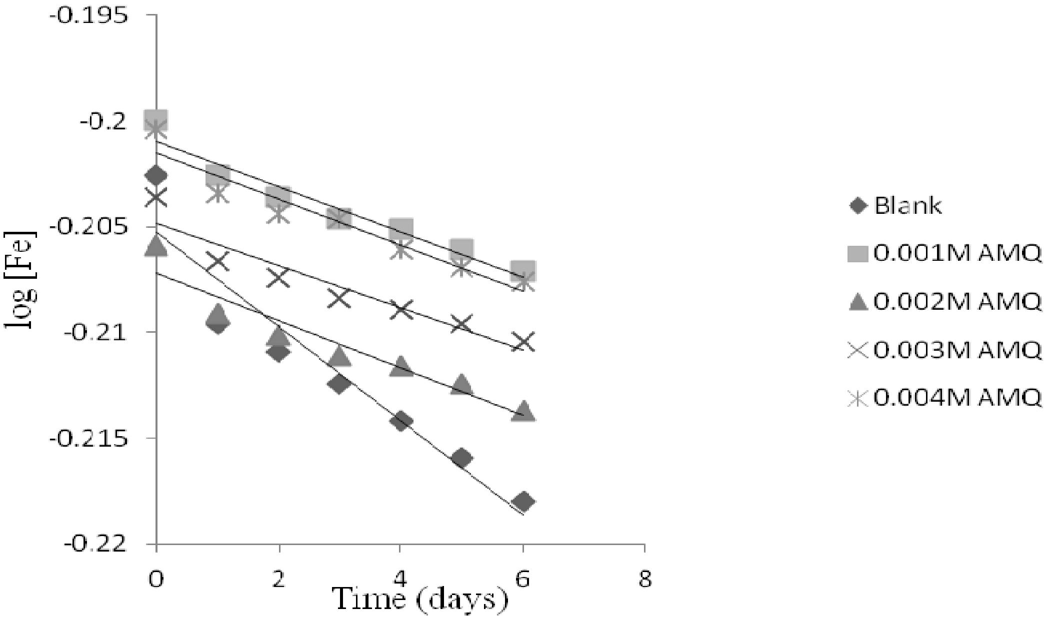

Fig. 3 Logarithm of the concentration of mild steel *versus* exposure time for mild steel corrosion in 0.1M HCl in the presence of different concentrations of amodiaquine.

could be fitted to a straight line and the coordinates of the Langmuir's adsorption isotherm are given in Fig. 4. This type of isotherm assumes that there is no strong interaction between the adsorbed molecules and the metal surface [25].

3.4 Proposed mechanism of action of amodiaquine as corrosion inhibitor

The adsorption of amodiaquine on mild steel can be attributed to the presence of polar groups containing nitrogen, oxygen and chlorine atoms. Possible adsorption centers include unshared electron pairs available on the heteroatoms, and π-electrons of the aromatic rings. The approximately homogenous distribution of nitrogen atoms throughout the structure of the molecule may aid in effective adsorption only if these are not protonated, since protonated nitrogen atoms would repel the positively charged metal surface. On the other hand, protonated nitrogen atoms may form a double layer with negatively charged chloride ions close to the metal surface, thereby hindering attacks by the oxonium ions. In addition to the interaction of the nitrogen atoms, the oxygen atoms may provide coordination with vacant *d*-orbitals of the metal atoms at the interface, by means of donor-acceptor interaction with electron pairs.

Conclusion

From the study of the inhibitory effect of an environmentally friendly and easily accessible drug, amodiaquine, on the corrosion of mild steel in 0.1M HCl by the weight loss method at room temperature, the following conclusions may be drawn:

1. Amodiaquine acts as a good inhibitor for mild steel in 0.1M HCl.
2. The inhibition efficiency increases with increasing inhibitor concentration.
3. The corrosion process and its inhibition follow first-order kinetics.
4. The adsorption process obeys a Langmuir's adsorption isotherm.

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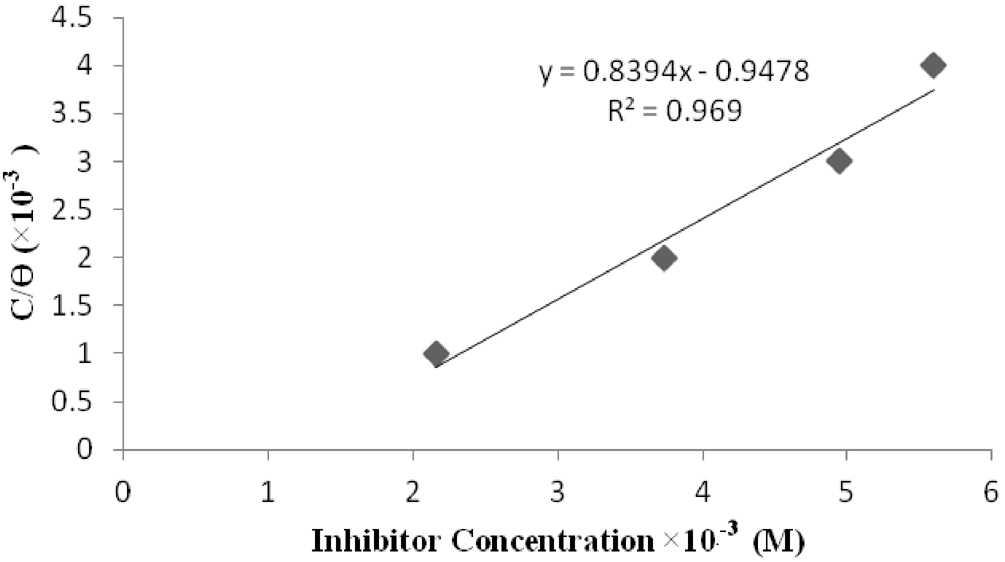

Fig. 4 Langmuir's adsorption isotherm for mild steel corrosion in 0.1M HCl containing amodiaquine as inhibitor.

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