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Study of Valine as Green Corrosion Inhibitor for 304 Stainless Steel in Saline Solution

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Abstract

Effectiveness of amino acid valine in preventing corrosion of 304SS in a sodium chloride (0.6 M NaCl) solution as a green inhibitor was investigated both with and without the organic inhibitor at temperatures between 298 and 328 K. With the use of potentiodynamic polarization approach, the electrochemical performance related to the amino acid valine had been investigated. Using scanning electron microscopy (SEM), The metal surface was researched. The findings demonstrated that is inhibition efficiency increased with inhibitor concentration increase, it decreased as temperature increased. According to polarization measurements, valine has physically adsorbed on stainless steel surface, is regarded as cathodic inhibitor, and complies with the Langmuir adsorption isotherm. To illustrate the corrosion inhibition process, a few thermodynamic parameters like Gibbs free energy (ΔG_{ads}) as well as activation energy (E_a) were calculated. Arrhenius theorem has been used to assess the kinetic limitations. A suitable mechanism for the corrosion of stainless steel in saline solution had been predicted.

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1. INTRODUCTION

A substance's deterioration of its qualities due to interactions with its environment is referred to as corrosion which is a neutral process occurring for metals. Growing awareness of the need to preserve the universe's metal resources has made corrosion research essential. Due to the increasing use of metals in all technological domains, there is presently a great focus on controlling metallic corrosion. [1,2]. Stainless steel has many desirable properties like stability, high strength, good corrosion resistance, weld ability, and workability, stainless steel has various desirable properties that could be utilized in a variety of construction applications, including construction materials, desalination plants, thermal power plants, the pharmaceutical industry, pickling processes, oil and petroleum sectors and chemical cleaning [3]. Its passive film contains chromium and nickel, which contribute to its great corrosion resistance [4]. Stainless steels, on the other hand, are vulnerable to a number of corrosion processes in marine environments [5-7]. Once the chromium content regarding the depleted zone drops below around 12 wt.%, stainless steel is vulnerable to corrosion, and the passive film in that region loses its protective qualities. Corrosion inhibitors could reduce metallic corrosion, which is mostly an electrochemical process that cannot be halted [8]. One of the most effective and real-world strategies for protecting metals against corrosion in various corrosive conditions is the application of inhibitors [9]. Corrosion inhibition was identified as the best method to prevent metals from corroding, particularly stainless steel. As a result, research on stainless steel's corrosion inhibition was crucial. The utilization of inhibitors is one of many approaches for corrosion control. Small amounts of a chemical compound called an inhibitor could stop metals from corroding. Research on organic compounds as corrosion inhibitors is extremely important and has received a lot of interest from environmentalists [10,11]. Numerous inorganic and organic compounds' effects on metal protection in various corrosive media have been studied [12,13].

Organic compounds with heteroatoms (S, N, P, and O) and numerous bonds, along with various functional groups, are considered the most effective inhibitors of corrosion. Additionally, organic compounds with -COOH, -OH, NH2, etc., are said to be excellent corrosion inhibitors. Amino acids are a type of encouraging compounds that could be utilized as a corrosion inhibitor. These biomolecules are fundamental to all organisms and are the building blocks of proteins and several other crucial substances, including neurotransmitters, hormones, and nucleic acids [14]. This paper uses a potentiodynamic approach to examine the inhibiting effect of the amino acid valine on 304SS corrosion in saline solutions at a temperature range of 298–313K. The kinetic and activation factors that control metal corrosion have been studied.

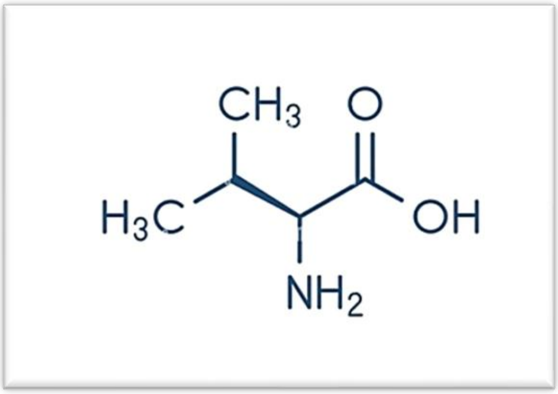


Figure 1. l-valine structure

2. METHOD

2.1.MATERIALS

The 304SS sheet, one of the stainless-steel specimens examined in this investigation, was purchased from a local market. Composition (wt%): 2.0 % Mn, 0.080 % C, 1.0% Si, 0.045 % P, 8 % Ni, 18 % Cr, and the balance Fe Before being immersed in the tested solutions, the SS electrodes were first cut into a circle with a 2 cm diameter and a 2mm thickness. They were then successively ground with various grade emery papers (300, 400, 800, 1500, and 2000), cleaned with alcohol, washed with distilled water, and dried. The surface area that has been exposed to the aggressive medium had a diameter of 1 cm.

2.2. POTENTIODYNAMIC POLARIZATIOM MEASURMENT

Electro chemical measurements was carried out using Three electrodes and 304 stainless-steel serves as the working electrode in the corrosion cell utilized in potentiodynamic polarization. The reference electrode was silver-silver chloride, and the counter electrode was Pt. Following the establishment of a steady state potential in either anodic or cathodic direction, polarization measurements have been made at potentials ranging from -200mV to +200mV at a 2mV/s scan rate. Every measurement has been carried out in a 3.50% NaCl saline solution with and without five distinct amounts of the amino acid valine. The cathodic and anodic curves of tafel plots were extrapolated to get the current density (i_{corr}) as well as corrosion potential (E_{corr}). In order to determine the current density (i_{corr}) and corrosion potential (E_{corr}), Tafel plots regarding cathodic and anodic curve were extrapolated. Each one of the experiments has been carried out at least twice, and results have been reproducible.

3. RESULTS AND DISCUSSION

3.1. POTENTIODYNAMIC POLARIZATION

Figure2 shows potentio-dynamic polarization findings regarding a 304 stainless-steel electrode in 0.6M sodium chloride, Figure3 at varying valine concentrations. The corrosion parameters have been determined from curves of polarization using Tafel extrapolation approach. Table1 presents the resetting results, which indicate that corrosion current density (i_{corr}) decreased as concentration of amino acids increased. When valine is added to a test, corrosion potential (E_{corr}) moves to higher negative values. Inhibitors were adsorbed to cathodic areas, according to this result. Cathodic type inhibitor is what Valine stands for. Table 1 evaluates and illustrates electro-chemical parameters like corrosion potential (E_{corr}), cathodic (β_c), corrosion current density (i_{corr}), anodic (β_a) Tafel slopes and inhibition efficiency (η%). It is possible to assess the inhibition efficiency (η%) using Eq. [15]:

$$\eta\% \equiv \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100\% \qquad (1)$$

In which i_{corr} and i^0_{corr} represent corrosion current density values in inhibitor existence and nonexistence. With 0.5 g/L of valine, the maximum efficiency value has been discovered to be 79.67% at 303K.

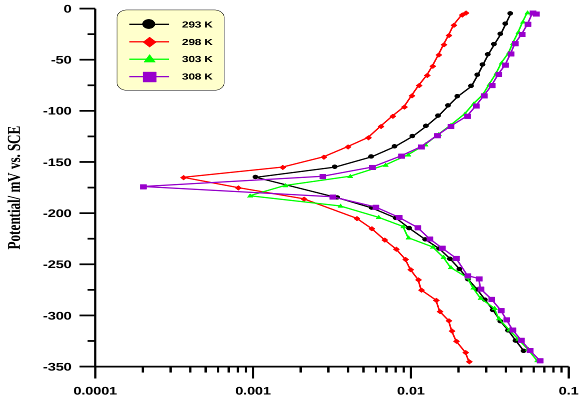
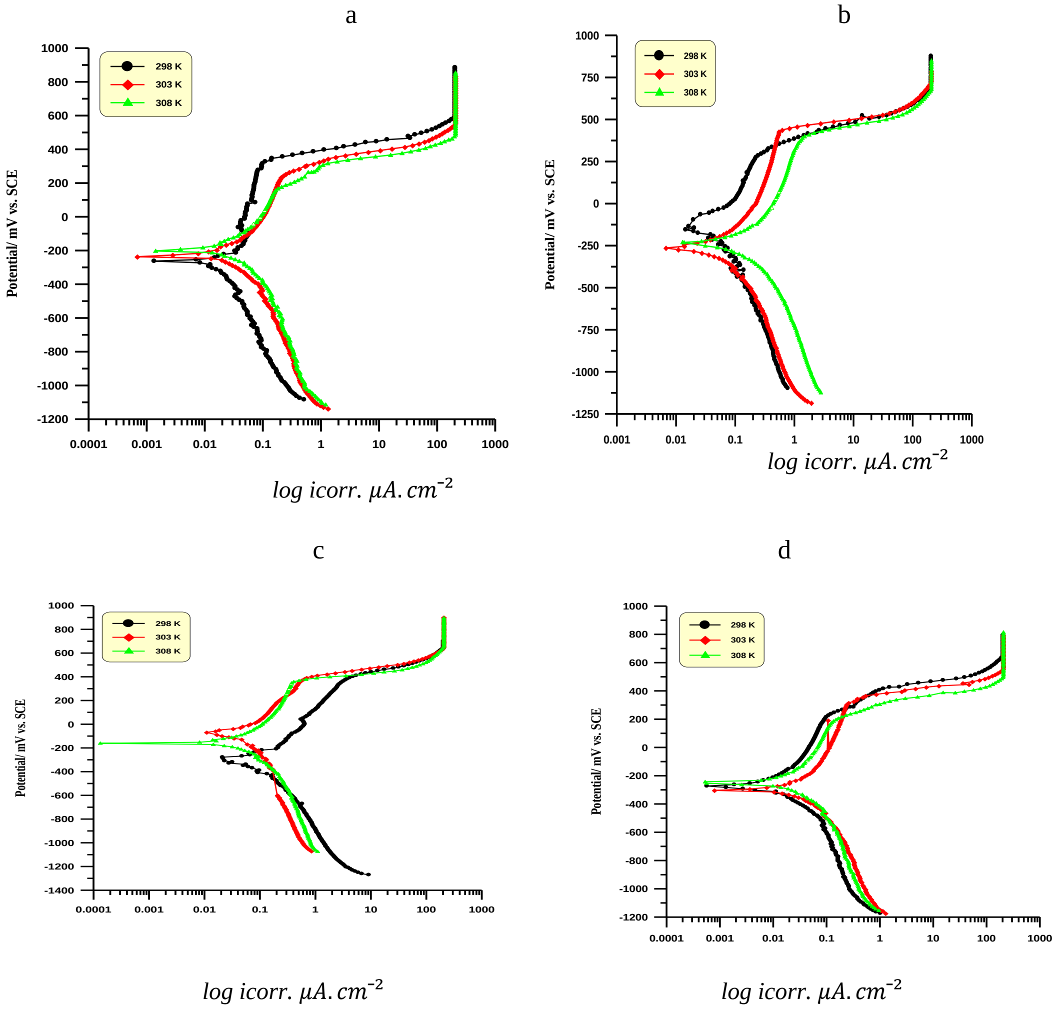


Figure2 . Potentiodynamic polarization curves of 304stainless steel in 0.6M NaCl



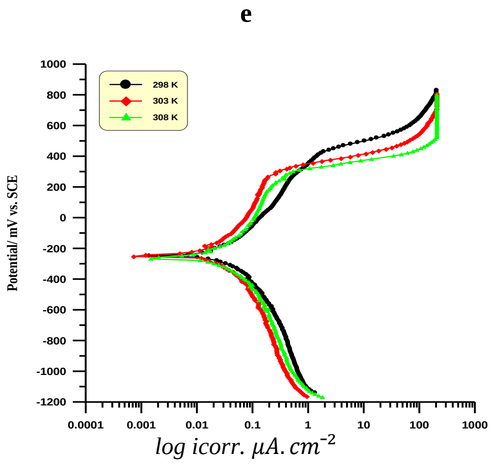


Figure3 . Potentiodynamic polarization curves of 304 stainless-steels in sodium chloride solution with different concentration of valine (a-0.1, b-0.2, c-0.3, d-0.4, e-0.5g/L) at different temperatures.

From the potentiodynamic results in Table1,it is clear that the existence of inhibitor, in saline medium minimize rate of corrosion. The decrease in i_{corr} is because of valine molecules adsorption on the ss alloy surface. The magnitudes of βa and βc varied to some extent with raising inhibitor concentration specifying the effect of them on the kinetics of metal corrosion. Compounds containing several active sites, like hetero-atoms make them a successful and effective option using for corrosion inhibition,they are feasibly subject to the adsorption inhibitors [16].

Table1. Electrochemical parameters acquired from potentiodynamic polarization measurements of stainless steel in sodium chloride solution in an existence and non-existence of diverse concentrations of amino acid valine.

T /K	**Conc. g/L**	**-E$_{corr.}$ mV vs sec**	**i$_{corr.}$ μAcm^{-2}**	**β$_{c.}$ mV dec^{-1}**	**β$_{a.}$ mV dec^{-1}**	**θ**	**η%**
298 K	Blank	151	10.23	-361.9	366.1	…..	…..
	0.1	262	3.15	-62.4	102.1	0.6921	69.21
	0.2	245	2.29	-42.8	27.8	0.7761	77.61
	0.3	280	2.18	-91.6	38.2	0.7869	78.69
	0.4	205	2.13	-48.0	28.1	0.7920	79.2
	0.5	265	2.08	-74.3	71.0	0.7967	79.67
303 K	Blank	178	11.48	-241.9	296.3	…..	…..
	0.1	283	3.83	-45.2	75.7	0.6664	66.64
	0.2	260	2.66	-140.8	165.7	0.7683	76.83
	0.3	263	2.63	-69.2	62.0	0.7702	77.09
	0.4	298	2.61	-42.1	56.4	0.7726	77.26
	0.5	250	2.52	-72.0	73.9	0.7804	78.04
308 K	Blank	191	13.49	-236.1	414.5	….	…..
	0.1	308	4.30	-36.1	101.3	0.6812	68.12
	0.2	277	3.20	-28.3	79.8	0.7628	76.28
	0.3	280	3.09	-48.9	46.3	0.7709	77.09
	0.4	277	3.03	-28.0	52.0	0.7754	77.54
	0.5	250	3.00	-27.0	59.6	0.778	77.8

E_{corr} magnitudes change to more negative ones when the amino acid valine is added. A compound is often classified into either the cathodic or anodic classes based on change in E_{corr} magnitude following the presence of an inhibitor. Values changed to more negative values than when valine was not present, which could mean that valine functions as a cathodic inhibitor and that the anodic reaction is likewise reduced [17]. The corrosion inhibition mechanism could be inferred from the analysis regarding the cathodic and anodic Tafel slopes. A region of an activation-controlled hydrogen evolution reaction and diffusion-controlled reduction reaction of the dissolved oxygen are visible in cathodic branch of the polarization curve when an organic inhibitor is present. As the concentration of organic inhibitor increased, the cathodic current related to oxygen reduction steadily decreased. Additionally, the cathodic Tafel slope increased, indicating that organic inhibitor molecules strongly interfere with the process of oxygen reduction. In such case, cathodic reaction rate controls the corrosion rate. Two distinct regions are shown on polarization curves' anodic branch: a region with diffusion-limited current follows a region with a rapid increase in current, defined by characteristic Tafel behavior, because of SS's anodic dissolution, close to the corrosion potential. The anodic Tafel slope increases with inhibitor concentration, which explain that the SS dissolution is likewise slowed down in a presence of inhibitor [18].

3.2. KINETICS PARAMETER

effect of temperature on the corrosion process was studied by varying temperature because it has a significant impact on metal electrochemical corrosion rate since it is an accelerator in most chemical reactions. Temperature impact (298–308 K) on the corrosion regarding stainless steel in presence and absence of organic inhibitor was also examined for the purpose of getting insight about nature of inhibitor's adsorption process. According to the results in Table 1, we discovered that while inhibition efficacy decreases as temperature increased, i_{corr} increased. This is because the equilibrium between adsorption and desorption has shifted in favor of desorption. The SS surface has so physically adsorbed the organic inhibitor. The Arrhenius equation has been used to calculate activation energy [19].

$$(i_{corr}) = A\ exp\left(-\frac{E^*}{RT}\right) \qquad (2)$$

Here, E^*mean: - activation energy, A mean: - pre- exponential factor and i_{corr} represents the corrosion rate. Figure4 depicts Arrhenius plot log i_{corr} vs. 1/T in absence and presence of amino acid valine. Activation energy that has gotten from the slopes of straight lines that have been listed in Table2.

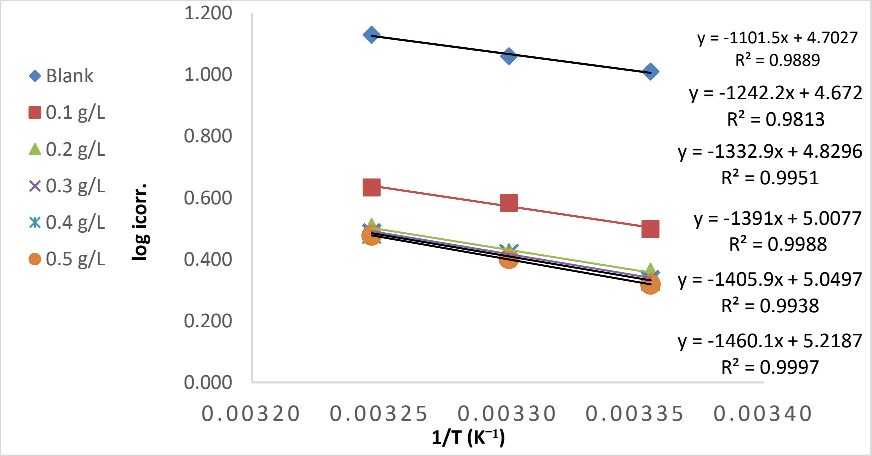


Figure4. Arrhenius Plot relating Log (i_{corr}) to 1/T for stainless steel corrosion in 0.6M NaCl solution in existence and absence of dissimilar concentration levels of valine in temperatures range of (298-308)K.

The theory of the transition state has been used for calculating corrosion process's enthalpy and activation entropy (ΔH^*, ΔS^*) [20]:

$$icorr. = \frac{RT}{Nh}\exp(\Delta S\ *)\ \exp\ (\frac{-\Delta H*}{RT}) \qquad (3)$$

Thus, h denotes Plank's constant, N denotes Avogadro's number, ΔS^* denotes an entropy of activation and ΔH^* denotes an activation enthalpy.[15]

Fig5 provides a depiction of log i_{corr}/T vs.1/T from slopes and intercepts of straight lines we acquired $\Delta H^*$and ΔS^*respectively.

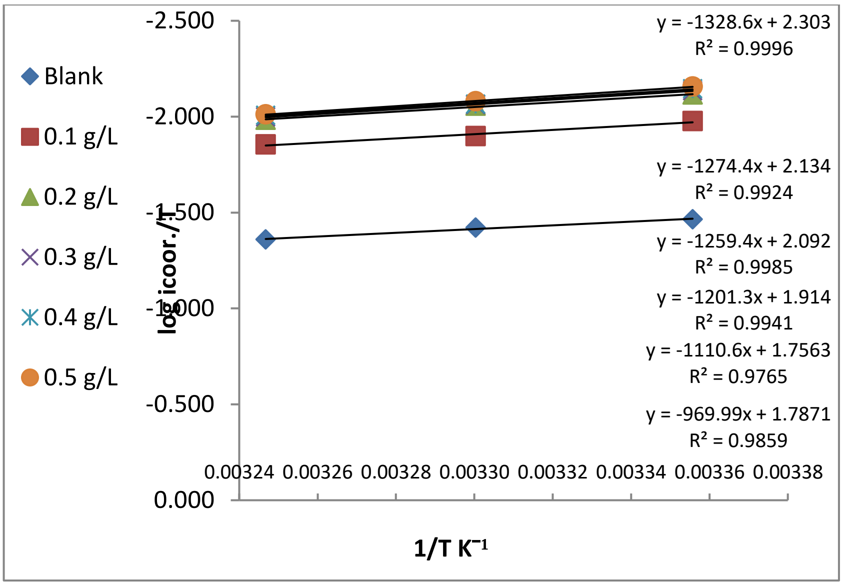


Figure 5 . Log (i_{corr} /T) to 1/T for stainless steel corrosion in 0.6M NaCl solution in presence and absence of diverse concentration levels of valine at temperatures ranged from 298 to 308 K

The values E^{*}, $\Delta S^{*}$and $\Delta H*$ were calculatedfor stainless steel in polluted NaCl in existence of diverse doses of the organic inhibitor in ranged temperature from 298 to 308K as show in Table (2).

Table2. Kinetic-thermodynamic corrosion parameters for stainless-steel corrosion in nonexistence and existence of numerous concentration levels of valine

Conc.	E^{*} kJ.mol^{-1}	-ΔH kJ.mol^{-1}	ΔS J.mol^{-1}K^{-1}
Blank	21.1	18.6	196.6
0.1 g/L	23.8	21.3	196
0.2 g/L	25.5	23.0	199
0.3 g/L	26.6	24.1	202
0.4 g/L	26.9	24.4	203
0.5 g/L	28	25.4	206

The inhibitor presence was associated with increased E^{*} values and E^{*}magnitudes. As an illustration of electro-static character of the inhibitors' adsorption on SS surface, adding an inhibitor increases energy barrier for corrosion. The activation entropy magnitudes were positives the activated complex's rate-determining step is an dissociation step, not a step of association. In particular, relative to the initial state, the activated molecules have not been in an advanced order state. The corrosion process was under exothermic conditions, as indicated by the negative magnitudes of ΔH^{*} [21, 22].

3.3. ADSORPTION ISOTHERM

Many adsorption isotherm models are used for expressing adsorption in a highly suitable method. Depending on the inhibitor's chemical arrangement, two primary types of interaction could be used to describe adsorption of inhibitors on metal surface, like chemisorption and physisorption. Surface coverage data is useful when analyzing adsorption features with the use of isotherm adsorption since it describes the addition of inhibitor molecules that interact with the metal's surface. The effect of the inhibitor (amino acid valine) on the concentrations of inhibitor solutions ($Cinh$) and the working electrode (SS) surface coverage (θ) is examined using adsorption isotherms. The optimal Langmuir isotherm is described by the next equation [23].

$$\frac{Cinh.}{\theta} = \frac{1}{Kads.} + Cinh. \qquad (4)$$

Where, Kads.denotes equilibrium constant of adsorbing / desorbing processes, and it denotes inhibitor molecules' affinity on the way to surface adsorption sites.

After that, measured Kads is for the calculation of Gibbs free energy levels for adsorption through [24]

$$\Delta G°ads = -RTln\ (55.50Kads) \qquad (5)$$

Where, R represents universal gas constant, T represents absolute temperature, whereas 55.50 denotes water concentration in solution.

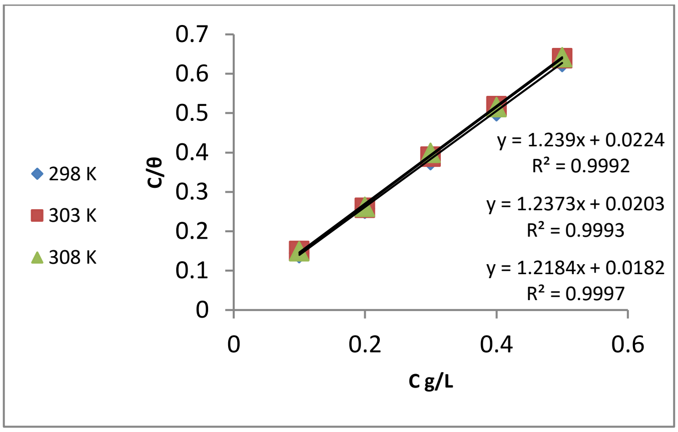


Figure 6. A linear form of Langmuir adsorption isotherm of valine on SS surface in (0.6 M NaCl)solution

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Thermodynamic adsorption parameters like $\Delta H°_{ads}$ and $\Delta S°_{ads}$are computed from combined form of vant'Hoff eq. [25]:

$$\ln K_{ads} = (-\Delta H°_{ads}/RT) + (\Delta S°_{ads}/R) + \ln(1/55.50) \qquad (6)$$

Fig7 explains response of $\log K_{ads}$vs.1/T exhibiting straight lines with slope = $(-\Delta H°_{ads}/RT)$ and intercept = $(\Delta S°_{ads}/R)+\ln(1/55.50)$

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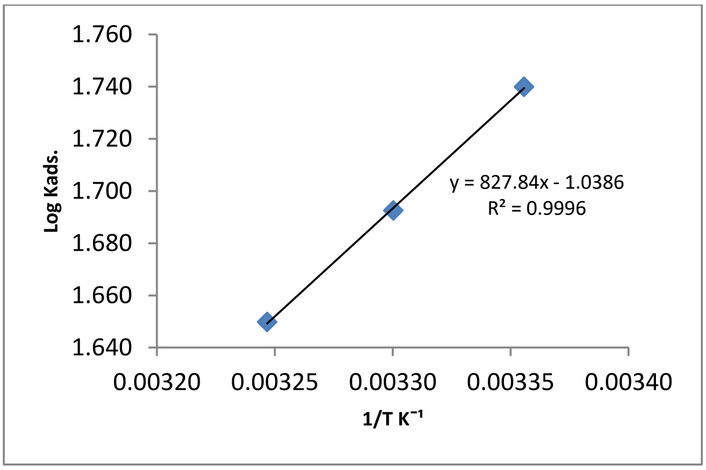

Figure7 . Log K_{ads}vs. (1/T) curves for stainless-steel corrosion in 0.6 M NaCl solution in nonexistence and existence of valine at different temperatures.

Table3. Thermodynamic parameters for adsorbing of valine on stainless steel surface at diverse temperature

Temp. K	K_{ads}	$-\Delta G_{ads}$ $kJ.mol^{-1}$	ΔH_{ads} $kJ.mol^{-1}$	ΔS_{ads} $J.mol^{-1}K^{-1}$
298	54.9	19.877	- 15.85	-79.87
303	49.3	19.935		
308	44.6	20.012		

Adsorption enthalpy values with negative magnitudes. According to ΔH_{ads}, the valine adsorption process on the surface of stainless steel represents an exothermic mode. Exothermic adsorption is accompanied by negative ΔS_{ads} magnitudes. This is consistent with what would be expected in an exothermic adsorption process. Conversely, it ought to be accompanied by a reduction in entropy change [26]. Table (3) has determined and described standard free energy of adsorption.

The spontaneous adsorption regarding valine on stainless steel surface is shown by negative ΔG°_{ads} values. Generally, ΔG_{ads} values reach -20kJ/mol measured as an electrostatic for charged molecules interrelating with outer metal layers (physisorption). Nonetheless, the ΔG_{ads} amounts are in greater negative level than -40kJ/mol as charges transfer from the inhibitor molecules to the metal surfaces or creating coordinate covalent bonds (chemisorption)[27]. This paper's ΔG_{ads} magnitudes fell between 19.9 and 20 kJ. mole^{-1},indicating that physical adsorption are responsible for the inhibitor's adsorption onto stainless-steel alloy surface [28].

3.4. SCANNING ELECTRON MICROSCOPE (SEM).

SEM experiments were carried out to investigate surface morphology of 304 SS, SEM images of 304 SS surface immersed in 0.6 M NaCl both prior to and following valine was added are displayed in Fig. 6. Both without and with the corrosion inhibitor, the 304 SS surface has significantly improved. As seen in figure8, 304 SS's surface is depicted in Fig. 8a prior to the corrosion process. Figure (a) depicts polished 304 stainless steel before to corrosion, (b) shows 304 stainless-steel immersed in NaCl solution with surface damage and roughness, and (c) shows 304 stainless-steel immersed in a 0.6M solution of NaCl with 0.5 g/L of valine present. An excellent inhibiting effect of the amino acid valine is seen by comparing SEM micrographs taken with and without the amino acid. the amino acid valine is seen by comparing SEM micrographs taken with and without the amino acid.

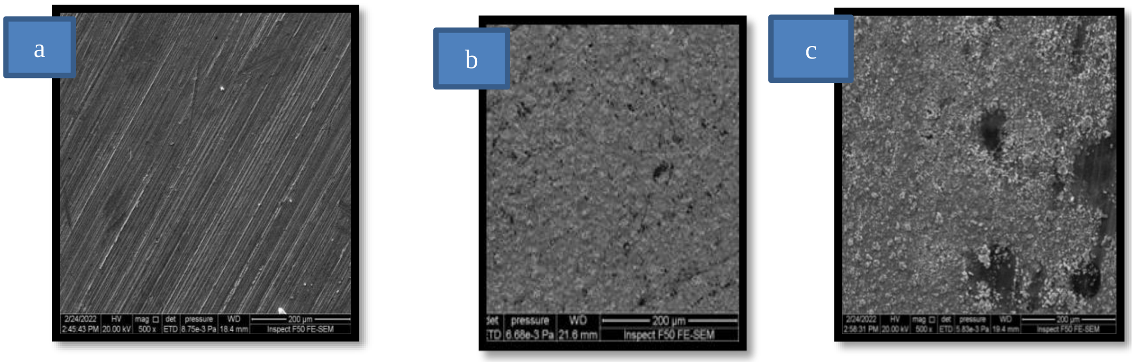

Figure 8. Scanning electron micrographs (a) polished SS 304, (b) shown SS 304 immersed in 0.6M NaCl, and (c) shown SS 304 in (0.6M) NaCl solution in presence of 0.5 g/L of valine.

4. CONCLUSION

The corrosion behavior regarding stainless steel specimens immersed in 0.6M NaCl saline medium was examined in relation to the amino acid valine. Negative ΔG_{ads} values indicate that the inhibitors adsorb on metal surface spontaneously. The observed Ea and ΔH values for the process of corrosion support this conclusion rate. Since the activation complex in rate-determining stage indicates an association instead of dissociation for ΔS^{*}_{ads}, all inhibited and blank solutions are negative. Langmuir adsorption isotherm was used to model the adsorption data for l-valine on a 304 SS surface, and the results showed good agreement with this model. The efficiency of protection of the inhibitor offered increased with its concentration. In l-valine, the highest value is 79.76% at 0.5g/L.

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