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Synthesis, Structural Properties and Complex Corrosion Inhibition Cu (II) With Amino Acid (DL-α-Alanine)

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ABSTRACT

We began, in this work, by the synthesis of the Cu(II) complex with DL-α-alanine which is characterized by powder X-ray diffraction, the UV-visible spectroscopy and the infrared spectroscopy. The RXs show that the complex has the formula $C_6H_{12}N_2O_4Cu$, $2H_2O$ while the experimental data show that the ligand is bidentate and the studied complex adopts octahedral stereochemistry. We then studied the inhibitory effect of Bis (DL-α-alaninato) copper dihydrate complex on ordinary steel in 1M HCl solution. The corrosion inhibition study of this complex was carried out by the electrochemical method (stationary and transient). The measurements carried out by this method gave a maximum efficiency of 88% to 10^{-5} M of Bis (DL-α-alaninato) copper dihydrate complex on an ordinary steel surface of 1 to 2 cm dimension in the presence of a 1M HCl solution. The obtained results show that the adsorption process of the Bis (DL-α-alaninato) copper dihydrate complex on the metal surface obeys the Langmuir adsorption isotherm.

Keywords: Bis (DL-α -alaninato) copper dihydrate, Corrosion, Inhibitor, 1M HCl.

INTRODUCTION

Copper is an essential element for many life forms since it is present in plants, animals and it used in various application industriel[1,2]. This metal forms stable complexes with amino acids[3].

The latter have both the amine function and the carboxylic acid function. The general formula in most cases is H2N CH R COOH where R is an organic substituent which is known under the name “side chain”)[4,5]. Nine of the 20 standard amino acids are called “essential” amino acids for human beings as long as they cannot be created from other compounds. They should be taken as food supplements[6,7]. Others may be conditionally essential for certain ages or medical conditions[8-10].

Amino acids, which represent the unity of proteins, are attractive because they can bind to metal cations like other organic ligands which are rich in coordination sites (one or two carboxylic groups, amino group). Moreover, their mode of coordination is flexible (monodentate, bidentate or tridentate ligands)[11].

The current interest in Cu complexes derives from their potential use as antimicrobial, antiviral, anti-inflammatory, anti-tumor agents, enzyme inhibitors, and chemical nucleases[12].

The literature studying the effect of metal complexes as an inhibitor of steel corrosion in an acidic solution is very limited[13-16].

Corrosion is a phenomenon of degradation of metallic materials by the environment[17]. This phenomenon concerns most industrial sectors, notably the aeronautics industry, the automotive industry and the chemical and petrochemical industries[18] in which the economic stakes are therefore considerable. Corrosion is not only a source of wastage of raw materials and energy but can also cause serious accidents and therefore contributes to environmental pollution[19].

The use of low-concentration inhibitors is one of the most practical methods for protecting and limiting the attack of metallic materials, which is easy to implement and inexpensive[20,21]. Acid solutions are widely used in industry, with the main areas of application being steel pickling, cleaning of facilities, stimulation of oil wells, and crude oil refining[22,23]. As an acid medium, HCl is one of the most widely used agents in many industrial processes, causing metal degradation due to its aggressiveness, either by chemical or electrochemical reactions.

Our objective is to synthesize the Bis (DL-α-alaninato) copper dihydrate complex from ligand alanine with good yield. This complex has the advantage of being soluble in aqueous media. After purification, the complex is analyzed by powder X-ray diffraction, the UV-visible spectroscopy and the infrared spectroscopy. The inhibitory efficacy of Bis (DL-α-alaninato) copper dihydrate reaches a maximum value of 88% at 10-5 M.

MATERIALS AND METHODS

Instruments

Infrared spectra (KBr disks) were recorded IRTF Vertex 70 Infrared Spectrophotometer in the range of 4000 to 400 cm^{-1}.

The UV-visible spectrophotometric studies were performed in the range of 200-800 nm by using an SP-2000UV Spectrophotometer with a 1 cm cell at a concentration of 10-3 M in water at room temperature.

The studied phase was characterized by X-ray powder diffraction and the diffractogram was recorded at room temperature on a pure sample by using a PANalytical X'Pert3 Powder diffractometer, which operates with copper Kα radiation (λ = 1.5406 Å).

The preparation of the Cu (II) complex with the amino acid (DL-α -alanine)

The Bis (DL-α-alaninato) copper dihydrate was synthesized according to the classical literature method[24].

This complex is prepared with stirring at room temperature. 1.8067 g (2.0310^{-2} mol) of alanine dissolved in 20 ml of water was introduced into an erlenmeyer flask. 2.0503 g (2.0310^{-2} mol) of triethylamin was added to deprotonate the amino acid.

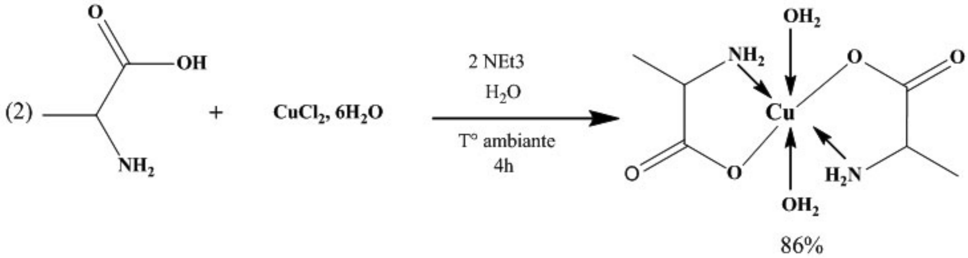
A solution consisting of 2.6862 g (1.1110^{-2} mol) of copper chloride hexahydrate in 10 ml of water was added dropwise with the aid of a burette. When the addition was complete, the reaction is kept under stirring at room temperature for 4 hours.

A precipitate formed. The blue precipitate was filtered on a frit with a vacuum flask and washed with ethanol. A blue powder was obtained and was dried in an oven at 60°C. The calculated yield from the obtained dry powder is equal to 86%.

The obtained solid was recrystallized from a mixture (1/2) H_2O / MeOH, blue crystals appear.

Analytical Results: Found: C, 26.13; Cu, 23.04; H, 5.85; N, 10.16; O, 34.81 Calculated for Cu (C3H6NO2)2, 2H2O: C, 26.13; Cu, 23.06; H, 5.81; N, 10.16; O, 34.84%.

The complexing reaction of Cu (II) with DL-α-alanine can be represented as follows:



Scheme 1: reaction of the complexation of alanine with copper

The used materials

The material used in corrosion study is an ordinary steel whose chemical composition (%) is given in Table 1.

Solution

The Bis (DL-α-alaninato) copper dihydrate is used as an inhibitor in 1M HCl solution, prepared from commercial solution, hydrochloric acid (37%) by using double distilled water. The concentrations used for the inhibitor range from 10^{-3} to 10^{-6} M.

Electrochemical measurements

The electrochemical experiments are carried out in a pyrex cell equipped with a conventional three-electrode assembly: steel (1 cm 2) as working electrode (ET), platinum as auxiliary electrode and Ag / AgCl electrodes as reference electrodes.

The intensity-potential curves are obtained in the potentiodynamic mode. The potential applied to the sample varies continuously with a scanning rate of 1MV / s. We have chosen a relatively low scanning speed so as to be in the quasi-stationary mode. The measurements are made with a mounting including a galvanostat potentiometer PGZ100, of radiometer type, associated with the Voltamaster 4 software. Before the curves are plotted, the working electrode is maintained for 30 minutes at its abort potential. We first plotted the cathodic curves and then the anodic curves.

RESULTS AND DISCUSSIONS

Analyzing methods of the Bis (DL-α-alaninato) complex copper dihydrate

The structure of the complex was determined from the following spectral data: IR spectroscopy, UV-visible spectroscopy and X-ray powder diffraction.

Infrared Spectroscopy

The main infrared absorption bands (in cm^{-1}) of ligand and complex are shown in Table 2. The characteristic bands are in agreement with the data of the literature[25-31].

The examination of the IR spectrum of complex in comparison with corresponding ligand made it possible to notice the following points:

- The IR spectra of amino acids show localized bands in the 2934-3037 cm^{-1} region attributed to elongation vibrations ν (N-H)[25].
- The wave numbers in the 1393-1415 cm^{-1} and 1583-1664 cm^{-1} domains correspond to symmetrical and asymmetric elongation

Table 1: Mass Chemical Composition of Ordinary Steel

Elements	C	Si	Mn	Cr	Mo	Ni	Al	Cu	Co	V	W	Fe
(%) of Mass	0.11	0.24	0.47	0.12	0.02	0.1	0.03	0.14	<0.0012	<0.003	0.06	Balance

vibrations respectively involving the carboxylic group COO^{-}[25,26].

In the [Bis (DL-α-alaninato) copper dihydrate.complex, the NH2 functional band is shifted towards 3158.5 cm^{-1}, which proves that the binding of the -NH2 group in the complex is formed[27]. In alanine, two absorptions related to the two asymmetric and symmetric vibration modes are characteristic of the carboxyl ion COO^{-}[28]. In the alanine complex, the asymmetric ν (C=O) vibration band moves from 1593 to 1625 cm^{-1} and the symmetrical vibrating band ν (C=O) moves from 1410 to 1395 cm^{-1}. The slipping of the position of the bands ν(C=O)as and ν (C=O) s in the complex with respect to the ligand suggests that alanine is coordinated with copper by the COO- group[29,30].

- The elongation vibrations of the O-H function corresponding to the Cu water coordination are in the range of 3586-3384 cm^{-1}[31].
- Two other bands appear at lower energies. The first at 408.3 cm^{-1} assigned to the (Cu-O) bond and the second at low intensity at 584.6 cm^{-1} characterizes the binding (Cu-N)[31].

The UV-visible spectrophotometry

The electron spectrum of copper (II) complex with alanine was recorded in water at the concentration of 10^{-3} M. The obtained results are summarized in Table 3.

The UV-Visible electron spectrum of the ligand in water has two bands: one at 322 nm and the other at 389 nm. This bands are attributed to the transition (n → π*)[32].

The UV-Visible electron spectrum of the Cu(II) complex shows the following bands at 389, 441 and 620 nm. The first band is attributed to ligand-metal charge transfer (L → M), while the last two bands are attributed to the transitions d–d (^{2}Eg $^2T_2$g). This transition is characteristic of an octahedral geometry[33,34].

X-ray diffraction study

The experimental powder diffraction pattern is depicted in Figure 1. Indexing results show Bis(DL-α-alaninato) copper dihydrate complex is monoclinic with space group C2 and unit-cell parametersa=12.0862(9)Å, b=9.6048(9)Å,

Table 2: the main infrared absorption bands of ligand (alanine) and complex (Bis (DL-α-alaninato) copper dihydrate)

	ligand		complex	
bands	experimental	literature	experimental	literature
ν (O-H) (H_2O)	—-	—-	3394,9	3586–3384
ν (N-H)	3087	2934-3037	3158,5	3085
ν_{as} (C=O)	1593	1583-1664	1625,1	1646-1609
ν_{s} (C=O)	1410	1393-1415	1395	1396
ν (Cu-O)	—-	—-	584,6	589–576
ν (Cu-N)	—-	—-	408,3	423

Table 3: The main bands of the ligand and the complex electron spectrum

	λ_{max} (nm)	ε_{max} (l.mol^{-1}.cm^{-1})	Transition
Ligand	322	7	n→π*
	389	31	n→π*
Complex	620	62	d - d
	441	37	d - d
	389	74	L → M

c=8.9915(6)Å, β=110.887(3)°,unit-cell volume V=975.19Å³, Z=4, and space group C2 (Table 4). After Pawley refinement, the unit-cell parameters of Bis(DL-α-alaninato) copper dihydrate complex were solved. All lines of powder data were indexed and consistent with the C2 space group.

Electrochemical study

Polarization curves

Fig1 shows the polarization curves of the ordinary steel in 1M HCl in the absence and presence of Bis (DL-α-alaninato) copper dihydrate at various concentrations ranging from 10^{-3} to 10^{-6} M at 298 K.

The (EI%) inhibition efficiency is defined as follows:

$$\mathrm{EI\%} = \frac{\mathrm{i_{corr}} - \mathrm{i_{corr/inh}}}{\mathrm{i_{corr}}} \times 100 \qquad \text{...(1)}$$

Where icorr and icorr / inh are the corrosion current densities in the absence and in the presence of the inhibitor respectively, obtained by extrapolating the cathodic and anodic Tafel line to the corrosion potential (Ecorr).

Fig 2 illustrates the cathodic and the anodic polarization curves of ordinary steel in 1M HCl in the absence and the presence of the Bis (DL-α-alaninato) copper dihydrate complex at different concentrations. The analysis of these polarization curves shows that adding the complex causes a shift in corrosion potential towards more cathodic values. This displacement is accompanied by a marked reduction in the cathodic current densities. It is clear from Table 5 that the cathodic current density decreases with decreasing the inhibitor concentration to one at a concentration of 10^{-5} M, which indicates the inhibition of the reaction of the hydrogen release. It can be concluded that this is a cathodic inhibitor, and the parallel cathode Tafel curves show that the evolution of hydrogen is controlled by the pure activation mechanism[37,38].

The electrochemical parameters as well as the inhibitory efficiency obtained from the polarization curve are given in Table 5. We notice that the inhibitory power of the complex tested increases with the decrease of the concentration to reach a maximum value of 88% at 10^{-5} M.

Study by the electrochemical impedance spectroscopy (EIS)

We used the techniques of EIS to confirm the results which were obtained by the polarization curves and to have more information about the mechanism of corrosion of ordinary steel.

The inhibition efficiency is evaluated from the transfer resistance (ERct%) which is defined by using the following equation:

$$E_{R_{ct}}\% = \frac{R_{ct/inh} - R_{ct}}{R_{ct/inh}} \times 100 \qquad \text{...(2)}$$

Where Rct / inh and Rt are the charge transfer resistors in the presence and the absence of the inhibitor respectively.

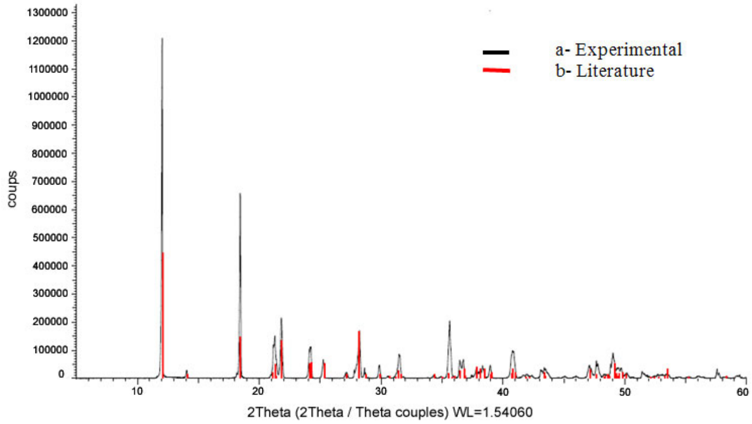


Fig. 1: X-ray powder diffraction pattern of (a) Bis(DL-α-alaninato) copper dihydrate complex experimental and (b) literature [35,36]

The impedance spectra for ordinary steel in 1M HCl with and without the Bis (DL-α-alaninato) copper dihydrate complex at different concentrations and at 298 K are shown in the form of the Nyquist diagrams which is given in Fig 3. According to the diagrams, we find that for all concentrations, there is a single capacitive loop corresponding to the charge transfer resistance whose diameter increases with the decrease in the concentration of the Bis (DL-α-alaninato) copper dihydrate complex.

The results in Table 6 are showing that:

The charge transfer resistance increases with decreasing concentration of the Bis (DL-α-alaninato) copper dihydrate complex to one at a concentration of 10^{-5} M while the capacity of the double layer decreases. This decrease in Cdl is due to the adsorption of the inhibitor on the surface of the steel.

The inhibitory efficiency increases with the decrease of the concentration of the inhibitor to reach a maximum value of 87% at 10^{-5} M.

Adsorption Isotherm

The recovery rate values (θ) for the different complex concentrations, which are obtained from the electrochemical measurements of the 298 K temperature bias curves (Table 5), were used to determine the isotherm corresponding to the adsorption process of the complex. Thus, different isotherm corresponding to Langmuir, Temkin and Frumkin were tested to find the suitable adsorption isotherm (Fig 4, 5 and 6). These adsorption isotherms were used for other inhibitors [39. . According to these isotherms, θ is connected to the inhibitor concentration Cinh by the following equations:

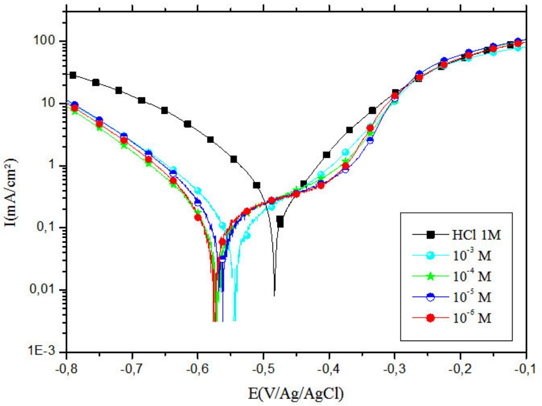


Fig. 2: The polarization curves of ordinary steel in 1M HCl at different concentrations of Bis (DL-α-alaninato) copper dihydrate at T = 298K

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

(Langmuir adsorption isotherm) ...(3)

$$exp(-2a\ \theta) = k\ C_{inh}$$

(Temkin adsorption isotherm) ...(4)

$$\frac{\theta}{1-\theta} exp(-2a\ \theta) = k\ C_{inh}$$

(Frumkin adsorption isotherm) ...(5)

Where *a* is an interaction constant between adsorbed particles, K_{ads} is the equilibrium constant of the adsorption process and C_{inh} is the concentration of the inhibitor in the electrolyte.

The θ values are present graphically according to the suitable adsorption isotherm. Only the Cinh/θ curve in view of the concentration is linear with a correlation coefficient greater than 0.99 for the complex (Fig 4), which shows that the adsorption of the complex on the steel surface in the hydrochloric medium obeys to the adsorption isotherm of Langmuir.

Temperature effect

Temperature is one of the factors which

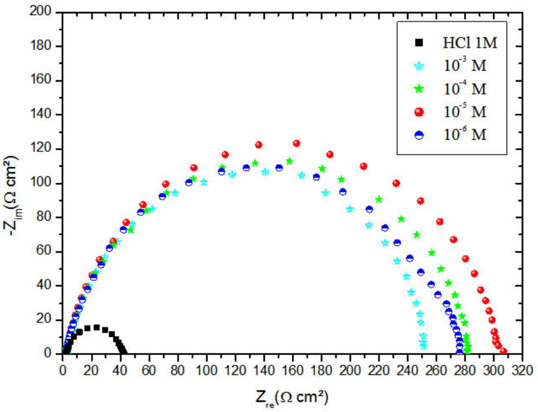


Fig. 3: Diagrams of electrochemical impedance of ordinary steel in 1M HCl in the absence and the presence of the complex at different concentrations and at 298 K

Table.4: Indexed X-ray powder diffraction data of Bis (DL-α-alaninato) copper dihydrate complex, C6 H12 Cu N2 O4 ·2 H2 O. Only the peaks with I_{obs} of 1 or greater are reported [a =12.0862(9)Å, b = 9.6048(9)Å, c = 8.9915(6)Å, β = 110.887(3)°,unit-cell volume V = 975.19Å³, Z = 4, and space group C2. . All measured lines were indexedand are consistent with the C2 space group. The d-values were calculated using CuKá1 radiation (θ = 1,54056Å).

$2\theta_{obs}$(°)	d_{obs}(Å)	I_{obs}	h	k	l	$2\theta_{cal}$(°)	d_{cal}(Å)	$\Delta 2\theta$
12.0740	7.324090	100	1	1	0	11.7590	7.519521	0.315
14.0790	6.285250	3	1	1	-1	13.0697	6.76824	1.009
18.4530	4.804110	33	0	2	0	18.4590	4.8024	-0.006
21.1280	4.201520	5	0	0	2	19.7309	4.49575	1.397
21.2860	4.170690	11	0	2	1	20.9492	4.23605	0.336
21.3740	4.153710	2	2	0	-2	24.6609	3.60705	-3.286
21.8070	4.072210	30	1	1	-2	23.0271	3.85868	-1.220
24.1640	3.680070	12	2	2	-1	25.6601	3.46872	-1.496
24.3050	3.659040	13	2	2	0	23.6437	3.75976	0.661
25.3890	3.505220	12	3	1	0	23.9324	3.71515	1.456
27.1690	3.279470	3	3	1	-2	31.2056	2.86384	-4.036
28.1970	3.162200	37	0	2	2	27.1474	3.28203	1.049
28.7520	3.102410	3	2	2	1	25.6606	3.46872	3.091
29.8800	2.987810	3	1	3	-1	30.5225	2.92636	-0.642
31.2160	2.862920	1	4	0	-2	35.7757	2.50778	-4.559
31.4290	2.844000	6	1	1	-3	32.1225	2.78415	-0.693
31.6641	2.823420	3	4	0	0	29.5387	3.02155	2.125
34.3560	2.608100	3	1	3	-2	35.1750	2.54922	-0.819
35.0609	2.557260	1	4	2	-1	36.4966	2.45989	-1.435
35.5570	2.522710	4	2	2	-3	38.3761	2.34362	-2.819
35.8589	2.502160	1	3	3	2	41.2006	2.18924	-5.341
36.0570	2.488870	2	2	2	-2	30.9806	2.88412	5.076
36.5080	2.459150	6	4	2	0	35.0581	2.55745	1.449
37.8390	2.375650	9	1	3	-2	35.1750	2.54922	2.663
38.1150	2.359080	8	3	3	2	41.2006	2.18924	-3.085
38.9740	2.309040	3	0	4	-2	42.6524	2.11802	3.678
39.0560	2.304380	5	5	1	-1	39.7027	2.26832	-0.646
40.7101	2.214490	4	2	4	0	40.3862	2.23149	0.323
41.8839	2.155100	1	1	1	-4	41.9123	2.15370	-1.001
42.1500	2.142110	1	3	1	2	31.2056	2.86384	10.94
43.3740	2.084450	5	0	4	-2	42.6525	2.11802	0.721
48.4130	1.878610	2	5	1	-1	39.7027	2.26832	8.710
48.5930	1.872070	3	1	5	-3	57.4247	1.60337	-8.831
48.7611	1.866010	2	2	4	2	45.3332	1.99881	3.427
49.1611	1.851760	12	2	4	-2	45.3332	1.99881	3.427
49.2081	1.850100	6	6	2	0	48.9970	1.85757	0.211
49.3409	1.845430	4	5	3	-1	48.2053	1.88621	1.135
49.4410	1.841930	2	6	2	-2	53.3170	1.71679	-3.876
49.5049	1.839700	4	4	4	0	48.3781	1.87988	1.126
49.8101	1.829140	5	4	4	-4	64.5727	1.44206	-14.76
52.1551	1.752280	1	6	2	-4	65.0873	1.4319	-12.93
52.4108	1.744330	1	6	0	-1	46.1420	1.9656	6.268
52.7969	1.732480	1	3	5	2	56.8662	1.61778	-4.069
53.5219	1.710710	8	3	5	4	56.8662	1.61778	-3.344
55.2331	1.661690	1	1	3	4	50.1140	1.81875	5.119
60.0821	1.538650	1	6	4	-2	63.7027	1.4596	-3.620
60.9351	1.519140	2	7	3	-2	64.6936	1.43966	-3.758
62.1148	1.493090	3	5	5	4	72.0849	1.2499	-13.97
69.2000	1.356500	1	5	5	-1	62.5708	1.48329	6.629

are likely to modify both the behavior of steel in a corrosive medium and the nature of the metal / inhibitor interaction.

The increase in temperature has a significant effect on the formation of the inhibitor film. Indeed, a rise in temperature favors the inhibitor desorption as well as rapid dissolution of the formed organic compounds or complexes. This leads to the weakening of the corrosion resistance of the steel[40].

In order to examine the influence of this parameter on the inhibitory efficiency of Bis (DL-α-alaninato) copper dihydrate for the optimal concentration 10^{-5}M, we performed stationary electrochemical measurements in potentiodynamic mode in a temperature ranging from 298K to 328K.

We plotted the polarization curves of steel with and without Bis (DL-α-alaninato) copper dihydrate (Figs. 7 and 8).

In order to study the effect of temperature on the inhibition efficiency of Bis (DL-α -alaninato) copper dihydrate, the parameters are determined from the potentio-static polarization curves. The measurements are carried out in the absence and the presence of an inhibitor at 10^{-5} M in the temperature range 298-328 K. The parameters gathered in table 7 suggest that Bis (DL-α-alaninato) copper dihydrate is well adsorbed on the surface of steel in the 1M HCl solution at all the temperatures studied. They also show that the corrosion current density increases with increasing temperature. The increase in temperature usually accelerates the corrosion reactions which translates a dissolution of metal with a higher velocity. The inhibitory efficiency of Bis (DL-α-alaninato) copper dihydrate increases with temperature to reach a maximum value of 88% at 298K for a concentration of 10^{-5} M. The calculation of the activation parameters for the corrosion process is carried out by using the Arrhenius equations (6 and 7)[41].

$$I_{corr} = A\exp\left(\frac{-Ea}{RT}\right) \qquad ...(6)$$

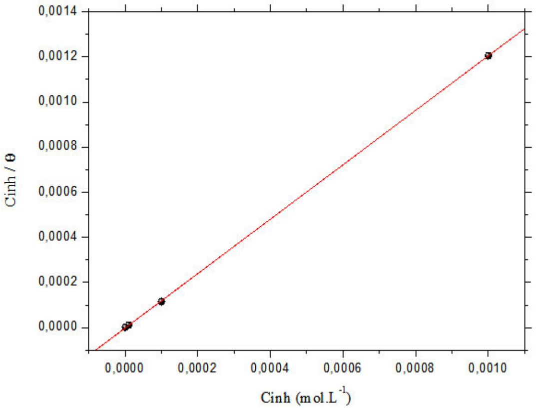


Fig. 4: Langmuir adsorption isotherm of ordinary steel in 1M HCl in the presence of the complex at 298K

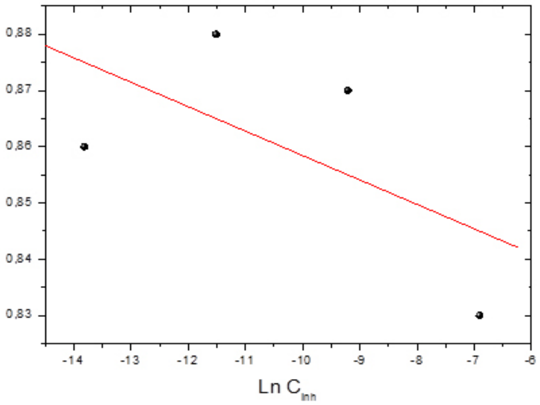


Fig. 5: Temkin adsorption isotherm of ordinary steel in 1M HCl in the presence of the complex at 298K

Table 5: The electrochemical parameters of ordinary steel in 1M HCl at different concentrations of Bis (DL-α-alaninato) copper dihydrate at 298K

Concentration (M)	E_{corr}(mV/Ag/AgCl)	i_{corr}(μA/cm²)	βc (mV dec^{-1})	E%
HCl 1M	-498	467	-220	-
10^{-3}	-546,3	81	-108,5	83
10^{-4}	-573	63	-67,2	87
10^{-5}	-565,9	57	-65,3	88
10^{-6}	-575,8	65	-70,8	86

From where :

$$Ln(I_{corr}) = -\frac{Ea}{RT} + Ln(A) \quad ...(7)$$

Table 6: Electrochemical impedance parameters in the absence and the presence of the complex at different concentrations

Conc. (M)	Cdl (μF/cm²)	Rct (ohm.cm²)	E%
HCl 1M	440	40	-
10^{-3}	101	251	84
10^{-4}	71	282	86
10^{-5}	68	307	87
10^{-6}	72	278	86

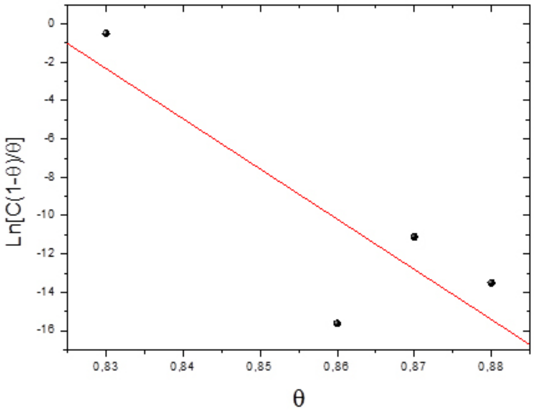


Fig.6: Frumkin adsorption isotherm of ordinary steel in 1M HCl in the presence of the complex at 298K

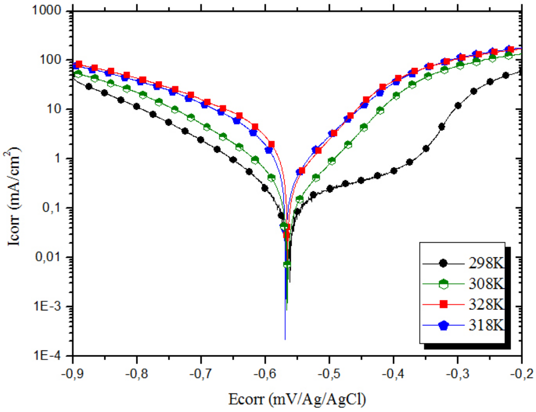


Fig. 8: The polarization curves of ordinary steel in 1M HCl in the absence and the presence of 10^{-5}M Bis (DL-α-alaninato) copper dihydrate at different temperatures

Ea: the activation energy (kJ.mol-1)
R: the perfect gas constant (J.mol-1.K-1)
T: the absolute temperature (K).
A: a pre-exponential factor.

The Enthalpy of activation ΔH^0_{abs} and activation entropy ΔS^0_{abs} determined from equations (8 and 9)[42,43]:

$$Ln\left(\frac{I_{corr}}{T}\right) = -\frac{\Delta H^{\circ}_{abs}}{RT} + B \quad ...(8)$$

$$I_{corr} = \frac{RT}{Nh}\exp\left(\frac{\Delta S^{\circ}_{abs}}{R}\right)\exp\left(\frac{\Delta H^{\circ}_{abs}}{RT}\right) \quad ...(9)$$

h : Plank Constant
N : Number of Avogadro

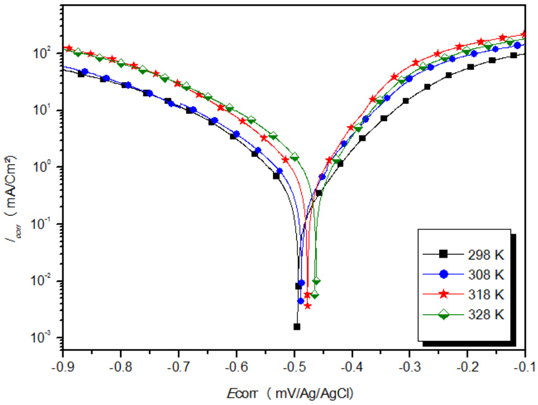


Fig.7: the potentiometric polarization curves of ordinary steel in 1M HCl at different temperatures

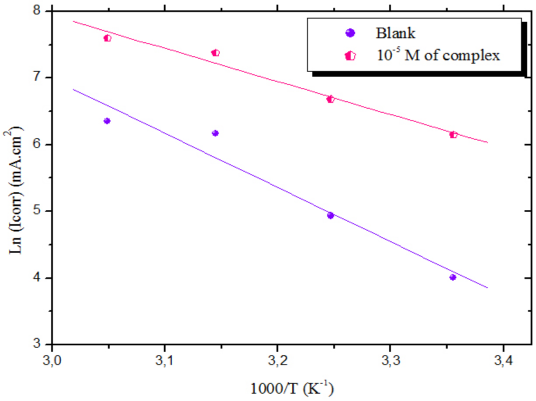


Fig. 9: Arrhenius lines calculated from the corrosion current density of steel with and without the addition of 10^{-5}M Bis (DL-α-alaninato) copper dihydrate

Fig 8 and 9 show the variation of the logarithm of the corrosion current density respectively Ln (I_{corr}) and Ln(I_{corr} / T) of the ordinary steel in HCl alone and in the presence of Bis (DLα-alaninato) copper dihydrate at different concentrations, depending on the inverse of the absolute temperature (1000 / T).

We notice that the variations Ln(I_{corr}) = f(1/T) and Ln (I_{corr}/ T) = F(1/T)are substantially linear whose regression coefficient R is of the order 0.97. They obey the Arrhenius law both in the absence and the presence of Bis (DL- α-alaninato) copper dihydrate.

These results enabled us to calculate the apparent activation energies, the enthalpies and the entropies of the ordinary steel dissolution in the absence and the presence of our inhibitor.

Table 7: Settings electrochemical ordinary steel corrosion in 1M HCl at different temperature, in the absence and presence of 10^{-5}M Bis (DL-α-alaninato) copper dihydrate

Inhibitor	T (K)	-E_{corr}(mV/ Ag/AgCl)	Icorr(µA .cm^{-2})	EI(%)
	298	498	470	——
	308	491	800	——
blank	318	475	1600	——
	328	465	2000	——
	298	566	55	88
complex	308	564	139	83
	318	567	476	70
	328	546	574	52

Table 8: the activation parameters values ΔH^0_{abs} and ΔH^0_{ads} for ordinary steel in 1M HCl in the absence and presence of 10^{-5}M Bis (DL-α -alaninato) copper dihydrate

Inhibitor	Ea(KJ. mol^{-1})	(KJ. mol^{-1})	(J. mol^{-1}.K^{-1})
blank	41,1	38,5	-64,40
10^{-5}M	67,5	64,9	6,96

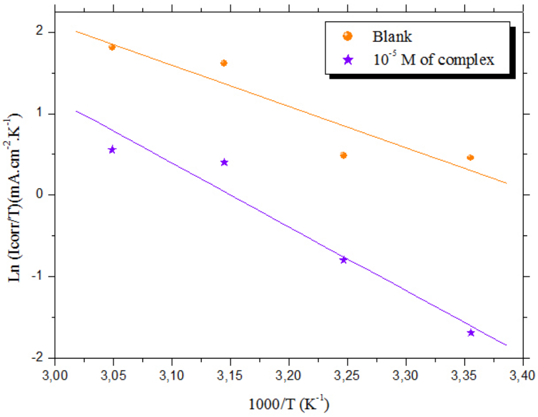


Fig.10: Variation of Ln (icorr / T) in view of the inverse of the temperature in the absence and the presence of 10^{-5}M Bis (DL-α-alaninato) copper dihydrate

The values of the relative thermodynamic quantities of this inhibitor derived from Fig 8 and 9 and those obtained by using equation (8) are given in Table 8.

The studied inhibitor is adsorbed on the surface by electrostatic bonds (physisorbed on the surface of the electrode). Indeed, the Ea value for Bis (DL-α-alaninato) copper dihydrate is greater than the Ea value which is obtained for the solution without inhibitor.

The positive signs of enthalpies ΔH^0_{abs} reflect the endothermic nature of the steel dissolution process. Indeed, the increase in the enthalpy of activation ΔH^0_{abs} with the concentration corresponds to a decrease in the dissolution of the metal[44].

The value ΔS^0_{ads} of in the presence of the inhibitor is high and positive, which indicates an increase in the disorder involved in the formation of the metal complex /adsorbed species [45,46].

CONCLUSION

We presented, in this work, the synthesis of the complexation of alanine with copper chloride hexahydrate. The structure of the complex was characterized by powder X-ray diffraction, the UV-visible spectroscopy and the infrared spectroscopy.

The study of the corrosion inhibition of this complex was carried out by the electrochemical method (stationary and transient), which led us to conclude that:

The Bis (DL-α-alaninato) copper dihydrate acts as an effective corrosion inhibitor for ordinary steel in 1M HCl acid medium.

- The decrease of the concentration of the inhibitor in a corrosive medium results in a decrease in the corrosion density.
- The inhibitory efficiency increases with the decrease of the concentration of the inhibitor to reach a maximum value of 88% at 10^{-5} M.
- The displacements of the potential show that it is an inhibitor of cathodic nature.
- The adsorption of Bis (DL-α -alaninato) copper dihydrate on the metal surface obeys the Langmuir adsorption isotherm.

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