EVALUATION OF CORROSION INHIBITOR ON PRE-CORRODED CARBON STEEL IN CO_2 MEDIUM BY IMPEDANCE SPECTROSCOPY

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The effect of pre-corrosion of carbon steel on the performance of a commercial amine based fatty acid corrosion inhibitor, KI384, was investigated in formation water solutions saturated with CO_2 using electrochemical impedance spectroscopy (EIS) measurements. The investigation was performed at constant partial pressure of CO_2 using an autoclave system with Rotating Cylinder Electrodes (RCE). Carbon steel was pre-corroded for periods up to 7 days at 35 and 80 ° C in the test solution prior to inhibitor injection. The results showed that when KI384 was applied on non-corroded carbon steel specimen, high inhibitor performance (ca. 99.8 %) was achieved independent of temperature. When KI384 was applied on pre-corroded carbon steel, inhibitor performance was found to be very much dependent on temperature and pre-corrosion time. It was evident from the results that the nature of the corrosion products formed during the pre-corrosion of carbon steel has a significant influence on the inhibitor efficiency, especially at 80 ° C.

***Keywords**: Corrosion, Corrosion inhibitor, Carbon steel, Carbon dioxide, Impedance.*

INTRODUCTION

The corrosion of steel in water containing dissolved carbon dioxide gas is a topic of considerable interest with practical applications and substantial economic impact in the oil and gas production and in the transportation industry. When carbon dioxide dissolves in water, it hydrates to form carbonic acid. This weak, partly dissociated acid is a cause of severe corrosion attacks on tubing and production equipment in water containing CO_2 [1]. In practice, corrosion inhibitors are commonly applied as the simplest and most cost effective way to diminish the corrosion in these systems. Despite the wide spread application, the detailed mechanism of action is poorly understood. Furthermore, survey of the literature [2,3] has shown that in most cases, laboratory testing of these corrosion inhibitors have been conducted on freshly polished samples, a situation that does not relate to the real practice. Usually metal surfaces are more or less corroded before application of corrosion inhibitors, and hence are certainly covered with corrosion products. It has been established by several investigators that the nature and properties of these corrosion products depend among other things on time of exposure and temperature [2-5]. The presence of these corrosion products on the metal surface can have significant influence on the inhibitor performance. It is not known whether corrosion inhibitors, which are effective on clean surfaces, will still be effective on surfaces covered with corrosion products. With such considerations the influence of pre-corrosion on the performance of inhibitor was studied using the AC impedance technique. The electrochemical impedance spectroscopy technique is a useful tool to study *in-situ* interface phenomena, and has been widely used to study corrosion inhibition [6-8]. The AC technique offers some advantage as compared to DC techniques. It uses very small current and voltage perturbations and hence several

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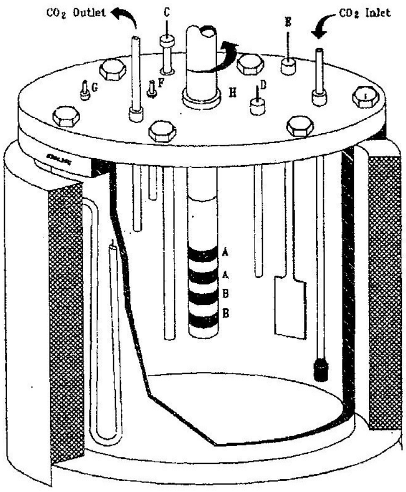
[§] Author to whom correspondence should be addressed, Email:jbuchwe@chem.udsm.ac.tz measurements can be taken without altering the properties of the surface. It can also provide possibility of studying corrosion reactions and measure corrosion rates in low conductivity media [7,8].

EXPERIMENTAL PROCEDURE

The investigation was carried out in an autoclave system with a Rotating Cylinder Electrode (RCE)-assembly, schematically shown in Figure 1. The carbon steel used in this work was an API type 5L-X60 with the following composition in weight percentage: 0.07 C, 0.25 Si, 1.30 Mn, 0.02 Cr, 0.01 Ni, 0.018 Al, 0.01 Cu, 0.10 Mo, 0.039 V and 98.183 Fe. The specimen had the shape of a cylinder with diameter of 2.5 cm, 1 cm long, this giving an exposed area of 7.85 cm^2. The exposed metal surfaces were polished with 1200 grits silicon carbide paper, ultrasonically cleaned with acetone, and finally rinsed with ethanol before the immersion in the test solution.



Key: A: Specimens for electrochemical measurements,
B: specimens for surface and gravimetric analysis
C: thermocouple
D: Reference electrode
E: counter electrode
F: pH-electrode
G: inhibitor inlet
H: mechanical seal (cartex)

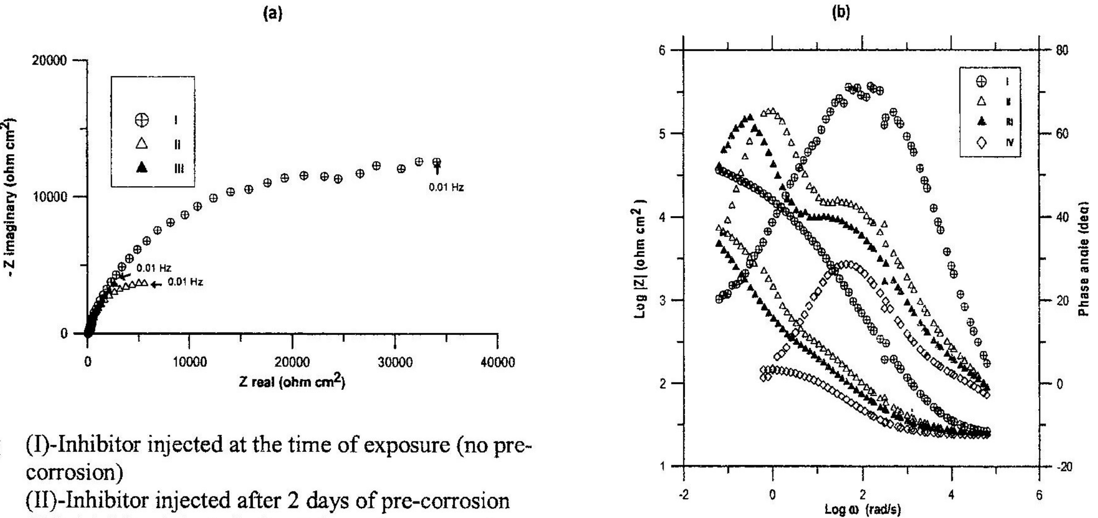
Figure 1: Electrochemical cell with RCE

The corrosive medium was prepared from analytical grade reagents in de-ionised distilled water and had the following chemical composition in g/l: 0.720-$NaHCO_3$, 21.620-NaCl, 0.350-KCl, 0.460-$CaCl_2 \cdot 2H_2O$, 1.320-$MgCl_2 \cdot 6H_2O$, 1.300-$NaCH_3COO$. The corrosion inhibitor used was a commercial water-soluble amine based fatty acid compound (called KI384) produced by Dyno Oilfield Chemicals, Norway. The test solution was deoxygenated and saturated with CO_2 by continuously purged with CO_2-gas before and during the experiments. The oxygen contents in the test solution were controlled by an Orbisphere oxygen indicator to be below 5 ppb. The pH of solution was monitored by a pH sensor installed in the autoclave and was 5.5 ± 0.5 after CO_2 saturation. The rotation speed for all experiments was set at a single speed of 1000 rpm.

Carbon steel was pre-corroded for periods up to 7 days at 35 and 80 ° C in the test solution prior the inhibitor injection. The concentration of corrosion inhibitor used was 50 ppm. Electrochemical impedance measurements were carried out at open circuit potential with perturbation amplitude of 10 mV and a frequency range from 10 kHz to 10 mHz measured between two identical cylinder electrodes of carbon steel separated by a Teflon spacer. A plate of stainless steel (70 cm^2) was used as a counter electrode, and saturated calomel as a reference electrode. The instrument used was a computer assisted frequency response analyser AUTOLAB-FRA.

RESULTS AND DISCUSSION

The effect of increased pre-corrosion time on the inhibited carbon steel at 35 °C is well illustrated by the results presented in Figure 2 (a) and (b). For clarity of features of impedance results both Nyquist and Bode plots are presented. The electrochemical impedance measurements were recorded 48 hours after the injection of 50 ppm of the corrosion inhibitor. For comparison purpose, in the Bode plot (Figure 2 (b)) typical impedance spectra for the carbon steel electrode corroded for six days in the same solution without inhibitor is also given. As can be seen in the Nyquist plot Figure 2 (a), a large size of semicircle (curve I) is obtained when the inhibitor is injected immediately (without pre-corrosion), indicating a significant reduction of corrosion process taking place on the metal surface.



Key (I)-Inhibitor injected at the time of exposure (no pre-corrosion)
(II)-Inhibitor injected after 2 days of pre-corrosion
(III)-Inhibitor injected after 7 days of pre-corrosion

Figure 2: (a) Impedance diagrams in Nyquist for rotating carbon steel electrodes (1000 rpm) in CO_2-saturated solutions at 35 °C, 48 hours after injection of 50 ppm KI384 inhibitor; (b) -Bode plots for the same data as in (a), also including 6 days exposed without inhibitor (curve IV)

When the same concentration of the inhibitor is injected on pre-corroded electrodes systems at 35 °C (curve II and curve III in Figure 2 (b)), the impedance diagrams change from a single to two capacitive loops. The size of the high capacitive semicircle is maintained constant whereas the low one decreases with the increase of pre-corrosion time. The impedance results for the system without inhibitor at the same temperature show only one time constant. The two capacitive loops result are well illustrated by the impedance diagram results (Nyquist formats) for the inhibited 2 days pre-corroded carbon steel at different exposure time presented in Figure 3.

One can notice that the size of the high frequency loop (inserted figure) does not change with time, while the low frequency loop increases significantly with exposure time. In order to understand better the influence of these two time constants, one extra experiment was performed. In this experiment the pre-corrosion time of the electrode before injection of inhibitor was maintained constant (i.e. 2 days) while the inhibitor concentration in the solution was changed between 20 and 50 ppm, the impedance results of which is presented in Figure 4. From these impedance results, it can also be noted that the size of the high frequency loop was maintained constant whereas the low process increases with inhibitor concentration. Based on the above two impedance experimental results the influence of the inhibitor on the corrosion process of carbon steel on pre-corroded electrodes at 35 °C, is therefore, apparently associated with the behaviour of the low frequency capacitive loop. The other high capacitive loop is related to the film (corrosion products) formed during pre-corrosion.

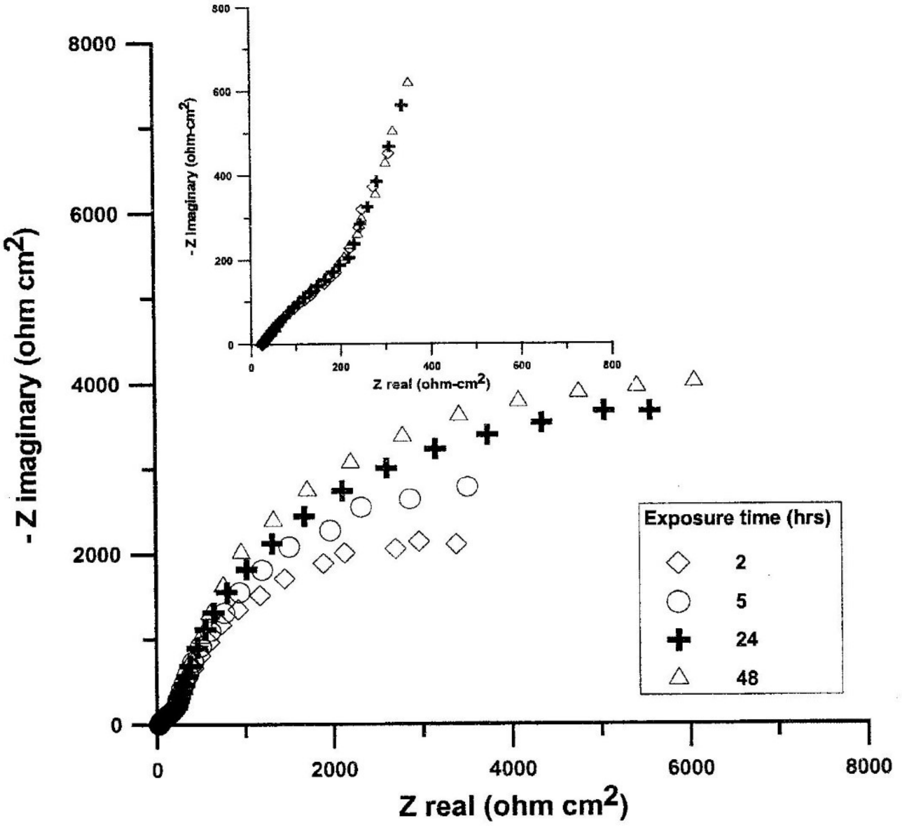


Figure 3: Influence of exposure time after inhibitor injection on the electrochemical impedance diagrams for rotating carbon steel electrodes (1000 rpm) in inhibited CO2-saturated solutions

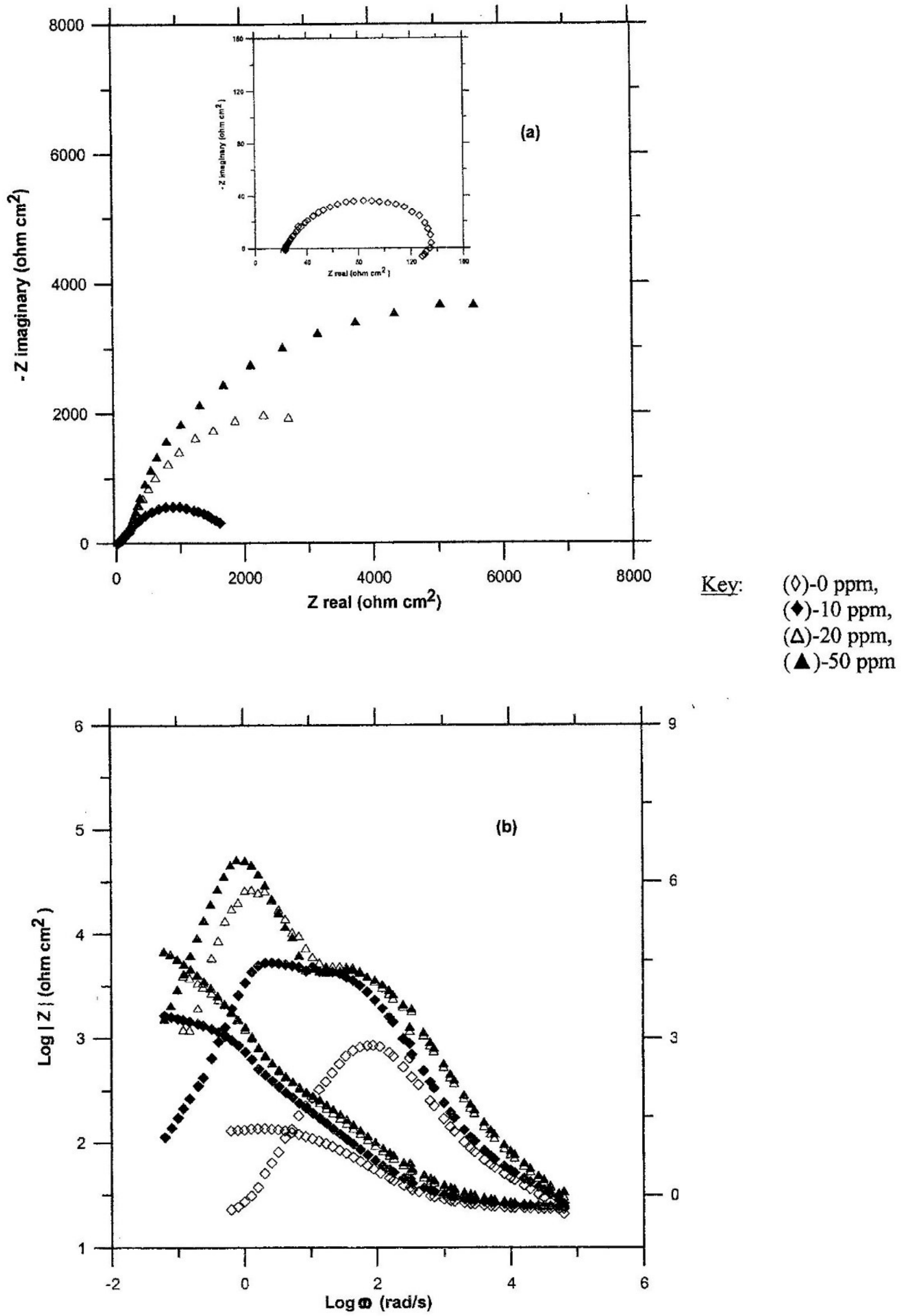


Figure 4: (a) Impedance diagrams in the Nyquist format for 2 days pre-corroded rotating carbon steel electrodes (1000 rpm) in CO_2-saturated formation water at 35 C prior to injection of inhibitor. Measurements were taken 24 hours after injection of inhibitor; (b) Bode plot for the same data as in (a)

Similarly, the effect of increased pre-corrosion time of carbon steel on the performance of KI384 by impedance measurements was also performed at an elevated temperature of 80 °C.

Typical impedance diagram results in Nyquist formats are presented in Figure 5 (a). The plots show only one time constant both on non-corroded and pre-corroded surfaces, which becomes smaller in size with increasing time of pre-corrosion. This diminution indicates an increase in corrosion rate, suggesting a drop in the inhibitor performance with an increase in pre-corrosion time. This is opposite to what was observed in the uninhibited solutions at the same temperature (Figure 5 (b)). The size of the semicircle increases with an increase of exposure time, suggesting formation of protective film of corrosion products as the immersion time increases. In combination of what was observed in the inhibited non-corroded as compared to pre-corroded electrodes, one would suggest that the protective film formed during pre-corrosion to be responsible for poor inhibitor performance. The film seems to obstruct the inhibitor molecule from reaching the metal surface while reactants in the corrosion process like water molecules, dissolved carbon dioxide species and H^+ ions are still able to penetrate the film to a certain extent. It is quite clear from the results that also at this temperature the inhibitor worked efficiently on freshly polished specimen, showing that thermal or chemical breakdown of the inhibitor could not explain the poor efficiency on the pre-corroded specimen.

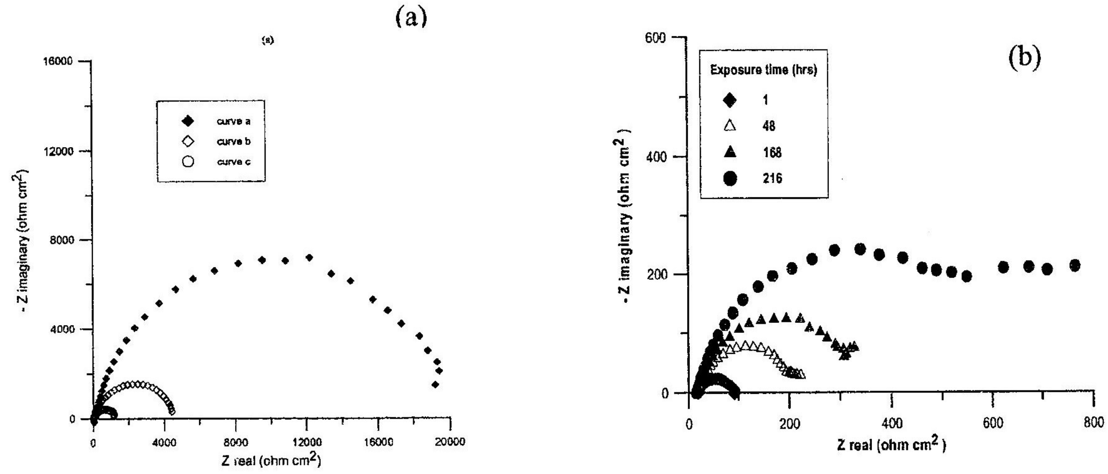
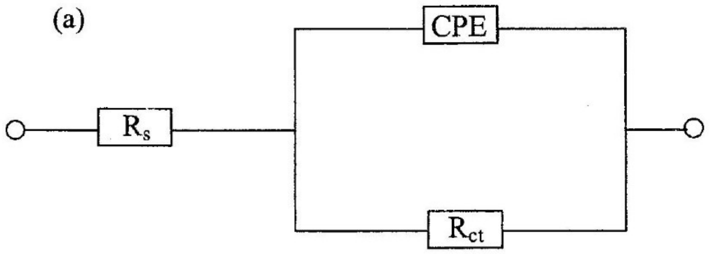


Figure 5: (a) Impedance diagrams in Nyquist format for rotating carbon steel in inhibited (50 ppm) CO_2-saturated formation water at 80 °C, 48 hours after inhibitor injection; (I)-No pre-corrosion, (II)-2 days pre-corrosion, (III)-7 days pre-corrosion. (b) Impedance diagrams in Nyquist format for rotating carbon steel in uninhibited CO_2-saturated formation water at 80 °C

The electrochemical impedance parameters (basically R_{ct}) were analysed by fitting the observed data to the equivalent circuits of the type shown in Figures 6(a) and (b), using a complex non-linear least square fitting program, EQUIVCRT [9]. The inverse of charge transfer resistance value, R_{ct}, is an indication of corrosion rate. The equivalent circuit models used to analyse experimental impedance spectra are given in Figure 6 (a) and (b). As can be seen from Nyquist plots of all the impedance results, the spectra are not perfect semicircles (i.e. are depressed) and hence a Constant Phase Element, CPE, was used instead of double layer capacitance [10-13]. Figure 6(a) is an equivalent circuit corresponding to a simple electrochemical cell. The circuit gives rise to only one time constant. The circuit, Figure 6(b), has been reported to represent an imperfectly covered electrode, as might be the case for a corroding metal coated with porous non-conductive film or imperfect coating [14]. This type of circuit has been used to analyse two time constants impedance results. An example of the fitting curve in Bode plot for the experimental and simulated data using this circuit (Figure 6(b)) is given in Figure 7. The figure shows that there is a very good agreement obtained between fitted and experimental results.



Key: CPE = Constant Phase Element, R_s = Solution resistance, R_{ct} = Charge Transfer Resistance and R_{po} = Pore Resistance.

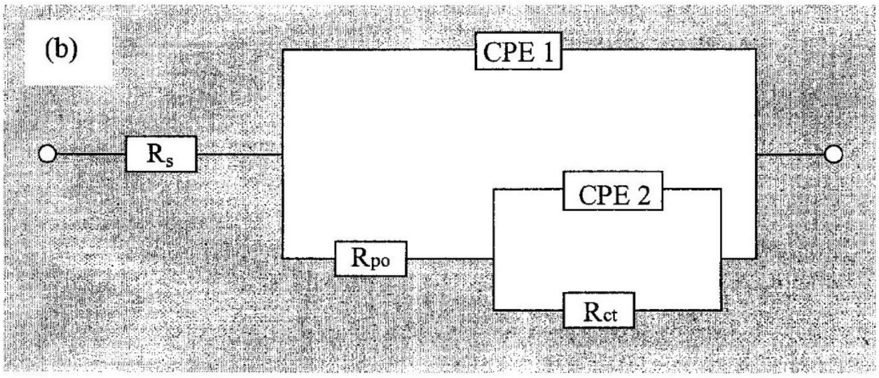


Figure 6: Randles type equivalent circuits used to analyse the EIS results; (a) one relaxation time constant, (b) two relaxation time constants (coated metal/solution interface)

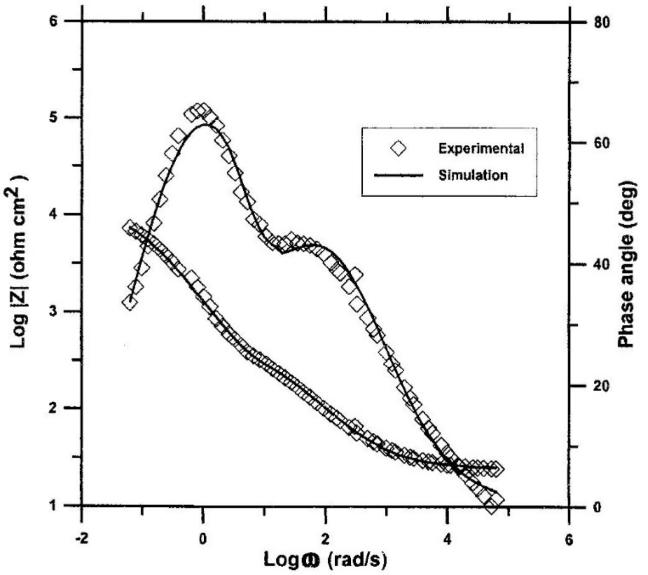


Figure7: Impedance diagrams (Bode plot) for 2days pre-corroded rotating carbon steel electrode (1000 rpm) as generated 48 hours after injection of 50 ppm KI384 inhibitor in CO_2-saturated formation water at 35 °C. The solid line represents simulated data obtained by equivalent circuit of Fig. 6 (b)

Based on R_{ct} values, inhibitor efficiencies (ϕ.) were calculated using the following relationship:

$$\phi = \frac{R_{ct,i} - R_{ct,u}}{R_{ct,i}} \qquad (1)$$

where, $R_{ct,i}$ is the charge transfer resistance for the system with inhibitor, while $R_{ct,u}$ is the charge transfer resistance for the reference system without inhibitor. The reference system is chosen to be the situation just before inhibitor injection.

Figure 8 (a) and (b) depict the variation of inhibitor efficiencies, with time of exposure after the injection of the inhibitor in the solutions at 35 °C and 80 °C, respectively. It is quite evident from this figure that high inhibitor performance was registered when KI384 was applied on freshly polished carbon steel surfaces (non-corroded) as compared to pre-corroded surfaces. The inhibitor efficiency reached to approximately 99.9% within the first hour and remained constant for the rest time of exposure at both temperatures.

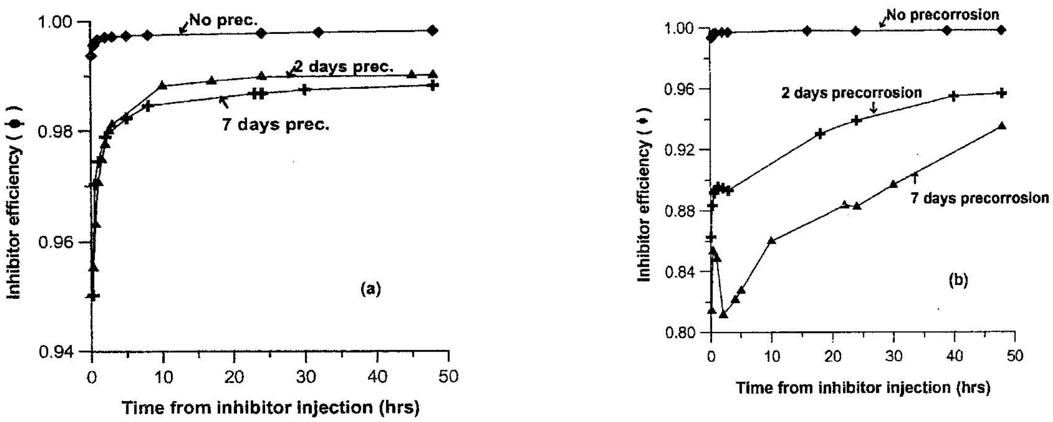


Figure 8: Inhibitor efficiency against time from inhibitor injection for rotating carbon steel electrodes (1000 ppm) in CO_2-saturated formation water at 35 °C (a) and 80 °C (b) with 50 ppm KI384 inhibitor

When the inhibitor was applied on pre-corroded carbon steel, at 35 °C, the inhibitor worked effectively on the steel that was pre-corroded for 2 days giving a final inhibitor efficiency of 98.8% after 10 hours which remains constant for the rest of 48 hours exposure. In a similar set of experiments at the same temperature, it was found that KI384 inhibitor worked efficiently even on carbon steel pre-corroded for 7 days in the test solution prior to injection of inhibitor. The pre-corrosion effect became more severe when the temperature was raised to 80 ° C. Similar experiments performed at 80 °C (Figure 8(b)) registered less inhibition percentage for pre-corroded carbon steel in CO_2-saturated medium. As the figure shows, on 2 days pre-corroded carbon steel, the inhibitor efficiency dropped to about 88% and gradually increased to about 95% after 48 hours exposure. Further increase of pre-corrosion time up to 7 days at 80 °C, the inhibitor performance dropped significantly to about 80% within the first four hours and gradually increases to 90% after 48 hours of exposure to the inhibited solutions. The above results indicate that it takes more time for the inhibitor to penetrate the film of corrosion products at 80 °C as compared to 35 °C. This could further suggest that the differences in porosity of film formed at two temperatures. The film formed at 80 ° C seems more compact that the film formed at 35 ° C, thereby making more difficult for the inhibitor to diffuse through and reach the metal surface.

The exact mechanism of how this particular inhibitor works is not known. However, it is assumed that lone pair electrons of nitrogen atom in the amine group of KI384 interact directly with the d-orbital of the metal iron atoms of the substrate. This may suggest that the inhibitor needs to reach the metal surface in order to be protective, and that adsorbing onto the corrosion products at the metal surface is not sufficient to block the corrosion process. The experimental findings in Figure 8 (b) may support this assumption, since pre-corroded electrodes are protected rather poorly and at a slower rate in the presence of the protective corrosion products (such as iron carbonate scale). These findings indicated that the surface conditions on the metal before inhibitor addition plays a big role on the performance of KI384 corrosion inhibitor. The results had also demonstrated the importance of considering the state of the metal surface conditions during inhibitor evaluations.

CONCLUSIONS

A commercial amine based fatty acid type of corrosion inhibitor has demonstrated high inhibition efficiency of carbon steel corrosion in carbon dioxide medium depending on the history of the metal surface to be protected. Significantly high inhibition was observed at two temperatures when the corrosion inhibitor was applied on non-corroded surfaces. Almost the same inhibitor efficiency (99.8%) was observed regardless of the system temperature.

The experiments have shown that corrosion products formed on the iron surface can have a significant influence on the performance of the corrosion inhibitor. At low temperatures i.e. at 35 °C, surface corrosion products (mainly iron carbide) formed by pre-corrosion of the carbon steel have only a minor influence on the inhibitor performance. At 80 °C the presence of a protective film of either iron carbonate film or iron carbide significantly diminish the performance of the corrosion inhibitor.

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NOMENCLATURE

CPE	Constant Phase Element
R_{ct}	Charge transfer resistance
$R_{ct,i}$	Charge transfer resistance with inhibitor
$R_{ct,u}$	Charge transfer resistance without inhibitor
R_{po}	Pore resistance
R_s	Solution resistance

Greek symbols

ϕ	Inhibitor efficiency

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