Expired Voltaren Drugs as Corrosion Inhibitor for Aluminium in Hydrochloric Acid

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The effectiveness of Expired Voltaren (EV) drug as corrosion inhibitor for aluminium in 1 M HCl was investigated by weight loss and electrochemical methods. Polarization curves revealed that the inhibiting action of the EV is mixed-type. The addition of the inhibitor molecules shifted the corrosion potential (E_{corr}) to more noble direction. The influence of temperature on the adsorption of inhibitor onto aluminium surface has been reported. Activated thermodynamic parameters were computed and discussed.The adsorption of the EV was found to obey the Langmuir adsorption isotherm. The inhibition efficiency of expired Voltaren, EV obtained by all methods was in good agreement with each other.

Keywords: Corrosion Inhibitor; Adsorption isotherm; Drugs; 2-(2, 6-dichloranilino) phenylacetic acid; Aluminum; Polarization.

1. INTRODUCTION

Aluminum and its alloys are widely used in many industries such as reaction vessels, pipes, aluminum–air technology, machinery, and chemical batteries, because of their advantages [1]. 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, 2]. Some non-ionic surfactants were also used to inhibit the corrosion of aluminum in HCl such as ethoxylated fatty acid [3] and tetradecyl 1, 2 diolpropenoxylates [4].

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 [4, 5]. Physical adsorption and chemisorptions are the principal types of interaction between organic inhibitors and the metal surface.

Despite the wide range of available organic compounds, the final choice of the inhibitor for a particular application is restricted by several factors, including increased environmental awareness and the need to promote environmentally friendly processes, coupled with the specificity of action of most acid inhibitors, which often necessitates the combined action of compounds to achieve effective corrosion inhibition. Consequently, there exists a need to develop inexpensive and environmentally friendly inhibitors. In recent years, researchers have paid attention to the development of drugs as inhibitors for the corrosion of metals in acid media [6-8].The use of expired drugs as corrosion inhibitors for metals are limited [9-12]. Voltaren drug is used as anti-inflammatory and analgesic. There is presently no report on use of Voltaren as a corrosion inhibitor for aluminum in hydrochloric acid.

The aim of the present work is to study the inhibitive action of the expired Voltaren (EV) towards the corrosion of aluminum in 1M HCl solution. Weight loss, Open circuit potential, and potentiodynamic polarization measurements were used to evaluate the inhibition efficiency of this compound at different concentrations and temperatures. Thermodynamic parameters obtained from the studies are also calculated and discussed.

2. EXPERIMENTAL

Aluminum metal with purity of 99.9 % provided by the "Aluminum Company of Egypt, NaghAmmady" was used in the present study. Aluminum sheets with dimention $2 \times 2 \times 0.2$ 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 bi distilled 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 hour. The average weight loss for each two identical experiments was taken and expressed in mg cm^{-2}. The temperature was adjusted to 30 ± 1 ^{o}C 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 bi distilled water.

3. RESULTS AND DISCUSSION

3.1. Evaluation of the used Expired Drugs as Corrosion Inhibitor

The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media. The choice of the inhibitor is based on two considerations [9-12].

First: It could be obtained conveniently from relatively cheap 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 [13-15]. In this respect, the present corrosion inhibitor was used from undesired expired medical drugs which have higher water solubility. Expired Voltaren of (a molecular weight of 296) from (EIPICO) pharmaceutical company was used for the study. Figure (1. a) shows the molecular structure of 'Voltaren'.
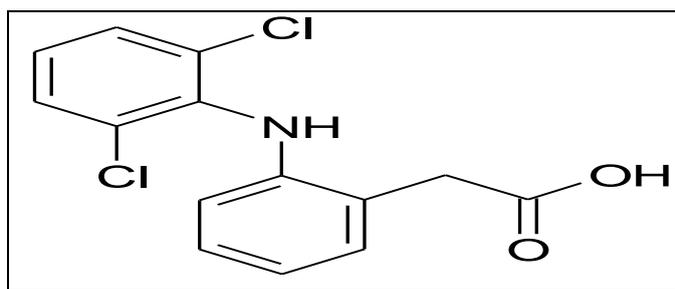

Figure 1. a). Molecular structure of 2-(2, 6-dichloranilino) phenylacetic acid (Voltaren)

The chemical structure of the expired voltarin (EV) was confirmed from their IR spectra. Figure (1.b) the presence of strong broad band at 3450cm^{-1} indicates the termination of the compound with hydroxyl groups of the carboxylic end group and the band observed at 810cm^{-1} is assigned to –CH out-of-plane bending of substituted phenyl. This confirms the presence of phenyl rings in expired drugs.
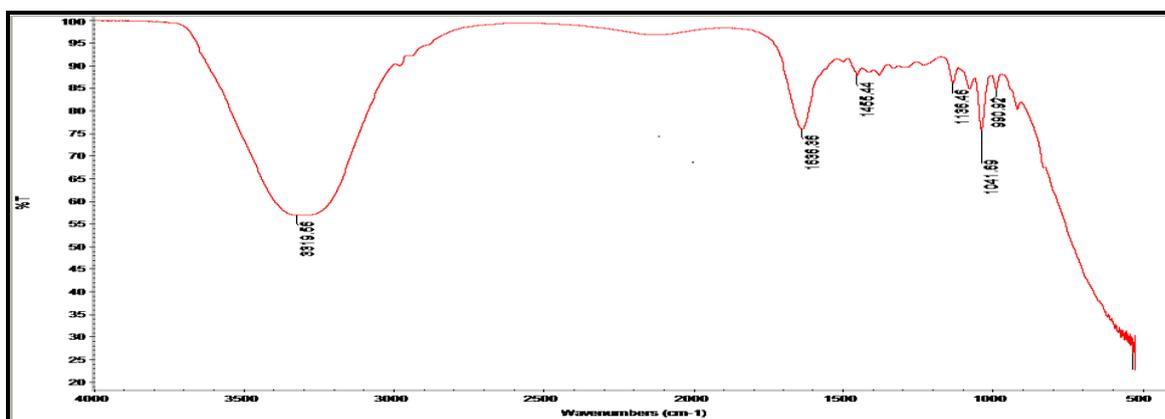

Figure 1. b). FT-IR Spectrum for expired voltaren (EV)

The presence of strong bands at 1636 and 1155cm^{-1}, which were assigned for C O stretching and C–O stretching of carboxyl groups, the band observed at 2900 cm^{-1} for the aliphatic –CH$_2$, appearance of a band at 3100cm^{-1}, which represents NH stretching for secondary amine group in the structure of the expired voltaren.

3.2. Open Circuit Potential Measurements

The time dependence of the open circuit potential (OCP) was recorded for 60minutes of immersion of the aluminum specimens in aqueous 1 M HCl solution without and with expired Voltaren at different concentrations (25 - 125 ppm).

A sharp drop in the E$_{OCP}$ was observed after the specimens were immersed in the solution followed by an increase to more positive values. The E$_{OCP}$ reached relatively stationary values after 20 minutes of immersion. Figure (2) the differences in E$_{OCP}$ values at the beginning of the exposure, due to the aggressiveness of the HCl solution. It was suggested that the initial negative shift would be related to the adsorption of inhibitor molecules on aluminum surface [16]. In the present study these alterations could possibly take place due to the interaction of the Voltaren molecules with metal surface. The results have shown that the addition of expired Voltaren (EV) molecules at the beginning shifts E$_{OCP}$ to more negative values. Although the trend in all cases is for E$_{OCP}$ to become more positive with time, due to oxide film growth [17]. In particular, initial values are more negative than steady state values, also the dependence of E$_{OCP}$ on concentration is much more marked this suggests that the inhibitors molecules are strongly and rapidly adsorbed at the steady state potentials [17].
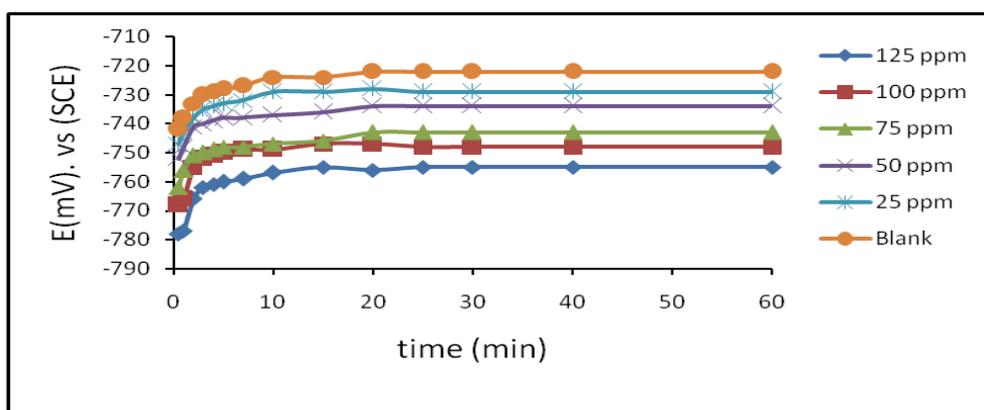

Figure 2. Potential- time curves for aluminum in 1 M HCl in absence and presence of different concentrations of (EV) at 303 K.

3.3. Potentiodynamic Polarization Measurements

Anodic and cathodic polarization curves for aluminum in 1 M HCl with and without various concentrations (25- 125 ppm) of inhibitor were represented in Figure (3). The curves were swept from -1400 to 0 Vs (SCE) with scan rate of 20 mVs^{-1}. Figure (3) illustrates the effect of adding progressive

addition (25- 125 ppm) from expired voltaren inhibitor on the cathodic and anodic polarization curves of aluminum in 1M HCl at 303 K
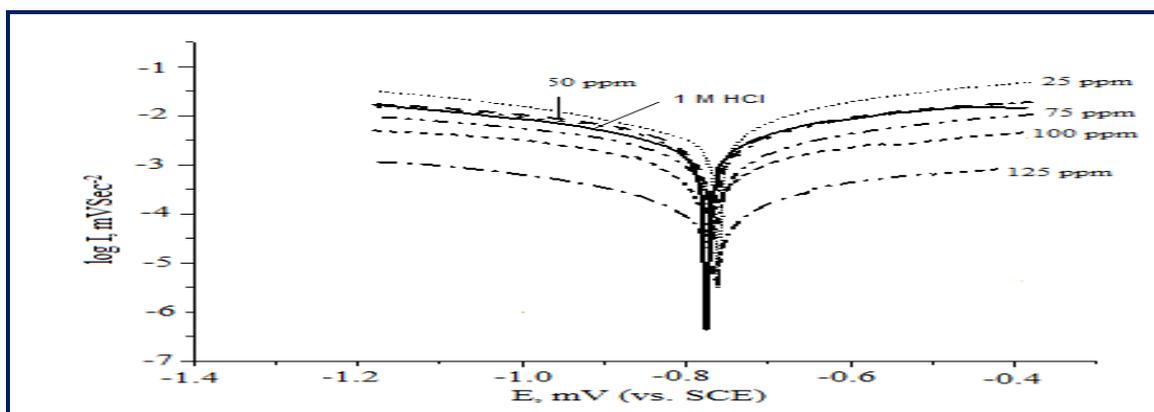

Figure 3. Potentiodynamic polarization curves of aluminum in 1M HCl in the absence and presence of different concentrations of (EV) at 303 K.

It is evident that presence of the inhibitor causes a prominent decrease in current densities, i.e. shifts the cathodic curves to lower values of current densities. It is known that corrosion behavior (resistance) of aluminum is determined essentially by the behavior of its oxide layer, in which the surface state plays a significant role and the oxide film on aluminum is in fact impossible to reduce electrochemically in aqueous solution [16]. As long as acid media are able to dissolve the oxide film spontaneously formed on aluminum surface during or before transferring electrode to the electrolytic cell with medium, it is expected that the combined action of acid and chloride leads to conditions similar to that of pitting [18]. Chlorides may substitute oxygen atoms in the oxide network, and this leads to a decrease in the oxide film resistance, which facilitates the release of aluminum atoms that diffuse into the hydrochloric acid solution.From Figure3.Is quite clear that in 1 M HCl solution without inhibitor there was no passive film formation during the anodic polarization, Strong dissolution of the preimmersion oxide air formed film occurs, probably due to the high concentration of H^+ ions , in other words, the dissolution rate of the film is greater than its rate of formation and a strongly local metal dissolution occur [19].

The shape of anodic curves observed in the HCl solution in presence of inhibitor molecules is quite different from those recorded in the solution without inhibitor, When inhibitor are added to the hydrochloric acid solution the existence of potential plateaus is observed [19]. The shape of the curves confirms that voltarin affects the cathodic hydrogen evolution, and blocked anodic electron transfer reaction, indicating the passive behavior of the aluminum surface due to the formation of a thin barrier passive film. It is quite obvious that the anodic process on Al in presence of expired voltaren is not only the simple dissolution of aluminum and that other processes are also involved such as adsorption of inhibitor molecules on electrode surface. Figure (3) was clear that, the addition of expired Voltarin drugs 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 towards the corrosion of aluminum in 1M hydrochloric acid solutions.

Corrosion potentials (E_{corr}), corrosion current densities (I_{corr}), cathodic Tafel slope values (bc) deduced from the polarization curves, corresponding inhibition efficiencies (I.E %) and surface coverage degrees (θ) are listed in Table (1).

Table 1. Polarization data of aluminum in 1 M HCl solution in the absence and presence of different concentrations of (EV) at 303 K

Sample	Conc., ppm	I_{corr}., mA/cm^2	$-E_{corr}$., mV	$-b_c$, mV/decade	θ	IE %
Blank	0	0.96	725	122	0	0
EV	25	0.25	789	85	0.739	73.9
	50	0.21	811	120	0.78	78
	75	0.16	825	127	0.83	83
	100	0.09	832	131	0.906	90.6
	125	0.08	843	137	0.917	91.7

The shift of corrosion potentials in the cathodic direction and decrease of corrosion currents with the increase of inhibitor concentration indicate the adsorption of these molecules at the cathodic site of the aluminum surface [16]. By addition of expired Voltaren to the HCl solution, the change in the mechanism of corrosion process and an improvement in corrosion behavior are obvious. This could be mainly attributed to the physical adsorption process of active molecules, which additionally form protective layer on aluminum surface [20].

3.4. Weight Loss Measurements

3.4.1. Effect of the inhibitor concentrations

Table 2. Corrosion rate, surface coverage (θ) and inhibition efficiency (% IE) obtained from weight loss measurements for aluminum in 1 M HCl in the absence and presence of different concentrations of (EV) at 303 K, after 8h immersion time

Conc., ppm	Corrosion rate mg.cm^{-2} hr^{-1}	θ	% IE
Blank	1.95	0	0
25	0.37	0.81	81
50	0.32	0.835	83.5
75	0.27	0.86	86
100	0.23	0.88	88
125	0.20	0.897	89.7

The weight loss results of aluminum in 1M HCl in the absence and presence of various concentrations of the inhibitor are summarized in table (2). The I.E (%) was calculated using the following equation:

$$\text{I.E (\%)} = (W_2 - W_1/W_1) \times 100 \tag{1}$$

Where, W_1 and W_2 are weight loss of aluminum in the presence and absence of the inhibitor respectively.

The inhibition efficiency increased with increase in the concentration of the inhibitor.

3.4.2. Effect of Temperature

To elucidate the mechanism of inhibition and to determine the kinetic parameters of the corrosion process weight loss measurements were performed at 303,313,323,333K. The effect of temperature on the corrosion inhibition efficiency of aluminum in the presence of the inhibitor is graphically represented in figure (4).
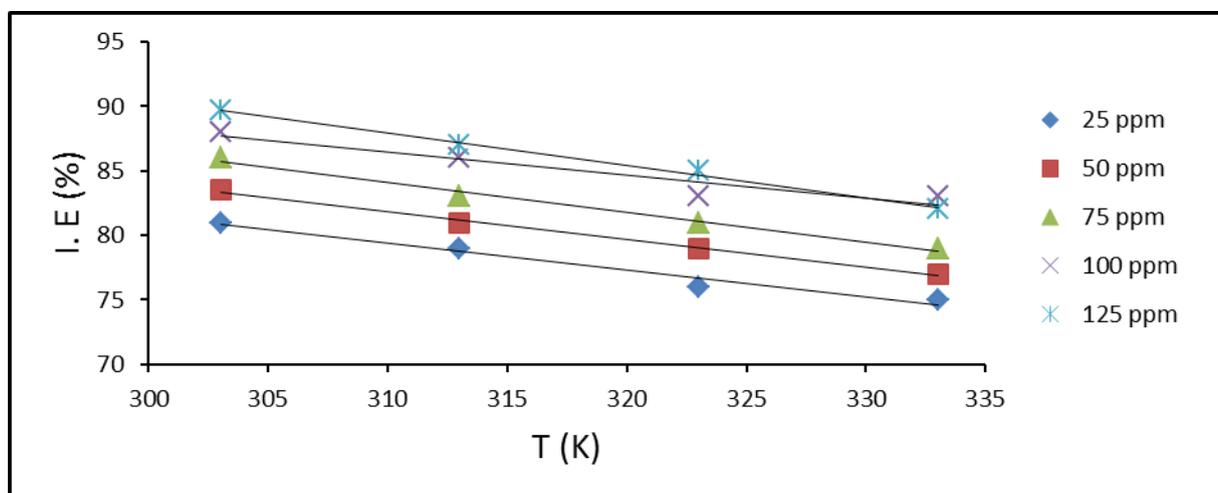

Figure 4. Effect of temperature on I.E for aluminum in 1M HCl in the presence of different concentrations of (EV) inhibitor

The inhibition efficiency decreased with increase in temperature, leading to the conclusion that the protective passive filmof these compounds formed on the aluminum surface is less stable at higher temperature; which may be due to the desorption of some adsorbed molecules from the surface of the aluminum at higher temperature due to which greater area of the metal is exposed to the acidic environment.The apparent activation energy (E_a) of metal corrosion in acid media can be calculated from the Arrhenius equation [10, 21]:

$$\ln C_R = (E_a/RT) + A \tag{2}$$

Where E_a is the apparent activation energy for the corrosion of aluminum, R is the universal gas constant, A is Arrhenius pre exponential factor and T is the absolute temperature. Figure (5)

depicts the plot of log CR vs. 1/T and the values of E_a obtained from the slope of the plot are given in table (3).

Table 3. Values of activation parameters for Aluminum in 1M HCl in the absence and presence of different concentrations of the (EV) inhibitor

Inhibitor Conc. (ppm)	E_a (kJmol^{-1})	ΔH_a (kJmol^{-1})	$-\Delta S_a$ (J k^{-1} mol^{-1})
Blank	33.12	32.88	123.44
25	43.1	40.4	127.2
50	45.92	43.3	124.8
75	46.88	46.96	120.6
100	49.2	50.16	118.24
125	52.4	52.56	114.96

The higher value of activation energy (E_a) in the presence of inhibitor than in its absence is attributed to its physical adsorption, its chemisorption is pronounced in the opposite case [10, 21].
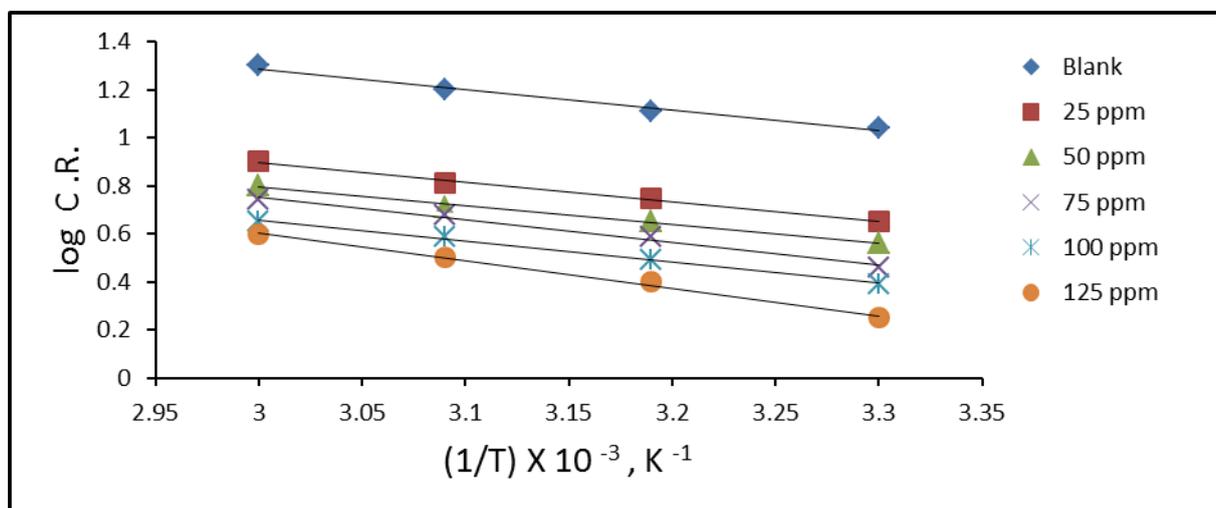

Figure 5. Arrhenius plot for Aluminum in 1M HCl solution in the absence and presence of various concentrations of (EV) inhibitor

In the present study the higher value of E_a for aluminum in presence of expired Voltaren (EV) compared to that in its absence is attributed to its physical adsorption. Szauer and Brand [15] explained that the increase in E_a can be attributed to an appreciable decrease in the adsorption of the inhibitor on the metal surface with increase in temperature and a corresponding increase in corrosion rates occurs due to the fact that greater area of metal is exposed to acid environment. An alternative form of Arrhenius equation is the transition state equation [18]:

$$CR = (RT/Nh) \exp(\Delta S_a/R) \ \exp(-\Delta H_a/RT) \tag{3}$$

Where, h is the Plank's constant, N is the Avogadro's number, ΔS_a is the entropy of activation, and ΔH_a is the enthalpy of activation.

A plot of log (CR/T) vs. 1/T gave a straight line as shown in Figure (6) with a slope of ($-\Delta H$ /2.303R) and an intercept of [log(R/Nh) + (ΔS /R)], from which the values of ΔH_a and ΔS_a were calculated and listed in table (3).
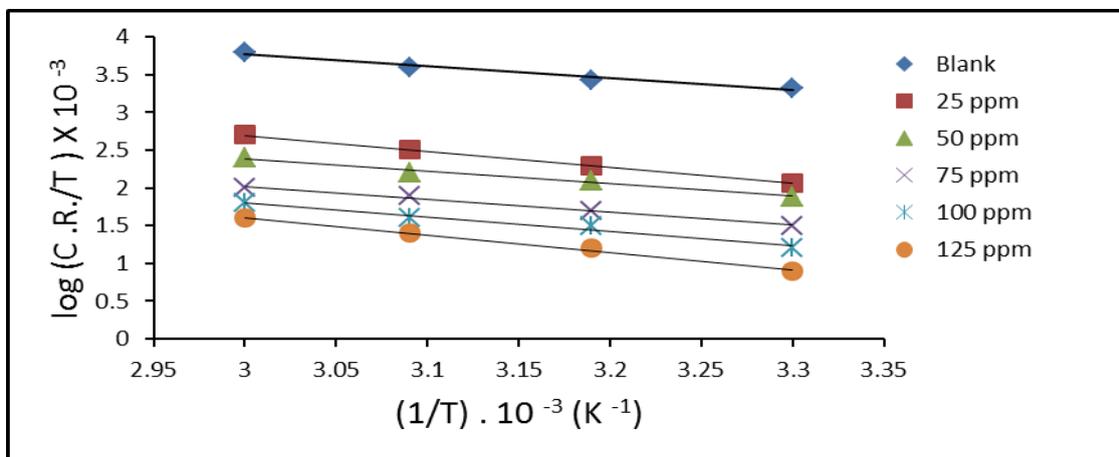

Figure 6. Transition state plot for Aluminum in 1M HCl solution in the absence and presence of various concentrations of (EV) inhibitor

The positive values of ΔH_a for corrosion of aluminum in the presence and absence of the inhibitor reflect the endothermic nature of metal dissolution process. The increase in ΔH_a with increase in the concentration of the inhibitor for aluminum corrosion reveals that decrease in aluminum corrosion rate is mainly controlled by kinetic parameters of activation [18].

The entropy of activation values are less negative for inhibited solutions than that for the uninhibited solutions. This suggests that an increase in randomness occurred while moving from reactants to the activated complex [22].

3.4.3. Adsorption Isotherm and Thermodynamic Parameters

The adsorption behavior of the organic adsorbate on the metal surface should be known to in order to understand the mechanism of corrosion inhibition. The degree of surface coverage (θ) for different concentration of the inhibitor (C_i) has been calculated. The data were tested graphically by fitting to various isotherms. A straight line with correlation coefficient nearly equal to 1.0 was obtained on plotting C_i/θ against C_i as shown in figure (7), suggesting adsorption of the compound on the mild steel surface followed Langmuir adsorption isotherm model. It is interpreted from the graph that, adsorption of the inhibitor on the aluminum surface followed Langmuir adsorption isotherm at all studied temperatures.
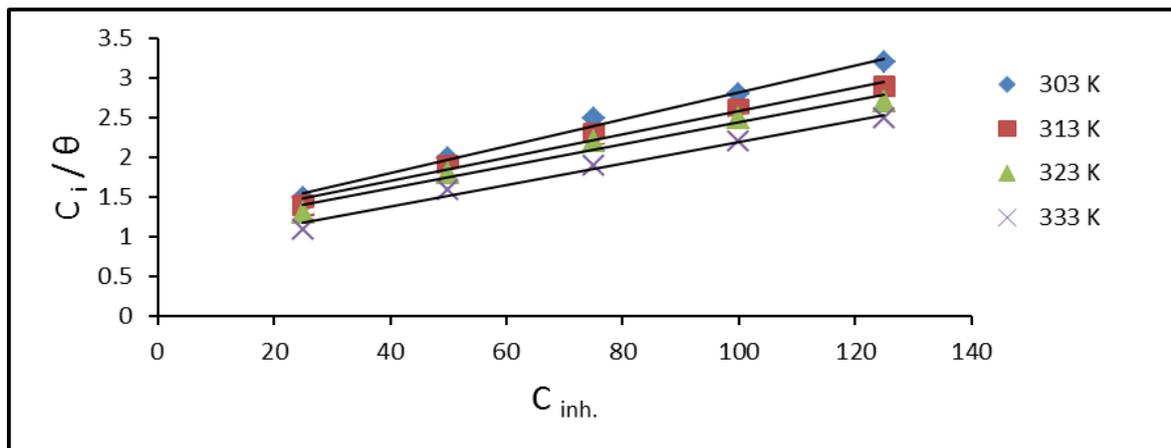
Figure 7. Langmuir adsorption isotherm for Aluminum in 1M HCl solution at various temperatures

According to this isotherm, the surface coverage (θ) is related [12] to inhibitor concentration C_{inhi} by equation (4)

$$C_{inhi} / \theta \quad = \quad 1/ K_{ads} + C \tag{4}$$

Where, K_{ads} is equilibrium constant of the equilibrium adsorption process. This isotherm assumes that adsorbed molecule occupies only one site and it does not interact with other adsorbed species.

The K_{ads} values can be calculated from the intercept lines on the C_{inhi}/ θ axis. This is related to the standard free energy of adsorption (ΔG_{ads}) by equation (5):

$$\Delta G_{ads} \quad = -RT \, lin \, (55.5 \, K_{ads}) \tag{5}$$

Where, R is the gas constant and T is the absolute temperature. The constant value of 55.5 is the concentration of water in solution in mol/L. The values of ΔG_a for the inhibitor on the surface of aluminum are given in table (4).

The negative value of ΔG_a indicated spontaneous adsorption of the inhibitor on the aluminum surface. Generally, the magnitude of ΔG_a around -20kJ/mol or less negative indicates electrostatic interactions between inhibitor and the charged metal surface (i.e., physisorption). Those around -40kJ/mol or more negative are indicative of charge sharing or transferring from organic species to the metal surface to form a coordinate type of metal bond (i.e., chemisorptions)[20]. In the present work, the calculated values $\Delta G°$ at 303K for aluminum is -33.2 kJ/mol, which indicate that adsorption of the inhibitor on the aluminum surface involves both physical and chemical process[23-25]. But the inhibition efficiency decreased with increasing temperature indicating inhibitor adsorbed predominantly physically on the surface of mild steel. The enthalpy of adsorption (ΔH_{ads}) can be calculated from the rearranged Gibbs-Helmholtz equation:

$$\Delta G_{ads}/T = (\Delta H_{ads} /T) \quad + \quad K \tag{6}$$

The variation of $\Delta G_{ads}/T$ with 1/T gave a straight line with a slope of ΔH_{ads} as shown in figure (6). The entropy of adsorption ΔS_{ads} was calculated using the following thermodynamic equation:

$$\Delta S_{ads} = (\Delta H_{ads} - \Delta G_{ads})/ T \tag{7}$$

The calculated values of heat of adsorption and entropy of adsorption are listed in Table (4).
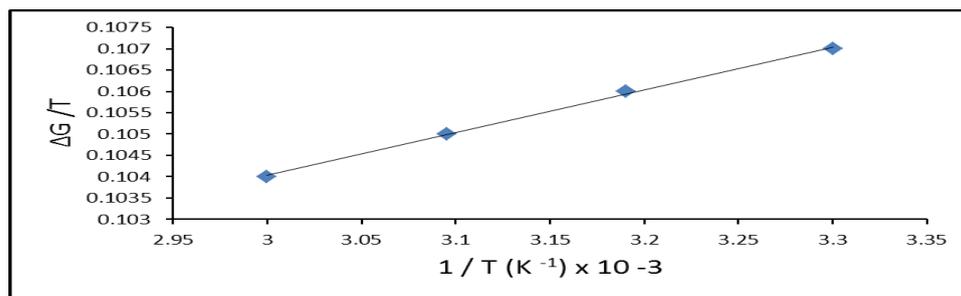

Figure 8. $\Delta G_{ads}/T$ versus $1/T$ plot for Aluminum in 1M HCl solution.

Table 4. Values of thermodynamic parameters for the adsorption of the inhibitor in 1M HCl on the Aluminum at different temperatures

Temperature (K)	K (mol^{-1})	$-\Delta G_{ads}$ (kJmol^{-1})	$-\Delta H_{ads}$ (kJmol^{-1})	ΔS_{ads} (J k^{-1} mol^{-1})
303	43926	32.48	8.5	78.4
313	37296	33.2	8.5	77.6
323	42561	34.1	8.5	78.88
333	37910	34.8	8.5	78.4

It is well known fact that adsorption is an exothermic phenomenon accompanied by a decrease in entropy [26]. In aqueous solutions the adsorption of the organic molecule is generally accompanied by desorption of water molecules [20, 27].

Inhibitor $_{(sol)}$ + x H$_2$O $_{(sol)}$ $\rightleftarrows$ Inhibitor $_{(ads)}$ + x H$_2$O $_{(sol)}$

The negative sign of ΔH_{ads} indicated the exothermic process of adsorption of the inhibitor on aluminum surface in HCl. The positive value of ΔS_{ads} in the presence of inhibitor can be attributed to the increase in the solvent entropy and more positive desorption entropy. It is also interpreted that the increase of disorderness is due to more water molecules which can be desorbed from the metal surface by one inhibitor molecule. Therefore it is revealed that decrease in the enthalpy is the driving force for the adsorption of the inhibitor on the surface of aluminum [21, 27].

4. CONCLUSIONS

Expired Voltaren (EV) ampoules act as good corrosion inhibitors for aluminum in 1 M HCl solution. Corrosion inhibition efficiency was increase with increasing inhibitor concentrations, but decrease with increasing temperatures. Potentiodynamic polarization curves for aluminum in 1 M HCl show that the used inhibitor molecules act as mixed type inhibitors.The addition of expired Voltaren (EV) molecules at the beginning shifts E_{OCP} to more negative values. Although the trend in all cases is

for E_{OCP} to become more positive with time, due to oxide film growth.Thermodynamic parameters show that the inhibitor under investigation is adsorbed on aluminum surface by spontaneous exothermic process, indicating that the adsorption mechanism of expired voltaren (EV) on aluminum in 1 M HCl is physicochemical adsorption.

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