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Thermodynamic, kinetic and mechanistic approach to the corrosion inhibition of carbon steel by new synthesized amino acids-based surfactants as green inhibitors in neutral and alkaline aqueous media

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ABSTRACT

The inhibiting power of three synthesized amino acids based-surfactant molecules, namely, sodium Ndodecyl asparagines (AS), sodium N-dodecylhistidine (HS) and sodium N-dodecyltryptophan (TS) on the dissolution of carbon steel was inspected in 0.5 M NaCl and 05 M NaOH solutions at 25°C. The methods employed in this work were weight-loss (WL), potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS). The chemical structures of the synthesized surfactants were confirmed by FT-IR and ¹HNMR. The inhibition efficiencies were found to increase as the surfactants concentrations increase, while decreasing with increasing the concentration of the corrosive media (NaCl & NaOH) and temperature. Results obtained from the different techniques revealed that the inhibition efficiency of the compound TS was higher than those of both AS and HS. The inhibition efficiencies of the synthesized surfactants were declined in terms of strong adsorption of surfactants on the surface of carbon steel and forming a protective film and such adsorption was found to obey Langmuir isotherm. Both thermodynamic and kinetic parameters were evaluated which support the mechanism of physical adsorption of the inhibitors. The tested surfactants were found to act as mixedtype inhibitors with anodic predominance. The surface morphology of the carbon steel surface was examined by scanning electron microscopy (SEM). The inhibitory mechanism of carbon steel corrosion was suggested. Results obtained from all employed methods are consistent with each others.

Keywords: Amino acids-based surfactants; Inhibitors; Sodium chloride; Sodium hydroxide; Corrosion; Carbon steel.

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1. Introduction

Carbon steel is used in a different applications, and it is generally exposed to the corrosion phenomenon in many environments resulting in the deterioration of the beneficial properties of steel alloys due to their interactions with the environment. Therefore, a great effort has been made to develop more efficient, economical and environmentally compatible methods to prevent iron corrosion such as using corrosion inhibitors [1-7]. The inhibitory effect of these inhibitors is due to their absorption into the metal surface and its blocking, thereby preventing corrosion [8-15]. Costs, health issues and environmental regulatory constraints have led researchers to focus on the development of non-toxic and economical organic compounds used as corrosion inhibitors [15].

Surfactant molecules are widely used where they exist in various industrial applications due to their great impact on the surface and interface properties. Therefore, the surface probe adsorbed on the surfaces of metals is very significant in electrochemical studies such as inhibition of corrosion because of the surface ability to assemble in an interface and in a solution that changes the corrosion resistance property of the metal [16,17]. The surfactant is characterized by its ability to migrate to the surface, and the adsorption layer protects the steel surface against corrosive solutions. The low critical micelle concentration values of nonionic surfactants indicate a greater tendency to absorb at solid surfaces at lower concentrations with higher efficiency expected at these lower concentrations [18,19]

Amino acids-based surfactants are of great interest in the field of novel surfactant research because they have excellent surface-active properties, quick biodegradation, low toxicity, excellent antimicrobial and antifungal activities in comparison to conventional surfactants [20]. The combination of various polar amino acids and nonpolar hydrocarbon chain compounds produces amino acids-based surfactants with high surface activity. The present work is aimed to evaluate the effectiveness of three synthesized new amino acids-based surfactants namely, sodium *N*-dodecyl asparagines (AS), sodium *N*-dodecyl histidine (HS) and sodium *N*-dodecyl tryptophan (TS) as corrosion inhibitors for carbon steel in NaCl and NaOH solutions using various techniques.

2. Experimental

2.1. Synthesis and characterization of amino acids-based surfactants

2.1.1. Preparation of amino acids ethyl ester hydrochlorides

In 100 ml round-bottom flak equipped with reflexing condenser, 0.1 M of amino acid (I) was transferred and 10 ml of freshly distilled thionyl chloride [21] was added slowly to the flask with continuous stirring. Then, a 40 ml of dry ethanol was added dropwise, and the resulting mixture was

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refluxed under nitrogen atmosphere for 16h (TLC-controlled). The excess of thionyl chloride was removed under reduced pressure and residue was washed several times with water and the final product amino acid ethyl ester hydrochloride (**II**) as white power in high yield (81-89%).



Scheme 1. Synthesis of amino acids-based surfactants.

The chemical structure of the surfactant sodium *N*-dodecyltryptophan (TS), as an example, elucidated on the basis of FT-IR and NMR spectroscopic tools. The FT-IR spectrum of the compound (**I**), tryptophan, (Fig.1, red-font) showed the following absorption bands at 3284 cm⁻¹ (for NH groups), 3180, 1065 cm⁻¹ for (N⁺) 1743 cm⁻¹ for the ester carbonyl group.

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Fig. 1.FT-IR spectra of tryptophan I (red-font) and tryptophan ethyl ester hydrochloride II (black font)

In addition, the ¹HNMR spectrum of the compound (**II**) (trptophan ethyl ester hydrochloride) (Fig. 2) in DMSO shows the following signals at $\delta = 11.19$ (s, 1H, NH, exchangeable by addition of D₂O); 8.67 (s, broad, 3H, NH₃), 7.53 (d, 1H, J = 7.5, CH-arom.), 7.38 (d, 1H, J = 7.5, CH-arom.), 7.26 (s, 1H, CH-indole), 7.08 (t, 1H, J = 5.5, CH-arom.); 7.00 (t, 1H, J = 5.5, CH-arom.); 4.16 (s, 1H, CH); 4.06 (s, 2H, CH₂); 3.34 (q, J = 2.5, 2H, CH₂ of the ester group); 1.07 (t, J = 2.5, 3H, CH₃ of the ester group). The expanded ¹HNMR (Figs. SI and S2) and the ¹³C NMR spectra (Figs. S3-S5) are cited as supporting information.



Fig. 2. ¹H NMR spectrum of tryptophan ethyl ester hydrochloride II in DMSO.

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2.1.2. Synthesis of sodium N-dodecyl amino acids

In 100 ml round-bottom flask, a suspension of 0.01 mole amino acid ethyl ester hydrochloride (**II**) and 0.05 Mole of NaHCO₃ in 40 ml freshly distilled acetonitrile was stirred at room temperature during dropwise addition of 0.015 mole 1-bromododecane (**III**). After complete addition, the mixture was refluxed for 18 h under nitrogen atmosphere. After cooling to room temperature, acetonitrile was removed under vacuum and the white residue of ethyl dodecyl amino acid surfactant (**IV**) is dissolved in 30 ml dichloromethane. It was washed with 0.1 M HCl (25 ml \times 3) and distilled water (25 ml \times 2). Dichloromethane was evaporated to give the pure product (**V**) in 66-92% yield. The product obtained is dissolved in 30 ml of absolute ethanol and 3 ml of 3.0 M NaOH is added dropwise to the solution. The reaction mixture stirred at room temperature for 6 h. The precipitate sodium dodecyl amino acid surfactant (**VI**) was filtered-off and washed twice with absolute ethanol [22] in poor yield (22-46% yield). The reactions are represented in Scheme 1.

The chemical structure of the N-dodecyl tryptophan (**V**) was confirmed by both spectroscopic and analytical tools. For example, The FT-IR spectrum of surafancts (**V**) showed (Fig. black font) the following absorption bands at 3350 cm⁻¹ (braod, for OH), 3180-3250 (for two NH groups), 300-3008 (CH-aromatic), 2860-2950 (CH-aliphatic), 1727 cm⁻¹ for the acid carbonyl group.



Fig. 3. ¹H NMR spectrum of N-dodecyl tryptophan (V) in DMSO.

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In addition, the ¹H NMR spectrum of the compound (**V**) (Fig. 3) in DMSO shows the following signals at $\delta = 11.19$ (s, 1H, NH, exchangeable by addition of D₂O); 9.80 (s, 1H, NH), 9.28 (s, 1H, OH) 7.54 (d, 1H, J = 7.5, CH-arom.), 7.37 (d, 1H, J = 7.5, CH-arom.), 7.25 (s, 1H, CH-indole), 7.06 (t, 1H, J = 5.5, CH-arom.); 7.00 (t, 1H, J = 5.5, CH-arom.); 4.30 (s, 1H, CH); 3.99 (q, J = 2.5, 2H, CH₂ of the ester group); 3.11 (t, J = 2.5, 2H, CH₂), 0.99 (s, 20 H, 10 CH₂), 0.93 (t, J = 2.5, 3H, CH₃ The expanded ¹HNMR (Figs. S6 and S7) and the ¹³C NMR spectra (Figs. S8- S10) are cited as supporting information.

2.2. Evaluation of inhibition efficiencies of the synthesized surfactants

2.2.1. Materials

All solutions employed in this work were freshly prepared from Merck or Aldrich chemicals using bidistilled water. Stock solutions of the corrosive media (NaCl & NaOH) and other reagent solutions were prepared with bidistilled water and the desired concentrations were obtained by appropriate dilution. Each experiment was repeated at least three times under the same conditions to check the reproducibility and the average of the three replicated values was taken. On the other hand, corrosion tests were carried out on a cylindrical carbon steel sample which has chemical composition (wt%): 0.110 C, 0.250 Si, 0.450Mn, 0.050 S, 0.040 P, and the remainder is Fe.

2.2.1. Weight-loss (WL) measurements

WL measurements were performed in a temperature controlled system. The carbon steel samples used were cylindrical rods with closed areas of about 14 cm². These rods were mechanically polished first with sandpaper in successive grades from 200 to 1200, then washed with bidistilled water and finally with acetone. After accurate weighing, carbon steel samples were immersed in corrosion media (in the absence of different concentrations of inhibitors) and at different temperatures. After 6 h, the carbon steel samples were taken out, washed, dried and weighed accurately. Then, the average weight loss of at least three parallel steel samples, in each experiment, could be obtained. The corrosion rate (CR) was calculated in mils penetration per year (mpy) from the following equation [18]:

$$CR (mpy) = \frac{KW}{Atd}$$
(1)

where *K* is a constant (3.45 x 10⁶), *W* is the weight loss in grams, *A* is the specimen area in cm², *t* is time in hour and *d* is the density of mild steel (7.86 g/cm³).

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The inhibition efficiency (% IE) and the degree of surface coverage (θ) of the synthesized surfactants on the corrosion of carbon steel were calculated as follows [23]:

% IE =
$$\theta \ge 100 = \left[1 - \frac{CR_{inh}}{CR}\right] \ge 100$$
 (2)

where CR and CR_{inh} are corrosion rate values without and with addition of the inhibitor, respectively.

2.2.2. Electrochemical measurements

Potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) measurements were carried out using PGSTAT30 potentiostat/galvanostat in a three-electrode cell containing platinum counter electrode (CE), reference electrode (RE) and the working carbon steel electrode (WE). All measurements were performed at a constant temperature in a temperature-controlled system where a double-jacket cell connected to a thermostat was used. The experiments were performed after immersing the electrode in electrolyte solutions for 30 minutes. The values of % IE and θ of the tested surfactants were calculated from the relation [24]:

% IE =
$$\theta \ge 100 = \left[1 - \frac{i_{corr(inh)}}{i_{corr}}\right] \ge 100$$
 (3)

where, i_{corr} and $i_{corr(inh)}$ are corrosion current densities without and with the inhibitor, respectively. The values of corrosion current densities were determined by extrapolation of the slopes of cathodic and anodic Tafel lines (β c, β a), of the polarization curves with the corrosion potentials.

EIS measurements were performed in a frequency range of 100 kHz to 0.1 Hz with an amplitude of 4.0 mV peak-to-peak using AC signals at OCP. The % IE was computed from the charge transfer resistance (R_{ct}) data using the following equation [24]:

% IE =
$$\left[1 - \frac{R_{ct}}{R_{ct(inh)}}\right] \times 100$$
 (4)

where R_{ct} and $R_{ct(inh)}$ in absence and presence of inhibitor, respectively.

2.2.3. Surface examinations

JEOL Scanning Electron Microscope (SEM) model T-200, was used to examine the surface morphologies of carbon steel samples after immersion in 0.5 M NaCl and in 0.5 M NaOH in the absence and presence of 900 ppm of the three amino acids based-surfactant molecules.

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3. Results and discussion

3.1. Weight-loss measurements and the effect of temperature

3.1.1. Effect of corrosive media concentrations

Figure 4 shows the plots of weight-loss versus immersion time for carbon steel samples in various concentrations of NaCl and NaOH solutions (0.1 - 1.0 M) at a temperature of 25 °C. The values of the CR are computed and are listed in Table 1. The obtained results indicated that the CR of carbon steel increases with increasing the concentration of the NaCl and NaOH solutions. It can be observed that the corrosion rates of carbon steel in NaCl solution are about 3.5 times higher than those recorded in NaOH solutions. This was explained due to the presence of the aggressive Cl⁻ ions which accelerates the dissolution of the steel.

Figure 5 a and b represents the effect of different concentrations of NaCl and NaOH solution on the inhibition efficiencies of 500 ppm concentration of the investigated surfactant molecules From Fig. 5, it is clear that inhibition efficiencies decreased with increasing the concentration of the corrosive media indicating that such surfactants are more effective at low concentration of NaCl and NaOH (0.1 M).



Fig. 4. Weight-loss versus immersion time for carbon steel in different concentrations of: a) NaCl, and b) NaOH solutions at 25 °C.





Fig. 5. Effect of concentration of: a) NaCl, and b) NaOH solutions on the inhibition efficiencies of 500 ppm of amino acids based-surfactants for the corrosion of carbon steel at 25 °C.

Table 1. Corrosion rates (CR) in mpy for carbon steel in different concentrations of NaCl and NaOH solutions.

Concn. (M)		0.1	0.3	0.5	0.7	1.0
CR	NaCl	11.29	13.35	14.65	15.61	16.48
(mpy)	NaOH	2.19	2.93	3.77	4.48	5.39

3.1.2. Effect of added surfactants

WL measurements of carbon steel in 0.5 M NaCl and in 0.5 M of NaOH solutions were investigated at different time intervals in the absence and presence of various concentrations of the tested surfactant molecules (100 - 900 ppm) at different temperatures (15 - 45 °C); only the weight-loss versus time curves obtained at 25 °C are shown here in Fig. 6. The values of the CR, θ and % IE of the surfactant molecules are also listed in Table 2. From Table 2, it is evident that, for all investigated surfactants, that CR values get decreased and inhibition efficiencies increased with the inhibitor concentrations. This is due to increasing adsorption coverage of inhibitors on the surface of carbon steel with concentration which decreases the dissolution rate of steel. Therefore, the investigated surfactants are considered as efficient inhibitors for carbon steel dissolution in NaCl and NaOH solutions. Also, the results showed that % IE of TS was higher than those of both AS and HS.



Fig. 6. Plots of weight-loss versus immersion time for carbon steel in the absence and presence of different concentrations of the amino acids based-surfactants in 0.5 M of NaCl solution, (a) AS, (b) HS, (c) TS, and in 0.5 M NaOH solution, (d) AS, (e) HS, (f) TS, at 25 °C.

Table 2. Corrosion rates (CR) in mpy of carbon steel, degrees of surface coverage (θ) and inhibition efficiencies (% IE) of the amino acids based-surfactants at different concentrations in 0.5 M NaCl and 0.5 M NaOH solutions at different temperatures.

Medium		Inhs.	Temperature (°C)											
(0.5 M)	Inhs.	Concn		15			25			35			45	
(0.5 M)		(ppm)	CR	% IE	θ	CR	% IE	θ	CR	% IE	θ	CR	% IE	θ
		0	13.11			14.65			16.46			18.33		
		100	5.90	55	0.55	7.31	50	0.50	8.66	47	0.47	10.26	44	0.44
		300	4.46	66	0.66	5.57	62	0.62	7.08	57	0.57	9.16	50	0.50
	AS	500	3.28	75	0.75	4.39	70	0.70	5.60	66	0.66	7.15	61	0.61
		700	2.49	81	0.81	3.66	75	0.75	4.77	71	0.71	6.23	66	0.66
		900	2.23	83	0.83	3.22	78	0.78	4.44	73	0.73	5.68	69	0.69
		100	5.64	57	0.57	6.59	55	0.55	7.90	48	0.48	10.63	42	0.42
		300	4.19	68	0.68	5.42	63	0.63	6.42	61	0.61	8.06	56	0.56
NaCl	HS	500	3.28	75	0.75	4.25	71	0.71	5.27	68	0.68	6.78	63	0.63
		700	3.15	76	0.76	3.79	74	0.74	4.61	72	0.72	6.24	66	0.66
		900	2.75	79	0.79	3.45	76	0.76	4.45	73	0.73	5.87	68	0.68
		100	4.33	67	0.67	5.12	65	0.65	7.41	55	0.55	9.53	48	0.48
		300	3.02	77	0.77	4.39	70	0.70	6.09	63	0.63	7.88	57	0.57
	TS	500	2.49	81	0.81	3.66	75	0.75	4.94	70	0.70	6.60	64	0.64
		700	2.10	84	0.84	3.11	79	0.79	4.28	74	0.74	5.68	69	0.69
		900	1.97	85	0.85	2.93	80	0.80	3.78	77	0.77	5.13	72	0.72
		0	3.32			3.77			4.27			4.69		
		100	1.56	53	0.53	1.91	49	0.49	2.48	42	0.42	3.05	35	0.35
		300	1.03	69	0.69	1.52	60	0.60	1.88	56	0.56	2.35	50	0.50
	AS	500	0.73	78	0.78	1.17	69	0.69	1.54	64	0.64	1.97	58	0.58
		700	0.70	79	0.79	0.95	75	0.75	1.32	69	0.69	1.64	65	0.65
		900	0.63	81	0.81	0.88	77	0.77	1.19	72	0.72	1.45	69	0.69
		100	1.59	52	0.52	1.90	50	0.50	2.52	41	0.41	3.14	33	0.33
		300	1.26	62	0.62	1.55	59	0.59	2.01	53	0.53	2.49	47	0.47
NaOH	HS	500	0.96	71	0.71	1.36	64	0.64	1.71	60	0.60	2.02	57	0.57
		700	0.83	75	0.75	1.20	68	0.68	1.54	64	0.64	1.69	64	0.64
		900	0.73	78	0.78	1.03	73	0.73	1.37	68	0.68	1.64	65	0.65
		100	1.20	64	0.64	1.47	61	0.61	1.96	54	0.54	2.53	46	0.46
		300	0.93	72	0.72	1.29	66	0.66	1.71	60	0.60	2.06	56	0.56
	TS	500	0.76	77	0.77	1.15	70	0.70	1.45	66	0.66	1.92	59	0.59
		700	0.66	80	0.8	0.94	75	0.75	1.24	71	0.71	1.73	63	0.63
		900	0.53	84	0.84	0.83	78	0.78	1.11	74	0.74	1.45	69	0.69

3.1.3. Effect of temperature

The effect of rising temperature on the CR of carbon steel in 0.5 M NaCl and in 0.5 M NaOH solutions, and on the inhibition efficiencies of the investigated surfactants at different concentrations has been studied in the temperature range of (15 - 45 °C) using WL measurements. As the temperature increases, the CR increase and the %IE of the additives decreases as listed in Table 2. The observed values of %IE decrease with raising temperature indicating that physical absorption is the predominant mechanism [25,26].

3.1.4. Adsorption isotherms

It is reported that [27,28] the surfactant molecules demonstrate the effect of inhibition by adsorption of these molecules on the metal surface. The adsorption processes are influenced by the chemical structure of the inhibitor, the charge on the metal surface and the type of the aggressive medium. In general, two modes of adsorption can be considered, physical (physisorption) and chemical (chemisorption) [29]. In order to obtain further information about the adsorption method, experiments were performed to fit experimental data with various adsorption isotherms such as Temkin, Langmuir, Freundlich, Frumkin, Bockris–Swinkels and Flory–Huggins, where the most frequently used isotherm is Langmuir.

For testing the adsorption isotherm of the investigated inhibitors obeyed by this system, the plots of fractional surface coverage values (C_{inh}/θ) versus inhibitor concentrations (C_{inh}) at all the studied temperatures were drawn. Straight lines with almost unit slopes and correlation coefficients of $(0.994 \le R^2 \le 0.998)$ were obtained as illustrated in Figure 7 indicating that the adsorption of the investigated inhibitors on carbon steel surface in both NaCl and NaOH solutions agrees with the Langmuir adsorption isotherm which is given by following equation [30]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$
(5)

where K_{ads} is the adsorptive equilibrium constant. Langmuir adsorption isotherm supposes that the adsorbed species occupy only one surface site and there is no interaction between the adsorbed species. Values of K_{ads} (listed in Table 3) were found to decrease with rising temperature indicating strong adsorption of the inhibitors on the carbon steel surface at lower temperatures but when the temperature becomes relatively higher, the adsorbed inhibitors tend to desorb from the steel surface.



Fig. 7. Langmuir adsorption isotherms for the amino acids based-surfactants adsorbed on the carbon steel surface in 0.5 M NaCl solution, (a) AS, (b) HS, (c) TS, and in 0.5 M NaOH solution, (d) AS, (e) HS, (f) TS, at different temperatures.

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3.1.5. Thermodynamic parameters

Thermodynamic parameters for the adsorption of inhibitor can provide valuable information about the mechanism of corrosion inhibition. The standard free energy of adsorption (ΔG^{o}_{ads}) is related to the adsorption constant (K_{ads}) according to the following equation [31],

$$\Delta G^{0}_{ads} = -RT \ln(55.5K_{ads}) \tag{6}$$

where, the value 55.5 is the molar concentration of water in solution.

The values of (ΔG^{o}_{ads}) for the three studied surfactants at a concentration of 500 ppm for each were calculated at various temperatures (Table 3). The obtained large negative values of (ΔG^{o}_{ads}) suggest spontaneity of the adsorption process and stability of the adsorbed layer on the carbon steel surface [32]. Moreover, the high values of (ΔG^{o}_{ads}) obtained for the surfactant TS indicated that this compound is more strongly adsorbed on steel surface in the corrosive media than the other surfactants. On the other hand, the obtained values of ΔG^{o}_{ads} indicated that the adsorption mechanism of the investigated surfactants on carbon steel in both NaCl and NaOH solutions is a mixed from physical and chemical adsorption [33,34].

The standard adsorption heat (ΔH^{o}_{ads}) can be calculated according to the Van't Hoff equation [35]:

$$\ln K_{\rm ads} = \frac{-\Delta H^o{}_{ads}}{RT} + \text{Constant}$$
(7)

Figure 8 represents the relation between $\ln K_{ads}$ vs. 1/T. A straight lines were obtained with slopes of $-\Delta H^{o}_{ads}/R$ The values of $-\Delta H^{o}_{ads}$ were obtained and are presented in Table 3. The obtained negative values of ΔH^{o}_{ads} reveal that the adsorption of inhibitors molecules is an exothermic process with a physical nature (physisorption).



Fig. 8. Van't Hoff plots for a 500 ppm of the synthesized amino acids based-surfactants adsorbed on the carbon steel surface in 0.5 M of: (a) NaCl, and (b) NaOH.

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The standard adsorption entropy (ΔS^{o}_{ads}) can be obtained from the following rearranged Gibbs– Helmholtz equation:

$$\Delta G^{\rm o}_{\rm ads} = \Delta H^{\rm o}_{\rm ads} - T \Delta S^{\rm o}_{\rm ads} \tag{8}$$

The calculated values of ΔS^{o}_{ads} are listed in Table 3. The obtained positive values of ΔS^{o}_{ads} showed a random increase in the metal interface / solution during adsorption of the inhibitor molecules on the carbon steel surface. This increase of disorder is because water molecules may desorb the surface of the metal with inhibitory molecules [36].

Table 3. Values of thermodynamic parameters and adsorptive equilibrium constant (K_{ads}) for the corrosion of carbon steel in 0.5 M NaCl and in 0.5 M NaOH solutions in the presence of a 500 ppm of the amino acids based-surfactants at different temperatures.

Medium	T 1 1 1 1	Temp.	10 ⁻³ K _{ads}	ΔG^{o}_{ads}	ΔH^{o}_{ads}	ΔS^{o}_{ads}
(0.5 M)	Inhibitor	(°C)	l mol ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹	J mol ⁻¹ K ⁻¹
NaCl		15	3.51	-29.17		70.21
		25	3.10	-29.87	-8.25	72.56
	AS	35	2.87	-30.68	0.23	75.28
		45	2.51	-31.32		77.42
		15	5.14	-30.07		53.62
	нс	25	4.29	-30.68	14.00	55.66
	115	35	3.65	-31.29	-14.09	57.71
		45	2.92	-31.72		59.15
		15	10.21	-31.72		17.30
	TS	25	6.93	-31.86	-26 56	17.76
		35	4.51	-31.83	-20.50	17.67
		45	3.69	-32.33		19.35
	AS	15	4.05	-29.51		19.79
		25	2.75	-29.57	-23.61	19.99
		35	2.01	-29.77	-23.01	20.67
		45	1.60	-30.13		21.87
		15	3.39	-29.08		20.30
NaOH	нс	25	3.01	-29.79	-23.03	22.69
	115	35	2.35	-30.17	-23.03	23.96
		45	1.66	-30.23		24.16
		15	6.36	-30.59		47.97
	т	25	5.32	-31.21	-16 29	50.05
	10	35	4.26	-31.69	10.27	51.66
		45	3.34	-32.08		52.97

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3.1.6. Kinetic-thermodynamic parameters

The dependence of corrosion rate on temperature is expressed by Arrhenius equation as follows [37]:

$$\ln CR = \ln A - \frac{E_a^*}{RT}$$
(9)

where, E_a^* is the activation energy and A is the Arrhenius constant.

Figure 9 represents the Arrhenius plots (ln CR vs. 1/*T*) for carbon steel in 0.5 M NaCl and in 0.5 M NaOH in the absence and presence of different concentrations of the studied surfactant molecules. The linear regression coefficients of all plots are higher than 0.99 indicating the validity of the used kinetic mode. The calculated values of E_a^* listed in Table 4 showed that the higher values of E_a^* in the presence of the surfactant molecules are higher than those in free solutions. This behavior indicates lower corrosion rates and physical adsorption of the inhibitors on steel surface [38]. Also, values of E_a^* were lower than the threshold value of 80 kJmol⁻¹ (required for chemical adsorption) confirming the physical adsorption of the inhibitors are consistent with those based on the values of both ΔG^o_{ads} and ΔH^o_{ads} confirming the validity of the obtained results.

The enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) of metal dissolution are calculated using transition state equation [40]:

$$\ln\left(\frac{CR}{T}\right) = \left(\ln\frac{R}{Nh} + \frac{\Delta S^*}{R}\right) - \frac{\Delta H^*}{R}\frac{1}{T}$$
(10)

where, N is Avogadro's number and h is Planck's constant.

Plots of ln(CR/??) versus 1/T gave good straight lines as illustrated in Figure 10. Values of Δ ??* and Δ ??* are obtained from the slopes and intercepts of such plots, respectively, and are presented in Table 4. The positive sign of ΔH^* reflects the endothermic nature of the dissolution process. High values and negative sign of ΔS^* in both the absence and presence of the surfactant molecules which means that in the rate-determining step the activated complex denotes an association rather than dissociation resulting in a decrease in disturbance [41].



Fig. 9. Arrhenius plots for the corrosion of carbon steel in the absence and presence of different concentrations of the amino acids based-surfactants in 0.5 M NaCl solution, (a) AS, (b) HS, (c) TS, and in 0.5 M NaOH solution, (d) AS, (e) HS, (f) TS.



Fig. 10. Transition state plots for the corrosion of carbon steel in the absence and presence of different concentrations of the amino acids based-surfactants in 0.5 M NaCl solution, (a) AS, (b) HS, (c) TS, and in 0.5 M NaOH solution, (d) AS, (e) HS, (f) TS.

		Inhibitors	E_{a}^{*}	ΔH^*	ΔS^*
Medium	Inhibitor	Concn. (mg l ⁻¹)	kJ mol ⁻¹	kJ mol ⁻¹	J mol ⁻¹ K ⁻¹
		0	8.56	6.03	-141.75
		100	13.88	11.39	-154.22
		300	18.21	15.71	-166.70
	AS	500	19.62	17.13	-169.19
		700	22.95	20.45	-178.33
		900	24.03	21.28	-180.83
		100	15.71	13.22	-160.04
		300	16.21	13.72	-160.11
NaCl	HS	500	18.21	15.71	-164.20
		700	17.04	14.47	-159.21
		900	19.25	16.63	-165.86
	TS	100	20.79	18.21	-175.01
		300	24.19	21.95	-184.97
		500	24.69	22.16	-184.16
		700	25.19	22.70	-184.99
		900	23.78	21.28	-179.58
		0	8.89	6.32	-131.78
	AS	100	17.21	14.71	-155.06
		300	20.45	18.04	-163.37
		500	24.94	22.28	-175.84
		700	21.95	19.45	-164.20
		900	21.37	18.87	-161.73
		100	17.63	15.13	-155.89
		300	17.46	15.05	-154.23
NaOH	HS	500	18.79	16.29	-155.87
		700	18.29	15.63	-153.39
		900	20.78	18.21	-160.86
		100	19.12	17.04	-159.21
		300	20.37	17.88	-161.71
	TS	500	22.95	20.37	-168.36
		700	24.11	21.62	-171.68
		900	25.27	22.86	-174.18

Table 4. Activation parameters for the corrosion of carbon steel in 0.5 M NaCl and in 0.5 M NaOH solutions in the absence and presence of different concentrations of the amino acids based-surfactants.

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3.2. Potentiodynamic polarization (PP) measurements

3.2.1. Effect of corrosive media concentrations

Figure 11 (a,b) represents the PP curves recorded for carbon steel electrode in various concentrations of NaCl and NaOH solutions, respectively. The associated electrochemical parameters of the corrosion process, i.e. corrosion potentials (E_{corr}), corrosion current densities (i_{corr}), cathodic and anodic Tafel slopes (β c, β a) were derived from polarization curve and are listed in Table 5. The data showed that the values of i_{corr} of carbon steel increased with corrosive media concentrations indicating an enhancement of steel corrosion with media concentrations.



Fig. 11. Potentiodynamic polarization curves for carbon steel in different concentrations of: a) NaCl, and b) NaOH solutions at 25 °C.

 Table 5. Corrosion parameters obtained from potentiodynamic polarization measurements for carbon

 steel in different concentrations of NaCl and NaOH solutions at 25 °C.

Modium	Concn.	-E _{corr}	βa	-β _c	icorr
Wieulum	(M)	(mV(SCE))	(mV/decade)	(mV/decade)	(µA/cm ²)
	0.1	513	327	363	26.2
NaCl	0.3	534	362	342	33.0
	0.5	542	387	349	36.9
	0.7	551	375	315	38.8
	1.0	559	361	295	42.3
	0.1	531	218	213	5.6
NaOH	0.3	529	227	209	7.7
	0.5	524	209	201	9.2
	0.7	521	222	204	11.3
	1.0	513	217	196	14.1

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3.2.2. Effect of added surfactants

The PP curves for carbon steel in 0.5 M NaCl and in 0.5 M NaOH solutions in the absence and presence of different concentrations of the investigated surfactant molecules are clarified in Figure 12. Values of corrosion parameters including E_{corr} , i_{corr} , βc , βa , βIE and θ were calculated from PP curves and are given in Table 6. From Figure 12 and Table 6, it can be observed that addition of the amino acids based-surfactant molecules to the blank solutions (0.5 M) shifted both anodic and cathodic branches of the polarization curves of carbon steel towards lower current density values at all investigated surfactant concentrations indicating retardation of both anodic and cathodic reactions and then inhibition of carbon steel corrosion. The values of % IE were found to increase with increasing the inhibitor concentrations and the value of % IE of TS was higher than those of both AS and HS. These results could be explained by the adsorption of the inhibitor molecules at the active sites of the mild steel surface, which retards both iron dissolution and hydrogen evolution, and consequently, decreases the corrosion rate [42]. The observed higher IE at higher inhibitors concentrations can be attributed to a complete and stable protective film of the inhibitory molecules formed at such concentrations. Because the inhibitors showed obvious anodic and cathodic inhibition effects with markedly shifting E_{corr} to more anodic potentials compared with that recorded for the free solutions, it could be concluded that the synthesized surfactants act as mixed-type inhibitors with anodic predominance. The values of b_a and b_c are nearly constant indicating that these compounds are of mixed type inhibitors. i.e. reduce the anodic and retard the cathodic hydrogen evolution reaction.



Fig. 12. Potentiodynamic polarization curves for carbon steel corrosion in the absence and presence of different concentrations of the surfactants in 0.5 M NaCl solution, (a) AS, (b) HS, (c) TS,and in 0.5 M NaOH solution, (d) AS, (e) HS, (f) TSat 25 °C.

Medium	Inhs.	Inhibitors	-Ecorr	βa	-βc	İcorr	% IE	θ
(0.5 M)		Concn.(mg/l)	(mV(SCE))	(mV/decade)	(mV/decade)	(µA/cm ²)		
		0	542	387	359	36.90		
		100	536	333	238	19.18	48	0.48
		300	535	311	231	14.02	62	0.62
	AS	500	532	289	222	9.96	73	0.73
		700	528	157	206	7.01	81	0.81
		900	529	217	208	5.53	85	0.85
		100	539	193	293	14.39	61	0.61
		300	537	187	288	10.33	72	0.72
NaCl	HS	500	536	251	254	7.75	79	0.79
		700	528	197	251	5.90	84	0.84
		900	535	205	235	5.17	86	0.86
	TS	100	542	227	255	14.76	60	0.60
		300	539	222	251	9.95	73	0.73
		500	538	219	357	6.64	82	0.82
		700	519	212	354	4.80	87	0.87
		900	524	237	266	4.06	89	0.89
		0	524	209	201	9.2		
		100	516	136	145	3.50	62	0.62
	AS	300	517	127	147	2.58	72	0.72
		500	512	138	155	1.93	79	0.79
		700	507	132	146	1.38	85	0.85
		900	503	125	129	1.01	89	0.89
		100	523	138	166	3.77	59	0.59
		300	518	128	113	2.48	73	0.73
NaOH	HS	500	516	117	131	1.47	84	0.84
		700	520	108	119	1.10	88	0.88
		900	522	103	126	0.92	90	0.90
		100	523	141	166	3.13	66	0.66
		300	517	130	132	2.12	77	0.77
	TS	500	505	124	147	1.37	85	0.85
		700	516	129	126	1.00	89	0.89
		900	512	96	104	0.74	92	0.92

Table 6. Polarization data for carbon steel corrosion in 0.5 M NaCland 0.5 M NaOH solution in the absence and presence of different concentrations of the amino acids based-surfactants at 25 °C.

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3.3. Electrochemical impedance spectroscopy (EIS) measurements

The behavior of carbon steel corrosionin 0.5 M NaCl and in 0.5 M NaOH solutions was studied in the absence and presence of different concentrations of the investigated surfactant molecules at 25°C and after immersion of carbon steel electrode in the corrosive medium for about 30 min. by the EIS measurements. Nyquist plots of carbon steel corrosion in the corrosive media containing various concentrations of the inhibitors are illustrated in Figure 13. The values of R_{ct} (charge transfer resistance) obtained from Nyquist plots, % IE values which calculated from the values of R_{ct} (using Eq. (4)) and θ values are given in Table 7. It is apparent from Nyquist plots that the obtained impedance spectra consist of one capacitive semicircle suggesting that adsorption of inhibitors occurs by simple surface coverage and the surfactants act as primary interface inhibitors, and the corrosion of carbon steel is mainly controlled by charge transfer process [43,44]. The size of the capacitive semicircle of carbon steel in the inhibitor-free neutral and alkaline media increased significantly after addition of the inhibitors to the corrosive medium indicating a decrease in the corrosion rate of carbon steel and increasing the inhibition efficiencies, and the latter were found to increase with increasing inhibitor concentrations. Also, it can be observed that the general shape of the curves is similar in the absence or presence of inhibitors at different concentrations indicating that no alter in the corrosion mechanism [45].

It is apparent from the values of R_{ct} listed in Table 7 that the addition of the inhibitors in the corrosive media leads to increasing the value of R_{ct} obtained in the blank solution. This indicates that the synthesized surfactants act as inhibitors via adsorption at the metal/solution interface which decreases their electrical capacities as they displace water molecules and other ions originally adsorbed on the surface [46]. Also, increasing R_{ct} value with inhibitor concentrations indicates that the amount of the inhibitor molecules adsorbed on the steel surface increases which form protective films on the steel surface resulting in increase in % IE [47]. With an increase in concentration of the synthesized surfactants, the protection efficiency increases which further confirms that the inhibitor acts as an efficient inhibitor for carbon steel in in 0.5 M NaCl and in 0.5 M NaOH solutions. Finally, the results of the inhibition efficiencies of the inhibitors obtained from EIS measurements were found to be in good agreement with that obtained from both PP and WL measurements.

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Table 7. Values of charge transfer resistance (R_{ct}) and inhibition efficiencies (% IE) of different concentrations of the amino acids based-surfactants for the corrosion of carbon steel in 0.5 M NaCl and in 0.5 M NaOH solutions at 25 °C.

Medium	Inhibitors	Α	AS		HS		TS	
(0.5 M)	Concn. (mg l ⁻¹)	Rct	% IE	R _{ct}	% IE	Rct	% IE	
	0	335		355		355		
	100	755	53	935	62	1228	71	
N-Cl	300	1012	68	1225	71	1615	78	
NaCl	500	1544	77	1690	79	2363	85	
	700	1870	81	2088	83	3225	89	
	900	2365	85	2218	84	3552	90	
	0	540		540		540		
	100	1235	56	1150	53	1635	67	
NaOH	300	1805	70	1505	64	2570	79	
	500	2570	79	2160	75	3375	84	
	700	3005	82	3008	82	4155	87	
	900	3175	83	3605	85	4910	89	

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Fig. 13. Nyquist plots for the corrosion of carbon steel in the absence and presence of different concentrations of the amino acids based-surfactants in 0.5 M NaCl solution, (a) AS, (b) HS, (c) TS, and in 0.5 M NaOH solution, (d) AS, (e) HS, (f) TSat 25 °C.

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3.3. Surface examinations

SEM micrographs of carbon steel samples in 0.5 M NaCl and in 0.5 M NaOH in the absence and presence of 900 ppm of the investigated surfactants are shown in Figure 14 (a-c). Image 14a shows the pure carbon steel surface before immersion in the corrosive media. Images 14 b and c show carbon steel surface in case of its immersion in inhibitor-free 0.5 M NaCl and in 0.5 M NaOH, respectively, for 12 h. The facets seen in these images were a result of corrosion occurred due to exposure of carbon steel to the corrosive media. Images (b1, b2, b3) and (c1, c2, c3) show SEM micrographs of the carbon steel surface after treatment with 900 ppm of the investigated surfactants in the 0.5 M NaCl and in 0.5 M NaOH, respectively. It is obvious that when the surfactant molecules were added to the corrosive media, the surface of the carbon steel suffered a marked change from its predecessor. The surface was devoid of drilling and was much smoother. A good protective layer on the surface of the steel is assumed to be randomly distributed over the whole surface. This can be attributed to the adsorption of the surfactant molecules on a solid steel surface incorporated into the passive film to prevent active sites on the surface and the participation of inhibitor molecules in the interaction with the active sites, showing excellent sequencing properties of corrosion inhibitor [48]. This film is responsible for high inhibition by these surfactants.

3.4. Mechanism of corrosion inhibition

From the observations drawn from the different employed methods; Wl, PP, EIS and SEM, it can be concluded that corrosion inhibition of carbon steel in both NaCl and NaOH solutions by the amino acids synthesized surfactants were found to depend on the concentration and nature of the surfactant. The inhibition efficiency of the compound TS was higher than those of both AS and HS. The proposed inhibition mechanism is based on the experimental observation involves adsorption of the synthesized surfactants on the carbon steel surface immersed in the corrosive media. The synthesized surfactants contain polar groups such as oxygen and nitrogen atoms. Each atom is a center of adsorption and the % IE depends on the electron density around this center. Furthermore, the higher values of % IE may be due to the higher number of carbon atoms of the hydrophobic tail which results in the increase in the electron density on the N and O atoms.

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Fig. 14. SEM micrographs of carbon steel surface: (a) before immersion in the corrosive media, (b) and (c) after 12 h immersion in 0.5 M NaCl and 0.5 M NaOH, respectively, (b1 & c1), (b2 & c2) and (b3 & c3) after 12 h immersion in the corrosive media containing900 ppm of the synthesized amino acids based-surfactants AS, HS and TS, respectively, at 25°C.

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4. Conclusions

- 1) Three new amino acids-based surfactants were synthesized and their chemical structures were confirmed by FT-IR and ¹H NMR.
- 2) The synthesized surfactants acted as good inhibitors for the corrosion of carbon steel in both NaCl and NaOH solutions.
- 3) The synthesized surfactants are considered as mixed type inhibitors with anodic predominance.
- 4) Adsorption of the inhibitors on carbon steel followed Langmuir isotherm.
- 5) The obtained thermodynamic parameters of adsorption indicate that the adsorption process was spontaneous and endothermic, and the type of adsorption was physical.
- 6) The results obtained from all employed techniques are consistent with each other.

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Highlights

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