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Fractal Analysis of the Corrosion Inhibition of Carbon Steel in a Bromide Solution by Lithium Chromate

E. Sarmiento, J. G. González-Rodriguez, J. Uruchurtu, O.Sarmiento, M. Menchaca*

Universidad Autonoma del Estado de Morelos-CIICAp Av. Universidad 1001,Col. Chamilpa, 62209-Cuernavaca, Mor., Mexico
*E-mail: juch25@uaem.mx

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Electrochemical noise results obtained for mild steel corrosion conditions under a lithium bromide-ethylene glycol solution and in the presence of different concentrations of lithium chromates (Li_2CrO_4) as corrosion inhibitor are shown. The evaluation was performed from the fractal dimension of the electrochemical noise-time series obtained using the so called the Rescale Range Analysis (R/S) proposed by Hurst. The steel under different inhibitor concentrations were exposed to a lithium bromide environment and electrochemical potential/current noise measurements were performed. Afterwards, the fractal dimensions were calculated from the time series obtained for the different condition signals. This dimension is obtained from the empirical law $R/S = (\tau/2)^H$ where R represents the difference between the maximum and minimum values of the variable, S the standard deviation of the time series, τ is the period of time measured and H the Hurst exponent between $0 < H < 1$. The calculation of the Hurst exponent and fractal dimension of the time series comes from the slope of the R/S plot. For comparison electrochemical impedance spectroscopy was also performed. The fractal analysis of electrochemical noise helps to evaluate the inhibitor protection performance under the corrosion conditions tested.

Keywords: Steel, inhibition, bromide solution, Fractals, Hurst.

1. INTRODUCTION

The cheapest and first structural material candidate one can have is carbon steel that has been used since ancient times. However, it is not precisely the most corrosion resistant for many industrial environments especially in the presence of chlorides [1-3]. For this reason, the expected high corrosion effects of the LiBr aqueous solutions, solutions used in absorption heat transformers [4] which are some of the most promissory elements to make an improvement of the industrial waste heat. Lithium bromide (LiBr) heavy brines are one of the most widely used absorbents, however, extremely corrosive [5-8]. An alternative system that reduces some of the disadvantages of the mixture water/LiBr is to add ethylene glycol to this system [5] because some thermo-physical properties of the LiBr/water mixture, such as thermal conductivity, viscosity, maximum concentration etc…, are improved [5]. Alternatively, corrosion, inhibitors can be used for corrosion control in closed systems and as an alternative of efficiency-cost for materials use. The affectivity of some corrosion inhibitors depends upon the type of material, its properties and the corrosive environment. Molybdate (MoO_4^{2-}) is a very effective passivating inhibitor at relatively high levels. Molybdates are inorganic, passivating inhibitors which have been used satisfactorily in many corrosive environments. For instance, they have been used to prevent mild steel [9] and cold rolling steel [10] corrosion in simulated cooling water, in the zinc corrosion inhibition in acidic solutions [11], used to seal phosphate coatings on hot-dip galvanized steel [12] or on the bacterial corrosion or iron [13]. In a similar way, they have been used on the corrosion inhibition of galvanized steel and aluminum[14] and zinc [19] in NaCl solutions, for the zinc corrosion inhibition in acidic solutions [15], on the pit initiation of pure aluminum in HCl solutions [16] or even used in sol-gel coatings for mild steel [17].

Electrochemical impedance spectroscopy (EIS) is a technique widely used to evaluate inhibitors performance, since it provides information about the corrosion process taking place on the metal surface. Particularly, it gives information about the polarization resistance values R_p (more precisely the charge transfer resistance R_{tc}), the double layer capacitance C_{dl}, solution resistance R_s as well as kinetic information.

Sometimes impedance data obtained at the corrosion potential, have the shape of a depressed semicircle with its centre, on the real axis. The simplest equivalent electric circuit corresponds to a parallel combination of a capacitance and a resistance. For better quality constant phase elements, CPE, replacing the capacitor, are often used in data fitting of depressed semicircles. The impedance of a CPE is given by:

$$Z=Z_o(j\omega)^{-n} \qquad [1]$$

where n take values between 0 and 1, depending of the circuit element represented. The complex impedance $Z(j\omega)$ of a depressed semicircle could be expressed as:

$$Z = R_s + R_{ct} / [1 + (j\omega C_{dl} R_{ct})]^{n} \qquad [2]$$

being ω the depression angle:

$$\omega = (1-n) \times 90^{\circ} \qquad [3]$$

Parameter n is 1 for an ideal capacitor. In real systems, the ideal capacitive behaviour is hardly observed due to surface roughness, heterogeneities or other effects that cause uneven current distributions over the electrode surface. In the case when n =1, the term $(j\omega C_{dl}R_{ct})^n$ reduces to $j\omega C_{dl}R_{ct}$ where C_{dl} is the interfacial double layer capacitance. This can be interpreted as an indication of the degree of heterogeneity of the metal surface [18]. When n takes values slightly higher than 0.5, corresponds to a severe heterogeneity, but when *n is equal* to 1, the metal surface is completely smooth. This degree of heterogeneity has been associated to the fractal dimension of the surface [19]. A "fractal" is an object with complex structure, revealing new details at increasing degrees of magnification [11, 12].

Taking into account the degree of depression of the semicircle in the Nyquist impedance plot, it is possible to determine the fractal dimension of the electrode surface by means of the following equation [9]:

$$n = 1/\,(D_{fs} - 1) \qquad [4]$$

where D_{fs} is the fractal dimension of the surface. D_{fs} can take values between 2, for a surface completely smooth, to values close to 3, for a rough surface. It has been demonstrated that the fractal dimension of an electrode can be determined by means of electrochemical impedance measurements and correlated with atomic force microscopy [10].

Electrochemical noise (EN) is a non-intrusive technique used highly successful in different corrosion conditions. EN data are collected in the form of potential and/or current time series or ensembles of sufficient length. Analysis methods for EN data include visual inspection, statistical and spectral analysis of time records [13-18]. Previous studies have suggested that EN time records contain valuable information about corrosion protection by inhibitors, however statistical and visual analysis have not revealed information about mechanisms of corrosion inhibition [19]. Spectral analysis have also been used to study the periodicity of the structure of EN time records. The slope of the spectral density function (SDF) at higher frequencies typically has the form of $(1/f^{\beta})$. Different values of the β exponent have been reported for specific modes of corrosion [20, 21].

Alternatively, the structure of the EN time record can be analysed in the time domain and described by the Hurst exponent H [20]. The development of fractal geometry by Mandelbrot [21] has provided mathematical tools for the analysis and characterization of the structure and scaling exponents of fractal time records. An EN time record is a "random" fractal, where the levels of detail are similar but not identical, sharing the same statistical properties. The fractal dimension D_f describes the structure of a fractal, e.g., the "roughness" of an EN time record, and the fractal geometry provides the explanation for the values of D_f, H and β that are observed for some of the EN time series parameters, and noise spectra. Specifically, the fractional brownian motion (fBm) technique of Mandelbrot provides the connection between the structure of the EN time record and SDF (characterized by D_f, H and β) and the microscopic behaviour (oxidation reactions) responsible for corrosion. The fractal dimension D_f is defined as:

$$D_f = 2 - H = (5-\beta)/2 \qquad [5]$$

For example, the Hurst exponent H which is formally related to β. reveals long-term time dependence in a time series and can be evaluated from the oscillations occurring in the data. When the variation in the time record over a specific time interval (the lag time) is proportional to the lag time raised to the power H, the time series is said to be fractal. According to Hurst´s rescaled range analysis based on his empirical law proposed [20]:

$$R/S = (\tau / 2)^{H} \qquad [6]$$

where R represents the difference between the maximum and minimum values of the variable, S the standard deviation of the time series, τ is the period of time measured and H the Hurst exponent. The parameter H describes both the appearance of the time series (“roughness”) and the characteristics: when $0.5 < H < 1$ undulating signal or “persistence”, or $0 < H < 0.5$ jagged signal “anti-persistence”. When H is equal to 0.5 the process is said to be completely random, that is statistically independent of each other. These are associated to the physicochemical process, e.g., corrosion [20-23].

The aim of the present work is to study the performance of lithium molybdates as corrosion inhibitor by comparing the results obtained by two electrochemical techniques i.e. electrochemical noise and electrochemical impedance spectroscopy measurements. Special emphasis has been made to determine the morphology of the metal surface expressed as the fractal dimension of the surface as obtained by electrochemical impedance spectroscopy and comparing the dimension with the Hurst exponent calculated from noise measurements. The purpose is to explore the possibility to evaluate corrosion resistance characteristics of the different inhibitor concentrations.

2. EXPERIMENTAL PART

The material tested was 1018 carbon steels, encapsulated in a commercial MC-40 resin. Cylindrical probes with 5.9 mm in diameter and an exposed area of 0.2728 cm^2 to the solution were used. All of them were abraded with 600 SiC emery paper, and finally rinsed with distilled water and ethanol. Solution used was a LiBr + ethylene glycol + H_2O mixture at room temperature, in a concentration of 614 and 217 g/l for LiBr and ethylene glycol respectively, with additions of 5, 20 and 50 ppm of lithium chromate, Li_2CrO_4, as corrosion inhibitor. The electrochemical free corrosion potential of the working electrode, E_{corr}, was measured versus a saturated calomel reference electrode (SCE), whereas a platinum wire was the auxiliary electrode. Triplicate electrochemical measurements were obtained by using a fully computerized potentiostat and the average values were obtained. EIS measurements were done with a Gamry EIS 300 equipment in the interval of frequency of 0.005 to 10000 Hz with an amplitude of ±10mV at the free corrosion potential, 5 minutes after immersion into the solution. Afterwards, for the different inhibitor concentrations the depression angle from the Nyquist plots were obtained using a commercial software.

Electrochemical noise measurements (EN) in both current and potential were recorded using two identical working electrodes and a reference electrode (SCE). The electrochemical noise measurements were made recording simultaneously the potential and current fluctuations at a sampling rate of 1 point per second for a period of 1024 seconds. A fully automated zero resistance ammeter (ZRA) from ACM instruments was used in this case. Removal of the DC trend from the raw noise data was the first step in the noise analysis when needed. To accomplish this, a least square fitting method was used. Finally, the noise resistance, R_n, was then calculated as the ratio of the potential noise standard deviation over the current noise standard deviation ($R_n = \sigma_v / \sigma_i$). From the EN time records, the Hurst exponent H was also calculated as to have one quantitative parameter in order to compare signals. This exponent was evaluated using the Hurst rescaled range analysis based on his empirical law proposed in 1965 [12]. Finally, corroded surfaces were analyzed in a LEO E300 scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

Nyquist impedance plots of steel in the bromide solution with different inhibitor concentrations are shown in Fig.1. Lithium chromate effectively reduced the corrosion rate and this inhibition effect is affected by the inhibitor concentration. The Nyquist plot are similar, presenting a depressed charge transfer resistance semicircle with a second low frequency loop or semicircle associated to mass transfer effects, typical of a mixed control inhibitor. The charge transfer resistance was obtained by extrapolation of the charge transfer semicircle corresponding to the diameter of the semicircle.

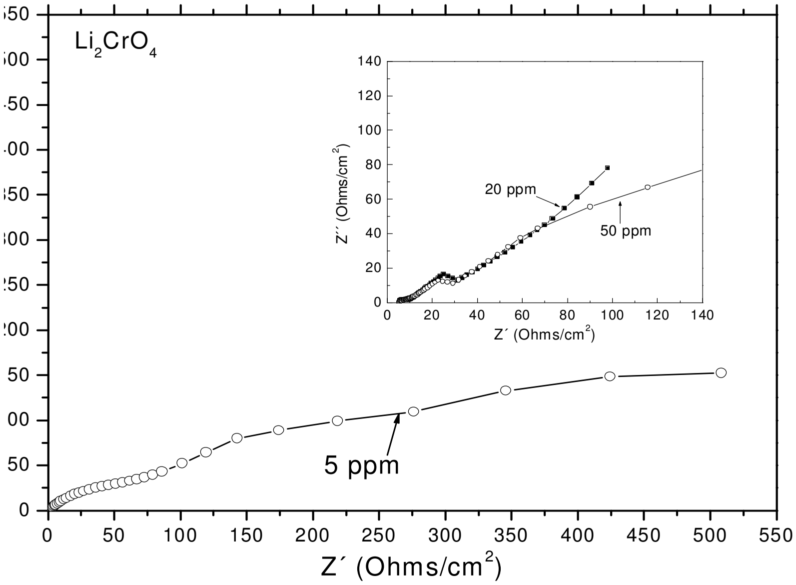

Figure 1. Nyquist diagram for Li_2CrO_4 at E_{corr} (-880, -885 and -930 mV for 5, 20 and 50 ppm of inhibitor concentration respectively)

Electrochemical parameters have been calculated from the obtained impedance data considering electric circuits shown on Fig. 2. In this circuit, R_f represents the resistance of the inhibitor film, C_f is its capacitance, R_{ct} represents the charge transfer resistance and C_{dl} represents the double layer capacitance. The experimental results are presented in table 1. The corrosion potential shows a tendency to be more negative as the inhibitor concentration increases and correspondingly the charge transfer resistance values are higher. Efficiencies were obtained for the different inhibitor concentrations being the best (91.38%) at 20 ppm inhibitor concentration although this difference was marginal. The impedance plots obtained at corrosion potential having the shape of depressed semicircles, with the center of the circle below the real axis, can be modeled in terms of parallel resistances and constant phase elements, being the charge transfer semicircle representing the surface roughness and being also the measured depression angle used to calculate the fractal dimension of the metal surface.

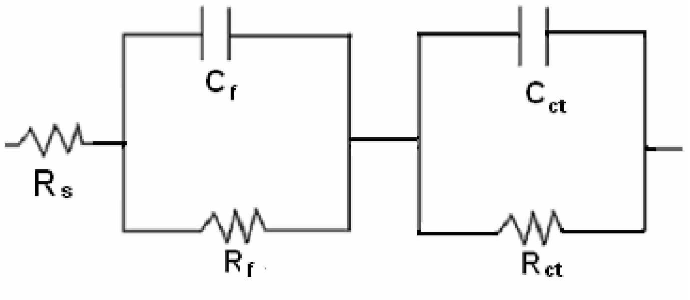

Figure 2. Electric circuits used to simulate EIS data

The fractal geometry of the metal surface as a function of inhibitor concentration is presented in Table 1. The fractal dimension describes the structure of a fractal, e. g. the irregularity of the electrochemical noise time record. It can be noticed that fractal dimension is sensitive to inhibitor concentration. Without inhibitor, the fractal dimension value is one of the lowest, maybe due to the polished surface and the effect of the corrosion process itself. The fractal dimension is highest at 20 ppm, which also offers the maximum corrosion resistance. The effect of the inhibitor could be clearly seen for different inhibitor concentrations. This change in fractal dimension could be due to passive film formed and promoted by the inhibitor reaction, which is known to occur with nitrate inhibitors used as oxidizers for active passive metals such as iron. This suggests that the main form of attack is localized such as pitting attack [22-24].

Table 1. Electrochemical parameters

Conc. (ppm)	Ecorr (mV)	Rtc (ohm/cm^2)	Cdl F/cm^2	Efficiency. (%)	Depression angle (°)	D_{fs}	2do.ang. (°)	R_f (ohm/cm^2)	C_f F/cm^2	R_{sol}: ohms.cm^2
0	-860	762	3.91E-04	-	26.18	2.4102	20.85	3.95E+02	1.04E-03	3.38E+00
5	-889	0.06	9.52E-03	87.33	32.72	2.5712	57.34	1.72E+02	4.46E-04	2.06E+02
20	-739	46.70	3.46E-02	83.68	27.53	2.4407	30.51	2.35E+01	2.11E-02	5.59E+00
50	-929	51.80	3.84E-02	85.29	26.55	2.4184	39.97	7.39E+01	4.05E-02	6.29E+00

As an example, electrochemical potential and current noise time records for the blank solution (without inhibitor) and for 50 ppm of inhibitor, are shown in Fig.3. The general appearance or structure of electrochemical potential and current time records appeared to be similar for the two time series conditions, although a transient associated to local events can be observed at the end of the time series, for the uninhibited solution. The ratio between the noise in potential and the noise in current gave the noise resistance time series (R_N). The results are presented in Fig. 4 for the different inhibitor concentrations, and we can see that the average noise resistance value consistently decreased as the inhibitor concentration increased for almost three orders of magnitude. A decrease in the R_N value is associated to the rupture of the protective passive film, whereas the increase in its value corresponds to a repassivation, healing of the passive film. The noise resistance data indicated that in absence of the inhibitors, transient data were present indicating film rupture/repassivation events. When inhibitors were present, the frequency of these transients was decreased; indicating a lower susceptibility towards localized type of corrosion [25].

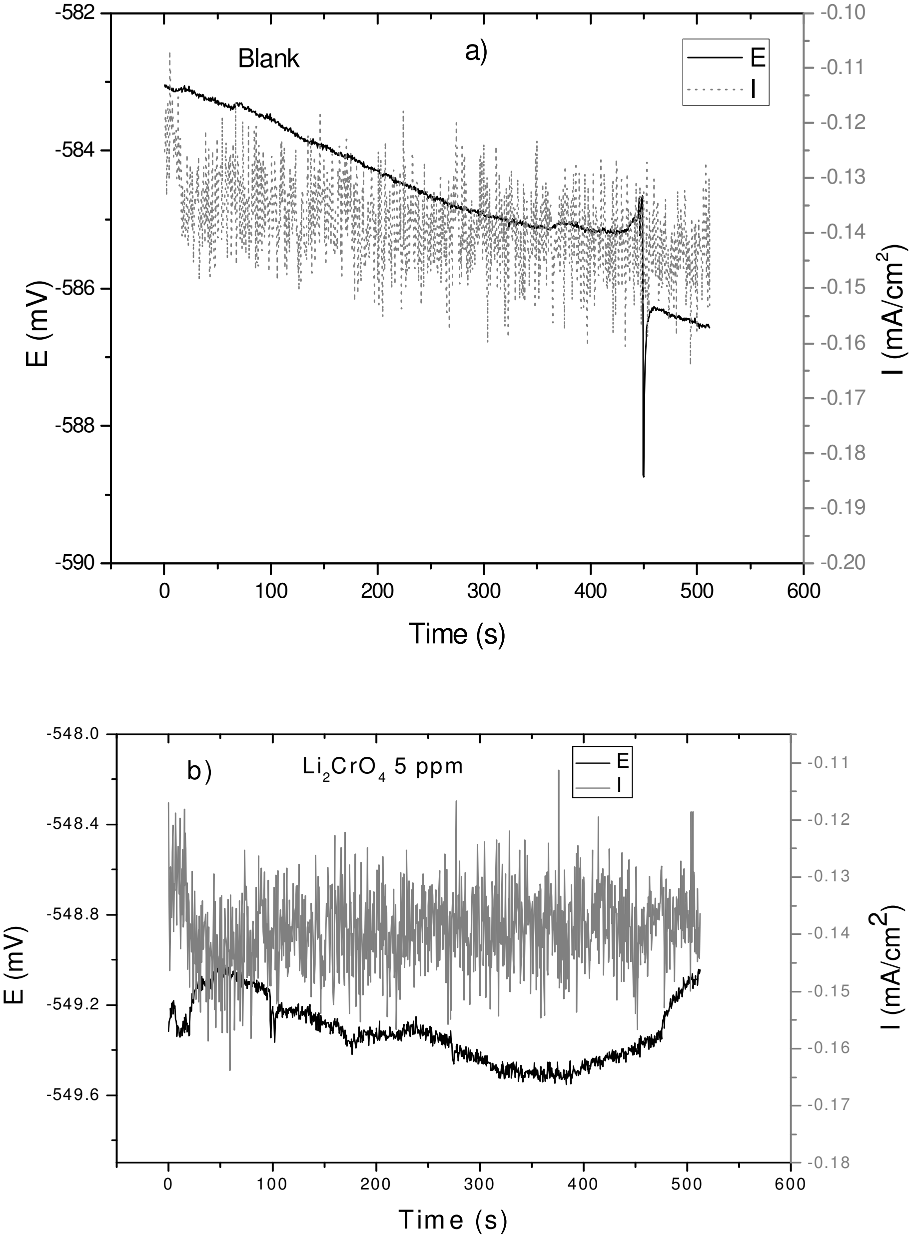

Figure 3. Electrochemical noise for 1018 steel a) without and b) with 5 ppm Li_2CrO_4

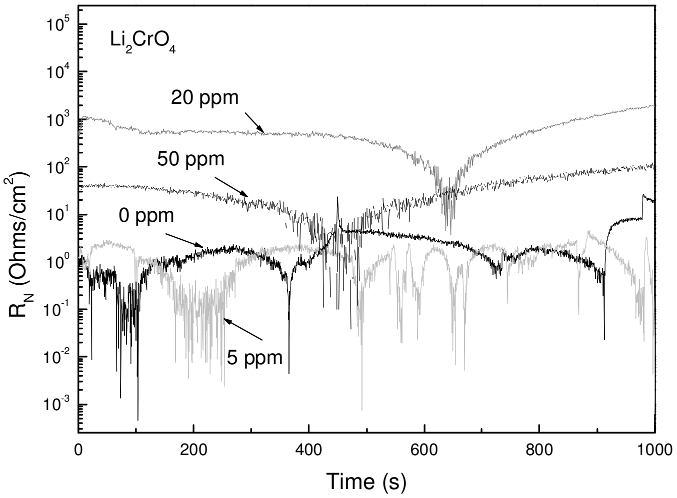

Figure 4. Change in the noise resistance value, R_n, with inhibitor concentration.

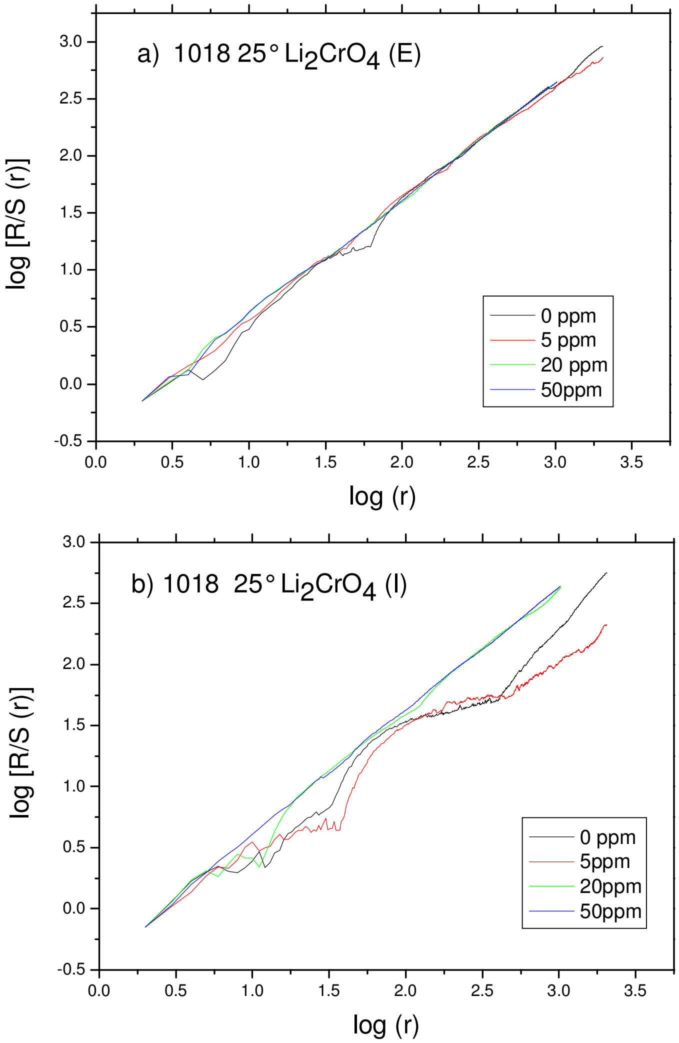

Figure 5. Rescaled range analysis for the electrochemical a) potential and b) current noise time series

Fig. 5 presents the rescaled range analysis for the electrochemical potential and current noise time series obtained for carbon steel in absence and presence of different inhibitor concentrations. From this graph, the H value was obtained by means of a statistical regression as the slope of the straight line. The slopes of the curves represent the Hurst exponent H, which characterizes the time series structure.

According to the model of fractional Brownian motion, the H value measures the persistence (or anti-persistence) in the increments of a time record. This persistence is presumably related to the processes generating the time record [9, 10, 24]. For corrosion processes, the electrochemical noise and the values of H, are reflecting the electrochemical reactions that take place at the electrolyte/substrate interface giving rise to corrosion. If this is true, then this is the reason that H can be sensitive to the level of corrosion resistance provided by the inhibitor.

The Hurst exponent is a measure of the memory effect of the system, which can be related with the form of corrosion [23]. When these values are between $0< H <0.5$ called anti-persistence zone associated to *noisy* signals, they represent a phenomena with a short memory effect. For $0.5< H <1$ called the persistence zone, they represent a phenomena with long term memory effect [12, 23]. For $H = 0.5$ the phenomenon is Brownian motion (random). Potential noise Hurst exponent results (H_E) show persistent conditions. Without inhibitor the current noise Hurst exponent (H_I) results, show persistency and for inhibitor concentrations, anti-persistent conditions do exist specially so for 5 ppm concentration. This could be due to the corrosion process taking place in those sites with subsequent film formation, which reduces the corrosion rate giving the anti-persistent condition at high inhibitor concentrations. An extension to the H range analysis, related to corrosion and coating performance was proposed, depending on 2H values [24, 26].

Table 2. Electrochemical noise statistical and fractal parameters

Inhibitor Concentration (ppm)	σ_v (mV)	σ_i(mA/cm^2)	R_n (Oms/cm^2)	Efficiency (%)	DOL	H_E	D_f(E)	H_I	D_f(I)
0	0.0275	0.102	179		0.66	0.521	1.478	0.512	1.487
5	0.02342	0.06609	329	45.38	0.6094	0.4780	1.5220	0.3413	1.6587
20	0.00977	0.02531	21413	99.16	15.8751	0.5128	1.4872	0.5018	1.4982
50	0.00804	0.00832	783	77.08	9.3315	0.5123	1.4877	0.5019	1.4981

For the experimental conditions statistical electrochemical parameters have been calculated from the obtained noise data, and presented in Table 2. The noise resistance show the highest values for 50 ppm inhibitor concentrations. According to these results the best result corresponds to the 50 ppm concentration corresponding with the highest R_n value, (18202 ohm.cm^2), As opposed to this, the optimum concentration obtained with impedance measurements was 20 ppm which offers the highest value of R_{ct}. This difference could be due to the sensitivity of electrochemical noise for localized corrosion as opposed to the electrochemical impedance spectroscopy. In any case, the difference suggests the best concentration could lie between 50 and 20 ppm.. The efficiencies calculated through the R_n values were somewhat lower than with impedance measurements. In this case, the efficiency values were calculated by using equation 7:

$$\text{Efficiency} = \frac{R_{ni} - R_n}{R_{ni}} \text{ x } 100 \qquad [7]$$

where R_{ni} is the noise resistance with inhibitor and R_n the noise resistance without inhibitor. The current variation coefficient or degree of localization attack (DOL) was calculated as follows:

$$\text{DOL} = \sigma_i / i_{mean} \qquad [8]$$

where σ_i is the current standard deviation divided by i_{mean}, the current mean value . The greater the DOL the more localized attack suffered by the metal surface [22]. The DOL revealed more localized attack for the 50 and 20 ppm inhibitor concentration. It is known that this inhibitor is an oxidizing agent promoting passive film formation, therefore with surface passive films the main form of attack is localized pitting. Oxidizers promote passive conditions but further inhibitor concentration film formation is disrupted, increasing the generalized corrosion attack over the surface.

Fig. 6 shows a comparison between the values of fractal dimension calculated from the depression angle of impedance plots and the fractal dimension obtained through the Hurst exponent *H*, determined from electrochemical noise potential and current time records as a function of inhibitor concentration. The behaviour of these fractal dimensions could be observed and associated to the morphology (roughness) of the metal surface and the electrochemical noise time series. The fractal dimension Dfs tend to increase as a function of concentration, while the potential noise fractal dimension Df(E) remained almost constant and the current noise fractal dimension Df(I) increased at 5 ppm, decreasing at 20 ppm with a slight increase at 50 ppm. This appears to be more sensitive to the changes in the experimental conditions.

Corrosion is a complex phenomenon, as evidenced from the electrochemical noise oscillations, especially during localized corrosion where transitions between stochastic and deterministic processes can occur. These are revealed by the presence of persistence or anti-persistence conditions. The conditions appear to be related to corrosion and film formation followed by stochastic breakdown-repair events and pit propagation.

Corrosion begins when aggressive ions attack a local site on the surface of the metal substrate [17, 18]. With further ion attack, corrosion spreads gradually and oxidize adjacent sites on the metal surface [19, 20]. On the basis of this model for uninhibited metal surface, it is expected that $H > 0.5$ and the electrochemical noise time records would become persistent. Diffusion of species present random conditions ($H=0.5$), and corrosion inhibition would be expected to reduce the persistency of the electrochemical noise ($H<0.5$), as obtained. Inhibition of corrosion may include passivity or the restriction of diffusion of aggressive ions to the substrate by corrosion products. After passive conditions pit nucleation and growth appear as the main form of corrosion, being a stochastic process. The fractal dimension results obtained are consistent with this model, when an inhibitor provided a high level of protection against corrosion, as proposed [15, 21, 22]. The Dfs suggests an increasing surface roughness and the Df(I) shows *noisy* time series associated to localized pitting corrosion specially so, for the 5 ppm inhibitor concentration (anti-persistent conditions) [21, 22].

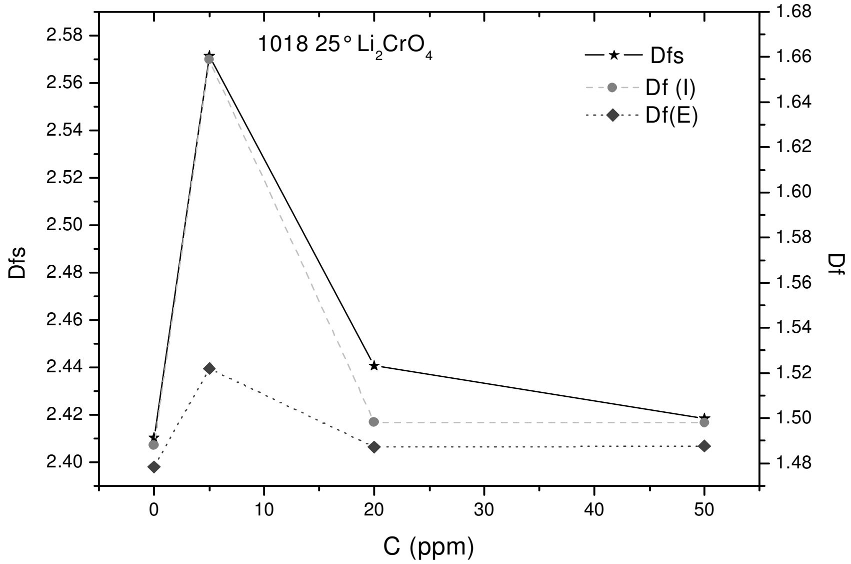

Figure 6. Fractal surface and time series, as a function of the inhibitor concentration.

4. CONCLUSIONS

The results obtained for the Hurst exponent demonstrate that electrochemical noise time series are fractals. The intensity of the corrosive attack clearly changes with the inhibitor concentration modifying the metal surface morphology. Electrochemical measurements suggest that the optimal concentration of lithium molybdate lies around 20 ppm. These were confirmed by fractal analysis that can provide a tool for the interpretation of the structure of electrochemical noise data related to surface morphology as well as a possible quantitative value to rank inhibitor performance and corrosion mechanism.

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