

## The Inhibition and Adsorption Processes of L-Cysteine Against the Corrosion of XC 18 Carbon Steel in 2N H<sub>2</sub>SO<sub>4</sub>

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**Abstract:** The inhibition effect of L-cysteine as environmentally friendly corrosion inhibitor for XC 18 carbon steel in stirred 2 N sulphuric acid has been investigated by electrochemical techniques. The impedance measurements showed that the inhibition efficiency increased with the increase of inhibitor concentration to reach more than 84% at 500 mg L<sup>-1</sup> and indicated that the amino acid act as mixed type inhibitor, while the adsorption followed the Langmuir isotherm. Effect of temperature is also studied in the 30-60°C range. The values of adsorption free energy ( $\Delta G_{ads}^0$ ) and activation energies ( $E_a$ ) reveal a physical adsorption of the inhibitor on the steel surface.

**Key words:** L-cysteine, ac impedance, corrosion inhibition, carbon steel, sulphuric acid

### INTRODUCTION

The use of inhibitor is one of the most practical methods to protect metals from corrosion, especially in aggressive media, in particular, in the chemical, petrochemical and oil industries (Hackerman, 1987; Nestle, 1973). Most of the effective inhibitors are compounds containing, in their structures, nitrogen, phosphorus and/or sulphur. Heteroatoms such as nitrogen, oxygen and sulphur are capable of forming coordinate covalent bond with metal owing to their free electron pairs and thus, acting as inhibitor (Hackerman, 1987; Flick, 1993). The inhibiting effect of these molecules is excellent but they are highly toxic as well for the environment as for the man (Ismail, 2007). Their progressive substitution by substances in biological matter, not toxic, biodegradable and potentially inhibiting takes an interest growing and represents a very required objective.

Many researchers were interested in biochemical compounds based on amino acids, which exhibit excellent properties such as good water solubility and rapid biodegradability (Morreti *et al.*, 2004; Ashassi *et al.*, 2004). These inhibitors, used in protection against the acid corrosion of certain metals such as nickel, cobalt, copper as well as iron and steel (Aksut and Bilgic, 1992; Morreti and Guidi, 2002), gave much satisfaction.

The amino acids are the building block of proteins. All amino acids have a central or alpha carbon, to which

are bonded four groups: hydrogen, an amino group, a carboxyl group and a unique side chain, also known as R-group (Aksut and Bilgic, 1992). These molecules differ in their unique side chain, which can be used to classify the molecules into functional types.

The original functional character of the amino acids is the simultaneous presence of two ionisable functions with an opposite chemical nature: the amine group with basic property and the carboxyl group with acid property. This amphoteric character enables them to form salts with the acids as with the bases. The ionized shapes of the amino acids are a function of the pH medium.

The inhibition of corrosion by organic compounds is primarily attributed to an adsorption process on the metal surface. This phenomenon is influenced by the nature and the surface charge of the metallic surface, the composition of the corrosive medium and the chemical structure of the inhibiting products. The physicochemical properties of the functional groups and the electron density at the donor atom play a significant part. The interactions of the  $\pi$ -orbital of the inhibitor with d-orbitals of the metallic surface atoms induce a strong adsorption of the inhibitor molecules onto the surface with the formation of a protecting film (Ali *et al.*, 2003; Bentiss *et al.*, 2000; Olivares *et al.*, 2006).

The aim of this research, is to investigate the inhibitive effect and to determine the mode of adsorption of an amino acid such as L-cysteine, usually available and

known for its antioxidant role in the organism, against the corrosion of carbon steel in 2 N H<sub>2</sub>SO<sub>4</sub> solution at various temperatures (30, 40, 50 and 60°C). For this purpose, polarization resistance, potentiodynamic polarization curves and the Electrochemical Impedance Spectroscopy (EIS) have been used to study the electrochemical behaviour of this interface.

### MATERIALS AND METHODS

The working electrode was a Rotating Disk Electrode (RDE) consisting of a cylindrical carbon steel (XC 18) with a 0.78 cm<sup>2</sup> cross-sectional area. The chemical composition of the steel specimens was given in Table 1. The working surface was polished with silicon carbide emery cloth (grade 800, 1000 and 1200), then rinsed with acetone in ultra-sonic bath and finally dried in air. The reference electrode was a saturated Hg/Hg<sub>2</sub>SO<sub>4</sub>/SO<sub>4</sub><sup>2-</sup>(aq) (SSE) and the auxiliary electrode was a large area platinum wire. The solutions were prepared from merck reagents (analytical grade) and bidistilled water. The experiments were performed in naturally aerated solutions. The electrolytic solution was 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> with L-cysteine at various concentrations. The Table 2 gives some properties of the L-cysteine and its developed form was illustrated in Fig. 1. All experiments were carried out under agitation at 750 rpm using RDE.

Table 1: The composition of XC 18 carbon steel used in this study

Elements	C	Cr	Mn	Ni	Mo
(Mass%)	0.16-0.22	<0.4	0.4-0.7	<0.4	<0.1

Elements	Si	p-value	V	S	Fe
(Mass%)	0.15-0.35	<0.035	--	<0.035	Balance

Table 2: Characteristics of l-cysteine (Roberts and Caserio,1977)

Name	Type of the R group	Masse molar		pK <sub>1</sub> (α COOH)	pK <sub>2</sub> (α <sup>+</sup> NH <sub>3</sub> )	pK <sub>r</sub> (R)
		weight (g mol <sup>-1</sup> )	pH <sub>i</sub>			
L-cysteine	Hydrophilic	121.16	5.05	1.92	10.70	8.37

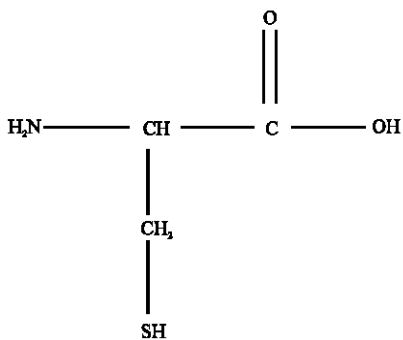


Fig. 1: L-cysteine structure

Potentiodynamic curves (Tafel slopes), polarization resistance Rp measurements are performed by using an Autolab PGSTAT 30 using GPES software. EIS measurements were carried out using as signals (5 mV) peak to peak at the Open Circuit Potential (OCP) in the frequency range of 10 kHz-50 mHz. Time interval of 60 min was given for steady state attainment of OCP and then ac impedance measurements were performed using FRA software.

The Eq. 1 was used to estimate Inhibition Efficiency (IE) (Dehri and Özcan, 2006):

$$IE\% = \left(1 - \frac{R_{t0}}{R_t}\right) \times 100 \quad (1)$$

where, R<sub>t</sub> and R<sub>t0</sub> are the charge transfer resistance, in inhibited and uninhibited solutions, respectively.

In order to examine the adsorption and corrosion inhibitive properties of L-cysteine, measurements were carried out at four temperatures: 303, 313, 323 and 333 K. The adsorption free energy of the adsorbed species was calculated using adsorption isotherms.

### RESULTS AND DISCUSSION

#### The Electrochemical Impedance Measurements (EIM):

Electrochemical impedance is a powerful tool in the characterisation of the corrosion and adsorption phenomena. It enables the fitting of the experimental results to a pure electronic model to represent the electrochemical interface. The experimental results when correlated to an equivalent circuit enable the verification of the mechanistic model for the interface. For instance, such a correlation leads to the calculation of the numerical values corresponding to physical and/or chemical properties of the electrochemical interface. The impedance data of XC 18 carbon steel plotted after immersion time of 1 h, in the presence of different concentration of L-cysteine and at various temperatures are presented as Nyquist and Bode plots in Fig. 2 and 3.

The measured corrosion potential and the calculated equivalent circuit parameters for XC 18 carbon steel in sulphuric acid containing different concentrations of L-cysteine are summarised in Table 3 for different temperatures.

**Effect of the L-cysteine concentration:** As can be seen in Fig. 2, the Nyquist plots are not perfect semicircles as expected from the theory of the ac-impedance technique. The deviation of Nyquist plot (more exactly a capacity loop) from a semicircle was attributed to frequency

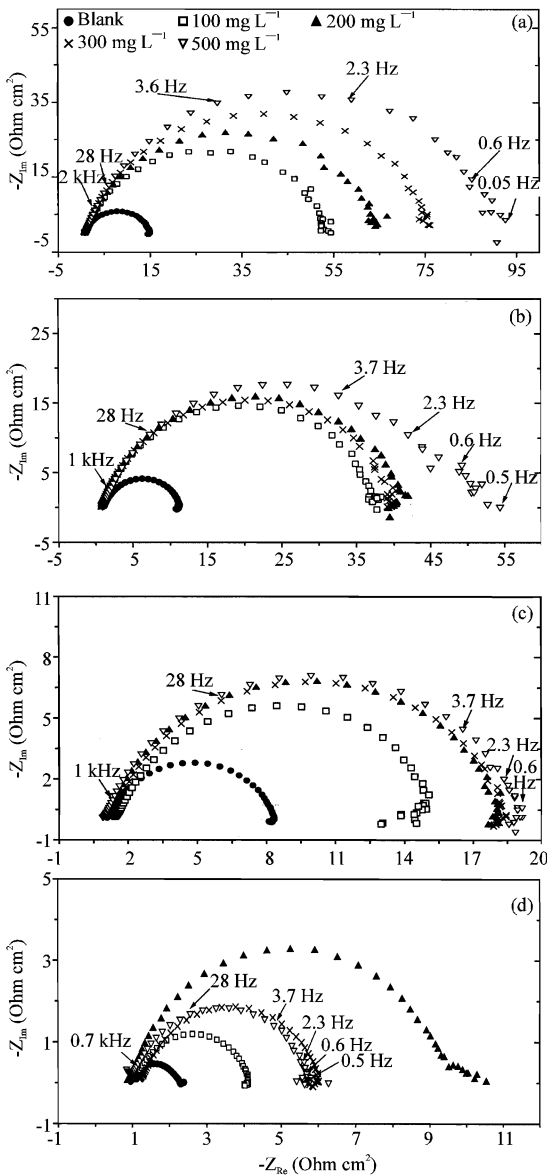


Fig. 2: Electrochemical impedance spectra (Nyquist plots) for XC 18 carbon steel in 2N H<sub>2</sub>SO<sub>4</sub> containing different concentrations of L-cysteine at different temperatures (a: 30°C; b: 40°C; c: 50°C; d: 60°C), RDE at 750 rpm

dispersion. The diameter of the Nyquist diagrams increase with increasing the inhibitor concentration indicating that the electrode surface gets more protection. On the other hand, it can be seen, at low frequencies, a small inductive loops characteristic of the sulphuric mediums. Such behaviour, is generally to be related to relaxation process of an adsorbed intermediate (Bokris and Reddy, 1973), simultaneously with the adsorption of anions such as sulphate ions  $SO_4^{2-}$  (Morad, 2000).

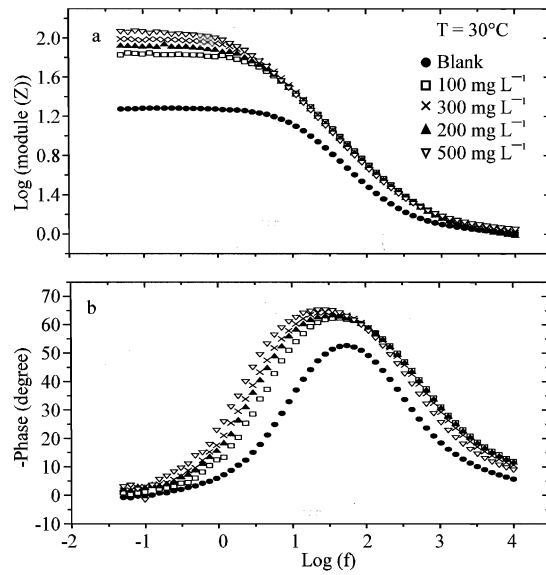


Fig. 3: Electrochemical impedance spectra (Bode plots) for XC 18 carbon steel in 2N H<sub>2</sub>SO<sub>4</sub> containing different concentrations of L-cysteine at T = 30°C, RDE at 750 rpm

Table 3: E<sub>corr</sub>, Equivalent circuits parameters and inhibition efficiency, IE%, for XC 18 carbon steel in 2N H<sub>2</sub>SO<sub>4</sub> solution, in the presence of different concentrations of L-cysteine. Influence of the temperature

Temp. (°C)	Conc. (mg L <sup>-1</sup> )	E <sub>corr</sub> mV/SSE	CPE			IE (%)
			R <sub>i</sub> Ω cm <sup>2</sup>	μF cm <sup>-2</sup>	n	
30	0	-918	14.03	710.37	0.89	-
	100	-892	52.30	344.43	0.87	73.18
	200	-889	63.70	418.47	0.88	77.96
	300	-883	74.45	425.65	0.90	81.17
	500	-882	89.50	445.50	0.89	84.32
40	0	-915	10.16	587.50	0.86	-
	100	-914	37.26	295.14	0.84	72.73
	200	-905	40.72	252.84	0.84	75.04
	300	-901	38.83	296.04	0.85	73.83
	500	-900	48.93	229.30	0.79	79.23
50	0	-918	7.23	599.30	0.84	-
	100	-919	13.87	413.60	0.87	47.90
	200	-915	17.09	355.70	0.85	57.70
	300	-912	17.20	391.90	0.85	57.92
	500	-909	18.13	311.70	0.84	60.13
60	0	-906	1.34	940.60	0.78	-
	100	-907	3.08	1396.20	0.84	56.56
	200	-895	8.64	1199.40	0.83	84.47
	300	-898	4.82	1155.06	0.84	72.21
	500	-903	4.96	1013.50	0.81	72.95

The Bode plots (Fig. 3) show only one time-constant, thus, indicating the predominance of an activation phenomenon in the electrochemical process. The impedance data of the XC 18 carbon steel electrode in 2N H<sub>2</sub>SO<sub>4</sub> solutions containing different concentrations of L-cysteine were analysed using the equivalent circuit shown in Fig. 4.

The electrode impedance, Z, can be represented by the following mathematical formulation (Ismail, 2007):

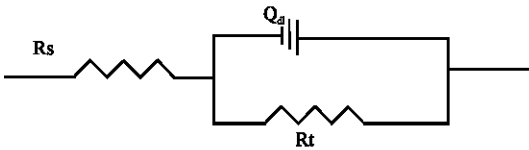


Fig. 4: Electrochemical equivalent circuit used to describe a XC 18 carbon steel electrode/solution in all solutions studied

$$Z = R_s + \frac{R_t}{1 + (2\pi f R_t C_{dl})^n} \quad (2)$$

where:

- $R_t$  = The charge transfer resistance
- $R_s$  = The solution resistance
- $C_{dl}$  = The double layer capacitance
- $f$  = The frequency in Hz
- $n$  = A coefficient ranging between 0 and 1

The above relation takes into account the deviation from the ideal RC-behaviour. In this study, the term  $Q_{dl}$ , a Constant Phase Element (CPE) is substituted for  $C_{dl}$  (Dehri and Ozcan, 2006):

$$Q_{dl} = C. (j\omega)^{-n} \quad (3)$$

where:

- $C$  = A constant depending on the specific analysed system
- $j$  = The imaginary unit ( $\sqrt{-1}$ )
- $\omega$  = The angular frequency

The physical meaning of CPE has been discussed in the literature and can be related to the surface heterogeneity (Dehri and Ozcan, 2006). Hence, this CPE represents, in addition to the double layer capacity ( $C_{dl}$ ), the capacity of the adsorbed layer ( $C_{ads}$ ) associated with the faradic process occurring on the metal surface (under adsorbed inhibitor film) through the film defects and its pores (Morreti *et al.*, 2004).

It can be seen, Table 3 that the corrosion potential is not influenced by the addition of the L-cysteine accordingly this amino acid acts as a mixed-type inhibitor. The charge transfer resistance ( $R_t$ ) increases after the addition of L-cysteine whilst  $Q_{dl}$  decrease. This increase in  $R_t$  value was caused by the adsorption of inhibitor molecules onto the metal surface by blocking the active sites (Dehri and Ozcan, 2006). This may explain the good inhibition performance obtained for a simple molecule like L-cysteine. These results can also be explained by the elimination of  $H_2O$  molecules from the metal surface and simultaneously L-cysteine molecules were adsorbed according to the following reaction:

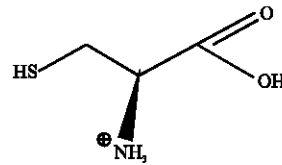
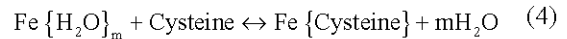


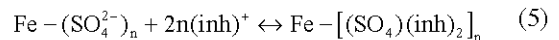
Fig. 5: Protonated form of L-cysteine



The behaviour of this inhibitor, in acid medium, can be interpreted by taking into account the relations between its molecular structure and its inhibiting properties. For this purpose, several mechanisms have been considered:

As the surface charge of the metal, in sulphuric medium, is positive (+) a specific adsorption of  $SO_4^{2-}$  ions creates an excess of negative charges (-), which supports the adsorption of the organic cations (Popova *et al.*, 2003; Abd El-Maksoud, 2004). In other words, the sulphate ions are adsorbed on the active sites of the surface leading to a negatively charged surface, which is suitable for the adsorption of the amino acid (Ismail, 2007) in its protonated form (Fig. 5).

In this study, it is supposed that the L-cysteine molecules are adsorbed onto the metal surface through the quaternary ammonium cation to form a complex at the metal surface, as illustrated by the following reaction:



where  $(\text{inh})^+$  is the protonated form of L-cysteine. The synergistic effect between the amino acid and sulphate anions leads to a stabilized adsorption of the amino acid molecules on the metal surface through the sulphate ions. In addition to the amino group, L-cysteine contains the -SH and -OH groups which induce an electronic high density (Abed *et al.*, 2004). Consequently, the adsorption of L-cysteine onto the metal surface is facilitated to form a blocking film which prevents the dissolution of iron.

The correction factor, n of the double layer capacity denotes an empirical parameter ( $0 \leq n \leq 1$ ) in the mathematical formulation Eq. 2 of the electrode impedance, Z, n is also called flatness factor of the semicircle (Nyquist plot), which depends on the surface heterogeneity and its roughness (Ismail, 2007; Morad, 2000), varies in the range of 0.8-0.9 (Table 3). These values indicate (Li *et al.*, 1996) also the predominance of the charge transfer in the electrochemical process. It can be noticed that the Inhibition Efficiency

(IE %) increases with the L-cysteine concentration where a maximum of 84.32% is reached at 30°C for L-cysteine concentration of 500 mg L<sup>-1</sup>.

**Adsorption isotherm:** Important information about the interaction between the inhibitors and metal surface can be provided by the adsorption isotherm. During corrosion inhibition of metals, the nature of inhibitor on the corroding surface has been deduced in terms of adsorption characteristics of inhibitor. If it is assumed for this purpose that the metal electrode is corroding uniformly in acidic medium, then the corrosion rate in the absence of inhibitors is representative of the total number of corroding sites. Therefore, the corrosion rate in the presence of inhibitors may be assumed to represent the number of potentially corroding sites that remain after blockage due to inhibitor adsorption.

In order to examine the adsorption properties of L-cysteine molecules, different models such as Temkin, Florry-Huggins, Langmuir and Frumkin adsorption isotherms were tested. The model which agrees more with our experimental results was that obtained with the Langmuir isotherm described by the following equation (Ateya *et al.*, 1984):

$$K C = \frac{\theta}{(1-\theta)} \quad (6)$$

where:

- $\theta$  = The degree of surface coverage
- C = The inhibitor concentration
- K = The equilibrium constant of adsorption

The parameter  $\theta$  is calculated according to:

$$\theta = \frac{IE(\%)}{100} \quad (7)$$

where, IE (%) is the inhibition efficiency. The equilibrium constant, K, obtained from the Langmuir isotherm was used to calculate the standard free energy of adsorption  $\Delta G^0_{ads}$  as follows (Olivares *et al.*, 2006):

$$\Delta G^0_{ads} = -RT \ln (55.5 \times K) \quad (8)$$

where:

- R = The universal gas constant
- T = The absolute temperature

The Langmuir isotherm, Eq. 6, can be rearranged to obtain the following expression:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (9)$$

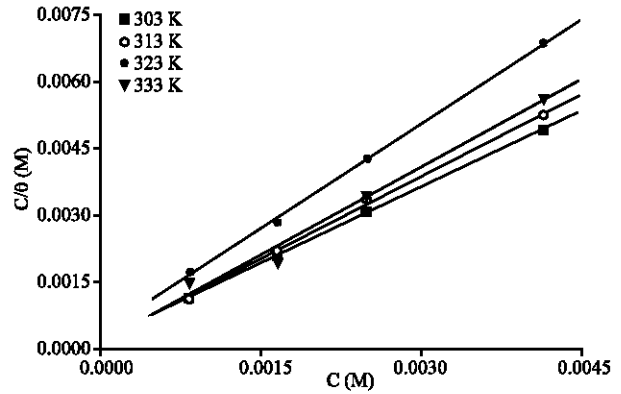


Fig. 6: Langmuir adsorption isotherms of XC 18 carbon steel in 2N H<sub>2</sub>SO<sub>4</sub> solution containing L-cysteine; RDE at 750 rpm, T= 303, 313, 323 and 333 K

Table 4: Thermodynamic parameters for the adsorption of L-cysteine on the carbon steel surface in contact with 2N H<sub>2</sub>SO<sub>4</sub> solution

Temperature (°C)	Slope	K	$\Delta G^0_{ads}$ (kJ mol <sup>-1</sup> )
303	1.14	4748.34	-31.43
313	1.24	6289.30	-33.20
323	1.57	2892.70	-32.17
333	1.31	7204.60	-35.70

The plot of C/θ as a function of C gives a straight line with a slope close to the unit as showed in Fig. 6. The adsorption free energy  $\Delta G^0_{ads}$  of L-cysteine, at different temperatures, is calculated using the slopes and the ordinate axis intercept of the straight lines. The deduced values are summarized in Table 4. It can be seen that the calculated slopes which differ from the unit, as predicted by Langmuir, would be probably due to the presence of SO<sub>4</sub><sup>2-</sup> ions. Therefore, an relatively insoluble layer of FeSO<sub>4</sub> can be formed on the metal surface thus, preventing the adsorption of the inhibitor (Bentiss *et al.*, 2000); so few molecules of L-cysteine are adsorbed.

The adsorption mechanism which is at the origin of the inhibiting action can be proposed starting from the calculated values of  $\Delta G^0_{ads}$ . Thus, Babic *et al.* (1996) have suggested the chemisorption in the inhibition of iron by the thiourea for a value of  $\Delta G^0_{ads} \approx -39$  kJ mol<sup>-1</sup>. Values of  $|\Delta G^0_{ads}|$  in the order of 20 kJ mol<sup>-1</sup> or lower indicate the electrostatic interaction between organic charged molecules and the charged metal in other words the physisorption; those around 40 kJ mol<sup>-1</sup> or higher involve charge sharing or transfer from the organic molecules to the metal surface to form a co-ordinate type of bond (chemisorption) (Morreti *et al.*, 2004; Morreti and Guidi, 2002).

The adsorption phenomenon of an organic molecule is not considered only through the values of  $\Delta G^0_{ads}$ . As a matter of fact, one takes also account of a wide range of conditions, ranging from the dominance of chemisorption

or electrostatic effects arising from other adsorption experimental data such as variations in metal charge, electric moment, temperature and the chemical potential of the organic molecules (Morreti *et al.*, 2004).

In the present research, as can be seen, Table 4, the calculated values of  $\Delta G^0_{ads}$  is ranged from -30 to -40 kJ mol<sup>-1</sup>. This indicates that the adsorption reaction of L-cysteine on the XC 18 carbon steel electrode occurs spontaneously. It's may also indicate the strong interaction (chemical or physical) involving the metal and the inhibitor molecules and the stability of the adsorbed layer on the metal surface derived from the inhibition process (Olivares *et al.*, 2006; Quraishi and Sardar, 2002).

**Temperature effect:** The temperature plays an important role in the evolution of the corrosion processes. Indeed, the corrosion rate generally increases with the rise of temperature. Figure 7 shows the evolution of the corrosion inhibition or the fraction of surface coverage ( $\theta$ ) for the XC 18 carbon steel electrode in 2 N H<sub>2</sub>SO<sub>4</sub> solutions containing different concentrations of L-cysteine as a function of the temperature. It can be noticed that the fraction of covered surface,  $\theta$ , decreases when the temperature increases from 30-50°C; whereas the opposite phenomenon is observed for T = 60°C.

As can be seen from Table 3 and Fig. 7, the L-cysteine revealed a good corrosion inhibition at all studied temperatures. The inhibition process as a function of temperature is depicted in Fig. 8. It is found that for 500 mg L<sup>-1</sup> of L-cysteine, the diameter of the capacitive loops and consequently the effectiveness of inhibition decrease with an increase of the temperature. This can be explained by the desorption of inhibitor molecules from metal surface at higher temperatures. Although, the Inhibition Efficiency (IE %) decreased when the temperature increased, the effectiveness preserved to a great extent with temperature increase.

According to the experimental and calculated results, the evaluation of corrosion inhibition as a function of the temperature can be explained as follows.

From 30-40°C, the decrease of  $\theta$  as can be seen on Fig. 7 is accompanied by a significant decrease of the capacitance ( $Q_{dl}$ ) values (Table 3). On the other hand,  $\Delta G^0_{ads}$  varies slightly from -31.43 to -33.20 kJ mol<sup>-1</sup>. The adsorption of inhibitor molecules trough the metal surface decrease the  $Q_{dl}$  value by reducing the dielectric constant between the metal and the solution and/or by increasing the thickness of the electrical double layer (Bentiss *et al.*, 2002).

From 40-50°C, in this range of temperature, a decrease in  $\theta$  as shown on Fig. 7 while an increase in  $Q_{dl}$  values is noted (Table 3);  $\Delta G^0_{ads}$  remains almost constant. The

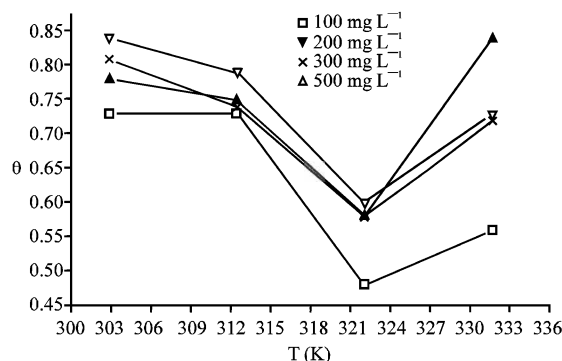


Fig. 7: Effect of temperature on the surface coverage for XC 18 carbon steel in 2N H<sub>2</sub>SO<sub>4</sub> solutions containing different concentrations of L-cysteine

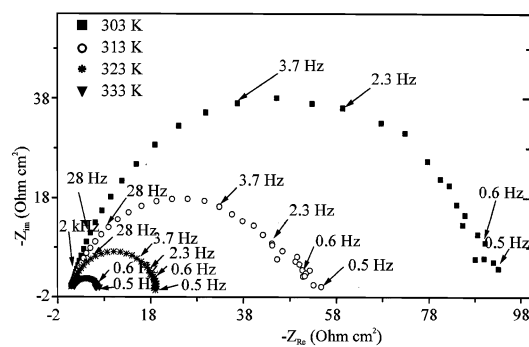


Fig. 8: Electrochemical impedance spectra (Nyquist plots) for XC 18 carbon steel in 2 N H<sub>2</sub>SO<sub>4</sub> containing 500 mg L<sup>-1</sup> of L-cysteine at different temperatures; RDE at 750 rpm

increase in  $Q_{dl}$  can be explained by the desorption of inhibitor molecules from the metal surface with the rise of temperature. Also, the presence of both FeSO<sub>4</sub> and few L-cysteine molecules adsorbed at the interface lead to the significant values of  $Q_{dl}$ .

From 50-60°C, we note a significant rise of the  $Q_{dl}$  value whilst the value of the surface coverage,  $\theta$ , increase again; the adsorption free energy,  $\Delta G^0_{ads}$ , decreases slightly from -32.17 to -35.70 kJ mol<sup>-1</sup>. This behaviour can be allotted to the presence of several functional groups on the molecule of L-cysteine which can constitute individually or together, by synergic effect, favourable sites of adsorption which depend on the temperature of the medium according to their nature.

The anion groups (-COO<sup>-</sup>, -CH<sub>2</sub>-S<sup>-</sup>) can be adsorbed on the anodic sites and the cation groups (-<sup>+</sup>NH<sub>4</sub>) on the cathodic sites of the carbon steel. The presence of both anion and cation groups in the molecular structure suggests an intermolecular synergistic effect for the L-cysteine. In this case, the competitive effect between

these ions groups to adsorb itself on the suitable sites and the temperature of the medium are responsible for the observed phenomena. The values of  $|\Delta G_{\text{ads}}^0| < 40 \text{ kJ mol}^{-1}$ , can be interpreted as an indication of physical adsorption.

**Activation energy:** To elucidate the mechanism of the inhibition process, comparison of the values of activation energy ( $E_a$ ) of the corrosion process both in the absence and in the presence of inhibitor and change of percent Inhibition Efficiency (IE %) with temperature variation can be used. In an acidic solution the corrosion rate is related to temperature by the Arrhenius equation (Dehri and Ozcan, 2006):

$$i_{\text{corr}} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (10)$$

where:

- $i_{\text{corr}}$  = The corrosion current density
- A = The pre-exponential constant
- $E_a$  = The activation energy of the corrosion process
- R = The universal gas constant
- T = The absolute temperature

The corrosion current density ( $i_{\text{corr}}$ ) can be determined from polarization curves. For a charge transfer controlled corrosion reaction, the extrapolation of anodic and/or cathodic Tafel lines gives the corrosion current density ( $i_{\text{corr}}$ ) at the corrosion potential ( $E_{\text{corr}}$ ). The charge transfer resistance ( $R_t$ ) deduced from impedance measurements can be used to estimate the corrosion current density according to Stern-Geary equation (Dehri and Ozcan, 2006):

$$i_{\text{corr}} = \left[ \frac{b_a b_c}{2.303 (b_a + b_c)} \right] \cdot \left( \frac{1}{R_t} \right) = \frac{B}{R_t} \quad (11)$$

where  $b_a$  and  $b_c$  are the Tafel slopes of the anodic and cathodic corrosion reactions, respectively.

In some cases, where the values of Tafel slopes are not known or it is difficult to determine, B values are determined between 0.020 and 0.027 V for technical metals (Dehri and Ozcan, 2006). Thus, in this study, the value of B is taken equal to 0.020 V.

The corrosion current densities ( $i_{\text{corr}}$ ) were determined using the values of  $R_t$  reported on Table 3 with Eq. 11 for uninhibited and inhibited acidic solutions containing different concentrations of L-cysteine at temperatures of 30, 40, 50 and 60°C. The obtained values were summarised on the Table 5. It can be shown that  $i_{\text{corr}}$  values increased with increasing temperature in the absence and in the presence of inhibitor.

Table 5: Activation energy,  $E_a$ , for the corrosion of XC 18 carbon steel in 2N  $\text{H}_2\text{SO}_4$  Solution containing various concentrations of L-cysteine and temperature dependence of corrosion current density ( $i_{\text{corr}}$ )

Conc. ( $\text{mg L}^{-1}$ )	0	100	200	300	500
$i_{\text{corr}}$ ( $\mu\text{A.cm}^{-2}$ )					
303 K	1430	382.4	313.9	268.6	223.4
313 K	1970	536.7	491.2	515.06	408.7
323 K	2770	1440	1170	1160	1100
333 K	14930	6490	2310	4150	4030
$E_a$ ( $\text{kJ mol}^{-1}$ )	61.18	78.86	57.40	75.31	79.67

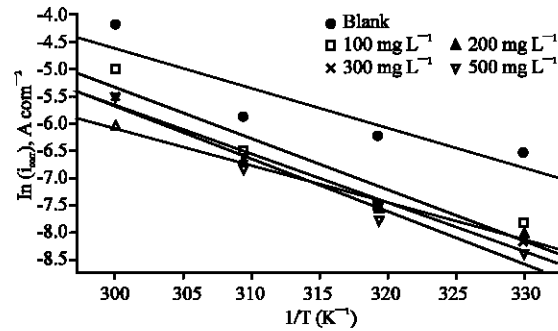


Fig. 9: Arrhenius plots for inhibited XC 18 carbon steel in 2N  $\text{H}_2\text{SO}_4$  solution containing different concentrations of L-cysteine; RDE at 750 rpm

The Fig. 9 shows straight-lines of the logarithm of the corrosion rate ( $\ln i_{\text{corr}}$ ) as a function of  $1/T$  (Arrhenius equation), for various concentrations of L-cysteine. The values of activation energy ( $E_a$ ) were determined using Arrhenius plots given in Fig. 9 for the corrosion current density ( $i_{\text{corr}}$ ) of XC 18 carbon steel in uninhibited and inhibited acidic solutions containing various concentrations of L-cysteine. The calculated values of activation energy ( $E_a$ ) are given in Table 5.

The higher value of the activation energy ( $E_a$ ) of the process in an inhibitor's presence when compared to that in its absence is attributed to its physical adsorption, its chemisorption is pronounced in the opposite case (Popova *et al.*, 2003; Olivares *et al.*, 2006). Indeed, chemisorption requires charge sharing or charge transfer between the metal surface and the inhibitor molecules. Electron transfer can be expected in the presence of a transition metal with low energy, empty electron orbitals and of an inhibitor with molecules having relatively loosely bound electrons or heteroatoms with lone pair electrons (Bentiss *et al.*, 2001).

The higher value of  $E_a$  in the presence of L-cysteine compared to that in its absence and the decrease of  $\theta$  with temperature increase (except 60°C) can be interpreted as an indication of physical adsorption. Physical adsorption is a result of electrostatic attraction between charged metal surface and charged species in the bulk of the solution. Adsorption of negatively charged species is facilitated if the metal surface is positively charged.

Positively charged species can also protect the positively charged metal surface acting with a negatively charged intermediate, such as acid anions  $\text{SO}_4^{2-}$  adsorbed on the metal surface (Dehri and Ozcan, 2006).

In addition to molecular form, the L-cysteine can also be present as protonated species in an acid solution. Its protonation results with the attachment of a proton ( $\text{H}^+$ ) to sulphur (S) atom. Both molecular and protonated species can adsorb onto metal surface.

According to the temperature investigations of L-cysteine, it can be concluded that the inhibitor can adsorb on the metal surface in 2 different ways:

- The protonated inhibitor molecule electrostatically adsorbs onto  $\text{SO}_4^{2-}$  anion covered metal surface, through its protonated form.
- The inhibitor molecules compete with acid anions for sites at the water covered surface and adsorb by donating electrons to the metal.

### CONCLUSION

The results showed that L-cysteine has good inhibiting properties at all temperatures studied, against the corrosion of XC 18 carbon steel under the most unfavourable conditions (strong concentration and stirred acid solution).

In addition to its non toxicity and its good solubility in aqueous medium, L-cysteine ensures an interesting effectiveness of inhibition. The effectiveness of L-cysteine depends on its structure as organic compound.

It was shown that deviation of a Nyquist plot from a semicircle caused by different behaviour of the double layer from a real condenser. Differential capacitance ( $Q_{dl}$ ) has been used instead of double layer capacitance ( $C_{dl}$ ) to represent experimental deviations of a Nyquist plot from a semicircle.

Inhibition of corrosion of XC 18 carbon steel electrode in acidic solutions by L-cysteine can be explained on the basis of adsorption of its molecular and protonated species. High corrosion inhibiting properties of this inhibitor may be attributed to the lone pair of electrons of O and S atoms and to the protonated species, which favour adsorption on the metal surface.

The results show also that the L-cysteine can act as mixed type inhibitor.

The thermodynamic parameters calculated from experimental data ( $\Delta G_{ads}^0$  and  $E_a$ ), indicate the spontaneous and physical adsorption of L-cysteine on the surface of the XC 18 carbon steel electrode. The adsorption process obeys the Langmuir equation.

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