THE EFFECT OF ROTATION AND TEMPERATURE ON THE INHIBITION PERFORMANCE OF CASHEW (*ANACARDIUM OCCIDENTALE L.*) NUT SHELL LIQUID ON CO_2 CORROSION OF CARBON STEEL

Buchweishaija, J. and Mkayula, L.L
Chemistry Department, University of Dar es Salaam,
P.O. Box 35061, Dar es Salaam, Tanzania.
E-mail: buchwe@chem.udsm.ac.tz

ABSTRACT

A natural extract of cashew nut shells, Cashew Nut Shell Liquid (CNSL) was investigated as a corrosion inhibitor for carbon steel in 3% NaCl solutions saturated with CO_2 gas using electrochemical techniques (i.e. potentiodynamic polarization and ac-impedance). The investigation was performed at different temperatures under static and dynamic conditions using a Rotating Disk Electrode (RDE). It was found that CNSL reduces the electrochemical processes taking place on carbon steel undergoing corrosion. The percentage inhibitor efficiency increases with increase in CNSL concentration and decreases with rise in temperature. Better performance at low CNSL concentration was registered under dynamic conditions and room temperatures. Thus CNSL is a potential corrosion inhibitor for carbon steel undergoing corrosion in CO_2 medium.

INTRODUCTION

Carbon dioxide corrosion is a major corrosion problem in oil and gas production and transportation systems/industry. The presence of CO_2 in the produced fluid is encountered more frequently due to the wide spread use of enhanced oil recovery technique involving CO_2 injection into the reservoir and also to gas production from deeper wells. When carbon dioxide dissolves in water, it hydrates to form carbonic acid. This weak, partly dissociated acid is a cause of corrosion attacks on pipes and equipment used in CO_2 containing systems (de Waard and Milliams (1975), McIntine et al. (1990)). Carbon steel is still the most common material in oil and gas production industry despite the developments in corrosion resistant alloys over the past decade. Carbon steel constitutes about 99% of the material used in this industry. It is usually the most cost effective option being 3 to 5 times cheaper than stainless steels. An important limitation for carbon steel is that it is highly vulnerable to CO_2 corrosion. One of the most effective methods of fighting corrosion is by the use of corrosion inhibitors. Hence, carbon steel is economically a material of choice when used in combination with corrosion inhibitors.

Organic compounds are normally used as corrosion inhibitors for protection against carbon dioxide corrosion of carbon steel in gas and oil production industries. Typical examples are usually large molecules with long alkyl chains such as fatty acid amine, cinnamic aldehyde, 2, 6-dialkyl quinoline and sodium salicylate (Trabanelli et al. (1971), Riggs (1973), Buchweishaija and Hagen (1997)). However, most of the corrosion inhibitors in current use are toxic and/or have adverse environmental impact, leading to increasing legislative pressure for their elimination. Research efforts have therefore begun to focus on non-toxic and environmentally friendly corrosion inhibitors (Abdel-Gaber et al. (2006), Bouklah and Hammouti (2006)).

Plants have been recognized as sources of a diversity of naturally occurring compounds, some with rather complex molecular structures and having a variety of physical, chemical and biological properties (Farooqi et al. (1997), Mukherjee et al. (1997)). Most of these compounds are currently enjoying use in traditional applications such as pharmaceuticals and biofuels (Nkunya (2002)). The naturally occurring chemicals are of interest because of their cheap and abundant availability and more importantly are environmentally acceptable

(green) materials. Recently, Philip et al (2001) have reported the use of Cashew (*Anacardium Occidentale L.*) Nut Shell Liquid (CNSL), oil extracted from the cashew nut shells as corrosion inhibitor of steel in CO_2 media. It was shown that CNSL reduced the extent of the electrochemical processes taking place on carbon steel surface undergoing corrosion. The corrosion rate of the carbon steel was reduced by over 90% with just 300 ppm of CNSL. However, their investigation focused only on the stationary conditions.

In oil and gas industry, liquids and gases are transported through piping during production and transmission. Therefore, flow has a major influence on both corrosion and inhibition of corrosion using inhibitors. Flow condition is one of the factors that complicate the application of corrosion inhibitors in these systems. For example most of the inhibitors applied in oil and gas systems are film-forming inhibitors which act by developing an adsorbed organic film on the metal surface. Their performance will obviously be linked to persistence against the prevailing flowing conditions (shear stress). It has been reported that severe flow regimes may have a negative impact on the inhibitor performance. Thus, high flow rates and turbulent conditions can lead to removal of inhibitor film from the metal surface causing its performance to diminish (Choi and Cepulis (1988), French et al. (1989), Schmitt (1995)). On the other hand an increase in flow rate may also lead to a better inhibitor distribution and transport resulting in high inhibitor performance (Stegmann and Asperger (1989)).

The present work was designed to gain further understanding of the inhibition mechanism of the extract. Particular attention was paid to the effect of flow on the inhibition efficiency of the inhibitor in order to ascertain the role of this abundant natural product in corrosion inhibition of carbon steel in oil and gas production and transmission systems. The behaviour of the carbon steel in the presence of corrosion inhibitor was investigated by electrochemical measurements using a rotating disc electrode.

EXPERIMENTAL

The electrochemical measurements were carried out with a conventional three electrodes Pyrex glass cell assembly at room temperature (30 ^{o}C). A Rotating Disk Electrode (RDE) assembly with adjustable speed was used as working electrode. The working electrode was a cylindrical carbon rod mounted in Teflon tube exposing the bottom surface area of 1 cm^2. The chemical composition of the tested material in weight percentage was 0.4 C, 0.1 Si, 0.21 Mn, 0.025 P, 0.06 S and 99.205 Fe. Prior to electrochemical tests, exposed metal surfaces were wet abraded by SiC paper to 4000 grit, ultrasonically cleaned with acetone, followed with polishing through 1 μm diamond paste and finally rinsed in ethanol before immersion in the test solution.

The test solution was 3% NaCl solutions prepared from analytical grade sodium chloride in distilled water. This solution was saturated with wet carbon dioxide gas for 12 hours prior to commencement of the experiment. The solution pH was measured using a Jenway Model pH meter and adjusted to pH 5.5 by adjusting it with either $NaHCO_3$ or and dil. HCl before the experiments. The solution pH is within the range for waters found in oil and gas production processes. The corrosion inhibitor used was oil extracted from cashew nut shells called Cashew Nut Shell Liquid (CNSL) and its performance was monitored at a concentration range from 0 to 500 ppm (v/v). For each corrosion inhibitor concentration experiment, a fresh solution as well as freshly polished electrode was used.

The corrosion inhibition process was followed by taking AC-impedance and potentiodynamic polarization measurements. The auxiliary electrode was platinum sheet electrode and the potential was measured with respect to Ag/AgCl as a reference electrode.

The AC impedance measurements were carried out by a computer controlled AutoLab Frequency Response Analyzer (FRA) at open circuit potential with perturbation amplitude of 10 mV vs Ag/AgCl in the frequency range of

10 kHz to 10 mHz at a sweeping rate of 10 points per decade, logarithmic division. At the end of each experiment the potentiodynamic polarization measurements were conducted starting at the open circuit potential and sweeping typically 300 mV vs Ag/AgCl below and over the open circuit potential. The cathodic and anodic curves were taken separately using a computer controlled AutoLab PGSTAT20 potentiostat. Typical scan rate was 1 mV/sec. The tests were performed both with and without corrosion inhibitor at different desired experimental conditions.

RESULTS AND DISCUSSION

It is well established that polarization curves can help to understand how a certain inhibitor works. Inhibitors can modify the anodic process, the cathodic process or both leading to a decreased rate of the global corrosion process. The inhibition effect of CNSL on carbon steel in CO_2 saturated 3% NaCl solution was investigated by polarization technique in both stationary and rotating (3000 rpm) systems. In all cases the polarization curves were recorded 10 hours after the injection of the CNSL in the test solution at 30 ^{o}C. Fig 1 shows some typical anodic and cathodic polarization curves of carbon steel in CO_2 saturated 3% NaCl in the absence and presence of various concentrations (20 ppm to 500 ppm) of CNSL. In Fig. 1a the inhibitor was applied in the solution under stationary conditions (0 rpm), while polarization curves taken on rotating specimen (3000 rpm) are shown in Fig. 1b.

In both Figures (Figs 1a and 1b), two important trends are evident. First it is clear that, CNSL was found to block the electrochemical processes taking place on the steel undergoing corrosion in CO_2 saturated 3% NaCl solution. It reduces both, rate of cathodic and anodic reactions by reducing the current densities on both sides of the polarization curves within the potential region studied. This factor suggests that the CNSL acts as a mixed type corrosion inhibitor. The current densities decrease with increasing CNSL concentration, indicating that the inhibitor is adsorbed on the surface and

hence inhibiting electrochemical processes taking place on a corroding surface. Secondly, CNSL shifts the open corrosion potentials towards less negative values with reference to the blank. The corrosion potential becomes more positive by increasing the inhibitor concentration. These two effects are found to be more pronounced on rotating specimen as compared to stationary specimen. This indicates that the effect of inhibition is enhanced on rotation. Obviously, this protection enhancement on dynamic system as compared to stationary is caused by the increased mobility of the inhibitor molecule to the metal surface.

From the polarization curves the electrochemical parameters listed in Table 1 were determined. These include corrosion potential ($E_{corr.}$), corrosion current density (i_{corr}) determined by extrapolation of the anodic and cathodic Tafel lines, corrosion rate (R_{corr}) and percentage inhibitor efficiency (IE%) both calculated using relations given elsewhere (Philip et al. (2001)). In the same table, the accelerating factor (α) which is the ratio of corrosion rate on stationary system to that of dynamic system at varied CNSL concentrations is also given.

It can be seen from Table 1 that the corrosion rates decrease tremendously at all inhibitor concentrations when the rotation is applied. The addition of 20 ppm of CNSL for stationary system caused the corrosion rate in mmpy of carbon steel to drop from 0.206 to 0.153 mm/y, which correspond to 26% efficiency whereas addition of the same concentration on dynamic system corrosion rate drops from 0.305 to 0.013 mm/y corresponding to 96% efficiency. It is generally quite clear that, under stationary conditions the concentration of CNSL has to be increased sixfold to get the same degree of inhibitor performance achieved under rotation. It can also be seen from the same table that the value of the accelerating factor increases with decreasing CNSL concentrations. Thus, it is higher at low concentration as compared to high concentration. The ratios vary from 0.63 at 500 ppm of CNSL to 11.8 at 20 ppm of CNSL.

This clearly shows that rotation has a dominant role in the adsorption process of the CNSL inhibitor. That rotation increases the mobility and access for the inhibitor to reach the metal surface especially at low concentrations.

The inhibition process of CNSL was also studied by electrochemical impedance spectroscopy technique. Impedance measurements in the Nyquist format for carbon steel in CO_2 saturated 3% NaCl solution containing different concentrations of CNSL at both stationary and dynamic conditions are shown in Figs.2a and 2b, respectively. The impedance results were analyzed by fitting the observed data in a Randles type circuit with one capacitive loop, using a Complex Nonlinear Least Squares fitting program to estimate equivalent circuit parameters (Boukamp (1989)). Equation used to calculate values of double-layer capacitance from impedance measurements is described elsewhere (Philip et al. 2001). Table 2 gives value of charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and percentage inhibitor efficiency (IE%) obtained from the above plots. Since, corrosion rate is inversely proportional to charge transfer, IE% was calculated by use of the relation used for the polarization results. It is seen from this table that as CNSL concentration increases, the R_{ct} values increase while the double-layer capacitance decreases. This indicates that it is corrosion inhibitive in nature. The decrease in the C_{dl} values in the presence of CNSL show that it adsorbs on the metal surface which results in decrease in double layer. The inhibition efficiencies obtained by impedance studies are in agreement with those obtained employing potentiodynamic polarization technique under stationary and dynamic conditions.

An attempt to change the rotation speed during the experiment has also been performed in the inhibited systems after injection of the optimum concentration of CNSL (i.e. 250 ppm) under dynamic condition at 30 °C. The rotation speeds were varied from 1000 rpm to 3000 rpm and impedance spectrum recorded after waiting for a period of 4 hours at each rotation. The impedance results in Nyquist format is shown in Fig.3. From this figure one would notice that with increased rotation speed the diameter of the semicircle increases. This indicates that the charge transfer resistance increases with an increase in rotation speed which suggests an increase in corrosion protection. This also suggests that the inhibitor (CNSL) film formed is quite stable and persistent against shear stress (Moldestad (1995), Buchweishaija (1997)).

For further understanding on the suitability of CNSL corrosion inhibitor, stability against temperature variation was also investigated. Temperature has a profound effect not only on corrosion rate but also it influences the inhibitor requirements as it affects inhibitor stability and solubility (Donham (1990)). Temperatures up to 80 °C were studied, using an optimal concentration of the inhibitor (i.e.250 ppm) under dynamic condition (i.e. 3000 rpm). The impedance spectra for carbon steel electrodes after 10 hrs immersion in the inhibited solutions at temperatures 30, 50 and 80 °C are shown in Fig.4. It can be seen from this figure that as the temperature increases, the size of the semicircle which represent the charge transfer resistance decreases. This suggests a reduction in the performance of the inhibitor as temperature increases. The same behavior was reported by Moldestad (1995), Buchweishaija (1997) under the study of carbon steel corrosion inhibition in carbon dioxide medium. This was explained to be due to the formation of semi protective $FeCO_3$ scale which hinders the inhibitor from reaching the electrode surface. On the other hand it could be due to the increase dissolution kinetics at elevated temperatures which competes with adsorption rate of the inhibitor. Using the fitted charged transfer resistances, the percentage inhibitor efficiencies were calculated and found to be 99%, 70% and 50% at 30 °C, 50 °C and 80 °C, respectively. It is quite clear that the inhibitor performance decreases significantly with increasing temperature. Therefore, change in temperature was found to have significant influence on the performance of the CNSL. This shows that CNSL is therefore temperature sensitive.

CONCLUSIONS

The present study focused on the effect of shear stress on the performance of CNSL inhibitor to inhibit CO_2 corrosion of carbon steel. The investigation was performed by injecting varied concentrations of CNSL at both stationary and dynamic (300 rpm) systems at temperature 30 ^{o}C. The results reveal that CNSL is an excellent corrosion inhibitor of carbon steel in CO_2 medium. The inhibitor has been found to perform well in both systems, but a better performance at very law concentration was registered under dynamic condition. Significantly high inhibitor performance about 96% was observed with just injection of 20 ppm of CNSL. Rotation was found to have a positive effect on the inhibitor performance suggesting that the formed protective inhibitor film to be resistive against flow (shear stress). The results also indicated that very low concentration is required on dynamic system to attain the maximum efficiency as compared to the stationary system. Furthermore, the results revealed that CNSL inhibitor is temperature sensitive. Its performance decreases with increasing temperatures. This inhibitor was found to work more efficiently at room temperature.

REFERENCES

1. Abdel-Gaber, A.M., Abdel-El Nabey, B.A., Sidahmed I.M, El-Zayady, A.M. and Saadawy, M.: Effect of Temperature on inhibitive action of Damsissa extract on the corrosion of steel in Acidic Media, Corrosion Vol. 62, No.4, 293-299 (2006).

2. Bouklah M., Hammouti, B.; Thermodynamics Characterization of steel corrosion for the corrosion inhibition of steel in sulphuric acid solutions by Artemisia; Portugaliae Electrochimica Acta 24, 457-468 (2006).

3. Buchweishaija, J. and Hagen G.; Adsorption isotherms for an amine based fatty acid corrosion inhibitor on carbon steel in CO_2 – saturated solution; Advances in Corrosion Control and Materials in Oil and Gas Production. European Federation of Corrosion Publications No. 26, (1999).

4. Buchweishaija, J.; Inhibiting properties and Adsorption of an amine based fatty acid corrosion inhibitor on carbon steel in aqueous carbon dioxide solutions, Dr. Ing. Thesis Norwegian University of Science and Technology (NTNU) (1997).

5. Choi, H.J. and Cepulis R.L.; Inhibitor film persistence measurements in carbon dioxide environments, Paper No. 371, CORROSION/88, NACE, Huston (1988).

6. de Waard, C. and Milliams, D.E.; "Carbonic acid corrosion of steel", Corrosion 31, 5(1975), p.177.

7. Donham, J.E.; The design of corrosion inhibitors to meet specific requirements for oilfield applications, in Chemical Inhibitors for Corrosion Control, Clubley, B.G. (Ed.), pg. 21 (1990).

8. Farooqi, H.I., Quraishi, M.A. and Saini, P.A., "Natural compounds as corrosion inhibitors for mild steel in industrial cooling systems", Proceedings from European Federation of Corrosion (EUROCORR.'97), Vol. I, Trondheim, sept. 22-25, pg.247-252 (1997).

9. French, E.C., Martin, R.L., Dougherty, J.A.; Review of corrosion inhibitors for gas wells; Materials Performance Vol. 28, No. 8, 46-49 (1989).

10. Gedam, P.H., and Sampathkumaran, P.S., "Cashew Nut Shell Liquid: Extraction, Chemistry and application", Progress in Organic Coatings 14, p.115-157 (1986).

11. McIntine, G., Lippet, J., and Yudelson, J.; "The effect of dissolved CO_2 and O_2 on the corrosion of iron", Corrosion vol.46, No. 2, p. 91-95 (1990).

12. Moldestad, G.; Corrosion inhibition of carbon steel in aqueous CO_2 solutions; Dr. Ing. Thesis, NTH (1995).

13. Mukherjee, D., Berchman, J., Rajsekkar, A., Sundarsanan, N., Mahalingam, R., Maruthamuthu, S., Thiruchelvam, T. and Karaikudi, D., "Plant-based alkaloids inhibit corrosion of marine alloys" Anti-Corrosion Methods and Materials, Vol. 44, No. 3, p. 186-194 (1997).

14. Nkunya M.H.H.; Natural Chemicals for Disease and Insect Management; Professorial Inaugural Lecture, Department of Chemistry, University of Dar es Salaam, Tanzania (2002).

15. Philip, J.N.Y., Buchweishaija, J., and Mkayula, L.L., "Cashew Nut Shell Liquid as an alternative corrosion inhibitor for carbon steels", Tanz. J. Sci., Vol. 27, p.9-19 (2001).

16. Riggs, O.L., "Theoretical Aspects of corrosion inhibitors and inhibition" in CORROSION INHIBITORS by C.C. Nathan (Ed.), NACE (1973).

17. Schmitt, G.; Hydrodynamic limitations of corrosion inhibitor performance, Proc. Of the 8th symposium on corrosion inhibitors (8SEIC) Ann. Ferrara, N.S. V, Suppl. No. 10 (1995).

18. Stegmann, D.W. and Asperger, R.G.; New test for oil soluble/water dispersible gas pipeline inhibitors; Proc. Corrosion/87, NACE, Huston (1987).

19. Trabanelli, G., Carrasiti, F., and Zucchi, F.; 3rd European Symposium on Corrosion Inhibitors, Ann. Univ. Ferrara, N.S., Sez. V., Suppl. No.5, p. 525 (1971).

(a)

(b)
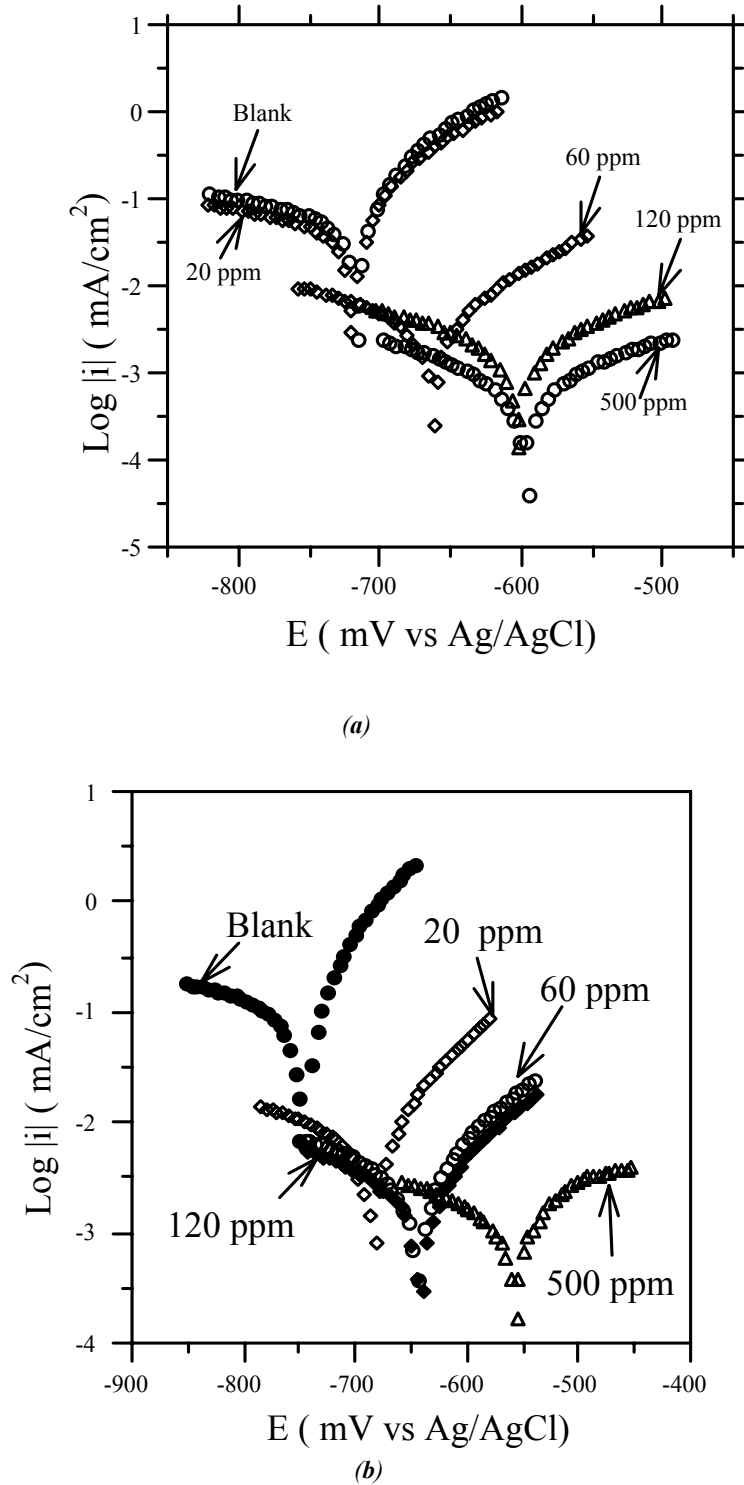
Fig.1:   *Cathodic and anodic polarization curves for carbon steel electrodes taken after 10 hrs of exposure in the absence and presence of different concentrations of CNSL in CO₂ saturated 3% NaCl solutions (pH 5.5) at 30 °C: (a) Stationary system; (b) Dynamic system (3000 rpm).*
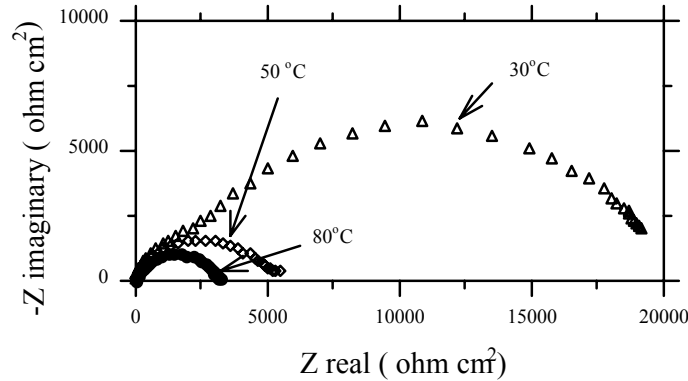
(a)

(b)
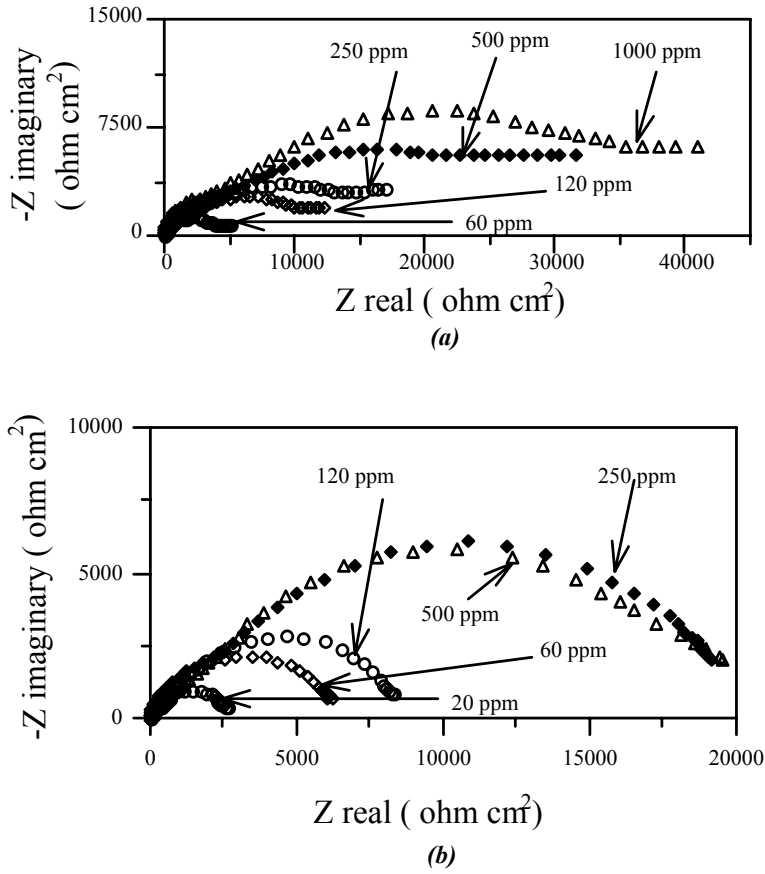
Fig.2: *Impedance spectra in Nyquist format for carbon steel electrodes taken after 10 hrs of exposure in the absence and presence of different concentrations of CNSL in CO_2 saturated 3% NaCl solutions (pH 5.5) at 30 ^{o}C: (**a**) Stationary system; (**b**) Dynamic system (3000 rpm).*
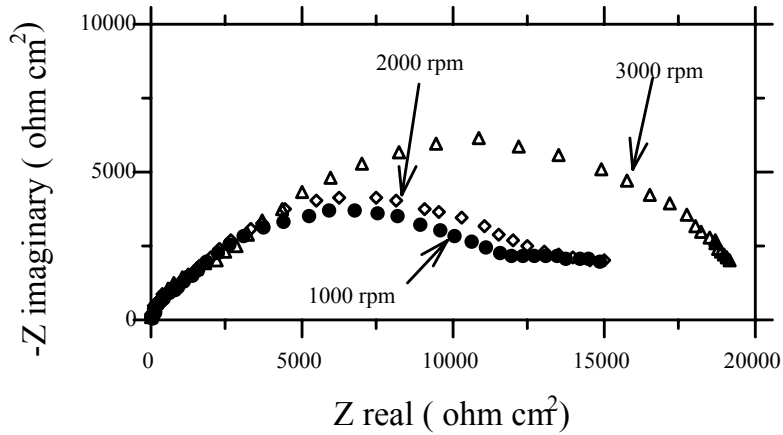
Fig.3: *Impedance spectra in Nyquist format for carbon steel electrodes recorded after 4 hours at each rotation in inhibited CO_2 saturated 3% NaCl solutions (pH 5.5, 250 ppm) at 30 ^{o}C.*

Fig.4: *Impedance spectra in the Nyquist format for rotating carbon steel electrodes (3000 rpm) in inhibited CO₂ saturated 3% NaCl solutions (pH 5.5) at different temperatures 10 hours after injection of 250 ppm of CNSL*

Table 1: *Electrochemical parameters from potentiodynamic polarization curves for carbon steel electrodes in the absence and presence of different CNSL concentrations in CO₂ saturated 3% NaCl solutions (pH 5.5) after 10 hours of exposure at 30 °C under stationary and dynamic (3000 rpm) conditions.*

C_{inh} (ppm)	STATIONARY SYSTEM				DYNAMIC SYSTEM				α $\dfrac{i_{corr}(a)}{i_{corr}(b)}$
	E_{corr} (mV vs Ag/AgCl)	$i_{corr}(a)$ (μA cm⁻²)	$R_{corr.}$ (mm y⁻¹)	IE (%)	E_{corr} (mV vs Ag/AgCl)	$i_{corr}(b)$ (μA cm⁻²)	$R_{corr.}$ (mm y⁻¹)	IE (%)	
0	-719	17.78	*0.206*	-	-746	26.30	*0.305*	-	-
20	-720	13.18	*0.153*	26	-684	1.12	*0.013*	96	11.76
60	-663	1.32	*0.015*	92	-645	0.87	*0.001*	97	1.52
120	-602	0.66	*3.65×10⁻³*	96	-644	0.44	*5.10×10⁻³*	98	1.50
250	-612	0.42	*4.87×10⁻³*	97	-545	0.29	*3.36×10⁻³*	99	1.45
500	-598	0.26	*3.01×10⁻³*	98	-557	0.41	*4.75×10⁻³*	98	0.63

Table 2: *Electrochemical parameters from impedance measurements on carbon steel electrodes in the absence and presence of different CNSL concentrations in CO₂ saturated 3% NaCl solutions (pH 5.5) after 10 hours of exposure at 30 °C under stationary and dynamic (3000 rpm) conditions.*

C_{inh} (ppm)	STATIONARY SYSTEM					DYNAMIC SYSTEM				
	R_{ct} (ohm cm⁻²)	C_{dl} (μF cm⁻²)	i_{corr} (μA cm⁻²)	$R_{corr.}$ (mm y⁻¹)	IE (%)	R_{ct} (ohm cm⁻²)	C_{dl} μF cm⁻²	i_{corr} μA cm⁻²	$R_{corr.}$ (mm y⁻¹)	IE (%)
0	287	1022	23.59	*0.273*	-	221	842	38.51	*0.446*	-
20	376	904	17.57	*0.204*	25	2672	61	2.78	*0.032*	93
60	4461	102	2.46	*0.029*	90	6381	30	1.41	*0.016*	96
120	12044	121	1.09	*0.013*	95	8628	22	0.71	*8.23×10⁻³*	98
250	16807	106	0.71	*8.23×10⁻³*	97	19848	12	0.51	*5.91×10⁻³*	99
500	29082	78	0.43	*4.98×10⁻³*	98	17744	7	0.58	*6.72×10⁻³*	98