Int. J. Electrochem. Sci., 14 **(2019)** 10227 – 10247, doi: 10.20964/2019.11.10

International Journal of
ELECTROCHEMICAL
SCIENCE
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Ketamine Drug as an Inhibitor for the Corrosion of 316 Stainless Steel in 2M HCl Solution

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Received: 15 June 2019 / *Accepted:* 15 August 2019 / *Published:* 7 October 2019

Ketamine drug was examined as an inhibitor of the corrosion of 316 stainless steel in 2MHCl solution using weight loss, galvanostatic polarization, potentiodynamic anodic polarization and electrochemical impedance spectroscopy measurements. The inhibitory efficiency was increased with increased concentration of ketamine and reduced at high temperature. The ketamine acted as mixed inhibitor. The inhibitory mechanism was interpreted by the formation of chelating compound strongly adsorbed onto the 316SS surface. The adsorption conformed Langmuir isotherm. Ketamine drug inhibits the pitting corrosion of 316SS by converting the pitting potential in the positive direction. The activation and adsorption of thermodynamic parameters were computed and clarified. A quantum calculation and its relationship to the inhibition efficiency of the ketamine drug was carried out using the density functional theory (DFT) by Hartree Fock (HF) level and Becke three-parameter DFT/B3LYP [26], together with Valence Triple Zeta plus Polarization and Diffuse 6-311++G (d, p).

Keywords: Ketamine drug, corrosion inhibitors, polarization, adsorption, DFT

1. INTRODUCTION

Stainless steel Type 316 (316 SS) is utilized in several industrial achievements due to its excellent mechanical properties and its effective protection against corrosion. These industries include ships, pipes, construction materials and many other industries [1-3]. The high resistance of 316SS results from its capability to form a passive layer on the surface and this layer has been often rich in iron oxides, chromium, nickel and other metals. When exposed to acidic medium, e.g., hydrochloric

acid or some halide ions, it leads to the destructive of the protective layer and causes pitting corrosion, which is one of the most serious.

Hydrochloric acid (HCl) solutions are used in several industrial applications [4-5]. Unfortunately, the acid causes dissolution of the stainless steel and therefore causes economic losses and one of the solutions to this problem and the most important add corrosion inhibitors. Inhibitors are generally organic compounds containing in their chemical composition hetro atoms and are effective when added to the corrosive solution at small concentrations [6-19]. These compounds have a significant ability to significantly diminish the corrosion rate of SS in acidic solutions by adsorbing it. The strength of adsorption process depending on several processes [20-22] such as the chemical structure, presence of electrodonating or repelling group and the presence of active centers which facilitate the adsorption process and other factors.

The main objective of this research is to try to minimize the corrosion rate of 316 SS in 2MHCl solution by using an environmentally friendly compound such as ketamine drug. The weight loss (WL), galvanstatic polarization (GP), potentiodynamic anodic polarization (PDAP) and electrochemical impedance spectroscopy (EIS) measurements were used in this study. Moreover, the effect of elevated temperature on 316 SS corrosion and some thermodynamic activation and adsorption parameters was investigated.

2. EXPERRIMENTAL METHODS

2.1. Electrode

316SS utilized in this manuscript had the chemical composition of: (wt. %) Ni 12.03, Cr 17.01, Mo 2.05, Mn 1.41, Si 0.42, P 0.028, C 0.026, S 0.003, and the rest is Fe

2.2. Techniques

2.2.1 Weight loss measurements.

The 316 SS strips with this dimension 1.0x 3.0 x 0.1cm^3 were furnished with a various degree of emery papers. The grease was then removed using acetone and washed with twice distilled water and finally dried. All chemicals used were of A.R. quality. Experiments were conducted at different temperatures ranging from 303K to 333 K $\pm 1^0$C using air thermostat. WL measurements were made as described earlier [23, 24].

2.2.2. Electrochemical measurements

A cylindrical rod of 316SS coated with Araldite with an exposed surface area of 0.68cm^2 was applied for GP, PDAP and EIS techniques. The same treatment of the electrode as is done in WL measurement. The cell utilized in these measurements containing three electrodes, working electrode (WE), saturated calomel electrode (SCE) and a Pt foil acted as auxiliary electrode. Measurements were conducted at 303 K$\pm 1^0$C.

GP and PDP measurements were performed using a PS remote potentiostat with PS6 software. The corrosion parameters was computed, e.g., anodic and cathodic slopes (β_a and β_c), corrosion potential (E_{corr}), and corrosion current density (I_{corr}). The I_{corr} was computed from the confluence of the of anodic and cathodic Tafel lines with E_{corr}. PDAP was carried out at a scanning rate 1mV s^{-1}.

EIS measurements were done using a potentiostate-controlled computer (Auto Lab 30, Metrohm). The EIS study was conducted at AC signals 5 mV peak to peak at OCP in the frequency range of 10 KHz to to 100 mHz. Measurements were carried out at a constant temperature at 303 ± 1 ° K. using a super-circulating thermostat.

2.3. Inhibitor

The corrosion inhibitor used in this study is ketamine. Ketamine is a drug that is used primarily to start and maintain anesthesia [25]. The chemical formula is $C_{13}H_{16}ClNO$, and the molar mass is 237.725 g/mol. The chemical structure of ketamine drug is shown in Fig. 1.

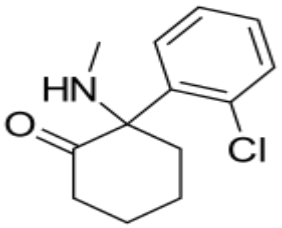

Figure 1. The chemical structure of ketamine drug.

2.4. Theoretical calculation

Theoretical calculations were conducted to support experimental data and to facilitate an explanation of observed experimental behavior. The Density functional theory (DFT) calculations were done using Hartree Fock (HF) level and Becke three-parameter DFT/B3LYP [26], together with Valence Triple Zeta plus Polarization and Diffuse 6-311++G(d,p) Basis set [27] implemented in the Gussian 9 program package [28,29].The geometry of the ketamine drug under study was determined by improving all engineering variables to determine the minimum energy structures.

All theoretical functions such as energy of the lowest unoccupied molecular orbital (LUMO), the energy of the highest occupied molecular orbital (HOMO), energy gap (ΔE), chemical hardness (η), softness (σ), ionization potential (I), electron affinity (A), electronegativity (χ), dipole moment (μ), electrophilicity (ω) and nucleophilicity (ε) of the investigated ketamine were called.

3. RESULTS AND DISCUSSION

3.1. WL measurement

3.1.1. Impact of ketamine drug concentration

The influence of various concentrations of ketamine on the WL –time curves of 316SS in 2M HCl solution were illustrated in Fig.2. From this figure as the concentration of ketamine rises the WL decreases indicating that the ketamine drug inhibits the corrosion of the 316 SS. The relation obtained in figure 1 is linear donating that the lack of surface film insoluble during corrosion

The corrosion rate ($R_{corr.}$) the percentage inhibition efficiency (IE %) and the surface coverage (Θ) of the ketamine drug were determined from the next equations [30]:

$$R_{corr.} = \Delta W / St \quad (1)$$

$$IE\% = (R - R_{add}) / R_f \times 100 \quad (2)$$

$$\Theta = 1 - (R_{add.} / R_f) \quad (3)$$

where, ΔW is the variation in WL, S is the surface area of the 316 SS coupons, t is the time inundation in minutes, R_f and R_{add} is the corrosion rate of 316 SS in free of and with ketamine drug, consecutively.

The values of $R_{corr.}$, IE% and Θ are listed in Table (1). Inspection of this table, it is obvious that the values of $R_{corr.}$ lowered, the values of IE% and Θ rises with augmented the concentration of ketamine drug. This led to the inhibiting impact of the ketamine drug compound toward the corrosion of 316 SS in 2MHCl solution.

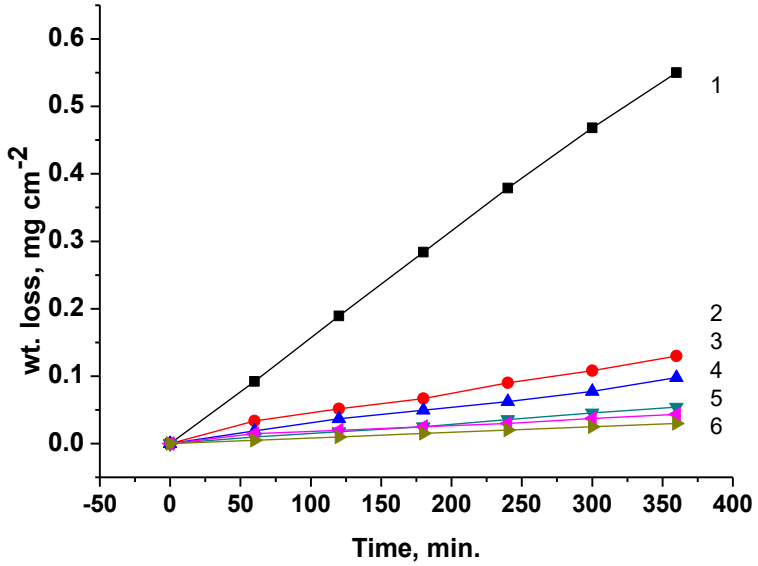

Figure 2. The relation between WL and time for the dissolution of 316SS in free 2MHCl solution and containing various concentrations of ketamine drug.

1) 2MHCl 2)2MHCl +100ppm ketamine 3)2MHCl +150ppm
4) 2MHCl +200ppm 5)2MHCl +250ppm 6) 2MHCl +300ppm

Table 1. The parameters obtained from the WL method for corrosion of 316SS in 2MHCl free and containing different concentrations of ketamine drug.

Conc,ppm	$R_{corr.}$, $x10^{-3}$ mg cm^{-2} min^{-1}	IE%	θ
2MHCl	5.09	-	-
100ppm ketamine drug.	1.20	76	0.76
150ppm ketamine drug	0.91	82	0.82
200ppm ketamine drug	0.50	90	0.90
250ppm ketamine drug	0.42	92	0.92
300ppm ketamine drug	0.33	94	0.94

3.1.2. Effect of iodide (I^-) ion

The effect of I^-ions on the corrosion of 316 SS in 2M HCl solution in with and without the ketamine drug was investigated by the WL method. The same curves in Fig.1 were obtained, but not appear.

Values of % IE for different concentrations of ketamine drug containing 0.01M of I^- ions are presented in table 2. It is evident that %IE of the inhibitor rises by adding I^- ions due to the synergistic effect [31]. The strong chemisorption of I^- ions with cation of the ketamine through the coulombic attraction, the cation is adsorbed on the surface of 316 SS while I^- ions are chemically adsorbed. θ and IE% are increased due to the stability of these anions absorbed with cations

Table 2. Effect of increasing concentrations of ketamine drug on the $R_{corr.,}$ I.E% and S_θ for corrosion of 316SS in 2MHCl+$1x10^{-2}$M KI at 303°K as determined from weight loss method

Conc, ppm	$R_{corr.}$, $x10^{-3}$ mg cm^{-2} min^{-1}	$IE_{(WL)}x100$	S_θ
100ppm ketamine drug.	0.82	84	0.91
150ppm ketamine drug	0.58	89	0.93
200ppm ketamine drug	0.26	95	0.96
250ppm ketamine drug	0.18	96	0.98
300ppm ketamine drug	0.08	98	0.99

The effect of synergy inhibition was assessed using the parameter, $S_{\theta,}$ determined from the θ values of the anion, cation, both of which were obtained. The synergism parameter S_θ was calculated by the subsequent equation [32].

$$S_\theta = 1-\theta`_{1+2} \quad (4)$$

where: $\theta_{1+2} = (\theta_1 + \theta_2)- (\theta_1\theta_2)$, θ_1 and θ_2 are the surface coverage of the anion and cation, respectively, and $\theta`_{1+2}$ is the surface coverage of both anion and cation.

S_θ values are registered in Table 1. These values are almost equal to the unit, suggesting that the improved inhibition efficiency of adding I^- ions to ketamine drug is fundamentally due to the synergistic effect.

3.1.3. Activation parameters for the corrosion of 316SS

The influence of rising temperature on corrosion of 316 SS in free 2MHCl and with some concentrations of ketamine drug was studied at temperature ranging from 303°K to333°K The same curves of fig. 1 was gained, but not appear. The obtained data are registered in Table 2. From this Table, it is evident that as the temperature raises the R_{corr} increases and the values of IE% and Ɵ are lowered. This detonates that the increase of temperature elevates the rate of desorption of ketamine drug from the 316SS surface. So, the inhibition efficiency is reduced.

Table 3. The effect of rising temperature on the parameters gained from the corrosion of 316SS in 2.0M M HCl solution in the absence and presence various concentrations of ketamine drug using WL measurements

T, ^oK	$R_{corr.}$, $x10^{-3}$ mg cm^{-2} min^{-1}	$IE_{(WL)}$**%**	Ɵ
2.0M HCl			
303	5.09	-	-
313	5.86	-	-
323	5.92	-	-
333	6.12	-	-
2.0MHCl +100 ppm ketamine			
303	1.20	76	0.76
313	1.68	71	0.71
323	2.06	65	0.65
333	2.56	58	0.58
2.0MHCl +150 ppm ketamine			
303	0.91	82	0.82
313	1.42	75	0.76
323	1.86	68	0.69
333	2.28	62	0.63
2.0MHCl +200 ppm ketamine			
303	0.50	90	0.90
313	1.22	79	0.79
323	1.64	72	0.72
333	2.05	66	0.67
2.0MHCl +250ppm ketamine			
303	0.42	91	0.92
313	1.04	82	0.82
323	1.48	75	0.75

333	1.82	70	0.70
2.0MHCl +300ppm ketamine			
303	0.33	94	0.94
313	0.86	85	0.85
323	1.18	80	0.80
333	1.45	76	0.76

The apparent activation energy E_a*, the enthalpy of activation ΔH* and the entropy of activation ΔS* for the corrosion of 316 SS in 2M HCl solutions with and without various concentrations of ketamine was determined from Arrhenius- equation [33,34]:

$$R_{corr.} = A \exp(-E_a^*/RT) \quad (5)$$

$$R_{corr} = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (6)$$

where, A, h, N and R are the frequency factor, the Plank's constant, the Avogadro's number and gas constant, respectively.

Fig 3. symbolizes the relationship between log $R_{corr.}$ vs. 1/T for corrosion of 316 SS in 2MHCl -free of and with containing different concentrations of ketamine drug. This relation gives straight line with slope equal to E_a*/2.303R. Value of E_a* was determined and given in Table 3.

Values of ΔH* and ΔS* were determined from the slope and of the intercept of the relation between log (R_{corr} /T) vs. 1/T Fig .4.

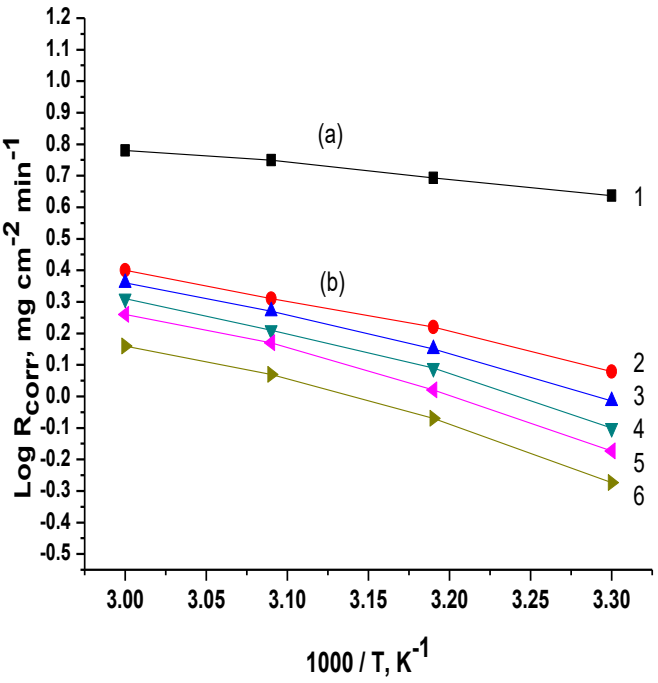

Figure 3. The relation between log $R_{corr.}$ Vs. 1/T for 316 SS in 2MHCl with and without of some concentrations of ketamine drug a) 1- 2MHCl b) 2-100ppm ketamine 3-150ppm 4-200ppm 5- 250ppm 6- 300ppm

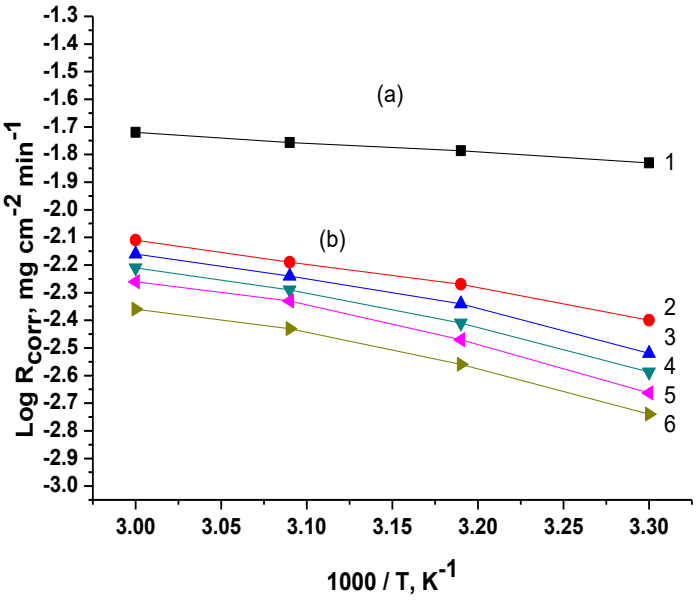

Figure 4. The relationship between log (R_{corr} /T) vs. 1/T for corrosion of 316 SS in 2MHCl with and without of some concentrations of ketamine drug a) 1- 2M HCl b) 2-100ppm ketamine 3-150ppm 4- 200ppm 5- 250ppm 6- 300ppm

It is apparent from Table 3 that, Ea * values rise in the presence of the ketamine drug and thus minimize the corrosion rate of 316SS. Also, E_a*increased by increasing the concentration of the ketamine. These data supported that performance of ketamine drug as an inhibitor by increasing E_a*of 316L SS corrosion by making a barrier to mass and charge transfer by their adsorption on 316L SS surface. Positive signs of ΔH^*indicate the 316SS corrosion are the endothermic nature. The high and negative values of ΔS^* indicate that the activated compound in the rate determining step is a link rather than a break-up step, which means that the reduction of disturbance occurs when moving from the reactants to the activated complex [34]

Table 4. The activation thermodynamic parameters for 316SS in 2.0 M HCl in with and without of some concentrations of ketamine drug.

Conc.,ppm	E_a(kJ. mol^{-1})	ΔH^*(kJ. mol^{-1})	$-\Delta S^*$(J. mol^{-1}. K^{-1})
2.0 MHCl	21.1	22.9	412.5
2.0 MHCl + 100 ppm ketamine	22.9	24.9	438.9
2.0 MHCl+ 150 ppm ketamine	25.9	26.9	452.6
2.0 MHCl +200 ppm ketamine	28.7	29.1	470.2
2.0 MHCl +250 ppm ketamine	30.9	31.7	482.4
2.0 MHCl+ 300 ppm ketamine	32.3	33.9	488.5

3.2. Galvanostatic polarization (GP)

GP curves of 316 SS in free 2M HCl solution and 2MHCl included some concentrations of ketamine drug are clarified in Fig.5. The numerical values of β_a, β_c $I_{corr.}$, $E_{corr.}$ and inhibition efficiency (%IE) with the of different concentrations of ketamine drug is given in Table 6.
The IE% values were determined from the values of $I_{corr.}$ using the next equation.
The IE% values are set from the $I_{corr.}$ values by the next equation:

$$\%IE = \left(1 - \frac{I\ corr\ in}{I\ corr.un}\right) x100 \quad (7)$$

where, $I_{corr.}$un and $I_{corr.}$in are the corrosion current in devoid of and containing ketamine drug.

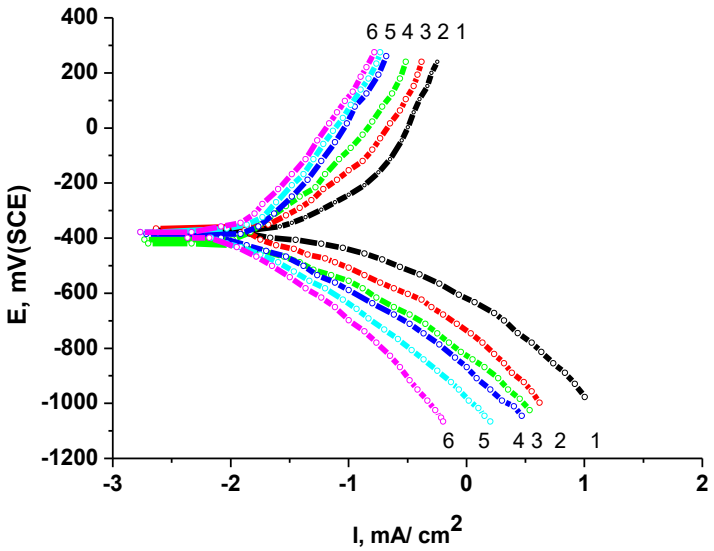

Figure 5. GP of 316 SS in free 2MHCl solution and containing different concentrations of ketamine drug.

1-0.00ppm ketamine 2-100 ppm ketamine 3-150 ppm ketamine
4- 200 ppm ketamine 5- 250 ppm ketamine 6- 300 ppm ketamine

This mentions that, the cathodic and anodic curves obtained show a Tafel behavior. The increased concentration of ketamine drug increased both cathodic and anodic overvoltage's and caused a parallel displacement to the more negative and positive values, respectively. This compound acts as an inhibitor of mixed species because they reinforce the anodic and cathodic Tafel slopes. The values of β_a and β_c are changing toward the more positive and negative direction but the cathode more polarized. So the ketamine drug is mixed inhibitor mainly cathodic. $E_{corr.}$ values shifted slightly toward negative values and $I_{corr.}$ values decrease with the increased concentration of ketamine drug which elucidates that the dissolution of 316 SS in 2M HCl solution is inhibited and the inhibition degree depends on the concentration and kind of the inhibitor used. IE% values increase until reaching 95.92% at 350 ppm of ketamine drug

Table 5. Corrosion parameters obtained from GP curves of 316SS in free 2M HCl solution and containing various concentrations of ketamine drug

Conc.	β_a mV dec^{-1}	- β_c mV dec^{-1}	-E_{corr},mV (SCE)	I_{corr} x10^{-3} (μAcm^{-1})	IE%
2MHCl	122	135	370	98	-
2MHCl+100ppm ketamine	145	148	365	22	78
2MHCl+150ppm ketamine	158	165	372	16	84
2MHCl+200ppm ketamine	170	186	378	10	90
2MHCl+250ppm ketamine	182	202	380	7	93
2MHCl+300ppm ketamine	198	226	384	4	96

3.3. EIS measurement.

Figure 6. shows a Nyquist plot of 316SS in free 2M HCl solution and 2MHCl + different concentrations of ketamine drug. From this figure, the impedance graph does not display full semicircular circles due to the roughness and the heterogeneity of the electrode surface [35, 36]. The increase in half-circle diameters by the concentration of ketamine drug proved an increase in the protection properties of the 316 SS surface. Thus, the capacitance semicircle is associated with dielectric properties and thickness of barrier-adsorbed film. A simple equivalent circuit model is used to fit the experimental data as mentioned above [37]. EIS diagrams have a semicircular shape; these graphs indicate that a charge transfer process fundamentally controls the 316 SS corrosion.

EIS parameters including charge transfer resistance R_t, and the double layer capacitance C_{dl}. are obtained from the Nyquist plots are inserted in Table 6. [38]. It has been noticed that R_t values increase with increased concentration of ketamine drug which in turn leads to a reduction in corrosion rate of 316SS in 2M HCl solution. The increase of R_t indicated the formation of a protective film at the 316SS/solution interface. With the increased concentration of ketamine, we find that the values of C_{dl} are reduced resulting from the water molecules at the electrode interface are substituted by ketamine drug of lower dielectric constant through adsorption. The values of IE% were computed from the following equation and listed in Table 6

$$\%IE = \left(1 - \frac{(R_t)_{un}}{(R_t)_{in.}}\right) x100 \qquad (8)$$

where, $(R_t)_{un}$ and $(R_t)_{in}$ are the charge transfer resistance in free HCl solution and with ketamine drug.

Inspection of the data in table 6, the values of IE% increase with the increasing of ketamine drug. Apparently, the IE % obtained from EIS technique is fully compatible with resulting from WL, GP and PDAP techniques, indicating the accuracy of the measurements used

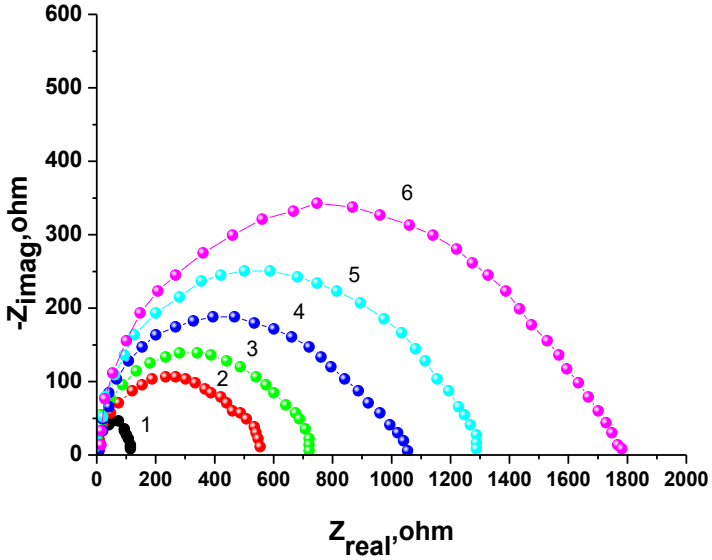

Figure 6. Nyquist plot of 316SS in free 2MHCl solution and with various concentrations of ketamine drug.

1-0.00ppm ketamine 2-100 ppm ketamine 3-150 ppm ketamine

4- 200 ppm ketamine 5- 250 ppm ketamine 6- 300 ppm ketamine

Table 6. EIS parameters of 316SS in free 2MHCl solution and with various concentrations ketamine

Inhibitor Concentration	R_{ct} ohm cm^{-2}	C_{dl} x10^{-6} µFcm^{-2}	I.E.$_{EIS}$ (%)
1M HCl	115	34	--
2.0 M HCl + 100 ppm ketamine	552	28	79
2.0 M HCl+ 150 ppm ketamine	715	22	83
2.0 M HCl +200 ppm ketamine	1045	18	88
2.0 M HCl +250 ppm ketamine	1285	15	91
2.0 M HCl+ 300 ppm ketamine	1775	13	94

3.4. Ketamine as pitting inhibitor

The impact of various concentrations from 100 ppm to 300 ppm of ketamine drug on the PDAP of 316SS electrode in 2MHCl+ 0.5 M NaCl at scan rate 1mVs^{-1} was shown in Fig.7. NaCl is used as pitting corrosion agent. It was noted that that in the anodic scan no any anodic peak is noticed proving the constancy of the oxide film formed on the surface of 316SS. The XPS study indicates that the film formed on the Cr-Ni steels containing Mo consist, mainly, of oxides of Cr^{3+}, Fe^{3+}, Ni^{2+} and Mo^{6+} [39-41]. These oxides strengthen passive film and achieve good corrosion resistance to pitting corrosion. At the passive region the current remains constant until at certain potential, the Cl^- ion break the passive film and the current is rapidly increasing. This potential is defined as pitting potential ($E_{pit.}$) [42, 43]. As the concentration of ketamine increases the values of $E_{pit.}$ is moved toward more positive (noble) direction. This denotes that the ketamine inhibits the pitting corrosion of 316SS.

Fig. 8 represents the variation of $E_{pit.}$ with the log $C_{ketamine.}$, Where $C_{ketamine.}$ is the concentration of ketamine. A straight line is acquired according to the next equation:

$$E_{pit.} = n + m \log C_{ketamine} \quad (9)$$

where, n and m are constants which dependent on both the concentration of inhibitor and the type of the metal or alloy used. It has been found that the pitting potential of 316 SS is moved toward noble values with increased concentration of the ketamine and this indicates increased resistance to the pitting attack.

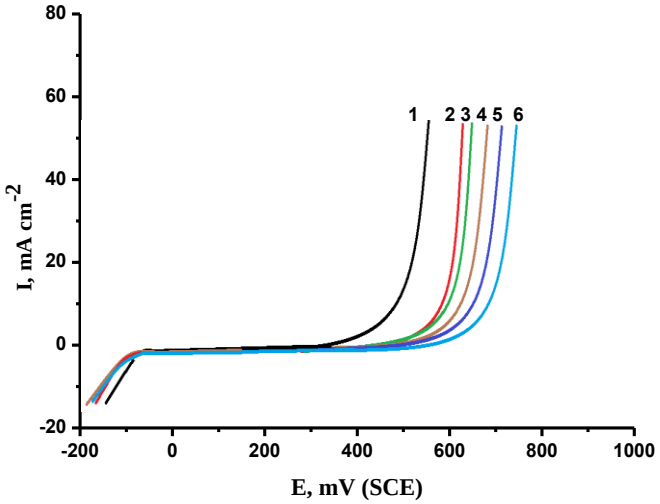

Figure 7. PDAP curves of 316SS in a 2MHCl solution + 0.5 M NaCl containing a various concentrations of ketamine drug at scan rate $1mVs^{-1}$

1-0.00ppm ketamine 2-100 ppm ketamine 3-150 ppm ketamine

4- 200 ppm ketamine 5- 250 ppm ketamine 6- 300 ppm ketamine

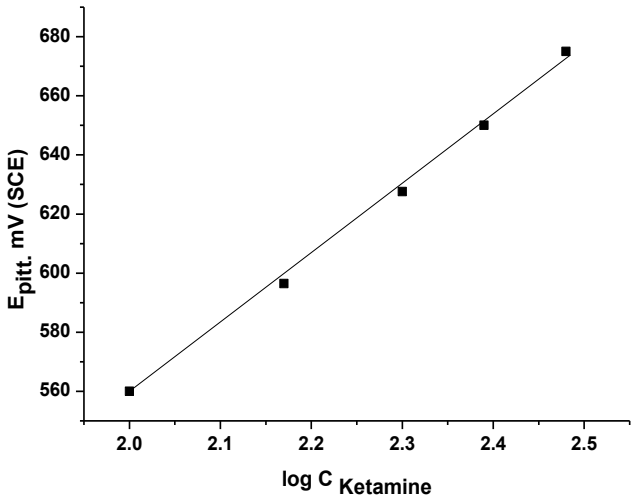

Figure 8. The relation between $E_{pitt.}$ and log $C_{ketamine}$ for 316 SS in 2MHCl + 0.5 M NaCl containing a different concentrations of ketamine drug

3.5. Adsorption isotherm and inhibition mechanism

Ketamine drug retards the corrosion rate of 316SS in 2M HCl by its adsorption on the electrode surface. The process of adsorption can be considered an alternative process where ketamine drug in the aqueous phase replaces a "n" number of water molecules adsorbed on the 316 SS surface,

$$\text{ketamine}_{(aq)} + n H_2O_{(surf)} \longrightarrow \text{ketamine}_{(surf)} + n H_2O_{(aq)} \quad (10)$$

where, n is defined as the number of adsorbed water molecules that are substituted by one ketamine. The intensity of adsorption depends on the chemical structure of the compound used as inhibitors, the nature of the metal and corrosive solution, the existence of electro donating or repelling groups and some active centers in the chemical structure of inhibitor facilitate the adsorption process and thus elevate the protection efficiency and other factors.

Several mathematical relations for adsorption isotherms are proposed to match the obtained results of the current manuscript. We confirm that the preferable adsorption isotherm is Langmuir due to the subsequent equation:

$$C_{ketamine}/\theta = C_{ketamine} + 1/K_{ads.} \quad (11)$$

where K_{ads} is the equilibrium constant of adsorption, $C_{ketamine}$ is the concentration of Ketamine drug.

Fig.9 shows the plots of $C_{ketamine}/\theta$ vs. $C_{ketamine}$ (Langmuir adsorption plots) to adsorb ketamine drug on the 316 SS surface in 2M HCl acid at various temperatures shown in Fig.(9). Straight lines are obtained with a slope approximately equal to the unit. This proving that the Langmuir temperature is suitable for this system. This isotherm assumes zero interaction between the absorbed molecules. From the intercept of the straight lines the values of K_{ads} can be computed. From these values, we can compute the standard free energy for adsorption ($\Delta G^{\circ}_{ads.}$) from this equation:

$$55.5\ K = \exp(-\Delta G^{o}_{ads}/RT) \quad (12)$$

where 55.5, T and R are the concentration of water in mol. L^{-1}, the absolute temperature and gas constant, respectively.

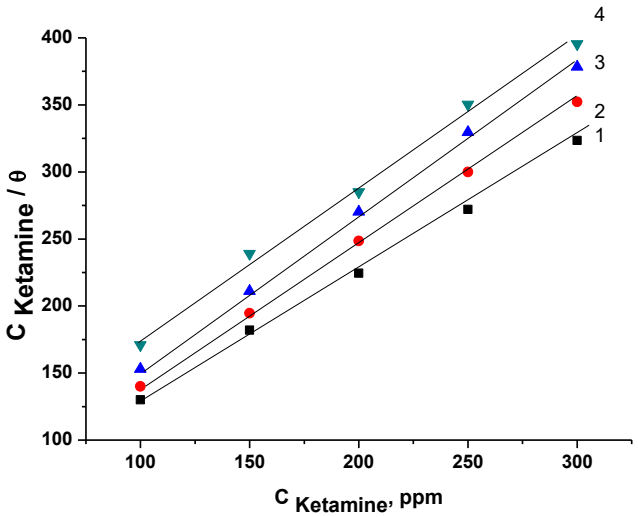

Figure 9. Relation between $C_{ktamine}/\theta$ versus $C_{ketamine}$ for 316SS in free 2MHCl and containing various concentrations of ketamine drug at various temperatures
1)303 K 2)313K 3)323 K 4)333K

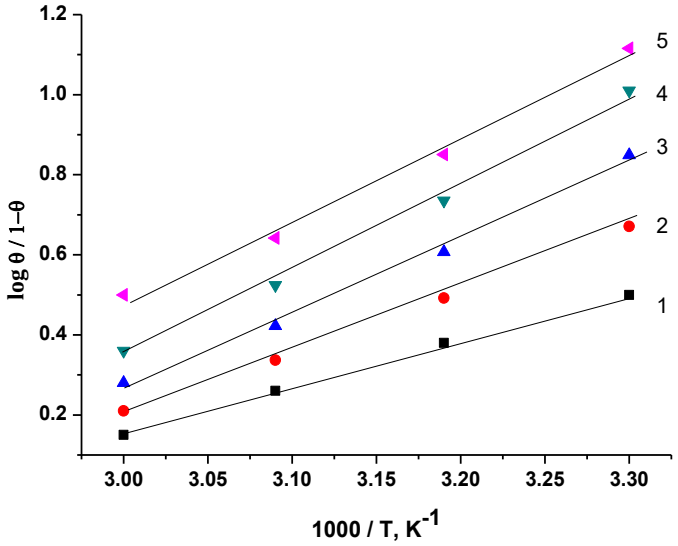

Figure 10. The relationship between log (θ / 1 – θ) versus 1/T for 316SS in 2 MHCl including different concentrations of ketamine drug

1-100ppm ketamine 2-150ppm 3- 200ppm 4- 250ppm 5- 300ppm

The computed values of $K_{ads.}$ are equal to 9.09,8.33,7.69 and 6.89 $x10^{-3}$ at 303, 313, 323 and 333 K, respectively. Also, the computed values of $\Delta G°_{ads}$ are equal to -56.75, -50.21, -46, 26 and -38.97 kJ. mol^{-1} at 303,313,323 and 333°K. From the values of K_{ads} and the negative values of $\Delta G°_{ads}$ denoting the strong spontaneous adsorption of ketamine on 316SS surface. K_{ads} and $\Delta G°_{ads}$ values are decreasing at elevated temperature. Thus, they are consistent with the inhibition efficiency, which also decreased at high temperature due to the desorption of some adsorbed ketamine drug from the 316SS surface. It is found that the values of $\Delta G°_{ads}$ are more than -40 kJ. mol^{-1} detonating the chemisorption of ketamine on the 316SS surface [44]. Langmuir equation can be written as follows [45].

$$(\theta/1-\theta)/ AC = \exp(-\Delta H°_{ads}/RT) \quad (13)$$

where, $\Delta H°_{ads}$, C and A are the enthalpy of adsorption, the concentration of ketamine drug and constant, respectively.

Fig.10. symbolizes the relation between (log θ /1 – θ) vs 1/T for 316SS in 2MHCl solution including various concentrations of ketamine drug. Straight lines were gained with slop equal to $-\Delta H°_{ads}/R$. The values of $\Delta H°_{ads}$ are computed and equal to -12.47, -14.96, -16.63, 18.29 and -19.95 kJ.mol^{-1} at the investigated different concentrations.

Negative values of $\Delta H°_{ads}$ that indicate the exothermic adsorption of ketamine drug on the surface of 316SS. The entropy of adsorption ($\Delta S°_{ads}$) is calculated from the next equation:

$$T\,\Delta S°_{ads} = (\Delta G°_{ads} - \Delta H°_{ads}) \quad (13)$$

Calculated values for $\Delta S°_{ads}$ are -0.169, -0.129, -0.092 and -0.053 kJ. mol^{-1} at the temperature tested. The negative values of $\Delta S°_{ads}$ mention a decrease in disturbance when moving from reactant to the metal adsorbed. This indicates the vigorous adsorption of the ketamine on 316 SS surface. Also, the more negative values of $\Delta S°_{ads}$ at low temperature. The values of adsorption thermodynamic functions are consistent with the low values of IE% at elevated temperatures.

The protective effect of ketamine drug toward the corrosion of 316 SS in 2M HCl solution using WL, GP, PDP and EIS techniques was established to depend on the concentration of the drug, temperature and its capability to form a complex.

The inhibition effect of ketamine drug can be interpreted due to its adsorption on the 316 SS surface.

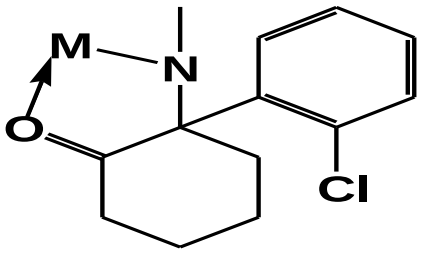

Figure 11. The formation of the complex between 316 SS (M) and ketamine drug

The existence of O and N atoms in the chemical structure of ketamine drug facilitates the formation of complex compounds by forming the coordination bond and covalent bond as shown in Fig. (11). The formation of a covalent bond between the nitrogen atom and 316SS, but the coordination bonds occurred due to the transfer of lone pairs of electrons from oxygen to 316 SS to give a stable chelate five membered ring. The adsorption of a chelating compound on the 316 SS increased the surface coverage and consequently the inhibition efficiency

3.6. Quantum Chemical Calculation and its relationship with corrosion inhibition

According to DFT-Koopmans' theorem [45], the ionization potential, $I = -E_{HOMO}$ while the electron affinity $A = -E_{LUMO}$. The electronegativity (χ) expressed as a finite difference approximation which is the negative of the chemical potential μ [46],

$$\chi = -\mu = \frac{I + A}{2}$$

The chemical hardness (η) is relevant to the resistance of a charge transfer, defined as [47],

$$\eta = \frac{\mathrm{I} - \mathrm{A}}{2}$$

The chemical softness σ defined as the chemical hardness inverse,

$$\sigma = \frac{1}{\eta}$$

The electrophilicity is one of methods expressed reactivity of chemical compounds [48,49].

$$\omega = \frac{\chi^2}{2\eta}$$

and the nucleophilicity is its inverse,

$$\varepsilon = \frac{1}{\omega}$$

Table 7. Quantum chemical parameters obtained from ketamine drug computed with DFT method.

parameters	HF/6-311++(d,p)	B3LYP/6-311++(d,p)
E_{HOMO}	-0.24571	-0.28652
E_{LUMO}	0.17005	0.23146
I	0.24571	0.28652
A	-0.17005	-0.23146
ΔE(L-H)	0.41576	0.51798
χ	0.03783	0.02753
μ	2.93796	2.70184
η	0.20788	0.25899
σ	4.81047	3.861153
ω	0.00344	0.001463
ε	290.516	683.440

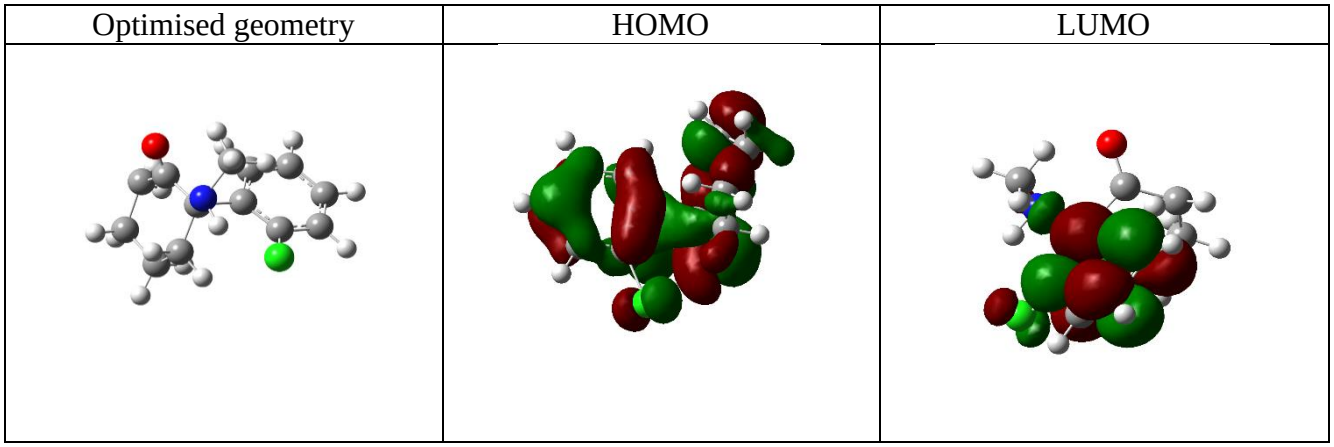

Figure 12. Optimized geometries and frontier molecular orbitals for ketamine calculated by DFT

The quantum chemistry parameters of ketamine which related to electronic structure were computed and given in Table 7 and optimized structure, HOMO, LUMO of structure studied is given in Fig. 12. As seen contribution of p-orbital of inhibitor molecule, this suggested the preferred active sites for electrophilic attack. HOMO and LUMO energies important factor that showed the chemical reactivity and stability of the molecule. These two parameters E_{HOMO} and E_{LUMO} are a useful tool to predict adsorption centers of ketamine molecule which accounts for interaction with SS surface [50].

The HOMO energy detonates the ability of ketamine molecule to give electrons to a convenient acceptor empty orbital (d-orbitals) in stainless steel. The higher HOMO energy indicates the greater of inhibitor to donate electrons to the unoccupied d-orbital of metal and offering high inhibitory efficiency and can promote the adsorption process. The increase in the HOMO energy (less negative)

demanding corrosion rate decrease. Therefore, the corrosion results will increase [51,52]. The lower the LUMO energy gives an assist the acceptance of electrons from 316SS in HCl acid solution. So, energy gap HOMO-LUMO quantum chemical parameter decreased and the efficiency of ketamine inhibitor improved. Therefor low value of the energy difference between HOMO and LUMO (ΔE) will provide best inhibition efficiency, due to the low excitation energy required to remove an electron from the last occupied orbital.

Table 7 also presents the calculated value of dipole moment μ for ketamine inhibitor. The dipole moment μ is another quantum chemical descriptor to obtain electronic distribution data on the molecule under study and is one of the properties that researchers used traditionally to compare and justify the structure and reactivity of many chemical systems [53]. A feedback from literatures that lowest dipole moment μ is related with high inhibition efficiency [54].

Electronegativity determines the attractive ability of electrons of chemical species. It determines the strong interaction with the316SS surface and higher inhibitory efficacy is observed. Two systems in contact 316SS surface and ketamine drug, electrons transferred from inhibitor to metal, until chemical potential equalized. The driving force of the electron transfer process is the difference in electronegativity. According to HSAB theory stainless steel surface is the Lewis acid [55].

Nucleophilicity and electrophilicity are also quantum parameters describe electronic behavior and can use to examine inhibitory efficacy of the molecule. Accordingly, a good corrosion inhibitor if a molecule has a high nucleophilic value, in addition, a poor corrosion inhibitor if a molecule has a high electrophilic value [56].

Based on Pearson hard–soft-acid–base principle (HSAB) theory [57]. This principle presents classification of molecules to soft which easy to polarize or give valence electrons to an electron acceptor molecule or surface. HSAB principle 'hard likes hard and soft likes soft' made the relationship between the chemical reactivity and softness or hardness [58, 59]. Generally, the energy gap of a molecule is indicated hardness or softness of molecular specie. Hard molecules are characterized by a large value of energy gap and are less reactive than soft molecules, which are characterized by a small energy gap and more reactive than hard molecules [60, 61]. An effective corrosion inhibitors should accept free electrons from the metal surface in addition to offer electrons unoccupied orbitals of the metal[62, 63].Therefore, it is clear that the smaller energy gap between HOMO and LUMO results in a high corrosion inhibition potential of a molecule strongly suggest soft-soft interaction.

The structure of ketamine drug contains heteroatoms nitrogen, oxygen and chloride as well as benzene ring. And therefore, the expected active centers on drug molecule are unshared electron pair of hetero-atoms and π-electrons clouds of aromatic ring. This will make it possible to provide electrons to the unoccupied d-orbitals of SS surface to form a stable co-ordination bond. HOMO location on ketamine drug is mostly located in N and O atoms as well as a benzene ring (figure 12) indicating the favor sites for the electrophilic attack from cation of metal located in N atoms. When studied ketamine adsorbs on the SS surface, electrostatic interaction takes place by partial transference of electrons from the polar atom N atom and π-electrons of the C=O of the ketamine molecule to the metallic surface. Therefor suggested in the studied system that has π-bonds, there are $\pi*$-antibonding molecule orbitals

(vacant orbitals). Ketamine molecules also adsorbed through planar pπ-orbitals of the benzene ring in a parallel situation to transition metal. In addition, it has been reported chloride atom showed poor corrosion efficiency or adsorption to metal surfaces [64]. Due to lone pairs and the presence of the benzene ring, more delocalized electrons increased, hence, softness is increased and the efficiency of ketamine drug to prevent corrosion justified. The high inhibition efficiency of ketamine drug is due to the presence of the phenyl ring which has sites susceptible to electrophilic attack as well as low HOMO energy, Low ΔE and low hardness. The other was the chemical adsorption of ketamine drug on stainless steel surfaces.

The mixed-inhibition mechanism is suggested by the polarization data. Ketamine drug is studied computationally in its neutral form. Ketamine drug can also present in the protonated form in hydrochloric acid. Both forms molecular and protonated species can adsorb on the transition metal surface. Adsorption of the protonated Ketamine drug on the cathodic sites on stainless steel surface retards the hydrogen evolution reaction. Adsorption on the anodic sites to inhibit the 316 SS surface from the corrosion process.

Adsorption of the drug on 316 SS surface area may supported by bond formation between ketamine and the SS surface. This type of adsorption should be more prevalent for protonated inhibitors due to conduction of the positive charge on the N-atom to the formation of hydrogen bonds. Unprotonated N-atoms may adsorb by direct chemisorption [65]. Ketamine drug thus can influence both the cathodic and anodic partial reactions, giving rise to the mixed inhibition mechanism observed.

In this study, parameter data listed in Table 7 mention that the selected drug will be expected to inhibit the stainless steel corrosion through adsorption of benzene ring and heteroatoms and donations of electrons to the metallic surface that will be the electron acceptor as indicated in, therefor, the exposed 316SS surface can be reduced by surface coverage of benzene ring and heteroatoms, leading to preventing the metal surface from the acid.

4. CONCLUSIONS

1. Ketamine drug considered as a good inhibitor for corrosion of 316 SS in 2MHCl solution
2. Galvanostatic polarization proved that the ketamine drug is mixed-type inhibitor.
3. The inhibiting action of the ketamine was explicated by its adsorption on the 316SS surface and the formation of a protective film.
4. The adsorption of ketamine on 316 SS surface follows Langmuir isotherm.
5. Ketamine drug acted as pitting corrosion inhibitors by moving the pitting potential in the noble direction.
6. A quantum calculation and its relationship to the inhibition efficiency of the ketamine drug was performed using DFT

ACKNOWLEDGEMENT
This research was funded by the Environmental Pollution Research Chair at Princess Nourah bint Abdulrahman University. (Grant no. EP-05).

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