MECHANISTIC STUDIES OF CARBON STEEL CORROSION INHIBITION BY CASHEW NUT SHELL LIQUID

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ABSTRACT

The inhibition mechanism of the Cashew Nut Shell Liquid (CNSL) on SAE 1008 carbon steel corrosion in CO_2 saturated 3% NaCl solutions has been studied by weight loss, UV/VIS and electrochemical techniques. The phenoxide, $\mathrm{R{-}Ar{-}O^-}$, *ions from the CNSL inhibitor were found to be responsible for the reduction of the corrosion rate of the carbon steel. Also, it was observed that the surface charge of the carbon steel electrodes was positive with respect to the solutions containing CNSL inhibitor. It is likely that the mechanism of the CNSL inhibitor adsorption involved the electrostatic attraction between the positively charged metal surface and the phenoxide ions via their negative ends.*

INTRODUCTION

A variety of organic inhibitors have been tested and used to protect metallic substrate from corrosion. Because of the very broad range under which these inhibitors are subjected and more importantly the awareness towards environmental pollution, existing formulations are continuously being improved and new types developed to substitute the pollutant and expensive commercial inhibitors in use. Recently, Cashew Nut Shell Liquid (CNSL) was reported to exhibit significantly higher corrosion protection of carbon steel in CO_2 than the conventional inhibitors (Philip *et al.* 2001). However, little if any attention has been given to investigate the mechanism of action.

Most of the papers dealing with the kinetics and mechanism of inhibition of metal corrosion agree that adsorption of the inhibitor onto the metal surface is the primary step in the action of organic corrosion inhibitors (Trabanelli 1989). The adsorption processes depend on many factors among others being the chemical structure of the inhibitor molecule, the nature and surface charge of the metal as well as the chemical composition of the aggressive medium (Trabanelli 1989).

In order to improve the chemistry of these corrosion inhibitors, increased fundamental understanding of the mechanism of action (adsorption) of molecules appears to be very crucial. The present paper reports on the mechanism of interaction of the CNSL with metallic substrate and how this affects the dissolution rate of the SAE 1008 carbon steel in CO_2-saturated NaCl solution.

METHODS

The electrochemical experiments were carried out in a three-electrode glass cell assembly as reported previously (Philip *et al.* 2001). A circular electrode of SAE 1008 carbon steel specimen with composition (% wt): 0.4 C, 0.1 Si, 0.21 Mn, 0.025 P, 0.06 S, and 99.205 Fe, served as the working electrode. The exposed area of the electrode was 0.80 cm^2. Two stainless steel rods each of 2 mm diameter were used as counter electrode and saturated Ag/AgCl as the reference electrode.

In addition to the electrochemical experiments, gravimetric measurements were performed. Mass loss coupons of identical composition, as above, with exposed area of 2.12 cm^2 were used. These experiments were performed in 300 ml conical flasks made of Pyrex glass each with a two holed rubber stopper as schematically shown in Fig. 1.

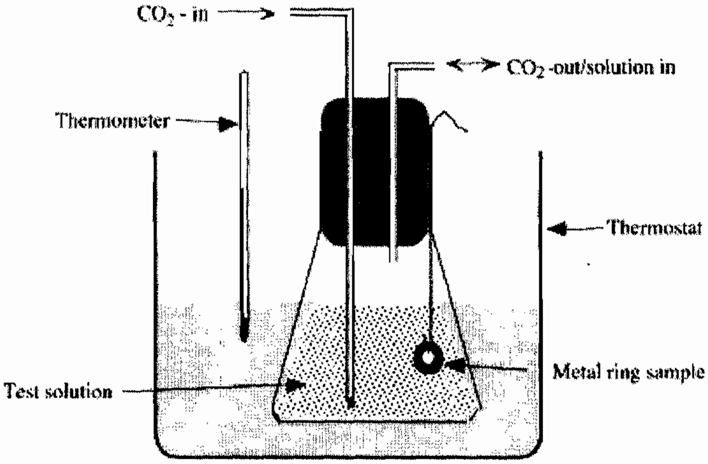


Fig. 1: Schematic drawing for the experimental set-up for weight loss measurements

Potentiodynamic polarization measurements were performed using a computer controlled AUTOLAB PGSTAT20 potentiostat. The cathodic and anodic polarization curves were taken separately, each over a range of 100 mV versus Ag/AgCl from the open circuit potential at the sweeping rate of 1 mV/s. The cathodic sweep was always taken first then the system allowed to return to its open circuit potential before being anodically polarized. Electrochemical Impedance Spectroscopy (EIS) measurements were also taken by use of a computer assisted AUTOLAB Frequency Response Analyzer in the frequency range of 10 kHz to 10 mHz at a sweeping rate of 10 points per decade, logarithmic division. The amplitude of the sinusoidal perturbation signal was 10 mV. All measurements were taken after 8 hours of exposure.

For the gravimetric measurements, the specimens with known weights and surface areas were suspended in both uninhibited and inhibited test solutions for a given period of time (1-28 days). The specimens were then removed from the test solutions and immediately immersed in another solution special for removing the corrosion products for approximately 10 minutes. The specimens were ultrasonically cleaned in acetone, air-dried and reweighed. The solution used to remove the corrosion products was prepared by mixing 200 g granulated zinc, 50 g sodium hydroxide and distilled water up to 1000 ml (Anon 1991).

The test solution was a 3% NaCl aqueous solution, prepared from analytical grade NaCl solid in distilled water. This solution was saturated with carbon dioxide by bubbling wet CO_2 gas for 12 hours prior to commencement of the experiment. The solution pH was measured using a Jenway Model 3015 pH meter and adjusted to the desired pH with either $NaHCO_3$ or HCl before the experiments. The pH values of the test solutions were adjusted to within the range (4.0 —7.0)for waters found in oil and gas production processes (Eriksrud 1983).

The water soluble CNSL was used as inhibitor. Prior to carrying out the electrochemical or gravimetric measurements, carbon steel samples were wet polished with a sequence of silicon carbide papers of different grits up to a 1000 grit surface finish, degreased with acetone, rinsed with ethanol, air dried and stored in a desiccator. All experiments presented here were carried out in CO_2-saturated solutions, with and without inhibitor at 30 °C. Before adding the inhibitor the solution pH values were adjusted to either 4.0 or 6.0.

RESULTS AND DISCUSSION

One of the crucial factors for the determination of the inhibition mechanism as well as the performance of the corrosion inhibitors is the solution pH. Most of the inhibitors are pH-selective. The nature of pH selectivity may depend on the molecular structure of the inhibitor, the corroding metal, the active species present in the solution and the composition of the inhibitor (Moldestad 1995). Figure 2 shows the polarization curves for carbon steel electrodes exposed to different solution pH with and without inhibitor. It can be seen from this plot that there is a drop in both cathodic and anodic currents as well as a significant anodic shift of the open circuit potentials on both uninhibited and inhibited solutions as the solution pH changes from 4 to 6.

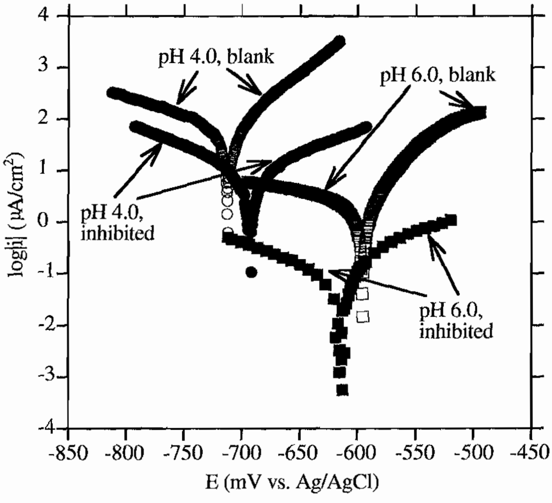


Fig. 2: The potentiodynamic polarization curves showing the effect of pH on the corrosion behaviour of SAE 1008 carbon steel electrodes in CO_2-saturated 3% NaCl solution without and with 1200 ppm CNSL inhibitor at 30 °C

The electrochemical parameters deduced from these curves by Tafel extrapolations are summarized in Table 1. These include Tafel constants (b_a and b_c), corrosion current densities (i_{corr}), open circuit potentials (E_{ocp}) and corrosion potentials (E_{corr}). In addition the calculated parameters such as corrosion rates in mmpy and inhibition performance/efficiency are also included in the same table. The corrosion rate (v_{corr}) and inhibitor performance (ϕ) were calculated using the following relations 1 and 2, respectively.

$$v_{corr} = 1.159 \times 10^{-2} i_{corr} \tag{1}$$

$$\phi = 100\left(1 - \frac{i_{corr,i}}{i_{corr,u}}\right)\% \tag{2}$$

where, i_{corr} is the corrosion current density. The subscripts i and u in equation 2 denote presence and absence of inhibitor, respectively.

Based on the above results on uninhibited solutions it can be seen that, changing the solution pH influences the corrosion behaviour of SAE 1008 carbon steel. The decrease of both anodic and cathodic current densities with an increase in pH shows the reduction of both anodic and cathodic reactions of carbon steel. In fact the carbon steel dissolution rate in the uninhibited solution dropped from 55.10 mA/cm^2 at pH 4.0 to 25.70 mA/cm^2 at pH 6.0. This indicates that the cathodic reduction of H^+ has significantly been reduced (Nesic *et al.* 1996), and possibly the remaining dominant cathodic reactions would either be the direct reduction of carbonic acid or the direct reduction of water (Nesic *et al.* 1996).

$$H_2CO_3(ads) + e^- \rightleftharpoons H(ads) + HCO_3^-(aq) \tag{3}$$

$$H_2O(ads) + e^- \rightarrow H(ads) + OH^-(aq) \tag{4}$$

The corrosion potential, E_{corr}, also shifts anodically as the pH values increases to 6.0 (Table 1). This is in line with the observed drop of current densities (when the electrolyte pH was increased) in the sense that the tendency of the carbon steel electrode to ionize was hindered when the concentration of H^+ was lowered. It can also be seen that the anodic Tafel constants (b_a) are slightly changed explaining a weak pH dependence of the anodic dissolution of the substrate in CO_2 solutions. A similar observation was reported by Nesic (Nesic *et al.* 1996). Similarly, the influence of pH on the cathodic Tafel slopes (b_c) was quite little and their values were within the range reported elsewhere (Moldestad 1995, Buchweishaija 1997).

Corrosion rate of the metal samples in inhibited solutions was found to be minimum for the solutions with pH 6.0. By comparing with those in blank solutions (Table 1), it can be seen that, in the presence of the inhibitor the anodic shift of the corrosion potential, with increase in solution pH was more significant. The inhibitor efficiency was found to be low (82 %) with the solution pH of 4.0 and high (99 %) with the solution pH of 6.0. Based on these results it can be generalized that the CNSL inhibitor performs more efficiently in solutions of higher pH≥ 6.0 (basic medium).

The corrosion rates and inhibitor efficiency from the gravimetric measurements are summarized in Table 2. The corrosion rate was determined according to the relation:

$$V_{corr}/mmpy = 2.2\times10^{-1}\frac{\Delta m\ (\text{mg})}{\Delta t\ (\text{day})} \tag{5}$$

where m is the weight loss (mg) of metal and t is the time of exposure (days) of the metal to the aggressive medium.

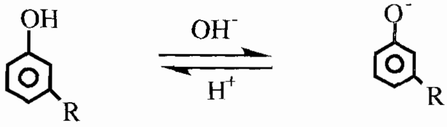
Table 1: Polarization parameters for the uninhibited (1200 ppm CNSL) systems with different solution pH, at 30 °C

Solution	pH	b_a (mV/dec)	b_c	E_{ocp} (mV vs. Ag/AgCl)	E_{corr}	i_{corr} (µ A cm^{-2})	V_{corr} (mmpy)	ϕ (%)
Blank	4.0	35	-94	-752	-715	55.10	0.6386	-
Blank	6.0	40	-87	-645	-605	25.70	0.2979	-
Inhibited	4.0	45	-94	-710	-700	9.70	0.1124	82
Inhibited	6.0	40	-98	-600	-580	0.21	0.0024	99

Table 2: The summary of the results obtained from mass loss measurements at various pH together with the calculated V_{corr} a and ϕ values ϕ

			1 day	1 week	2 weeks	4 weeks
pH 4.0	blank	mass loss (mg)	18.101	96.281	192.620	312.813
	blank	$V_{corr,u}$ (mmpy)	3.966	3.013	3.014	2.448
	inhibited	mass loss (mg)	7.06	43.0	106.0	184.7
	inhibited	$V_{corr,i}$ (mmpy)	1.547	1.346	1.659	1.445
		ϕ	61	55	45	41
pH 6.0	blank	mass loss (mg)	5.481	32.111	59.83	98.91
	blank	$V_{corr,u}$ (mmpy)	1.201	1.005	0.936	0.774
	inhibited	mass loss (mg)	0.603	3.86	5.39	10.9
	inhibited	$V_{corr,i}$ (mmpy)	0.132	0.121	0.084	0.085
		ϕ	89	88	91	89

These results are in agreement with those obtained from electrochemical experiments. The most probable explanation for the increased inhibitor performance with increase solution pH is based on the influence of pH on the solubility of CNSL inhibitor. Most phenols have their K_a values in the neighbourhood of 10^{-10} and thus are considered to be weak acids (Morrison *et al.* 1992). The equilibrium equation for phenols in acidic and basic media is given below and can best explain this phenomenon.



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At low pH
(Insoluble in aqueous media)

At high pH
(Soluble in aqueous media)

Thus, CNSL being phenolic is expected to have a low solubility in solutions of low pH and vice versa. To test the validity of this assumption, high concentration of the inhibitor (10,000 ppm) was added to the test solutions of different pH values. In the solution with pH 4.0, droplets of the CNSL were observed when the solution was left to stand undisturbed for 4 days, whereas, for the solution with pH 6.0, no droplets of CNSL were observed. Therefore, the effect of pH on the performance of CNSL inhibitor could be explained in terms of its solubility in aggressive medium. At low pH the solubility of the inhibitor was poor hence hindering its transportation to the metal surface. As the pH increases, its solubility also increases, thus, enhancing its transportation via the solution to the metal surface.

In addition to low inhibitor efficiency for the solutions of pH 4.0 there was also a drop of inhibitor performance from 61 % to 41% indicating a poor persistence of the inhibitor on the metal surface (Table 2). However, with solutions of pH 6.0 both performance and persistence of the inhibitor were high maintaining an efficiency of 89 – 2 % (see also Fig. 3).

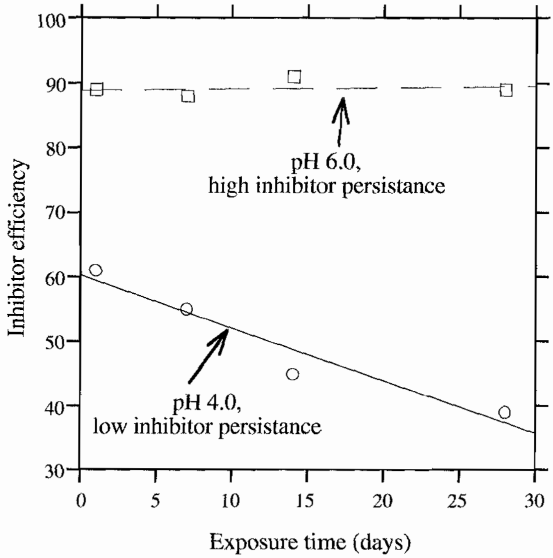
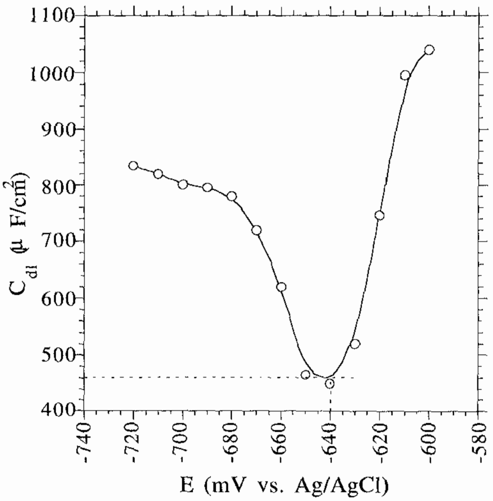


Fig. 3: The CNSL inhibitor persistence on SAE 1008 carbon steel electrodes in CO_2-saturated 3% NaCl solutions at 30 ßC of different pH

Since the primary step in the action of organic inhibitors is their adsorption onto the metal surface, the knowledge of factors that influence adsorption is quite important for an understanding of the mechanism of inhibition. Among the factors that influence adsorption are the nature and surface charge of the metal, the chemical structure of the inhibitor and the solution composition (Trabanelli 1989).

From the pH dependence results, the possibility of an ion adsorption by means of electrostatic forces is determined by the electric charge on the metal with respect to the solution, which is related to the difference, Δ, between the corrosion potential, E_{corr}, and the potential of zero charge, E_{pzc} (Riggs 1973). When Δ is positive, adsorption of negative charged molecules or anions is favourable and vice versa. Also the orientation of dipoles is determined by Δ. Thus differences in adsorption behaviour of inhibitor on various metals may be explained from considerations of Δ.

Therefore, the electrochemical impedance spectroscopy (EIS) technique was employed to determine the E_{pzc} for the carbon steel in the blank test solutions and UV/VIS to determine the adsorption of the CNSL inhibitor on the metal surface at different potentials. Freshly prepared SAE 1008 carbon steel metal specimens each of 0.8 cm^2 were used. The solution was CO_2-saturated 3% NaCl of pH 6.0 at 30ßC with and without inhibitor. Impedance measurements were performed after 8 hours of exposing the specimen in the blank solution at different applied electrode potentials in a range between -720 and -600 mV vs. Ag/AgCl. This range was about – 60 mV away from the open circuit potential. The electrochemical double layer capacitance, C_{dl}, values were then derived from the subsequent impedance data using a Complex Non-linear Least Squares (CNLS) fitting program, EQUIVCRT (Boukamp,1989), and plotted as a function of applied electrode potential as shown Fig. 4.



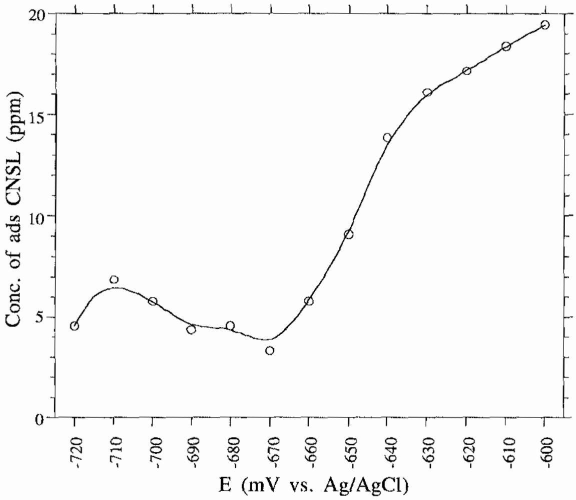
E(mV vs. Ag/AgCl)	C_{dl} (μ F/cm^2)
-720	834
-710	820
-700	801
-690	796
-680	780
-670	720
-660	621
-650	466
-640	450
-630	521
-620	746
-610	996
-600	1040

Fig. 4: A plot of double-layer capacitance (C_{dl}) as a function of applied electrode potential (E vs. Ag/AgCl) for the SAE 1008 carbon steel electrode in CO_2-saturated aqueous 3% NaCl solution of pH 5.5 at 30ßC

A parabolic curve with a minimum capacitance value at —640mV vs Ag/AgCl was obtained (Fig. 4). Hence, this value can be called the E_{pzc} of SAE 1008 carbon steel in CO_2-saturated 3% NaCl aqueous solution of pH 6 at 30ßC (Riggs 1973).

It was previously observed (Table 1) that, the open circuit potential for the inhibited SAE 1008 carbon steel in the CO_2-saturated 3 % NaCl solutions of pH 6.0 and 30 ßC was -600 mV vs. Ag/AgCl. Then it follows that $\Delta = E_{ocp} - E_{pzc} = -600 —(-640) = +40$ mV vs Ag/AgCl, indicating the metal surface of SAE1008 carbon steel to be positively charged in the inhibited solution with respect to E_{pzc} and hence anion species in the solutions would be directly adsorbed on the metal surface. Consequently, with increasing positive charge on the metal surface, adsorption of anion (phenoxide ion) would increase and its concentration in the solution would decrease.

The adsorption of the inhibitor on the metal surface was then followed as a function of applied potential by the UV/VIS techniques. Metal specimens of an area about 10 cm^2 were prepared (as for EIS above) and used in this experiment. 10,000 ppm of the CNSL corrosion inhibitor was added to CO_2-saturated 3% NaCl solutions. Large surface of the specimens and high concentration of the inhibitor were used in order to ensure working with inhibitor concentrations in the solutions within the detection limit of the UV/VIS instrument. The same inhibited solution was used for all experiments. Each metal specimen was immersed in 100 cm^3 of the inhibited test solution and subjected to the specified applied electrode potential. The potentials varying from —600to -720 mV vs. Ag/AgCl were applied to the specimens immersed in the test solution. Eight hours duration was allowed for each specimen. The specimens were then removed from the solutions, and the solutions were analysed by UV/VIS using the UV-240 spectrophotometer. One UV spectrum was obtained from the solution without immersing the specimen and used as a reference for calculation of concentration of the adsorbed CNSL after each exposure. The concentration of the adsorbed inhibitor on SAE 1008 carbon steel electrodes surface varied with the applied electrode potential (Fig. 5).



E (mV vs Ag/AgCl)	C_{inh} (ppm)
-720.00	4.5500
-710.00	6.8200
-700.00	5.7700
-690.00	4.3700
-680.00	4.5500
-670.00	3.3200
-660.00	5.7700
-650.00	9.0900
-640.00	13.810
-630.00	16.080
-620.00	17.130
-610.00	18.360
-600.00	19.410

Fig. 5: A plot of concentration of adsorbed CNSL inhibitor on SAE 1008 carbon steel at different applied potentials in aqueous CO_2-saturated 3% NaCl solutions of pH 6.0 at 30ßC

As the positive charge increased on the metal surface the concentration of the adsorbed CNSL on the metal surface also increased (Fig. 5). This supports our previous proposed inhibition mechanism, which suggested that the phenoxide ions were directly adsorbed on the positively charged metal surface electrostatically. It also shows that CNSL inhibitor is not effective at lower solution pH due to inability to ionize (refer equation 5). Schematic representation of the probable adsorption inhibition mechanism of CNSL on carbon steel in CO_2-saturated 3 % NaCl solutions is as given below (Fig. 6).

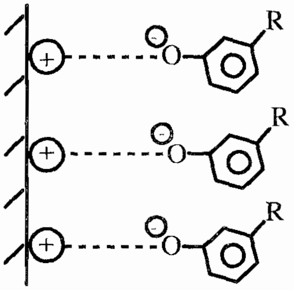


Fig. 6: The electrostatic adsorption of the anionic corrosion inhibiting species to the positively charged SAE 1008 carbon steel surface

CONCLUSION

CNSL inhibitor was found to be more effective at higher solution pH (i.e. a basic type inhibitor), and to act mainly anodically. Based on the experimental observations as well as the theoretical interpretation above it can be concluded that the phenoxide ions, $R—Ar—O^-$, of the CNSL inhibitor are adsorbed on SAE 1008 carbon steel surface in aqueous CO_2 -saturated 3 % NaCl solution by the electrostatic interaction (Fig. 6.).

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