



Serine and Alanine as Corrosion Inhibitors for 5083 AA in Aqueous Solutions

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Abstract

By means of potentiodynamic polarization methods, inhibiting the influence of serine and alanine on 5083 AA corrosion in 0.1 mol.dm^{-3} sodium hydroxide and $0.6 \text{ mol.dm}^{-3} \text{ NaCl}$ over temperature range (298-313) K was investigated. Potentiodynamic polarization results specified that these amino acids functioned as a functional inhibitor in an alkaline environment. The inhibiting efficiency raises as the inhibitor concentration raises. However, it drops as temperature rises. The maximum efficiency value found with alanine was 73 under 298 k and $10^{-2} \text{ mol.dm}^{-3}$ alanine concentration. The adsorption of the amino acids complies with Langmuir adsorption isotherm. Some thermodynamic parameter (ΔG_{ads}) and activation energy (E_a) have been computed to demonstrate the process of corrosion inhibition. The kinetic limitations have been evaluated by means of Arrhenius theorem. An appropriate mechanism has projected for 5083 AA corrosion in alkaline medium. The surface morphology of uninhibited and inhibited samples was investigated using an optical microscope.

Keyword: Corrosion inhibition, 5083AA, Amino acids, Free energy of adsorption, Adsorption mechanism.

Introduction

Corrosion investigations are essential as a result of growing attentiveness of the necessity to preserve the realms metal resources [1]. Currently, more consideration has been towards the metallic corrosion control because of cumulative usage of metals in the entire technology fields. The examinations of corrosion performance of aluminum (Al) in diverse aggressive surroundings have paid attention as a result of their widespread industrialized application and commercial concerns [2]. Al and its alloys have arisen as alternative materials in space and several biochemical processing productions.

They recurrently meet acids or bases throughout de-scaling, pickling, electrochemical etching that are expansively employed in chemical processing productions. The majority of the testified researches have been projected on corrosion of numerous alloys as well as metals in HCl and H_2SO_4 mediums [3, 4, 5]. Sodium hydroxide can be employed for degreasing determination.

Investigating the corrosion performance of Al and Al alloys in sodium hydroxide medium and corrosion mechanism can be adopted using green inhibitors [6]. To diminish Al corrosion, the foremost approach is to separate the metal from corrosive causes efficiently. This is possibly accomplished by means of corrosion inhibitors that have organic and inorganic materials. On the other hand, organic inhibitors can be employed the corrosion throughout film formation. Biological compounds have performance typically through adsorption processing on the metal surface and complex creation. Some biological corrosion inhibitors can be poisonous and consequently intolerable for the environment.

Current studies have been engaged concerning the unconventional inhibitors that can be organically tolerable, stable, non-toxic and obtainable at a reasonable cost. These compounds signified as "green", 'eco-friendly', or environmentally-friendly comprise for inorganic and organic inhibitors.

One of the green biological inhibitors is amino acids. They are entirely soluble in aqueous mediums and produce in considerable purity at small expenses. Furthermore, they contain heteroatoms like N, O, and S in a specific number of them that can produce protective films [7].

The present work investigates the inhibiting influence of amino acids including alanine and serine on Al corrosion in robust alkaline solutions with (3.5% w/w) sodium chloride at a temperature range (298-313) using a potentiodynamic technique. Activation and kinetic factors that manage metal corrosion have investigated.

Experimental Methods

Materials

Investigations have been done on 5083AA specimen sheet of the adopted composition (weight %): 4.5 Mg, 0.25Zn, 0.4 Si, 0.4 Fe, 0.1Cu, 0.5 Mn, and 0.2 Cr, which previously were cut to circular shape (2 cm diameter and 2 mm thickness), grinded with emery papers of dissimilar grades (200, 400, 800, 1200, and 2000), degreasing with acetone and bathed with purified water, dried amid dual filter papers. The exposed surface area to the aggressive medium was 1cm².

Solutions

Based on analytical grade chemicals and doubly purified water, a solution has been organized. Sodium hydroxide has been obtained from, but alanine and serine have been gotten from Aldrich chemical Co. Ltd. Each measurement has been done in alkaline solution (0.1mol.dm⁻³) having 3.5% NaCl that has an analogous level to seawater. Twice distilled water has been adopted in all the above preparations.

Methods and Techniques

Potentiostatic polarization investigations have been implemented in a conformist three-electrode glass cell with employed volume 1000ml by means of Wenking M lab potentiost at. An electrode had used with a sheet of circular shape with 2 cm diameter and 2 mm thickness that before were grinded with emery papers of diverse graded (200,

400, 800, 1200, and 2000). Then, they were polished mechanically with diamond paste using a smooth cloth to a surface mirror. The exposed surface area to the aggressive medium has been 1cm². Silver-silver chloride as the referencing electrode as well as Pt counter electrode has been employed. Polarization tests have been done under -200 to +200 mV potentials in the case of a scan rate of 2mV/s for steady-state potential in cathodic or anodic direction.

All investigations have been performed in alkaline solution (0.1mol.dm⁻³ NaOH) of 3.5% NaCl in the nonexistence and existence of 3 dissimilar inhibitor concentrations. The plots of Tafel of anodic and cathodic curves have been inferred to acquire current density (*i*_{corr}) along with corrosion potential (*E*_{corr}). The experimental results have been reproducible. Each experimentation has conducted at least twice.

Optical Microscopy Investigations

5083AA electrode surface has been investigated by means of optical microscope type (Nikon Eclipse ME 600, Japan) earlier and beyond to immersion in the aggressive solution in nonexistence and existence of the optimal concentration of amino acid under 25°C. The samples have been washed quietly with water, dried up sensibly and examined with no additional treatments.

Results and Discussion

Potentiodynamic polarized curves of 5083AA electrode in 0.1 mol.dm⁻³ sodium hydroxide and 0.6 mol.dm⁻³ sodium chloride without and with various concentration (1×10⁻³, 5×10⁻³ and 1×10⁻² mol.dm⁻³) of alanine and serine at temperature range (298-313)K were recorded.

Figs 1 and 2 show polarization curves of 5083AA in aggressive solution with and without a number of a concentration of alanine and serine under (298-313) K temperature range. Electrochemical limitations like corrosion current density (*i*_{corr}), corrosion potential (*E*_{corr}), cathodic (*β*_c), anodic (*β*_a), Tafel slopes and inhibiting efficiency (*η*%) have been computed as recorded in Table 1. The inhibiting efficiency (*η* %) were computed by [8] :

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

i_{corr}^0 and i_{corr} stand for corrosion current densities in nonexistence or existence of inhibitor correspondingly. A maximum value

of efficiency was found to be = 73 at 298 K and $10^{-2} \text{ mol. dm}^{-3}$ alanine

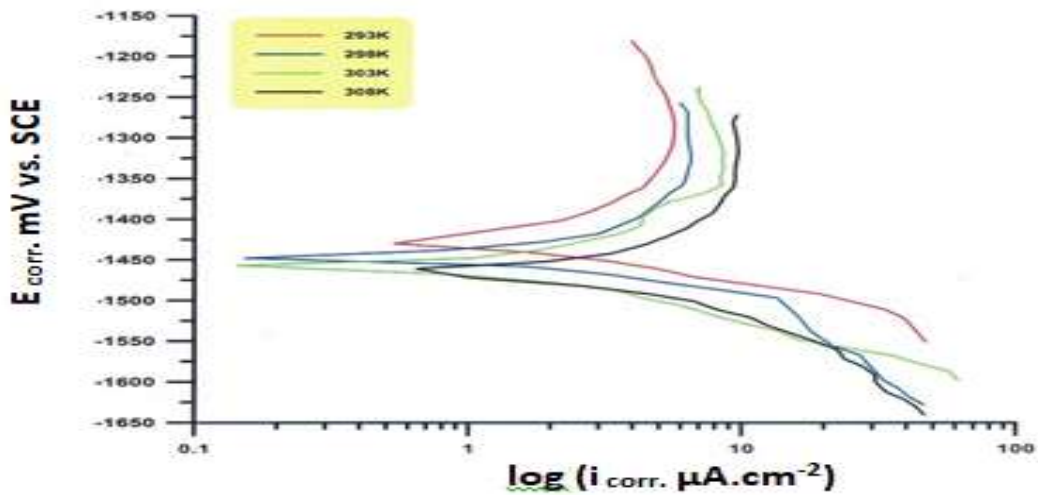
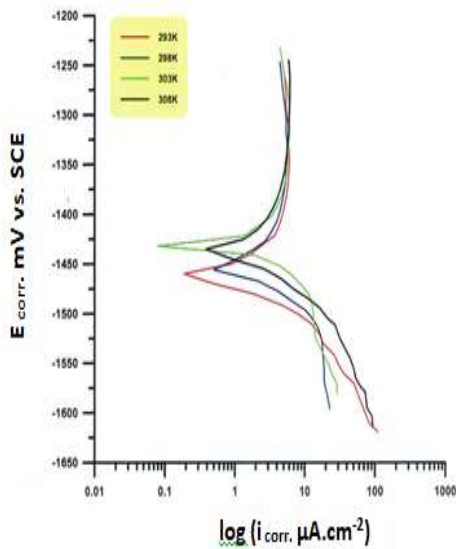
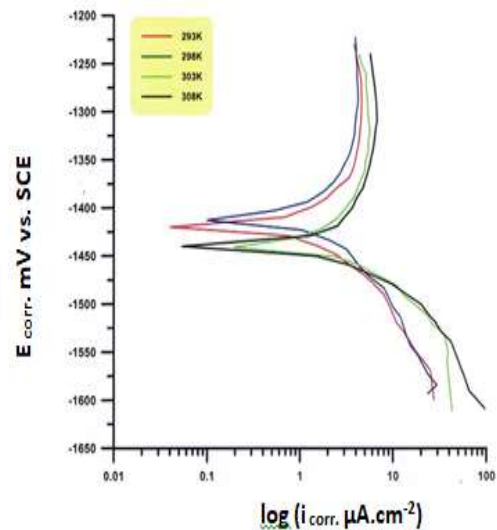


Figure1: Potentiodynamic polarization curves of 5083AA in 0.1 mol.dm⁻³+0.6mol.dm⁻³NaCl at different temperature

A



B



C

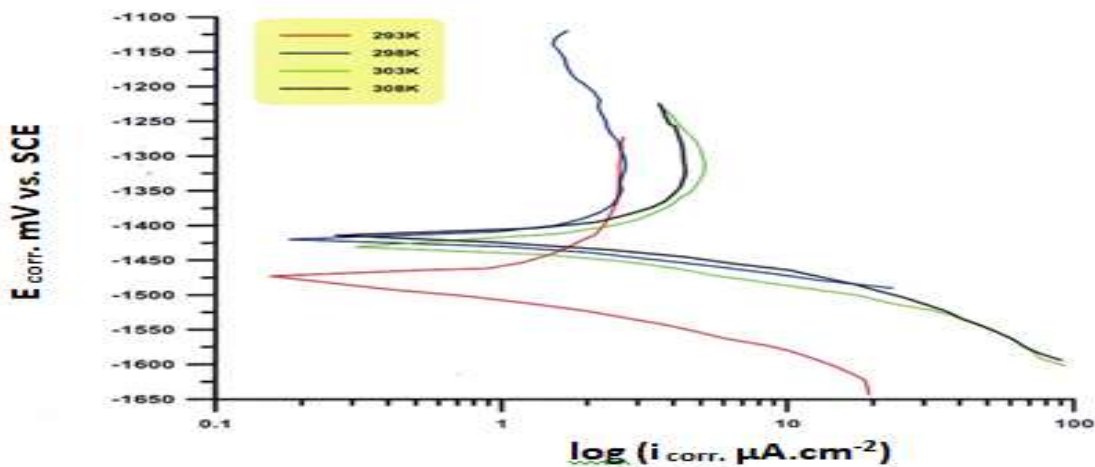


Figure 2: Curves of potentiodynamic polarization 5083AA in 0.1 mol.dm⁻³+0.6mol.dm⁻³NaCl with diverse concentrations of alanine (a- 1×10^{-3} b- 5×10^{-3} 1×10^{-2} mol.dm⁻³) at dissimilar temperatures

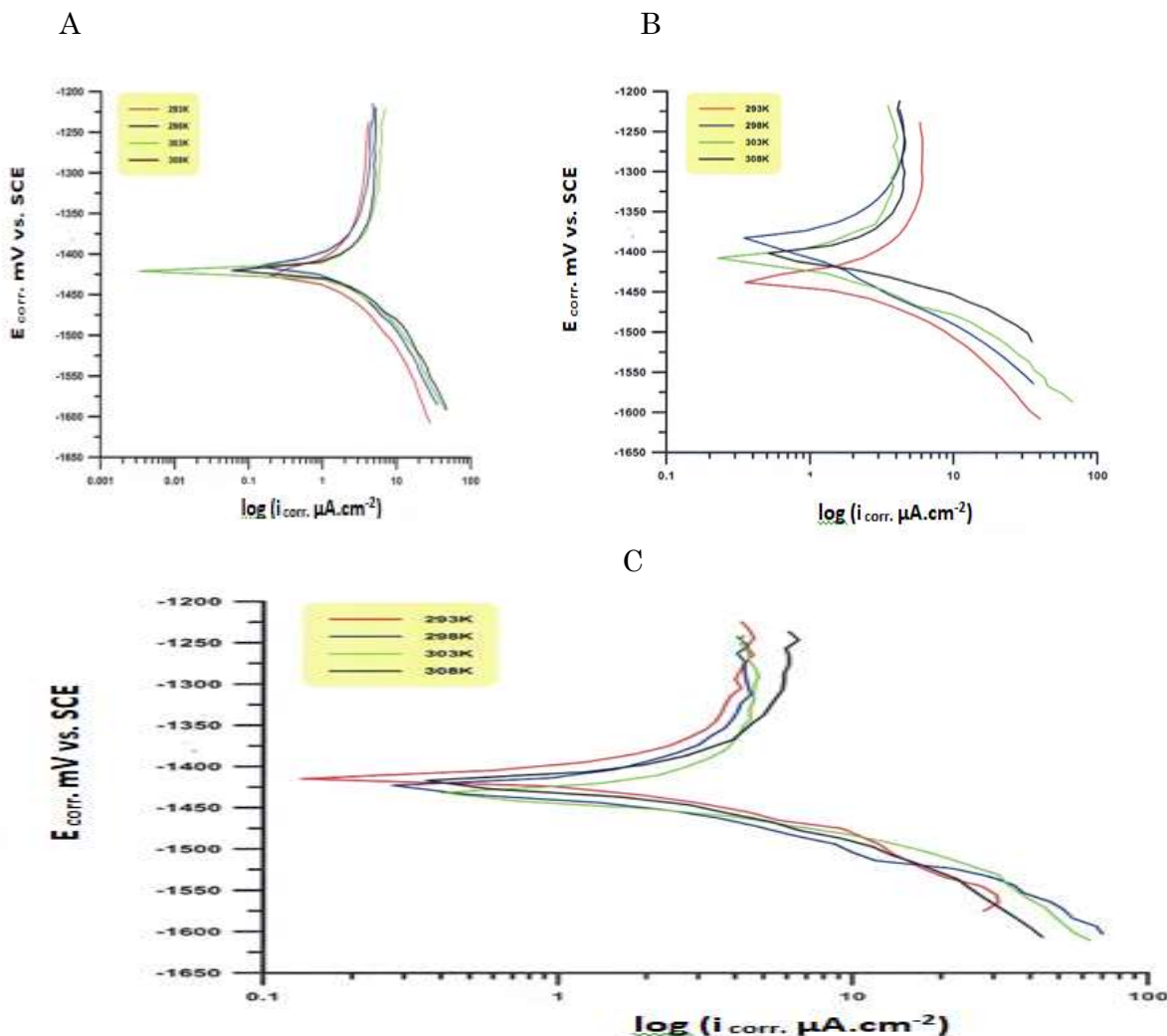


Figure 3: Curves of Potentiodynamic polarization of 5083AA in 0.1 mol.dm⁻³+0.6mol.dm⁻³NaCl with dissimilar concentrations of serine (a-1×10⁻³ b-5×10⁻³ 1×10⁻² mol.dm⁻³) at dissimilar temperatures

Based on potentiodynamic consequences reported in (Table1), the existence of amino acids, in diverse mediums, decreases the corrosion rate. The reduction in i_{corr} magnitude is attributable to inhibitor molecules adsorption. The magnitudes of β_a and β_c have been altered to some extent with

cumulative inhibitor concentration that points out the impact of these compounds on the metal dissolution kinetics. As a result of several active sites like hetero-atoms in the examined compound for adsorbing process, they can be as adsorbing inhibitors.

Table 1: Electrochemical factors obtained from potentiodynamic polarization records of 5083AA in 0.1 mol.dm⁻³ sodium hydroxide +0.6 mol.dm⁻³ sodium chloride solution in nonexistence or existence of dissimilar concentrations of alanine and serine at 298K

Comp	Conc. M	-E _{corr.} mV vs sec	i _{corr.} μA cm ⁻²	β _{c.} mV dec ⁻¹	β _{a.} mV dec ⁻¹	θ	η%
Serine	Blank	1439	1360	38	155
	1*10 ⁻³	1430	765	53	136	0.651	65.1
	5*10 ⁻³	1438	717	54	54	0.679	67.9
	1*10 ⁻²	1415	656	47	86	0.702	70.2
Alanine	1*10 ⁻³	1462	652	36	58	0.708	70.8
	5*10 ⁻³	1420	629	61	54	0.718	71.8
	1*10 ⁻²	1473	619	29	79	0.73	73.0

The addition of alanine and serine shifts E_{corr} magnitudes involving a lesser amount of negative quantities. In general, a compound is possibly categorized as cathodic or anodic kind in the case of in E_{corr} change is higher than 85 mV [9]. As the prevalent shift by dual amino acids has been about 60 mV as

revealed by table 1, these dual amino acids must be reflected as a mixed inhibitor type. Namely, the addition of these amino acids to 0.1 mol.dm⁻³ sodium hydroxide +0.6 mol.dm⁻³ sodium chloride solutions lessen anodic dissolution of 5083AA and retards cathodic reacting. Based on the computed inhibition

efficiency magnitudes as explained by Table 1, the sequence of increasing inhibition efficiency is: alanine >serine.

Kinetics Parameter

Temperature possesses an excessive influence on metal electrochemical corrosion

rate since it stands for acceleration element in the majority of chemical effects. It raises the reacted species energy and hence chemical reacting become considerably faster. It is found from Table 2 that i_{corr} raises as temperature increases while inhibition efficiency lessens as temperature increases.

Table 2: Electrochemical limitations gotten from potentiodynamic polarization measurements of 5083AA in 0.1 mol.dm⁻³ sodium hydroxide +0.6 mol.dm⁻³ sodium chloride solution in the presence of 1×10⁻²mol dm⁻³ of serine and alanine at different temperatures

Comp	Temp. K	-E _{corr.} mV vs sec	i _{corr.} μA cm ⁻²	β _{c.} mV dec ⁻¹	β _{a.} mV dec ⁻¹	θ	η%
Serine	303	1424	738	61	44	0.696	69.6
Alanine		1416	682	48	110	0.716	71.6
Serine	308	1453	878	51	76	0.688	68.8
Alanine		1427	805	51	72	0.713	71.3
Serine	313	1417	1100	60	102	0.657	65.7
Alanine		1414	930	37	88	0.710	71.0

The alteration of adsorption/desorption equilibrium is towards desorption. Namely, alanine and serine have been substantially

adsorbed on 5083AA surface. Energy of activation has been determined in line with Arrhenius equation [10]:

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

E_a stands for apparent activation energy, A represents the pre-exponential factor and k represents the rate of corrosion. Figures (3-4) indicate Arrhenius plot log i_{corr} vs. 1/T in the

deficiency or existence of alanine or serine. Activation energy which was gotten from straight lines slopes was specified in Table 3.

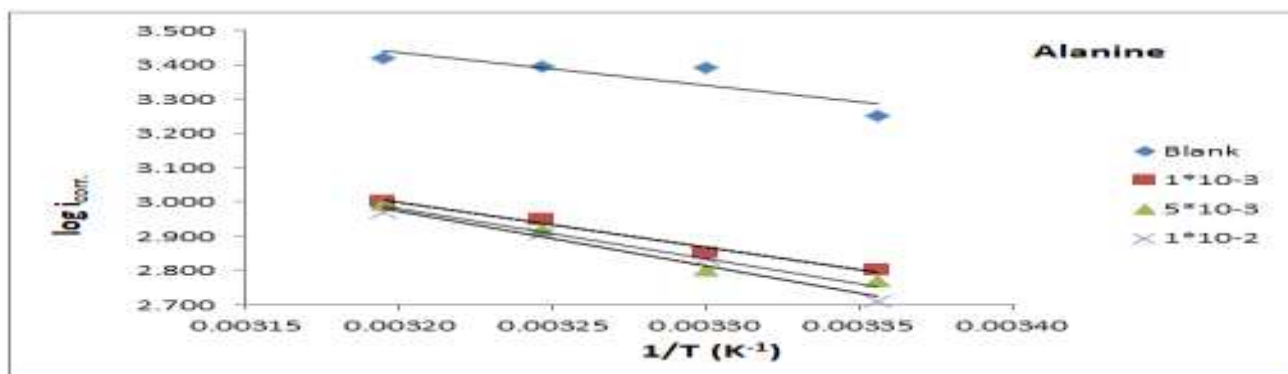


Fig 3: Arrhenius Plot relating Log (i_{corr}) to 1/T for the 5083 AA corrosion pH=13 with 0.6 mol. dm⁻³ NaCl solution in existence/nonexistence of dissimilar concentrations of alanine for four temperatures under (298-313) K range

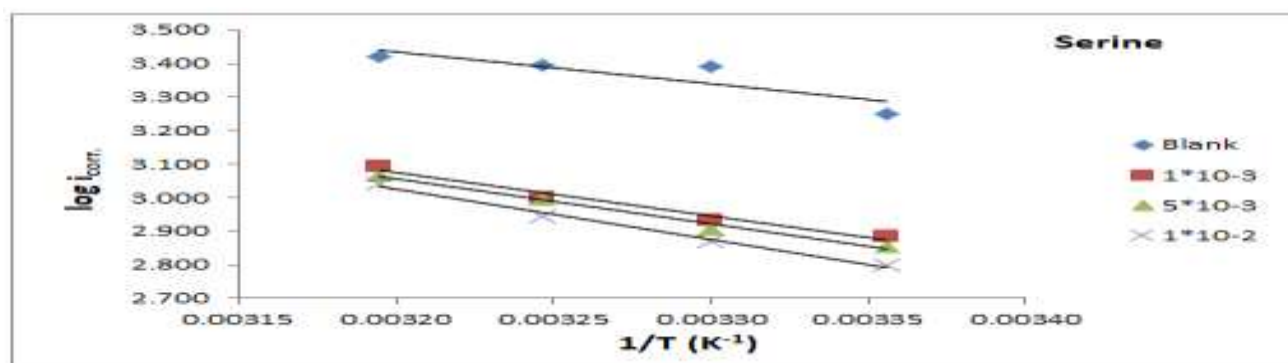


Fig 4: Arrhenius Plot relating Log (i_{corr}) to 1/T for the 5083 AA corrosion pH=13 with 0.6 mol. dm⁻³ NaCl solution in existence/nonexistence of dissimilar concentrations of serine for four temperatures under (298-313) K range

Enthalpy and activation entropy (ΔH^* , ΔS^*) for the

corrosion growth can be computed based on transition state concept by [11]:

$$i_{corr} = RT/Nh \exp(\Delta S^*)\exp(-\Delta H^*/RT) \quad 3$$

Accordingly, h stands for Plank’s constant, N stands for Avogadro’s number, ΔS^* stands for activation entropy while ΔH^* is activation enthalpy.

Fig 5and6 give an indication of the plot of $\log i_{corr}/T$ vs. $1/T$ from the slopes and catches straight lines based on gotten ΔH^* and ΔS^* correspondingly.

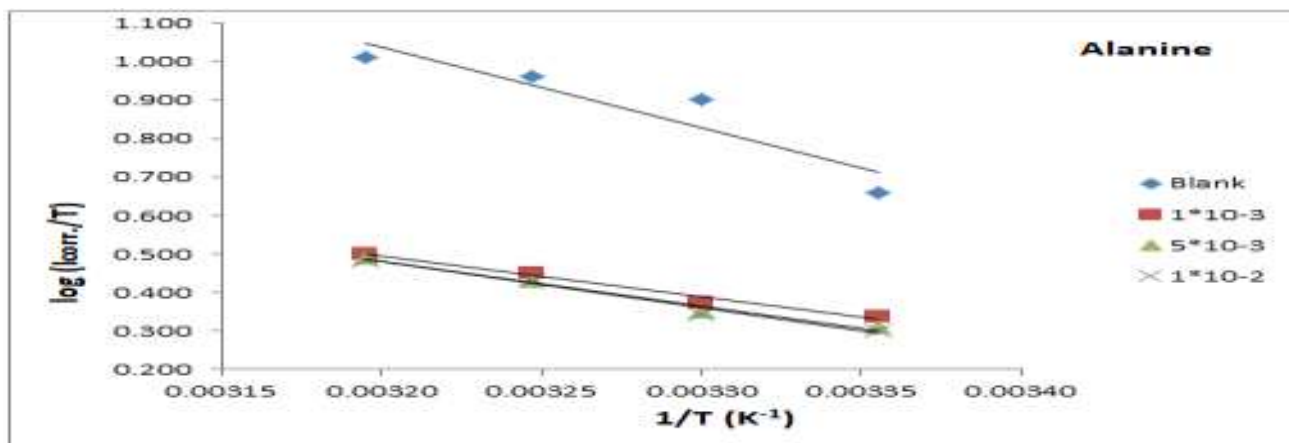


Fig 5: Log (i_{corr}/T) to $1/T$ for the 5083 AA corrosion pH=13 with 0.6 mol. dm^{-3} NaCl solution in existence/nonexistence of diverse concentrations of alanine for 4 temperatures within (298-313) K range

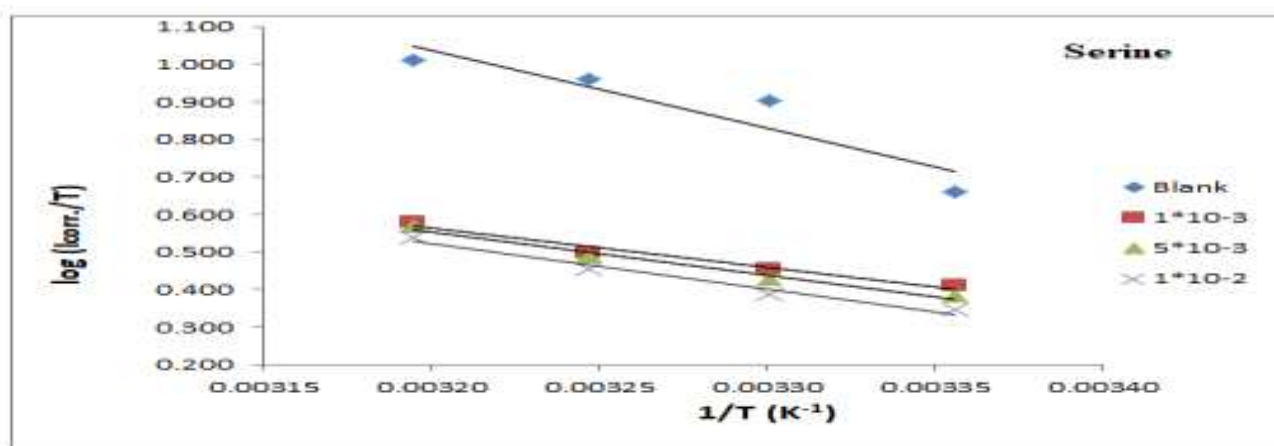


Fig6: Log (i_{corr}/T) to $1/T$ for the 5083 AA corrosion pH=13 with 0.6 mol. dm^{-3} NaCl solution in existence/nonexistence of diverse concentrations of serine for 4 temperatures within (298-313) K range

Table3: Kinetic-thermodynamic corrosion limitations for 5083AAcorrosion in nonexistence and existence of several concentrations of serine and alanine

Inhibitors	Conc. M	E_a kJ.mol^{-1}	$-\Delta H$ kJ.mol^{-1}	$-\Delta S$ $\text{J.mol}^{-1}.\text{K}^{-1}$
Serine	Blank	18.527	-39.9037	309.9597
	1×10^{-3}	24.886	-19.7431	236.3488
	5×10^{-3}	26.036	-21.9201	243.1280
	1×10^{-2}	28.522	-22.9565	245.8444
Alanine	1×10^{-3}	25.000	-20.0170	235.9103
	5×10^{-3}	28.338	-22.1552	242.5190
	1×10^{-2}	30.337	-23.0285	245.2924

The computed magnitudes of E^* , ΔS^* and ΔH^* have been depicted in Table (3). In the existence of every amino acid separately, intensification in E^* magnitudes has detected in the existence of the inhibitor. For instance, the insertion of inhibitor increases the energy barrier for the corrosive process highlighting

the electrostatic features of inhibitors adsorbing on 5083AA surface. The ΔS^* magnitudes are negative indicating the determining step for a motivated complex in the association before the dissociation step. Namely, activated molecules have been in advanced sequence state as compared with

an initial state. Based on negative ΔH^* values, the corrosion process stands for an exothermic process [12].

Adsorption Isotherm

Adsorption isotherms give elementary facts about interacting amid the inhibitor and 5983AA throughout several models of adsorption isotherm. Dual foremost kinds of interaction can define inhibitors adsorption on the metal surface. These types are chemisorption and physisorption, reliant on the chemical inhibitor organization, the corrosive medium kind as well as the charge and description of corrosive metal. In aqueous solutions, the metal surface is at all times covered with adsorbed water molecules. For that reason, the inhibitor

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

Accordingly, K_{ads} stands for the equilibrium constant of desorption/adsorption. It reflects a similarity of inhibitor molecules in the direction of surface adsorption locations. Based on the straight line interceptions on

$$\Delta G^\circ = -RT \ln(55.5 K_{ads})$$

From the above equation, R stands for the universal gas constant, T stands for the absolute temperature, while 55.5 value stands for water concentration in the solution. Standard free energy of adsorption has been computed and listed in Table (4), Negative ΔG°_{ads} values signpost spontaneous adsorption of amino acids on 5083AA surface [15]. Usually, ΔG°_{ads} magnitudes up to $20\text{kJ}\cdot\text{mol}^{-1}$ are connected with physisorption,

molecules adsorption from an aqueous solution is a quasi-substitute process [13]. The inhibitors have the capability for being adsorbed powerfully on the metal surface, and they will delay the closure reacting of the absorbed metal into the corrosive media.

The corrosion inhibition mechanism is defined with respect to the adsorption performance for the designed coverage degree [14]. The surface coverage along with amino acid concentrations of inhibitor has been examined by matching to numerous isotherms as in Temkin, Langmuir, and Freundlich. On the other hand, the finest fitting has been gotten from Langmuir isotherm as illustrated in Figure (6) based on [13]:

the C_{inh} / θ axis, Figure (6) indicates the equilibrium constant (K_{ads}) of desorption or adsorption of an amino acid process. This constant is associated with adsorption standard free energy as stated by [14]:

whereas those nearby $-40\text{kJ}\cdot\text{mol}^{-1}$ are in accordance with chemisorptions owing to charge allocation or make a transferal from inhibitor molecules to a metal surface to produce the coordinate covalent bond [16]. Subsequently, in keeping with considered ΔG°_{ads} magnitudes in this paper, adsorption of amino acid onto 5083 AA surface occurs through chemical and physical adsorption of a mixed category.

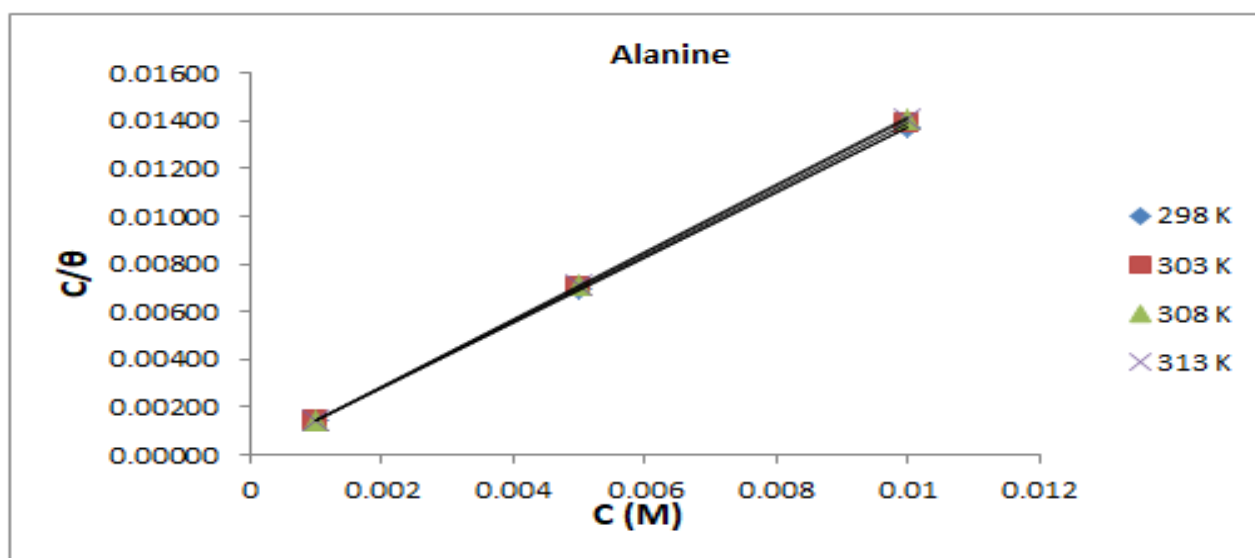


Fig7: Linearity of Langmuir adsorbing isotherm for alanine on 5083AA surface in $0.1\text{ mol}\cdot\text{dm}^{-3}\text{NaOH}+0.6\text{ mol}\cdot\text{dm}^{-3}\text{NaCl}$ solutions

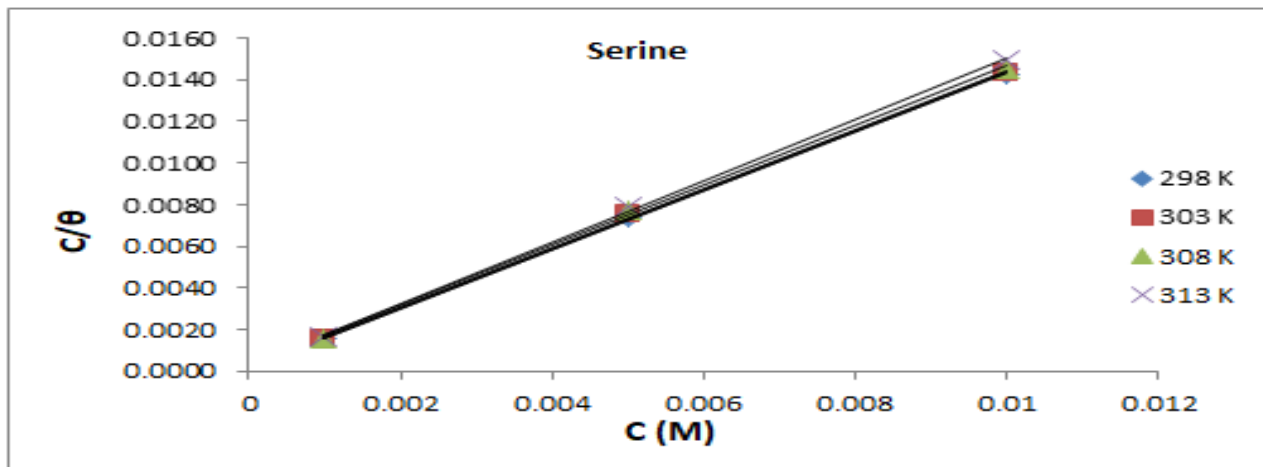


Fig8: Linearity of Langmuir adsorbing isotherm for serine on 5083AA surface in 0.1 mol.dm⁻³NaOH+0.6 mol.dm⁻³NaCl solution

Thermodynamic adsorption parameters such as ΔH°_{ads} and

ΔS°_{ads} are calculated from combined form of van't Hoff equation [17]:

$$\ln K_{ads} = (-\Delta H^{\circ}_{ads}/RT) + (\Delta S^{\circ}_{ads}/R) + \ln(1/55.5)$$

Figure 9 explains the response of $\log K_{ads}$ vs. $1/T$ that exhibits straight lines with

slop = $(-\Delta H^{\circ}_{ads}/RT)$ and intercept = $(\Delta S^{\circ}_{ads}/R) + \ln(1/55.5)$.

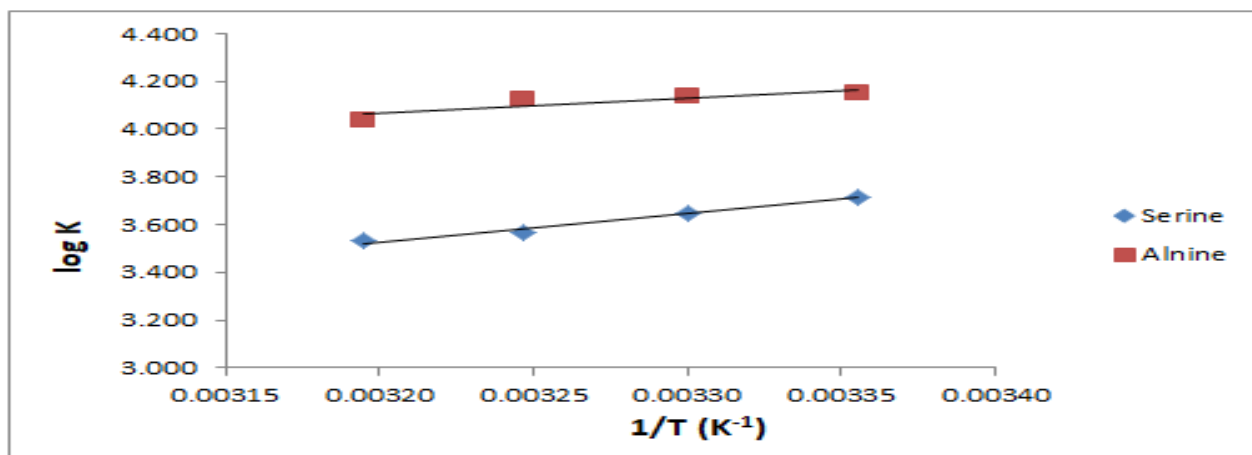


Fig9: Log K_{ads} vs. $(1/T)$ curves for 5083AA corrosion in 0.1 mol.dm⁻³ NaOH+0.6 mol.dm⁻³NaCl solution in nonexistence and existence of alanine and serine at dissimilar temperatures

Table 4: Thermodynamic factors for serine and alanine adsorption on 5083AA surface under diverse temperatures

Inhibitors	Temp. K	K_{ads}	$-\Delta G_{ads}$ kJ .mol ⁻¹	$-\Delta H_{ads}$ kJ .mol ⁻¹	$-\Delta S_{ads}$ J .mol ⁻¹ , K ⁻¹
Serine	298	5219.53	-31.159	-29	-106.8
	303	4455.44	-31.283		
	308	3705.48	-31.328		
	313	3397.82	-31.611		
Alanine	298	14152.15	-33.631	-33	-120.9
	303	13763.08	-34.125		
	308	13513.51	-34.641		
	313	13379.42	-35.177		

Negative magnitudes of enthalpy of adsorption ΔH_{ads} puts forward that the adsorption processing on 5083AA for serine and alanine surface stands for an exothermic mode. ΔH_{ads} is approximately – (29-33) kJ .mol⁻¹ that is higher as compared with typical physical adsorbing heat of 40 kJ.mol⁻¹,but lesser as compared with typical chemical adsorbing temperature of 100 kJ .mol⁻¹[18].

Explicitly, chemical and physical adsorptions have been taken place. Negative ΔS_{ads} magnitudes are gone along with the process of exothermic adsorbing. This is in agreement with the expected case in the adsorbing with an exothermic process. Vice versa, it should be gone along with by a lessening in the entropy change [19].

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