



Mechanism Investigations of Corrosion Inhibition of NST-44 Mild Steel in 1M Hydrochloric Acid by Caffeine Strychnine and Quinine

M. Alagbe

Department of Metallurgical Engineering, Institute of Technology,
Kwara State Polytechnic, Ilorin, Nigeria
E-mail: alagbemic@yahoo.com

Abstract - Mechanism investigations of corrosion of NST-44 mild steel in 1M hydrochloric acid containing caffeine ($C_8H_{10}N_4O_2$), strychnine ($C_{22}H_{22}N_2O_2$) and quinine ($C_{20}H_{24}N_2O_2$) have been studied using gravimetric and polarization techniques. The inhibitive potential of the three inhibitors were evaluated based on a determination of the corrosion rates in the presence and absence of the inhibitors and effectiveness of the three inhibitors at different levels of concentration for room temperature. The results show that the three inhibitors provide adequate inhibition of corrosion at molar concentrations of 10-2M. It was observed that quinine, strychnine and caffeine, however showed considerable potentials with inhibition efficiencies of about 84.8%, 78.3% and 70.2% respectively in 1M hydrochloric acid for NST-44 mild steel. Anodic and cathodic polarization data revealed that these compounds act as mixed corrosion inhibitors by interfering with both anodic dissolution of mild steel and cathodic evolution of hydrogen. The surface coverage (θ) values obtained from the corrosion rates and polarization techniques are in good agreement. The results of this work are expected to improve the corrosion resistance of NST-44 mild steel as a constructional material for petroleum and chemical industries in Nigeria.

Keywords: acid, corrosion, inhibition efficiencies, polarization, steel, surface coverage.

1. Introduction

The study of the influence of organic compounds on the corrosion of metals has been subject to pronounced practical significance. Their inhibitive properties arise from their ability to be readily absorbed onto a metallic surface, reducing the chemical reactivity of the metal/solution interface. Nitrogen containing organic compounds can function in deoxygenated, acid environments as contain inhibitors and a variety of these organic compounds have been screened as metallic corrosion inhibitors (Alagbe, 1997 and Damaskin, 1971). Among the theories of corrosion inhibition proposed by some researchers, the absorption theory is most significant as it take into account the nature of the metal, surface heterogeneity, nature of the inhibitors, magnitude of the charge at the metal-solution interface, solution composition and the cathodic reduction during corrosion (Tuan and Xianming, 2009, Damaskini 1971, Alagbe et al, 2006 Loto and Mohamed, 2000 and Evans 1961). A considerable interaction between the inhibitor molecules and the electrode surface during corrosion has been realized (Fontana and Greene, 1978 John et al, 1978).

The present drive to encourage oil and gas production in Nigeria has led the companies utilize acidizing to stimulate oil wells. One of the impeding factors to achieving the laudable objectives of companies is the frequency with which the machineries or oil bearing shale breakdown due to the corrosion of the parts, resulting from the contact with the aqueous acids at highly diluted concentrations between 1 and 15% (Acidizing – Schlumberger, 2017, Acidizing – Halliburton, 2017, Acidizing – Investopedia, 2015 and Growcock and Frenier, 1984). In the present study, the corrosion of mild steel in hydrochloric acid and its inhibition efficiency by using nitrogen containing organic bases such as caffeine ($C_8H_{10}N_4O_2$),

strychnine (C₂H₂₂N₂O₂) and quinine (C₂₀H₂₄N₂O₂) are to be investigated. The corrosion inhibition of mild steel is followed by weight loss and polarization measurements. In addition, the mechanism of corrosion inhibition is reported. The retardation of corrosion attack of machine part will go a long way to increase the life span of the machines and processing equipment.

2. Materials and Method

Caffeine (C₈H₁₀N₄O₂), strychnine (C₂H₂₂N₂O₂) and quinine (C₂₀H₂₄N₂O₂) were selected for this study, stored differently and varying concentrations of these were prepared in 100ml of 1M hydrochloric acid solutions. The type NST-44 mild steel test specimens used in this work had a percent nominal composition of 0.15C, 0.22Si, 0.04S, 0.50Mn, 0.04P, 0.10Cr, 0.1Ni, 0.045Sn, 0.25Cu and 0.11N, the balance being Fe.

Weight loss test specimens were from the steel samples whose compositions are given above. The original cylindrical rods were cut into 120 short pieces having a cross section of 8 mm and a gauge length of 40mm and their surface were given similar surfaces finishing using the same grades of energy papers 240, 320, 400 and 600 grits for each sample. They were washed with distilled water, degreased in benzene and dried. Before weighing, the specimens were left in the desiccators for 2 days to allow the oxide film on the surface reach steady state. Afterwards, the test specimens were weighed on FB 143 mettle Tolrdo digital weighing balance.

Different concentrations (10⁻⁵ to 10⁻¹M) of inhibitors were prepared and added to the environments. Then another medium without any inhibitor was used for the control experiment. Specimens were weighed in turn and their original weights recorded. They were then totally immersed in 100ml of 1M hydrochloric acid containing mixture of different concentrations of inhibitors. The specimens were removed after every 24hours and weighed after cleaning off the corrosion products, this lasted for 96 hours. The corrosion product formed on the surface of each specimen was removed by scrubbing under running water using fine energy paper. The specimens were then dried, re-weighed and the corrosion rates calculated in mills per year (mpy). Graphs of corrosion rates in mills per year (mpy) versus the exposure time were plotted for each inhibitor concentration in the media. The inhibitor efficiency (p) in 1M hydrochloric acid was determined from the relationship:

$$P = \frac{100(W_1 - W_2)}{W_1}$$

Where, W₁ and W₂ are the corrosion rates in the absence and presence of the inhibitors respectively. All chemicals used were of analytical grade. The solutions were made from freshly distilled water.

The cell for the polarization measurements consisted of three compartments separated by fritted glass discs to prevent the mixing of anolyte and catholyte. The reference electrode and working electrode compartments were separated by a luggin capillary to minimize the ohmic potential drop. A saturated calomel electrode and a carbon electrode were used as reference and auxiliary electrodes respectively. The galvanostatic polarization studies were performed using a constant current source (DB-300) and with the current densities range from 0.1 to 20mA/cm². The potentials during corrosion and polarization were measured using a digital multimeter (systronics model 435) with an accuracy of ±5mv. The experiments were repeated to confirm reproductively. The surface coverage (θ) data of caffeine, strychnine and quinine on mild steel surface were calculated using the expression.

$$1 - \theta = \frac{i_{\text{corr}}^*}{i_{\text{corr}}}$$

Where, i_{corr} and i_{corr}^* are the corrosion current densities without and with organic compounds respectively. The experiments were carried out for samples of mild steel under aerated stirred conditions at room temperature in the materials laboratory of the Department of Metallurgical Engineering, Kwara State Polytechnic, Ilorin, Nigeria.

3. Results and Discussion

The relationship between corrosion rates in mills per year (mpy) and the molar concentrations of inhibitors of NST-44 mild steel in 1M hydrochloric acid are shown in Fig. 1. The curves of Fig. 1 shows that in hydrochloric acid, quinine causes a continuous decreased in corrosion rates with increase in molar concentration although rate with increase in molar concentration followed by a sharp drop in rate of corrosion, after a critical inhibitor concentration. The three inhibitors provide inhibition at molar concentration of 10^{-2}M in acid medium. Examination of the curves shows that the inhibitive power in hydrochloric acid to be in order: quinine > strychnine > caffeine. Quinine, Strychnine and caffeine are able to inhibit corrosion by forming adherence of the absorbed species on surfaces of the steel to plug all corrosion sites. The absorption of inhibitors thus formed, probably tends to create a suitable barrier between the Fe^{2+} of the steel and the Cl^- ions of the hydrochloric acid thereby preventing the corrosion reaction according to equation (6). As inhibitor concentration is increased further, however, the chloride ion – inhibitor ratio decreases within the pores and breakdown process is again suspended and a reduction in corrosion rate is observed.

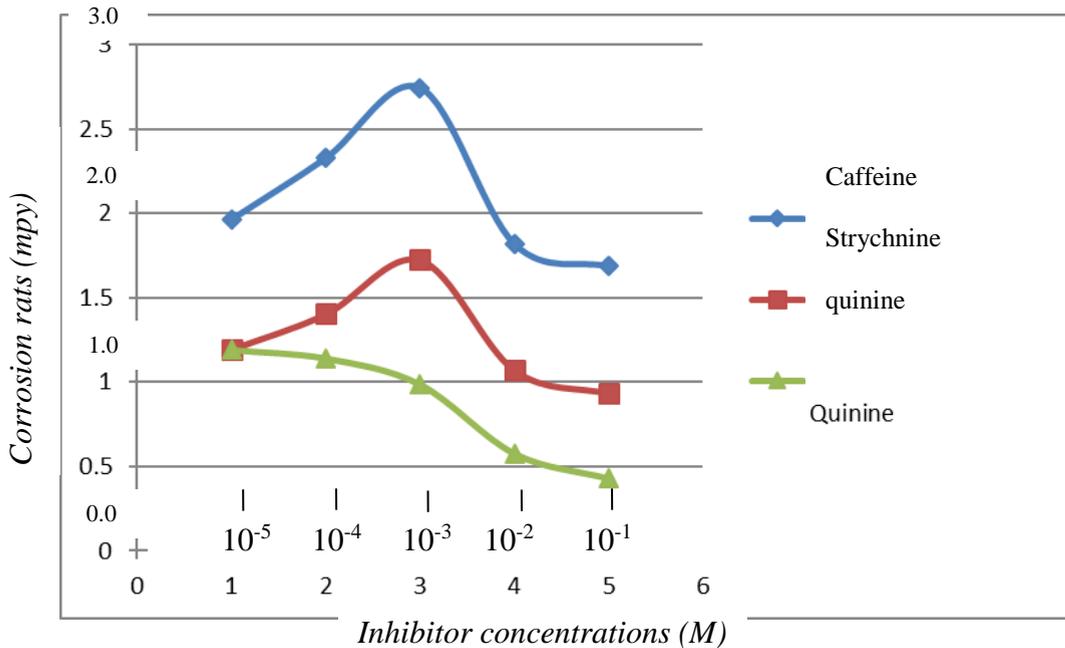


Fig. 1. Relationship between corrosion rates and inhibitor concentrations after 48hours of exposure in 1M HCl.

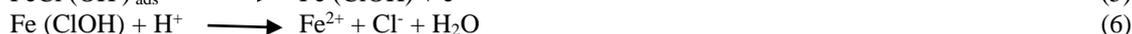
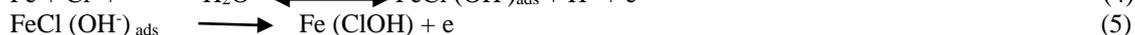
The metal surface in aqueous solution is always covered with absorbed water dipoles. Therefore, the absorption of inhibitor molecules from aqueous solution is a substitution process in accordance with equation (1) (Damaskin, 1971):



The corrosion of iron in acid solution is in accordance with equations (2) and (3) (Fontana and Greene, 1978).



However, each of the reactions proceeds with many consecutive steps depending on the acidity of the solution and the type of anions present in the solution. There are two main theories on the anodic dissolution mechanism of iron (John et al 1979). Both the theories indicate the participation of OH⁻ ions directly during the dissolution of iron both in alkaline and acid solutions. Anodic dissolution of iron in acid solution could be written as:



Absorption of anions on the electrode surface in acid solution affects the kinetics of anodic dissolution of iron and cathodic evolution of hydrogen. Relationships between efficiency of inhibition and inhibitor concentrations in 1M hydrochloric acid after 48hours of exposure are shown in Fig. 2. This relation shows the increase in efficiency of the inhibitor on increasing its concentration till it reaches a maximum value at a concentration of 10⁻²M. However, quinine, strychnine and caffeine showed considerable potentials with inhibition efficiencies of about 84.8%, 78.3% and 70.2% respectively in 1M hydrochloric acid for mild steel. Apparently, this value corresponds to the formation of a monolayer of the inhibitor at the corroding steel surface. The inhibition efficiencies of strychnine and caffeine are adequate, though quinine would be considered to be a marginally better inhibitor of carbon steel corrosion in 1M hydrochloric acid.

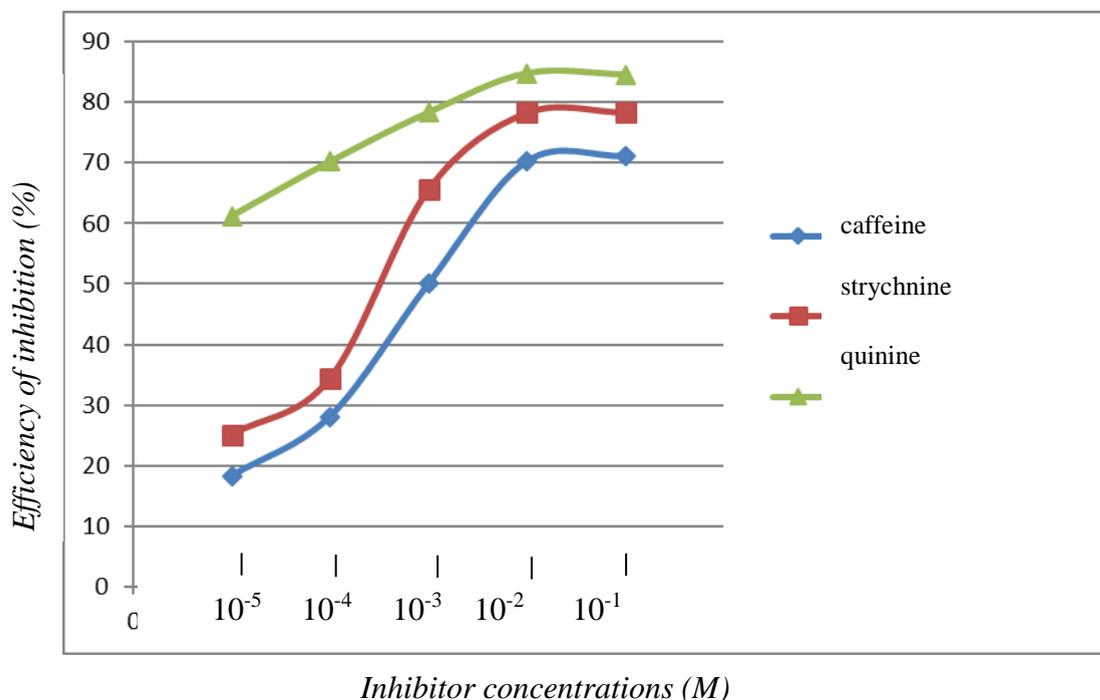


Fig. 2. Relationship between efficiency of inhibition and inhibitor concentrations in 1M HCl after 48hours of exposure.

The polarization curves shown in fig.3 are those measured for mild steel in 1M hydrochloric acid without and with various concentrations of caffeine, strychnine and quinine with the current densities range from 0.1 to 20mA/cm². At each current density, in 1M hydrochloric acid the over potentials both during anodic and cathodic polarizations decreased and attained steady values with time. The presence of these organic compounds in 1M hydrochloric acid shifted the anodic steady over potentials towards more noble direction whereas the cathodic over potentials towards less noble direction. This observation confirms the above prediction that the action of quinine, strychnine and caffeine is related to the absorption of anions on the electrode surface in acid solution affects the kinetics of anodic dissolution of iron and cathodic evolution of hydrogen and thus acting as mixed inhibitors.

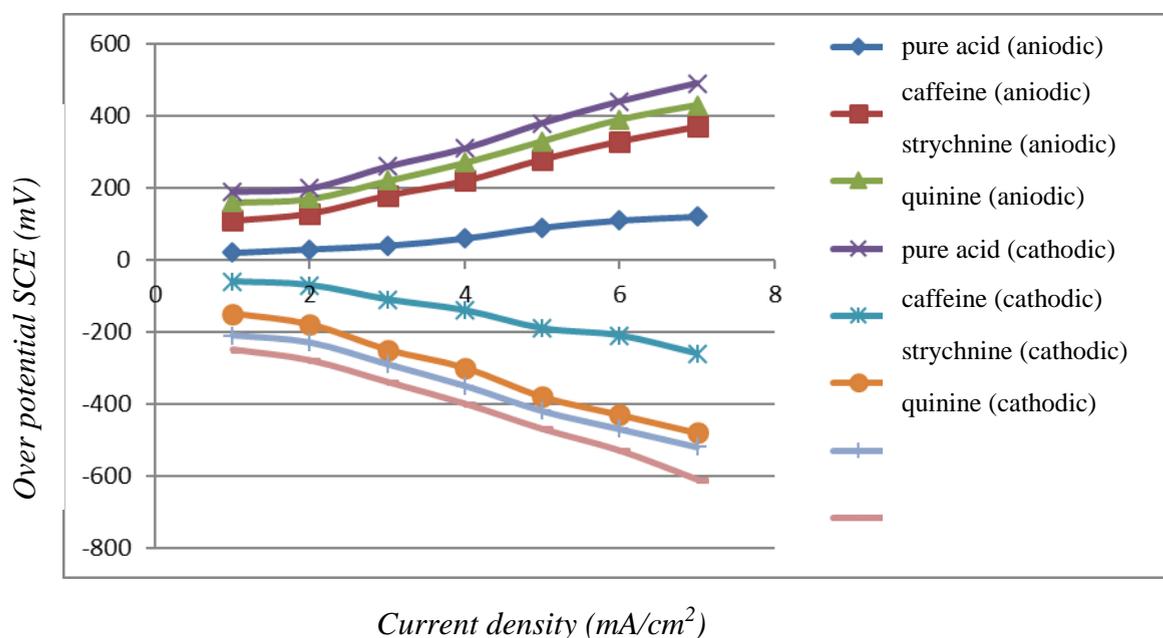


Fig. 3. Anodic and cathodic polarization curves (Tafel plots) for mild steel in 1M HCl containing 10⁻²M inhibitors.

Relationship between surface coverage and inhibitor concentrations after 48hours of exposure are shown in Fig.4 for 1M hydrochloric acid. The nature of the variation of surface coverage with inhibitor concentration is similar to the absorption isotherm. This shows the corrosion inhibition of mild steel in hydrochloric acid medium by the surface absorption of these organic compounds. The comparison of corrosion rate – concentration curves, inhibition efficiency – concentration curves, polarization curves and surface coverage – concentration curves, obtained for mild steel in 1M hydrochloric acid containing these nitrogen containing organic compounds has been shown that quinine is more efficiency inhibitor than strychnine and caffeine under the same condition.

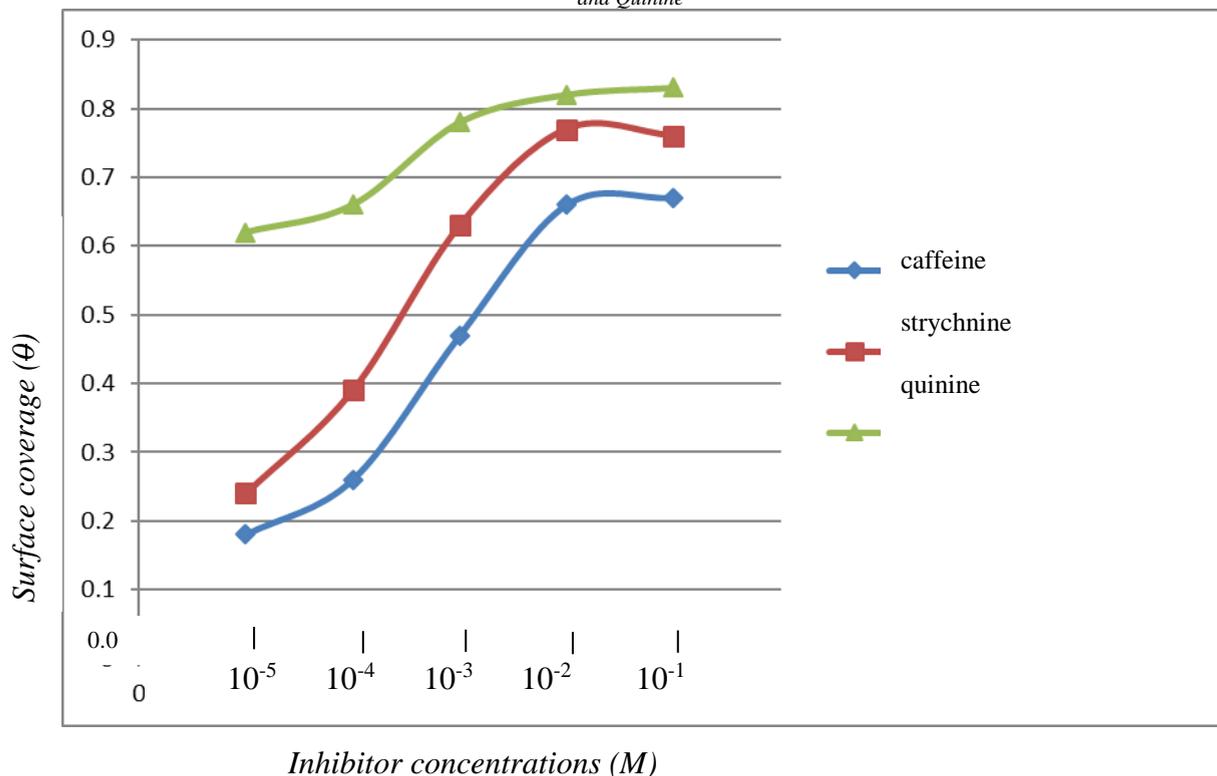


Fig. 4. Relationship between surface coverage and inhibitor concentrations after 48hours of exposure.

4. Conclusions

The main conclusions drawn from this investigation were:

- i. The corrosion of mild steel in 1M hydrochloric acid can be inhibited by quinine, strychnine and caffeine, to varying degrees.
- ii. The inhibitive power of these inhibitors increased with increase in concentration and the level of inhibition is therefore controlled by adsorption.
- iii. The efficiency of inhibition in 1M hydrochloric acid decreased in the following ranking order: quinine, strychnine and caffeine.
- iv. The mechanisms of all inhibitors investigated in 1M hydrochloric acid medium is suggested as being due to the absorption of the inhibitors on the metal surface thus forming a protective film which grows as the concentration of inhibitors increase.

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