EXPIRED RANITIDINE DRUGS AS CORROSION INHIBITOR FOR CORROSION OF ALUMINIUM IN HYDROCHLRIC ACID

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Abstract

The corrosion behavior of aluminum in 1M HCl solution in the absence and presence of expired Ranitidine drug was investigated using weight loss and electrochemical techniques. It was found that, the inhibition efficiency of Ranitidine depends on the concentrations. The inhibitive action of this compound discussed in terms of blocking the electrode surface by adsorption of the molecules through the active centers contained in its structure. The adsorption process follows Langmuir adsorption isotherm and El-Awady isotherm. The polarization curves indicate that this compound may act as mixed-type inhibitor. The variation of the open circuit potential of the aluminum electrode as a function of the period of exposure was measured and indicate that the addition of the inhibitor molecules, shift the corrosion potential (E_{corr}) to less noble direction. The effect of temperature on the rate of corrosion was also, studied. Activated thermodynamic parameters were computed.

Keywords*: Drugs; Inhibitors; Aluminum; Hydrochloric acid.*

Introduction

Aluminum and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries because of their advantages. Hydrochloric acid solution is used for pickling, chemical and electrochemical etching of aluminum. It is very important to add corrosion inhibitors to decrease the corrosion rate of aluminum in such solution. Numerous organic compounds serve effectively as corrosion inhibitors. Aliphatic and aromatic amines as well as nitrogen heterocyclic compounds were used as inhibitors for dissolution of aluminum in acidic media **[1-6]**. Some non-ionic surfactants were also used to inhibit the corrosion of aluminum in HCl such as ethoxylated fatty acid **[7]** and tetradecyl 1, 2 diol propenoxylates **[8].**

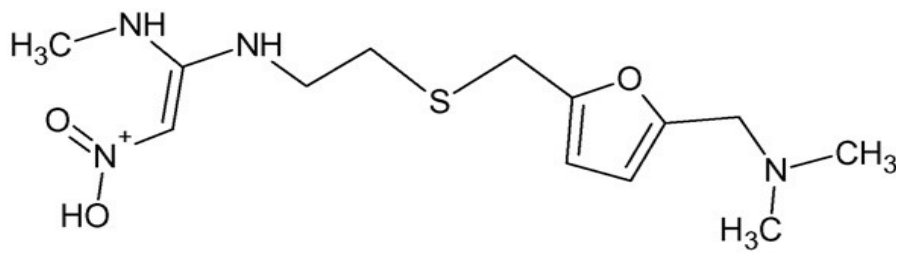
Generally, it has been assumed that the first stage in the reaction mechanism of the inhibitors in aggressive media is the adsorption of the inhibitors on to the metal surface. The processes of inhibition are influenced by the nature and surface charge of the metal, the chemical structure of organic inhibitors, the distribution of charge in the molecule, the type of aggressive electrolyte and the type of interaction

between organic molecules and the metallic surface **[9-13].** Physical adsorption and chemisorptions are the principal types of interaction between organic inhibitors and the metal surface.

The aim of the present work is to study the inhibitive action of the expired ranitidine towards the corrosion of aluminum in 1M HCl solution.

Weight loss and potentiodynamic polarization measurements were used to evaluate the inhibition efficiency of this compound. Also, the effect of temperature was studied.

Chemical Structure of Ranitidine Drug.



Experimental methods.

Aluminum metal with purity of 99.9 % provided by the “Aluminum Company of Egypt, Nagh Ammady” was used in the present study. Aluminum sheets with dimention 2 x 2 x 0.2 cm^3 were used for weight loss measurement. For electrochemical measurements, cylindrical rod embedded in araldite with exposed surface area of 1.0 cm^2 was employed. Prior to each experiment the surface of aluminum specimens were mechanically polished with different grades of emery paper, degreased with acetone and rinsed with bidistilled water. For weight loss measurements, the cleaned aluminum sheet was weighed before and after immersion in 100ml of the test solution for a period of time up to 7 hours. The average weight loss for each two identical experiments was taken and expressed in mg cm^{-2}. The temperature was adjusted to 30±1 ^oC using thermostat. All electrochemical experiments were recorded using a radiometer analytical, voltamaster (PGZ301, DYNAMIC ELS VOLTAMMETRY). Three compartment cells with a saturated

calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. The used drug was supplied by (SEDICO) pharmaceutical company. The aggressive 1M HCl solution was prepared by dilution of analytical grade HCl with bidistilled water.

Results And Discussion

Evaluation of the used drug as Corrosion Inhibitor:

The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media **[14]**. The choice of the inhibitor is based on two considerations:

First: it could be obtained conveniently from relatively cheep raw materials,

Secondly: it contains the electron cloud on the aromatic ring or the electronegative atoms such as nitrogen and oxygen in the relatively long chain compounds **[15]**. In this respect, the present corrosion inhibitor was used from undesired expired medical drugs which have higher water solubility.

Open circuit potential measurements:

The variation of the open circuit potential of the aluminum electrode as a function of the period of exposure was measured against (SCE) as indicated in **Figure (1)**. It is clear that, the corrosion potential (E_{corr}) of aluminum in 1M HCl (blank curve) tend toward less negative values firstly, giving rise to short step. Such behavior represents the break down of the pre-immersion, air formed oxide film present on the metal surface, and then the potential was shifted to less noble direction until the steady state potential is established. Addition of the inhibitor molecules produces a positive shift in (E_{corr}). the results clearly indicate that, as the concentration of the inhibitor increases, the corrosion potential ($E_{corr.}$) was shifted to less noble direction [**16].** The results of final steady state potential (E_s) without inhibitor is -737 mV (vs. SCE) while that using the best dose (300ppm) of the used inhibitor is -712 mV (vs. SCE).

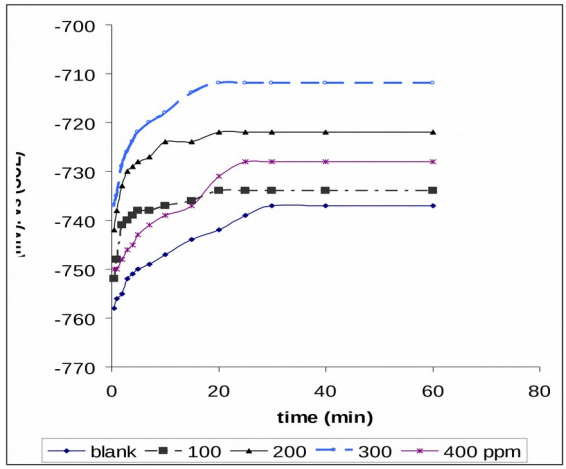


Figure 1: Potential- time curves for aluminum in 1 M HCl in absence and presence of different concentrations of the used inhibitor at 303 K

Potentiodynamic Polarization Measurements:

Anodic and cathodic polarization curves for aluminum in 1 M HCl with and without various concentrations (100-400 ppm) of inhibitor were represented in **Figure (2).** The curves were swept from –1000 to 0 Vs (SCE) with scan rate of 20 mVs^{-1}. **Figure (2)** illustrates the effect of adding progressive addition (100-400 ppm) of selected inhibitor on the cathodic and anodic polarization curves of aluminum in 1M HCl at 30ºC. The addition of the inhibitor decreases the corrosion current densities (I_{corr}). Furthermore, it was also found that the inhibitor behaved as a mixed-type, i.e. both cathodic and anodic polarization curves are affected by the inhibitor **[17]**. The variable values of the cathodic Tafel slopes suggested that the inhibition action of such compound occurs by simple blocking of the electrode surface area **[17]**. The cathodic current–potential curves give rise to parallel Tafel lines, which indicated that hydrogen evolution reaction was controlled **[18]**. Addition of inhibitor increases both the cathodic and anodic over potential of aluminum and causes displacement of the cathodic and anodic polarization curves. Therefore, this drug could be classified as mixed type (anodic/cathodic) inhibitor. These results indicated that the used expired drug inhibits HCl corrosion of aluminum via their adsorption on both anodic and cathodic active sites without modifying the mechanism of corrosion reaction. This means that the adsorbed inhibitor molecules block the

surface active sites and decrease the area available for hydrogen evolution and metal dissolution reactions **[18].**

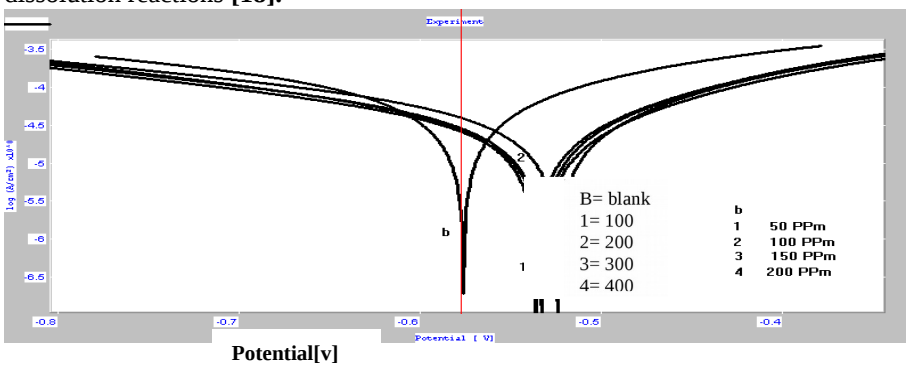


Figure 2: Potentiodynamic polarization curves of aluminum in 1 M HCl in absence and presence of different concentrations of expired Ranitidine inhibitor at 303 K

The corrosion potential, (E_{corr}) and the corrosion current density (I_{corr}) were determined from extra-pollation of cathodic I_c and anodic Tafel lines. The values of E_{corr}, I_{corr}, R_p, Tafel slopes (b_a, b_c), degree of surface coverage (θ) and inhibition efficiency (IE) were calculated for each sample and listed in Table (1). It is clear that the values of corrosion potentials E_{corr} remain almost unchanged and indicated that the used inhibitor act mainly as mixed type inhibitor **[19].** Addition of the used inhibitor to HCl solution decreases the values of I_{corr} and increases the values of R_p for aluminum.

The inhibition efficiency IE of inhibitor was calculated from polarization measurements by using the following equation:

$$IE = 1 - (I_{inh} / I_{uninh}) \times 100 \qquad (1)$$

Where: I_{uninh} and I_{inh} are the corrosion current densities in the absence and presence of inhibitor respectively. Also, the polarization resistance (R_p) can be calculated using Stren-Geary equation.

$$R_p = (b_a \times b_c) / (2.303\, i_{corr}\, (b_a + b_c)) \qquad (2)$$

The inhibition efficiency calculated from the polarization measurements were listed in **Table (1)**. It is obvious that the inhibition efficiency increases with increasing the concentration of inhibitor

Table 1: Polarization data of the used inhibitors.

Sample	Conc., ppm	$I_{corr.}$, mA/cm^2	$-E_{corr.}$, mV	Rp, ohm.cm^{-2}	b_a, mV/decade	$-b_c$, mV/decade	IE%	θ
Blank	0	2.012	61.84	38.73	186.9	226.4	0	0
R	100	0.532	493.2	88.3	129.6	169.1	73.5	0.735
	200	0.497	490.3	102.6	118.0	174.2	75.2	0.752
	300	0.362	482.5	157.4	120.1	144.3	82.2	0.822
	400	0.432	481.3	141.3	99.8	153.4	78.5	0.785

Adsorption Isotherms:

If one supposes that the adsorption of inhibitor follows the Langmuir adsorption isotherm, the surface coverage could be given by the equation:

$$C_i/\theta = (1/K_{ads}) + C_i \quad (3)$$

Where, C_i is the inhibitor concentration and K_{ads} is the adsorption equilibrium constant. The degree of surface coverage (θ) for different concentrations of the inhibitor in acidic media, **[20]** has been evaluated from potentiodynamic measurements by using the following equation:

$$\theta = 1 - (I_{inh}/I_{uninh.}) \quad (4)$$

Careful inspection of these results showed that, inhibition efficiency increases with increasing inhibitor concentration and surface coverage.

In the present work, it was observed that, the isotherm has slope less than unity. The deviation from unity may be explained on the basis of interaction between the adsorption species on metal surface **[20].** The inhibition of this compound may be due to their adsorption and formation of adsorbed monolayr at metal surface interface. The surface coverage values (θ) were tested graphically for fitting a suitable adsorption isotherm. The relation between Ci/θ and Ci was illustrated in **Figure (3)**.

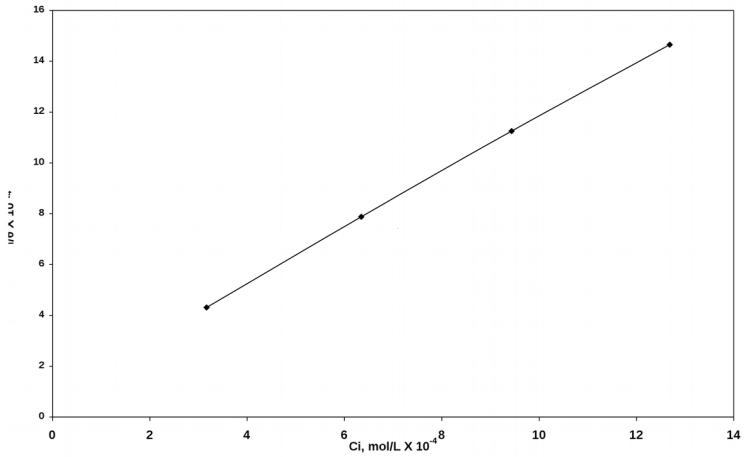


Figure 3: Langmuir adsorption isotherm for the used Inhibitor.

The relation between the calculated efficiency and concentrations of the selected compound were represented in **Figure (4).** S-shaped adsorption mode, appeared in **Figure (4),** proved that the mechanism of inhibition involves the formation of monolayer at the metal-solution interface. The shape of isotherm seems to reflect two modes of adsorption. At very low concentration, the inhibitor is adsorbed either at a vertical mode or the active sites on the surface are not fully occupied. The plateau form may be explained by the formation of a monolayer on the metal surface. Further increase of inhibitor concentration leads to the formation of a multilayer, generally at horizontal mode. The presence of hydroxyl,nitrosyl,NH groups, N,N- dimethyl,dialkylthioether chain and furanyl ring, all these active groups reinforces the adsorption phenomenon by inducing the anodic action.

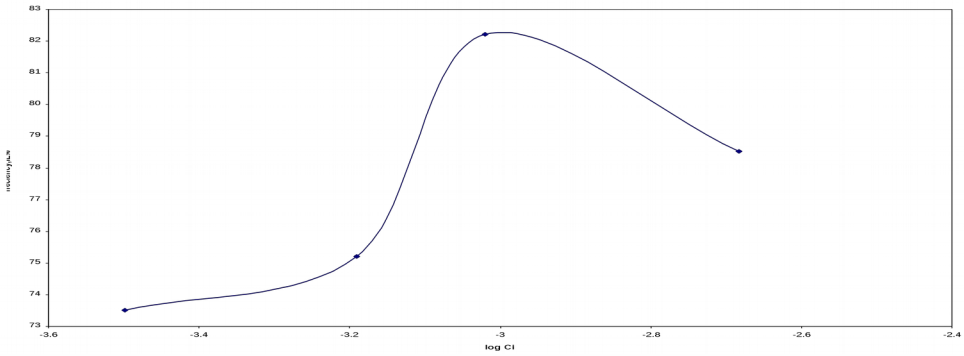


Figure 4: Variation of the efficiency for Al with the log. Ci (S-curve for the used inhibitor)

El-Awady isotherm: El-Awady equation was modified to the following one [**21**]

$$\log (\theta /1- \theta) = x \log K + 1/x \log Ci \quad (5)$$

Where K is the equilibrium binding constant, and "x" = number of sites on the metal surface which can be occupied by one molecule of the inhibitor. The slop value was near unity indicating a strong adsorption of inhibitor molecule on the metal surface. Straight lines of plotting log (θ /1- θ) against log Ci as shown in **Figure (5)**, indicate the validity of modified El – Awady isotherm.

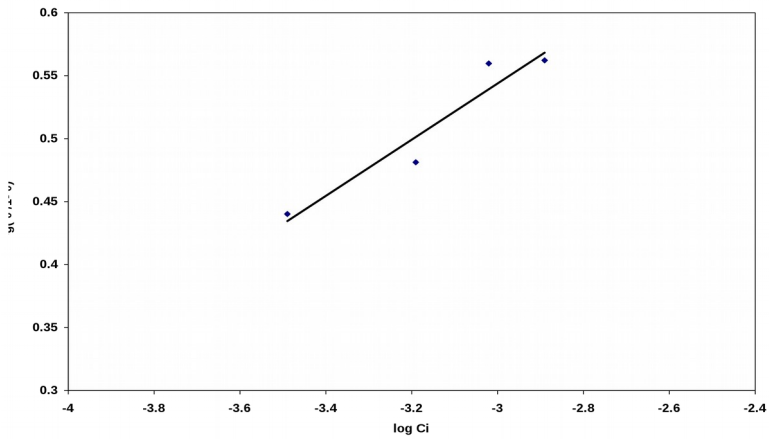


Figure 5: El – Awady isotherm.

Weight Loss Measurements:

Effect of Temperature:

Effect of temperatures on the corrosion behavior of aluminum in 1 M hydrochloric acid was studied by the weight loss method over temperature range (303–333 K). The data display that the rate of corrosion increases with an increase in temperature from 303 to 333K as represented in **Table (2).** Also, **Figures (6)** indicated that the weight losses of aluminum in 1 M HCl increase with increasing the immersion time. The results of aluminum inhibition efficiency of 300 ppm of the used drug at different temperatures show that the weight losses decrease (corrosion rate) with increasing temperature from 303 – 333K which indicate chemical adsorption **[19].**

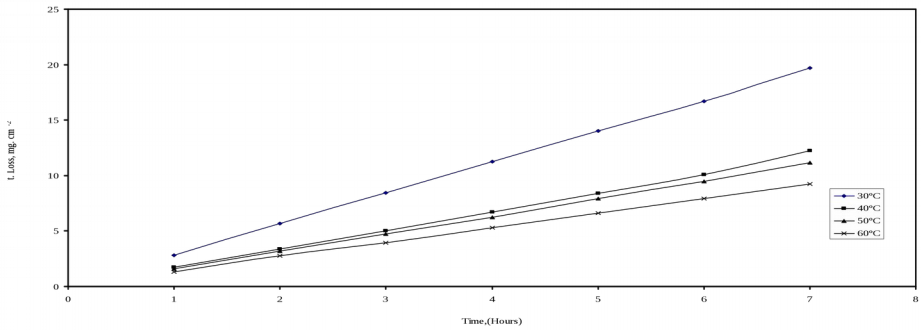


Figure 6: Weight loss-time curves of aluminum in 1 M HCl in the presence of 300 ppm of the used inhibitor at different temperatures

Activation Energy of corrosion:

Corrosion is an electrochemical phenomenon and consequently follows the laws of chemical kinetics. The corrosion rate increases with increasing temperature as a result of decreasing the apparent activation energy, E_a of the charge transfer reactions. Increasing temperature also enhances the rate of H^+ ion diffusion to the metal surface beside the ionic mobility, which increases the conductivity of the electrolyte. The effect of temperature on the inhibition efficiency of corrosion inhibitors is important in elucidation of the mechanism and kinetics of their action. Moreover, at lower temperature, adsorbed hydrogen atoms (exothermic process) blocked the cathodic area.

The activation energy (Ea) can be calculated from Arrhenius equation [**19].**

$$\log C.R. = \log A - Ea/2.303RT \qquad (6)$$

A is pre-exponentional factor related to concentration, steric effect and metal surface characteristics, etc. Plotting of log C.R. against 1/T for the free acid solution (blank) and in presence of 300 ppm of the used inhibitor were represented in **Figure (7)**. The activation energies were calculated and listed in **Table (2).** The results showed that the whole process is controlled by surface reaction **[22].**

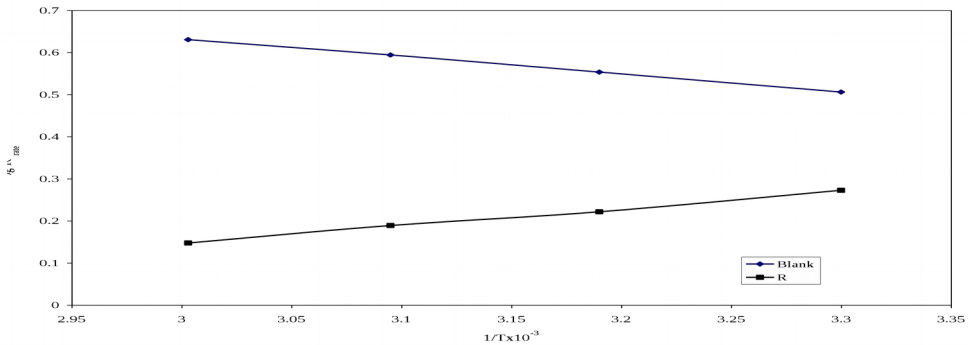


Figure 7: Relation between log C.R. against 1/T at different temperatures in absence and presence of 300 ppm of the used inhibitor.

Table 2: Degree of surface coverage (θ) and percentage of inhibition efficiency (IE) of the used inhibitors in 1M HCl at different temperatures calculated from weight loss data.

Compound	T, ºK	(1/T)x10^{-3}	R_{corr} mg.cm^{2}.day^{-1}	Log R_{corr}	IE	Θ	E_{active}, k.J.mol^{-1}
R1	303	3.3	1.042	0.01787	82	0.82	53
	313	3.19	0.96	0.0177-	84	0.84	
	323	3.09	0.81	0.0915-	85.4	0.854	
	333	2.91	0.76	0.1192-	88.7	0.887	

Activation Thermodynamic parameters

The free energy of adsorption (ΔG_{ads}*) at different temperatures was calculated from the following equation:

$$\Delta G_{ads}^{*}=RT\ (\log C.R. - \log KT/h) \quad (7)$$

K, is equilibrium constant, which is given by

$$K = \theta / Ci\ (1- \theta) \quad (8)$$

The values of E_a* and ΔG_{ads}* were listed in Table (3). The negative values of ΔG_{ads}* indicate the spontaneous adsorption of inhibitors on the surface of aluminum. The negative values of ΔG_{ads}* also suggest the strong interaction of the inhibitor molecules on to the metal surface **[23].** The thermodynamic functions of inhibitor adsorption, entropy, ΔS_{ads}*, enthalpy, ΔH_{ads}* and free energy, ΔG_{ads}* are calculated from the equations:

$$\Delta H_{ads}^* = E_a^* + RT \quad (9)$$

Where, R is the universal gas constant. Entropy of inhibitor adsorption (ΔS_{ads}^*) can be calculated using the following equation:

$$\Delta S_{ads}^* = (\Delta H_{ads}^* - \Delta G_{ads}^*)/T \quad (10)$$

The calculated ΔS_{ads}^* data were listed in **Table (3).** All obtained data show that ΔS_{ads} values are positive and increased by increasing temperature which indicates that the inhibitor more oriented and more ordered on the surface of the metal. **Table (3)** showed being that ΔH_{ads}^* has negative values, indicating that, the process is exothermic. On the other hand, the negative value of ΔH_{ads}^* indicated that the adsorption of inhibitors is of a chemical one and the inhibitor forms stable layer at the surface of the metal. This behavior protects aluminum form the environmental conditions (HCl) and decreased the corrosion rate.

The chemical adsorption can be explained on the basis of the effect of chemical structure of inhibitor on its inhibition efficiency. In this respect, the furan ring and the N=O group of the used inhibitor can form a big π bond. Accordingly, not only the π electron of the furan and nitrosyl enter unoccupied orbital of aluminum, but also the π*orbital can accept the electrons of the aluminum orbitals to form feed back bonds, which produce more than one center of chemical adsorption on the metal surfaces [**19,2**4]. On the other hand, the presence of the electron donating groups in the structure of the used inhibitors such as (-N $(CH_3)_2$), increases the electron density on the nitrogen of the NH group and increases inhibition efficiency by increasing the polarity of the inhibitor.

Table 3: Thermodynamic activation Parameters of adsorption for aluminum in 1 M HCl in absence and presence of 300 ppm of the used inhibitor at different temperatures.

Compound	Temp., °K	E_a^*	$-\Delta G^*$, k.J.mol^{-1}	$-\Delta H^*$, k.J.mol	ΔS^*, k.J.mol.k^{-1}
Blank	303	29	33.16	24.3	0.178
	313		34.26	24.9	0.186
	323		37.16	25.4	0.196
	333		39.3	26.2	0.198
R1	303	53	53.7	27.4	0.142
	313		56.9	27.8	0.148
	323		59.8	29.2	0.152
	333		61.7	30.9	0.159

Conclusions:

Based on the obtained results, the following conclusions are accomplished: -

1- The expired Ranitidine drug is very good inhibitor and act as a mixed type inhibitor for aluminum corrosion in hydrochloric acid solution.
2- Inhibition efficiencies increased by increasing inhibitor concentration and temperatures up to 333 K.
3- All entropy parameters for adsorption of inhibitor molecules on aluminum are positive and increased by increasing the temperature which indicates that the inhibitor being more oriented and more ordered on the surface of the metal.
4- The activation parameters of the adsorption (E^*, ΔH^* and ΔS^*) were calculated and showed that the used inhibitor decreased the rate of corrosion.
5- The adsorption of this inhibitor on surface obeys both Langmuir's and El-Awadi isotherms.

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