CASHEW NUT SHELL LIQUID AS AN ALTERNATIVE CORROSION INHIBITOR FOR CARBON STEELS

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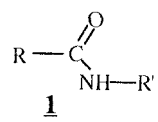
ABSTRACT

Cashew Nut Shell Liquid (CNSL) has been tested as a corrosion inhibitor for carbon steel in 3% aqueous NaCl solution (pH 6) saturated with carbon dioxide gas at 30°C under static conditions using ac-impedance and potentiodynamic polarisation techniques. It was found that CNSL reduces the extent of the electrochemical processes taking place on carbon steel undergoing corrosion. The corrosion rate of the carbon steel was reduced by over 92 % when only 300 ppm of CNSL was applied. This indicates that CNSL is a potential corrosion inhibitor for carbon steels in CO_2 environment.

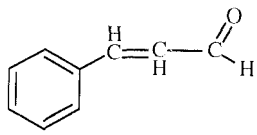
INTRODUCTION

Although carbon steel is widely employed as a storage and transportation material in oil and gas systems, it is highly vulnerable to carbon dioxide corrosion. In the aqueous phase, carbon dioxide (CO_2) forms carbonic acid (H_2CO_3) leading to an increased corrosion rate of the base metal. This corrosion problem, to a certain extent, can be mitigated by the use of corrosion inhibitors, thus making the use of carbon steels an economical choice when compared to stainless steels (Buchweishaija & Hagen 1997).

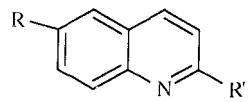
Organic compounds are normally used as corrosion inhibitors for the protection against CO_2 corrosion on carbon steels in oil and gas production industries (Ericksrud 1983). These compounds are usually large molecules with long alkyl chains (Ericksrud 1983). The schematic chemical structures of some of these molecules, found to be effective in CO_2 environment are shown below (**1** - **4**) (Buchweishaija 1997, Trabanelli 1971).



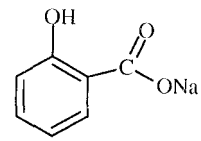
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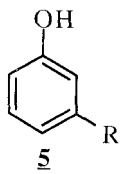
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Fatty acid amine Cinnamic aldehyde 2,6-Dialkyl quinoline Sodium salicylate

R or R' = C_3 - C_{18}; Saturated, unsaturated, chain or cyclic.

However, because of the production costs and environmental pollution caused by most of these compounds, cheaper and more environmentally friendly corrosion inhibitors are continuously being formulated, including those of natural products.

During thermal process of removing cashew kernel (*Anacardium occidentale)* from the nut, the Cashew Nut Shell Liquid (CNSL) oozes out from the shells as a by-product. CNSL is a naturally occurring mixture of phenolic compounds which amounts to about 20 % by weight of the whole nut. Because of their phenolic character and the long alkyl side chain which varies in its degree of unsaturation attached to the benzene ring of their molecules, the CNSL has become of a great research interests in various areas including natural products, electrochemistry and for industrial applications. The thermally extracted and purified CNSL is composed of mainly cardanol, (**5**) (Gedam & Sampathkumaran 1986).



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$R = C_{15}H_{31-n}$; n = 0, 2, 4, 6

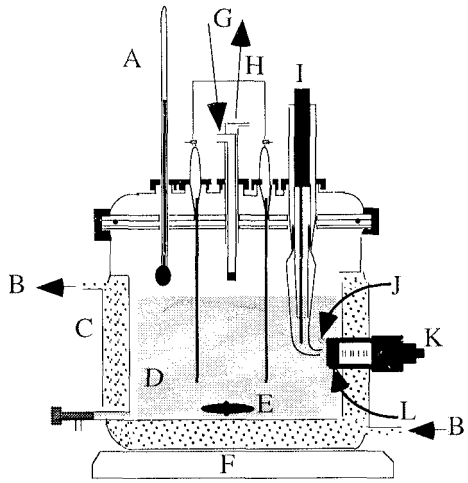
(n = 6, a triene is present in greatest proportion)

In some cashew nut processing industries, CNSL is not fully utilized in spite of having many applications, including the preparation of friction and heat resistant dust for break and clutch linings, wood binders and mould (Gedam & Sampathkumaran 1986). Instead CNSL is left to rot, thereby posing environmental problems.

Structurally, CNSL compounds resemble some of the well-known organic corrosion inhibitors used to inhibit CO_2-corrosion, though none if any study has so far been reported on its use as a corrosion inhibitor in aqueous environments. The paper reports the inhibiting action of CNSL on corrosion of SAE 1008 carbon steel in CO_2-saturated, 3 % aqueous NaCl solutions at ambient temperature.

EXPERIMENTAL

The electrochemical experiments were carried out in a three-electrode glass cell assembly (Fig. 1). A circular electrode of 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 approximately 0.80 cm^2. Two stainless steel rods, each of 2 mm diameter, were used as counter electrodes. The reference electrode consisted of saturated Ag/AgCl and was connected to the cell through a Luggin capillary tube.



A = Thermometer
B = Water in/out
C = Thermostatic jacket
D = Test solution
E = Magnetic bar
F = Stirrer table
G = CO_2 in/out and test solution in
H = Stainless steel rod counter electrode
I = Reference electrode
J = Luggin capillary tube
K = Sample holder
L = Metal sample (working electrode)

Fig. 1: Schematic drawing of the three electrode glass cell assembly.

Prior to carrying out the corrosion inhibition tests, 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.

The test solution was a 3% aqueous NaCl solution, prepared from analytical grade NaCl 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 pH 6.0 with either $NaHCO_3$ or dil. HCl before the experiments. The pH of the test solution is within the range for waters found in oil and gas production processes (Eriksrud 1983).

The CNSL was emulsified by dispersing it in ethanol and treating it with hydrazine hydrate in the presence of 0.1 M sodium hydroxide solution, to make it soluble in water. The performances of CNSL as a corrosion inhibitor were monitored at a concentration range from 0 to 1200 ppm (v/v.). For each corrosion inhibitor concentration experiment, a fresh solution as well as a

freshly polished electrode was used. Experiments presented here were all carried out at an ambient temperature of 30 °C.

Electrochemical Impedance Spectroscopy (EIS) measurements were carried out by 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. Measurements were taken at various time intervals ranging from 1 to 12 hours. Impedance spectral results were presented in both Nyquist and Bode format. EIS measurements were performed before polarization measurements because the technique use very small signal excitation amplitudes, often in a range of 5 to 10 mV peak-to-peak, which does not disturb the metal surface (Greef *et al.* 1990).

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. From the polarization curves, the corrosion currents and potentials were obtained by Tafel extrapolation (Greef *et al.* 1990). The sweeping rate was 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. All polarization curves were recorded at the end of each experiment.

RESULTS AND DISCUSSION

The impedance plots obtained were all semicircular (Fig. 2a), indicating that charge transfer was the controlling dissolution mechanism (Silverman 1993). The EIS results were analyzed by fitting the observed data in a Randles type circuit with only one capacitive loop, using a Complex Nonlinear Least Squares (CNLS) fitting program, EQUIVCRT (Boukamp 1989), to estimate equivalent circuit parameters. As can be seen from the Nyquist plot, the impedance spectra obtained are depressed semicircles. Deviations of this kind have been reported to be attributed to the roughness of the metal surface (Juttner 1990). Therefore, a Constant Phase Element (CPE), Q was used to calculate the electrochemical double layer capacitance (C_{dl}) using the relationship:

$$C_{dl} = Q(R_s^{-1} + R_{ct}^{-1})^{\frac{n-1}{n}} \qquad (1)$$

where Q is the complex admittance, R_s is the solution resistance, R_{ct} is the charge transfer resistance and n is a dimensionless parameter with value between −1 and +1 measuring the degree of distortion from the true capacitor (i.e. n = 1 means ideal capacitor (Brug *et al.* 1984).

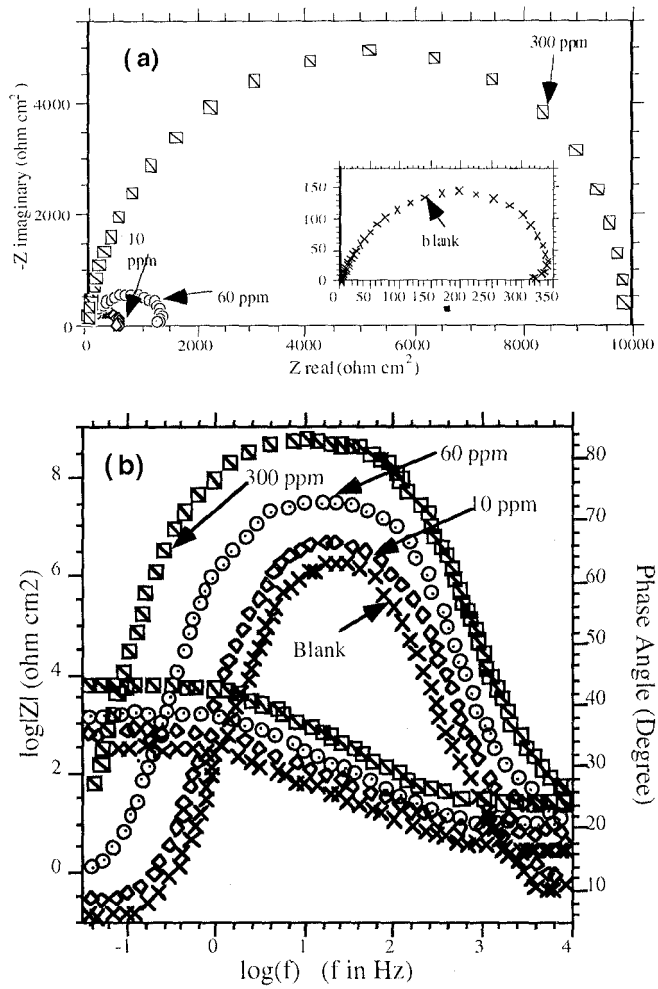


Fig. 2: EIS spectra in (a) Nyquist format (b) Bode format, for carbon steel electrodes taken after 8 hours of exposure in the absence and presence of different concentrations of CNSL in CO_2-saturated 3% NaCl solution (pH 6) at 30°C

Figure 2 (b) shows the same EIS experimental data in Bode format. It can be noted that the maximum phase angle increased with increase in inhibitor concentration. The continuous increase in the phase angle and continuous widening of the peak correlates with the inhibitor film growth (Tan *et al.* 1996). Thus, this observation clearly shows that the best protective film was formed at an inhibitor concentration of 300 ppm or higher.

For all CNSL concentrations, the R_{ct} and C_{dl} attained relatively constant values after 8 hours of exposure (Fig. 3 a and b). This suggests at least eight hours of immersion in the inhibited solution to be the shortest time required

for the CNSL inhibitor to be completely transported through the medium and get adsorbed on the metal surface. It can also be seen from this figure that, the immersion time in the inhibited solution is independent of CNSL concentrations. Similarly, the R_{ct} and C_{dl} values increase and decrease, respectively, as the CNSL concentrations increase. This could be attributed to reduction of the charge transfer at the metal/solution interface and consequently to corrosion rate (Buchweishaija 1997, Silverman 1993). Thus, the faradaic process that takes place on the metal surface uncovered by the inhibitor film decreases with increasing inhibitor concentration, hence reducing the surface area of the metal undergoing corrosion (Tan *et al.* 1996, Muralidharan *et al.* 1995).

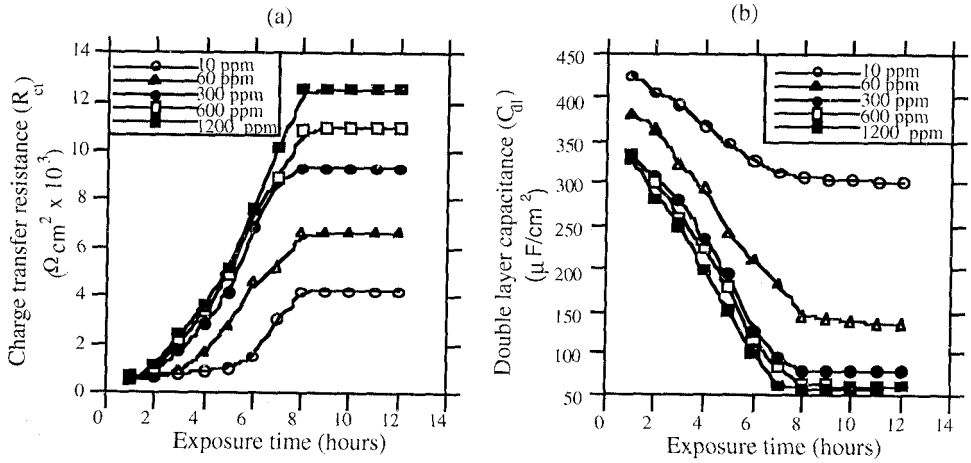


Fig. 3: Influence of exposure time on carbon steel electrodes in CO_2-saturated 3% NaCl solution (pH 6) with various concentrations of CNSL at 30°C. (a) R_{ct} versus time (b) C_{dl} versus time

From figure 2, the equivalent circuit parameters derived from the impedance plots after 8 hours exposure in the inhibited and uninhibited solution were used for comparison purposes. The calculated corrosion current densities (i_{corr}), corrosion rates (R_{corr}) and corrosion inhibitor efficiencies (ϕ_{inh}) after 8 hours of exposure are summarized in Table 1. Corrosion current densities were calculated using the Stern Geary equation (Buchweishaija 1997).

Table 1 Electrochemical parameters obtained from EIS and inhibitor efficiencies of carbon steel electrode in the absence and presence of CNSL in CO_2-saturated 3% NaCl solution (pH 6) after 8 hours at 30 °C n: regression coefficient

C_{inh} (ppm)	E_{ocp} (mV vs. Ag/AgCl)	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	n	Q (μF cm^2)	C_{dl} (μF cm^2)	i_{corr} (μA cm^{-2})	R_{corr} (mmpy)	ϕ (%)
Blank	-645	8.80	380	0.818	391	631	39.00	0.4520	-
10	-645	8.80	610	0.830	380	591	34.10	0.3952	13
20	-640	10.12	690	0.890	377	500	23.60	0.2735	39
30	-630	12.10	920	0.823	359	612	18.12	0.2100	54
60	-630	12.27	1230	0.802	336	593	12.80	0.1483	67
120	-626	14.25	1998	0.799	283	551	9.21	0.1067	76
180	-623	22.45	2983	0.810	238	493	5.70	0.0660	85
240	-619	26.78	3650	0.769	200	536	3.08	0.0356	92
300	-614	31.34	4996	0.791	113	280	2.54	0.0294	93
600	-601	32.29	8629	0.799	45	108	2.53	0.0293	93
900	-601	35.15	8640	0.786	48	126	2.53	0.0293	93
1200	-559	41.27	8636	0.801	50	126	2.54	0.0294	93

By assuming a uniform corrosion, the corrosion current density can be related to the corrosion rate in millimetres per year (mmpy) by Faraday's law using the equation (Trethewey & Chamberlain 1988)

$$R_{corr} = 1.159 \times 10^{-2} i_{corr} \qquad (2)$$

where i_{corr} is the corrosion current density in μA cm^{-2} (Table 1).

The inhibitor efficiencies, ϕ_{inh}, for the carbon steel samples in the inhibited systems has been calculated from the equation (Juttner 1990, Tan *et al.* 1996)

$$\phi_{inh} = 100\left(1 - \frac{R_{corr,i}}{R_{corr,u}}\right)\% \qquad (3)$$

where $R_{corr,u}$ and $R_{corr,i}$ are the corrosion rates without and with inhibitor, respectively.

It is clear from these results that increase in CNSL concentration up to 300 ppm caused a decrease in both C_{dl} and i_{corr} and consequently an increase in the corrosion inhibition efficiency. The decrease of C_{dl} values is indicative of the adsorption of the inhibitor on the metal surface. It has been suggested (Buchweishaija 1997) that on rough and porous electrode surfaces the surface

area is large and C_{dl} is high compared to that on a smooth surface. When the inhibitor is injected into the electrolyte the active sites are thought to be covered by the inhibitor forming a smooth surface, consequently C_{dl} decreases (Buchweishaija 1997, Trabanelli 1971). It has been proposed (Trabanelli 1971) that the adsorption of the inhibitor on the metal surface can occur directly on the basis of donor-acceptor interaction between the π or lone pair of electrons of the inhibitor (compound **5** contains π-electrons in the unsaturated part of the chain) and the vacant d-orbitals of iron surface atoms, hence forming a protective film. Therefore, with time, inhibitor molecules adsorb on the metal surface and the protective film grows until it covers all possible corroding sites by forming a thin mono-molecular film on the metal surface, hence reducing the C_{dl} values (Buchweishaija 1997, Trabanelli 1971). The observed decrease in C_{dl} values in EIS measurements is supported by this proposition.

Polarization studies on carbon steel samples exposed for 8 hours in the test solution were then performed for different concentrations of the CNSL in CO_2-saturated 3% aqueous NaCl solutions.

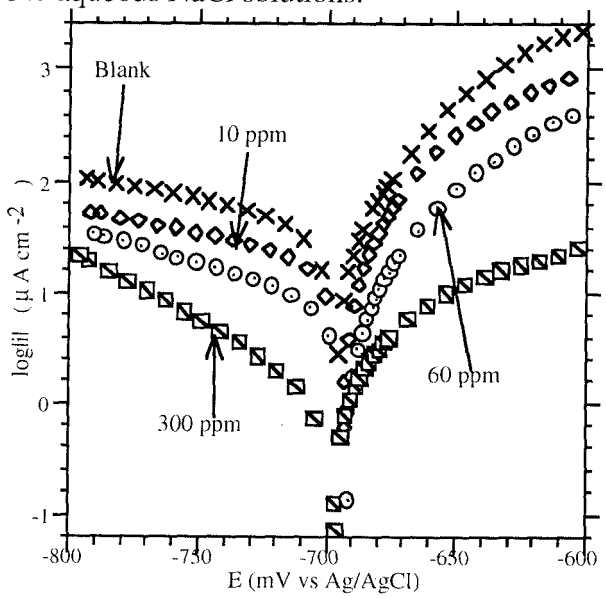


Fig. 4: Cathodic and anodic polarisation curves for carbon steel electrodes taken after 8 hours of exposure in the absence and presence of different concentration of CNSL in CO_2-saturated 3% NaCl solutions (pH 6) at 30°C

The presence of CNSL in the test solution reduced both the cathodic and anodic corrosion currents (Fig. 4). Moreover, increase in CNSL concentration in the test solution lowered the corrosion current densities and slightly shifted the open circuit potential (E_{ocp}) in the cathodic direction. This observation is characteristic of the cathodic behaviour of the inhibitor (Buchweishaija 1997).

However, one cannot conclude that this substance acts only as cathodic inhibitor because both anodic and cathodic branches of the polarisation curves were affected as the CNSL concentration increased. This, therefore, indicates that CNSL may be characterised as a mixed type inhibitor (Buchweishaija 1997).

The electrochemical parameters, i.e., Tafel slopes (b_a and b_c) obtained by Tafel extrapolation, corrosion current densities (i_{corr}) and corrosion potential (E_{corr}) obtained to the intersection point of the Tafel lines, calculated corrosion rate (Eqn. 2) and inhibitor efficiencies (Eqn. 3) are summarised in Table 2.

Table 2: Electrochemical parameters obtained from potentiodynamic measurements on carbon steel electrodes in the absence and presence of different concentrations of CNSL in CO_2-saturated 3% NaCl aqueous solution (pH 6) after 8 hours of exposure at 30 °C

C_{inh} (ppm)	b_a (mV/dec)	b_c (mV/dec)	E_{corr} (mV vs. Ag/AgCl)	i_{corr} mA cm^{-2})	R_{corr} (mmpy	ϕ (%)
Blank	40	-105	-630	34.60	0.4010	-
10	40	-105	-630	27.45	0.3181	21
20	40	-100	-628	22.67	0.2627	34
30	35	-100	-625	17.60	0.2039	49
60	35	-100	-625	13.00	0.1506	62
120	35	-98	-625	8.98	0.1040	74
180	35	-98	-615	5.51	0.0638	84
240	35	-99	-613	3.50	0.0405	90
300	50	-120	-610	2.55	0.0295	92
600	40	-128	-595	2.57	0.0297	92
900	40	-128	-595	2.53	0.0293	92
1200	40	-128	-595	2.53	0.0293	92

The corrosion current density values (Table 2) for carbon steel in the solutions containing CNSL are smaller than those of the blank solution. The i_{corr} reduction was found to depend on inhibitor concentration up to 300 ppm of the inhibitor, above which no significant change of i_{corr} with further increase in CNSL concentration was observed.

The corrosion rate for the carbon steel sample in the blank solution was about 0.4 mmpy (Table 2). However, R_{corr} values decreased with increase in CNSL concentration to a minimum value of about 0.03 mmpy when 300 ppm (or above) of the CNSL had been added to the test solution. This results in a corrosion inhibition efficiency of 92%. The corrosion current densities and the inhibitor efficiencies (Table 2) were in good agreement with those obtained from EIS measurements (Table 1).

It is interesting to note that the corrosion potential (E_{corr}) did not change significantly with increasing CNSL concentration. However, there was a slight shift of E_{corr} by ca. 35 mV versus Ag/AgCl in the anodic direction. This indicates a predominant anodic protection effect. The values of the cathodic Tafel slope, $|b_c|$ decreased with the increased inhibitor concentration range between 0 and 240 ppm but increased at higher CNSL concentrations. The values of the anodic Tafel slope decreased only slightly with low inhibitor concentration between 30 to 240 ppm. This behaviour indicates that CNSL is a mixed type corrosion inhibitor (Muralitharan *et al.* 1995).

CONCLUSION

In the present study, the corrosion inhibitive properties of cashew nut shell liquid were investigated on freshly polished SAE 1008 carbon steel samples in CO_2-saturated 3% aqueous NaCl solutions at pH 6 and at 30°C. The results sugget that CNSL inhibits the electrochemical processes taking place on carbon steel surface undergoing corrosion in CO_2 solutions. CNSL is capable of decreasing the corrosion rate by over 90% when its concentration in the test solution is about 300 ppm. Therefore, CNSL is a potential corrosion inhibitor for CO_2 corrosion on carbon steel in aqueous sodium chloride solutions.

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