

New Schiff base cationic surfactants as corrosion inhibitors for carbon steel in acidic medium: weight loss, electrochemical and SEM characterization techniques

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Abstract Two new Schiff base cationic surfactants were synthesized and their chemical structures confirmed using FTIR spectroscopy. The tensioactive and thermodynamic characteristics of their solutions were determined using surface tension/log concentration plots. The protection performance of the synthesized compounds against carbon steel corrosion in 1 M HCl solution was evaluated using weight loss and electrochemical techniques. The compounds were found to be excellent corrosion inhibitors, and their efficiency increased with increasing inhibitor concentration. The mode of adsorption obeyed the Langmuir adsorption isotherm. Polarization curves showed that the two compounds were mixed-type inhibitors. The temperature dependence of the corrosion rate in the absence and presence of these compounds was studied in a temperature range of 303 to 333 K using the weight loss data. Activation parameters E_a , ΔH_a^o , and ΔS_a^o were determined and discussed. In addition, the presence of a protective film on the carbon steel surface was confirmed using scanning electron microscopy (SEM).

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Introduction

Carbon steel is considered a vital structural material, and is one of the most common and popular construction materials across a number of industries; it has played an important role in national economic development, and accounts for approximately 85 % of annual steel production worldwide [1, 2]. Acidic solutions are widely used for industrial cleaning and oil well acidification and in petrochemical processes, especially hydrochloric acid, which is generally used in the pickling process of metal and alloys, and these aggressive solutions may come into contact with the carbon steel surface [3–5]. In all of these many applications, carbon steel is prone to suffer the effects of this aggressiveness, leading to serious corrosion problems. Numerous methods have been used to overcome corrosion issues, the most effective and economic of which is the use of corrosion inhibitors for the protection of metals, especially in acidic media [6, 7]. Organic compounds containing heteroatoms such as nitrogen, oxygen or sulphur and multiple bonds are well recognized as efficient corrosion inhibitors for metals and alloys that allowing greater adsorption on the metal surface [8, 9].

Surface-active compounds (surfactants) are a very important class of organic compounds that can be used as corrosion inhibitors [10–12]. They have many advantages, including low toxicity, safety, easy adsorption on the steel surface, low cost, ease of production, and high inhibition efficiency [13–19]. A surfactant compound is one that tends to accumulate at a surface or interface due to its high surface activity resulting from the adsorption of the surfactant molecules at the interface between bulk phases, forming aggregations called micelles, such as air and water, oil and water or electrode and solution [20–22]. The concentration at which surfactants aggregate is called the critical micelle concentration (CMC). An excellent surfactant inhibitor is one that aggregates or adsorbs at low concentrations. Surfactants with low CMC values are desirable because they adsorb at low concentrations; consequently, the CMC is a key indicator in determining the effectiveness of surfactants as corrosion inhibitors.

Among the large number of synthetic and naturally occurring heterocyclic organic compounds, Schiff bases have attracted the greatest interest. The presence of an azomethine group (–C=N–) in Schiff bases enhances their adsorption ability and corrosion inhibition efficiency [23]. Studies have shown that adsorption depends mainly on certain physicochemical characteristics of the inhibitors, such as electron density of the donor atoms, π -orbital character, and electronic structure of the molecules acting as reaction centres for the adsorption process [24, 25]. Such criteria are present in Schiff base molecules, allowing them to be easily adsorbed on the metal surface by the formation of a coordinate covalent bond (chemical adsorption) or electrostatic interaction between the metal and the inhibitor (physical adsorption).

Experimental

Chemicals

The raw chemicals and solvents used for the synthesis of Schiff base cationic surfactant compounds were obtained from Sigma-Aldrich; materials were of analytical grade and were used without further purification. All physicochemical properties were determined in bi-distilled water.

Synthesis of Schiff base compounds

Schiff base compounds were synthesized according to the Schiff base reaction, as follows: In a single-neck flask, 0.5 mol of N, N-dimethyl ethylene diamine was condensed with 0.5 mol of benzaldehyde in the presence of 200 mL ethanol as a solvent. The reaction mixture was refluxed for 6 h and left overnight until the product was precipitated. The solid product was recrystallized from ethanol and dried under a vacuum at 40 °C to obtain the Schiff bases.

Synthesis of Schiff base cationic surfactants (I and II)

In a single-neck flask, the synthesized Schiff base compounds (1 mol) were refluxed separately with 1 mol of (dodecyl, hexadecyl) bromide individually for 90 h in the presence of ethyl alcohol as solvent (Scheme 1 showing the chemical formulas of the two prepared compounds I and II). The solid product was recrystallized from ethanol and dried under a vacuum at 40 °C to obtain the Schiff base cationic surfactants [(*N*, benzylidene amino) ethylene- dodecyl dimethyl ammonium bromide, compound I] and (*N*, benzylidene amino) ethylene-hexadecyl dimethyl ammonium bromide, compound II]. The chemical structure of the synthesized compounds was confirmed by Fourier transform infrared (FTIR) spectra using the ATI Mattson InfinityTM Series benchtop spectrometer (model 961), controlled by WinFIRSTTM v2.01 software.

Tensiometry measurements

The tensioactive properties of the two synthesized compounds were identified by observing their behaviour in aqueous solutions. Surface tension was measured using a du Noüy tensiometer (KRÜSS K6) at different concentrations ranging from 4×10^{-2} to 1.9×10^{-5} M/L at 35 °C, controlled by a thermostatic water bath. The curves of surface tension versus log surfactant concentration ($\gamma \sim \log C$) were plotted and their CMC values calculated from the break points. At the same time, the surface tension corresponding to CMC, $\gamma_{\rm CMC}$, was obtained on the curves of $\gamma \sim \log C$.



Compound I, n =11

Compound II, n =15

Compound I: (N,benzylidene amino) ethylene- dodecyl dimethyl ammonium bromide and Compound II: (N,benzylidene amino) ethylene- hexadecyl dimethyl ammonium bromide.

Scheme 1 The synthetic route of the two new Schiff base cationic surfactants

Corrosion tests

Metal sample preparation

All experiments were carried out on carbon steel of the following composition (wt%): 0.19 % C, 0.05 % Si, 0.94 % Mn, 0.009 % P, 0.004 % S, 0.014 % Ni, 0.009 % Cr, 0.034 % Al, 0.016 % V, 0.003 % Ti, 0.022 % Cu, and the rest Fe. Rectangular carbon steel coupons having dimensions of length 5.6, width 2.7, and thickness 0.5 cm with an exposed total surface area of 38.54 cm² were used for gravimetric measurements. For electrochemical experiments, the carbon steel cylinder, embedded in epoxy resin with a surface area of 1 cm² exposed to the electrolyte, was used as working electrode. Before running all experiments, the surface of the carbon steel was abraded with emery paper at a series of grades (320–600–800–1000–1200) and then washed with bidistilled water and acetone.

Corrosive medium

The corrosive medium, 1 M HCl, was prepared by dilution of analytical-grade HCl 37 % with bi-distilled water. The concentration of the synthesized compounds used ranged from 100 to 1200 ppm. All solutions were prepared using bi-distilled water.

Gravimetric measurements

In order to perform gravimetric experiments, the coupons were dried and accurately weighed, and were immersed in 100 ml of 1 M HCl solution with and without the addition of different concentrations of the synthesized compounds. The effect of temperature was studied by carrying out the experiments at 303, 313, 323 and 333 K.

Electrochemical measurements

Electrochemical experiments were carried out using a VoltaLab 40 PGZ301 potentiostat in a conventional electrolytic cell with a three-electrode arrangement: saturated calomel reference electrode (SCE), a platinum wire as a counter electrode, and the carbon steel as working electrode (WE). All measurements were conducted at 303 K. Potentiodynamic polarization curves were obtained by changing the electrode potential automatically (from -800 to -300 mV vs. SCE) at open circuit potential with a scan rate of 2 mV s⁻¹.

Electrochemical impedance spectroscopy (EIS) measurements were carried out using a potentiostat (VoltaLab PGZ-301) attached to the Zsimpwin software program. Impedance spectra were obtained in a frequency range of 100 kHz to 50 mHz using 10 steps per frequency decade at the corrosion potential after 30 min of immersion in test solutions without and with different concentrations of the prepared inhibitor. An AC signal with 10 mV peak-to-peak amplitude was used to perturb the system. The EIS diagrams are given as Nyquist representations. All experiments were performed at 303 K under atmospheric conditions without stirring.

Scanning electron microscopy (SEM)

It is necessary to ascertain the morphological changes occurring on the carbon steel surface due to the corrosion process before and after the addition of inhibitors. For this purpose, SEM was used. The specimens were first immersed in 1 M HCl in the absence and presence of optimal concentrations (0.01 M) of the tested compounds for 48 h at room temperature. They were then extracted from the test solutions, cleaned with bi-distilled water and acetone, and dried with cool air. SEM images were acquired using a JEOL model JSM-53000 scanning electron microscope.

Results and discussion

Chemical structure confirmation

The chemical structure of the new synthesized Schiff base cationic surfactants was confirmed by FTIR spectroscopy. Figure 1 shows the characteristic bands of the two synthesized compounds. FTIR spectra showed absorption bands at 1643.8–1646.2 cm⁻¹ (imine group, CH=N), 2853.5 and 2852.2 cm⁻¹ (CH₂), and



Fig. 1 FTIR spectra of the synthesized Schiff base cationic compounds

2924.3 and 2921.3 cm^{-1} (N⁺) for surfactants I and II, respectively. The data confirmed the expected functional groups in the synthesized cationic surfactants.

Surface activity parameters

The surface tension of aqueous solutions of the synthesized Schiff base surfactants was measured at 35 °C with a surface tension technique and the results are depicted in Fig. 2. It is clear that surface tension decreases with increasing concentration of the surfactants due to increased migration of the surfactant molecules from the bulk to the interface of the solution [26]. Of note, the reduction in surface tension of surfactants at identical concentrations is greatly affected by the hydrophobic chain length of the respective compound under investigation. Hence, compound I contains a shorter hydrophobic chain (n = 11) and exhibits less reduction in surface tension



Fig. 2 Surface tension (γ) versus log C at various concentrations of the synthesized Schiff base compounds

than compound II (n = 15), suggesting a higher tendency of longer hydrophobic chains towards adsorption at the air/water interface, hence increasing number of hydrophobic chains, leading to increased repulsion between the aqueous medium and the hydrophobic chains due to differences in their polarity.

The CMC values of the two surfactants were determined by the intercept of the pre- and post-micellar trends at the break points of two straight lines fitted to the interval of concentration characterized by a linear decrease in surface tension (γ) and to the concentration region of nearly constant surface tension (Table 1). CMC is considered an important parameter because, at this concentration, most of the physical and chemical characteristics of the surfactant solutions present abrupt variations. It is evident that CMC values decrease as the length of the hydrophobic chains increases; the value is lower for compound II (3.6×10^{-3} M/L) and higher for compound I (3.9×10^{-3} M/L) [27]. However, this increase in hydrophobic chain length results in decreased solubility, leading to a concentration of the surfactant molecules at the surface and formation of micelles.

Table 1 Tensioactive and thermodynamic characteristics of the synthesized Schiff base cationic surfactants (I and II) at 35 $^{\circ C}$

Inhibitor	$\begin{array}{c} \text{CMC} \times \ 10^3 \\ \text{(M/L)} \end{array}$	π _{CMC} (mN/m)	$\begin{array}{l} Pc_{20}\times 10^5 \\ (M/L) \end{array}$	$\Gamma_{\rm max} \times 10^{11}$ (mol/cm ²)	A_{\min} (nm ²)	$\Delta G^{\circ}_{ m mic}$ (kJ/mol)	$\Delta G^{\circ}_{ m ads}$ (kJ/mol)
I	3.9	41.8	2	7.37	2.25	-14.2	-67.3
II	3.6	43.0	1	7.88	2.11	-14.4	-72.7

The surface tension of the surfactant solution at the CMC determines its effectiveness ($\pi_{CMC} = \gamma_o - \gamma_{CMC}$). Hence, increasing the hydrophobic chain length of the two surfactants increases the reduction in surface tension at the interface, while the efficiency (P_{C20}), i.e., the concentration of surfactant required to produce a 20 mN m⁻¹ reduction in surface tension, is decreased. At this value, the surfactant concentration is close to the minimum needed to produce maximum adsorption at the interface.

Another important factor determining the surface activity of surfactant molecules at the interface is the maximum surface excess, Γ_{max} , which can be evaluated by applying the Gibbs adsorption isotherm, as given in the following equation [28]:

$$\Gamma_{\rm max} = -\frac{1}{2.303nRT} \left(\frac{\delta \gamma}{\delta \log c} \right)_{\rm T},\tag{1}$$

where γ is the equilibrium surface tension in dyne/cm, Γ_{max} is the saturation adsorption amount in mol/1000 m², *R* is the gas constant (8.314 mol⁻¹ K⁻¹), *T* is the absolute temperature, *C* is the surfactant concentration, and $(\delta\gamma/\delta \ln C)$ is the slope in the surface tension isotherm when the concentration is near the CMC. The value of *n* expresses the number of solute species and is equal to 2 for conventional ionic surfactants.

The values of maximum surface excess at the interface are increased by increasing the hydrophobic chain of the two compound molecules, and this can be attributed to the increased hydrophobicity of the molecules that increases the tendency towards adsorption of surfactant molecules, and consequently $\Gamma_{\rm max}$ is increased, indicating higher surface concentration and increased number of surfactant molecules at the surface.

The values of the minimum surface area occupied by the synthesized Schiff base cationic surfactants at the interface, A_{\min} (nm²), when the surface adsorption was saturated were determined using the following equation:

$$A_{\min} = \frac{10^6}{N\Gamma_{\max}},\tag{2}$$

where N is Avogadro's number (6.023 \times 10²³), Γ_{max} is maximum surface excess in mol cm⁻², A_{min} in nm².

Basic information about the orientation mode of the molecules at the interface can be provided by determining the minimum surface area (A_{\min}) . An increase in adsorbed molecules at the interface leads to an increase in maximum surface excess values; accordingly, the area available for each molecule will decrease. As a result, a dense compacting layer of surfactant molecules will be formed at the interface.

The values of CMC, π_{CMC} , P_{C20} , Γ_{max} and A_{min} are presented in Table 1. Briefly, it is clear that compound II achieves the given values of surface tension at a lower concentration than compound I. Consequently, it can be concluded that compound II is more surface-active than compound I, revealing much better surface properties. Generally, CMC values are dependent on the structure of the compound and its quaternization by alkyl halide according to its alkyl chain length.

Thermodynamics of micellization and adsorption

The standard free energies of adsorption and micellization (ΔG_{ads}^{o} and ΔG_{mic}^{o}) at 35 °C were used to study the thermodynamic behaviours of the synthesized Schiff base cationic surfactants in their solutions. The thermodynamic free energy of adsorption is calculated from the following equation [29, 30]:

$$\Delta G_{\rm ads}^{\rm o} = \Delta G_{\rm mic}^{\rm o} - (0.6023 \times \pi_{\rm CMC} \times A_{\rm min}), \tag{3}$$

where $\Delta G_{\text{mic}}^{\circ} = \text{RT}$ In CMC, $\pi_{\text{CMC}} = \gamma_{\text{o}} - \gamma_{\text{CMC}}$, and γ_{o} is the surface tension of water and γ_{CMC} is the surface tension of surfactant solution at the same temperature. Data pertaining to the thermodynamic parameters of micellization and adsorption are listed in Table 1, from which it is clear that the values of the standard free energies of adsorption and micellization of the synthesized Schiff base cationic surfactants are always negative. This phenomenon indicates that the adsorption and micellization processes both occurred spontaneously. In addition, the standard free energies of adsorption of the two compound molecules at the air/water interface are more negative than those of the micellization, indicating that the adsorption process is more favourable than the mobilization. Moreover, the large difference between ΔG_{ads}° and ΔG_{mic}° values can be attributed to the fact that the adsorbed molecules at the interface are highly compacted, and consequently the water molecules do not interact significantly with these molecules.

Weight loss measurements

The weight loss method, given its simplicity and the reliability of its measurements, is the most commonly used non-electrochemical technique for evaluating the inhibition efficiency of any inhibitor [31, 32]. Table 2 shows the values of corrosion rate C_r (mg cm⁻² h⁻¹), surface coverage (Θ), and inhibition efficiency η_w (%) obtained from weight loss measurements for carbon steel after 6 h of immersion in 1 M HCl solution with and without the addition of different concentrations of the two synthesized compounds at temperatures of 303, 313, 323 and 333 K. The corrosion rate (C_r) was calculated from the following equation [33]:

$$C_{\rm r} = \frac{\Delta W}{At},\tag{4}$$

where *W* is the weight loss of the carbon steel coupons (mg), *A* is the total surface area of the carbon steel coupon (cm²), and *t* is the immersion time (6 h). The inhibition efficiency was obtained from the calculated corrosion rates as follows:

$$\eta_{\rm WL}(\%) = \frac{C_{\rm r}^{\rm o} - C_{\rm r}}{C_{\rm r}^{\rm o}} \times 100, \tag{5}$$

where C_r^o and C_r are the corrosion rates of the carbon steel coupons in the absence and presence of the inhibitor, respectively.

T (K)	Conc. (ppm)	Compound	ł I		Compound	II		
		$\Delta W (mg)$	$\begin{array}{c} C_{\rm r} \\ ({\rm mg} \ {\rm cm}^{-2} \ {\rm h}^{-1}) \end{array}$	$\eta_{\rm w}(\%)$	$\overline{\Delta W}$ (mg)	$\begin{array}{c} C_{\rm r} \\ ({\rm mg} \ {\rm cm}^{-2} \ {\rm h}^{-1}) \end{array}$	$\eta_{\rm w}(\%)$	
303	1 M HCl	93.0	0.4022	_	93	0.4022	_	
	100	45.4	0.1963	51.2	14.79	0.0639	84.1	
	300	21.2	0.0917	77.2	10.32	0.0446	88.9	
	600	17.8	0.0768	80.9	8.00	0.0346	91.4	
	900	15.7	0.0680	83.1	6.98	0.0302	92.5	
	1200	13.1	0.0567	85.9	4.84	0.0209	94.8	
313	1 M HCl	121.0	0.5233	-	121	0.5233	-	
	100	67.52	0.2920	44.2	26.86	0.1162	77.8	
	300	33.76	0.1460	72.1	19.72	0.0853	83.7	
	600	27.47	0.1188	77.3	15.61	0.0675	87.1	
	900	24.32	0.1052	79.9	11.62	0.0502	90.4	
	1200	21.78	0.0942	82.0	9.32	0.0403	92.3	
323	1 M HCl	154.0	0.6660	-	154	0.6660	-	
	100	89.47	0.3869	41.9	41.58	0.1798	73.0	
	300	47.89	0.2071	68.9	30.65	0.1325	80.1	
	600	41.89	0.1811	72.8	24.95	0.1079	83.8	
	900	36.81	0.1592	76.1	20.64	0.0892	86.6	
	1200	30.95	0.1339	80.0	15.86	0.0686	89.7	
333	1 M HCl	162.0	0.7006	-	162	0.7006	-	
	100	99.47	0.4302	38.6	50.38	0.2179	68.9	
	300	63.50	0.2746	60.8	41.31	0.1786	74.5	
	600	58.81	0.2543	63.7	35.80	0.1548	77.9	
	900	54.12	0.2340	66.6	29.0	0.1254	82.1	
	1200	47.79	0.2067	70.5	21.38	0.0925	86.8	

Table 2 Corrosion parameters obtained from weight loss data of carbon steel in 1 M HCl with and without various concentrations of Schiff base derivatives at different temperatures, with an immersion time of 6 h

Influence of inhibitor concentration

The corrosion rate (C_r) and inhibition efficiency data obtained from weight loss measurements are depicted in Table 2. It is clear that the weight loss values are decreased, leading to suppression of the corrosion rate with increasing inhibitor concentration, and that both compounds are highly effective against corrosion in acidic solution, suggesting adsorption of these compounds onto the carbon steel surface from acidic solutions [34].

The high protective performance of the synthesized inhibitors is due to the presence of the phenyl and azomethine group (-C=N-) of Schiff base moiety in their chemical structure, as well as the presence of protonated amine species, which

result in increased adsorption on the metal surface [35]. Consequently, these compounds exhibit excellent protective performance as corrosion inhibitors for carbon steel in an acidic medium, which is attributable to the presence of high electron density from the benzene ring and the azomethine group. Indeed, these groups are adsorbed onto the positive centre on the carbon steel surface, while the alkyl chains of alkyl halides are arranged on the metal surface, preventing contact between the metal surface and the aggressive solution, resulting in a reduction in the rate of carbon steel dissolution [36].

Figure 3 shows the effect of compounds I and II concentrations on the inhibition efficiencies of the carbon steel in 1 M HCl solution at different temperatures. In a comparison of protection efficiency between compounds I and II in acidic solution, the latter displays higher inhibition efficiency, which can be attributed to an increase in the side chain attached to the tested inhibitors during the quaternization reaction. Hence, inhibition efficiency is higher in the hexadecyl bromide derivative than the dodecyl bromide derivative.

Effect of temperature

Weight loss measurements were used to study the effect of temperature on inhibition efficiency percentage at 303–333 K for different concentrations of the synthesized Schiff base compounds. From Table 2 and Fig. 3, we note that the corrosion rates of carbon steel in both free and inhibited acid media increased with increasing temperature for both inhibitors. Inhibition efficiency was found to decrease as temperature increased. This phenomenon can be explained on the basis that an increase in temperature leads to a shift in equilibrium constant towards desorption of the inhibitor molecules at the surface of carbon steel, resulting in physical adsorption of the synthesized inhibitors onto the metal surface [37, 38].



Fig. 3 Inhibition efficiency dependence on concentration of Schiff base compounds in 1 M HCl solution at different temperatures

Adsorption isotherm

The application of adsorption isotherms is widely used for deducing basic information about interactions between inhibitors and carbon steel surface in acidic media. The adsorption capacity of the inhibitor on the carbon steel surface is significantly related to its degree of protection efficiency, which is dependent on the electronic characteristics of the inhibitor, the nature of the metal surface, temperature, stress effects, and the varying degrees of surface-site activity [39, 40]. Accordingly, the mode of adsorption as well as the adsorption isotherm can yield important information about the interaction between the inhibitor and the metal surface.

The degree of surface coverage (Θ) for different concentrations of the tested inhibitors in the studied temperature range (303–333 K) was evaluated by weight loss data and is presented in Table 2. Various models were used to fit the Θ values, including Langmuir, Temkin, Frumkin and Flory–Huggins. The linear relationships of C/Θ versus C presented in Figs. 4a and 5a suggest that the best fit was obtained with the Langmuir adsorption isotherm, and is described by the following equation [41]:



Fig. 4 Curves fitting the adsorption process of Schiff base compound I on carbon steel surface in 1 M HCl solution; a Langmuir adsorption isotherm, b Van't Hoff plot, and c variation of ΔG_{ads}^{o} against 1/T



Fig. 5 Curves fitting the adsorption process of Schiff base compound II on carbon steel surface in 1 M HCl solution; a Langmuir adsorption isotherm, b Van't Hoff plot, and c variation of ΔG_{ads}^{o} against 1/T

$$\frac{C_{\rm inh}}{\theta} = \frac{1}{K_{\rm ads}} + C_{\rm inh},\tag{6}$$

where C_{inh} is the inhibitor concentration, K_{ads} is the adsorption equilibrium constant, and Θ is the degree of surface coverage with the value of inhibition efficiency. The degree of surface coverage of each inhibitor and the inhibition efficiency at a given concentration can be determined using the following equations, respectively [33]:

$$\theta = \frac{W_{\rm o} - W_i}{W_{\rm o}} \tag{7}$$

$$\eta_{\rm WL}(\%) = \frac{W_{\rm o} - W_i}{W_{\rm o}} \times 100,\tag{8}$$

where W_o and W_i indicate weight loss in the absence and presence of inhibitors, respectively. Table 3 illustrates the strong correlation of the Langmuir adsorption isotherm obtained for compounds I and II. Both linear correlation coefficients and slope values are very close to unity, indicating adsorption of both compounds on the carbon steel surface according to the Langmuir adsorption isotherm. A slight

Table 3 Different thermodynamic parameters of	Inhibitor	<i>T</i> (K)	Slope	R^2	Kads
linear regression between C_{inh}/Θ and C_{inh} in 1 M HCl for the prepared compounds I and II at	Compound I	303	1.1153	0.9996	6363
		313	1.1499	0.9997	5012
various temperatures		323	1.1818	0.9989	4269
	Compound II	333	1.3497	0.9983	3924
		303	0.9356	0.9982	17,262
		313	0.9521	0.9977	11,823
		323	0.9795	0.9970	9946
		333	1.1319	0.9965	7559

deviation from unity is noted in slope values, indicating the presence of a repulsive force in the adsorption layer [42].

Equilibrium constant and standard free energy of adsorption (K_{ads} and ΔG_{ads}^{o})

It is well recognized that the adsorption equilibrium constant (K_{ads}) is related to the standard free energy of adsorption (ΔG_{ads}^{o}) deduced from the following equation [43]:

$$K_{\rm ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{\rm ads}^{\rm o}}{\rm RT}\right),\tag{9}$$

where *R* (8.314) is the universal gas constant, *T* is the absolute temperature, and 55.5 is the molar concentration of water in solution expressed in mol/L. The values of K_{ads} obtained for the two compounds at different temperatures are listed in Table 3. The relatively high values of the adsorption equilibrium constant reflect the higher adsorption capacity of these molecules on the carbon steel surface in 1 M HCl. It can also be seen from Table 3 that the adsorption equilibrium constant (K_{ads}) decreases with an increase in experimental temperature, which likely indicates desorption of some adsorbed inhibitor molecules from the metal surface at higher temperatures, confirming the physical adsorption of the inhibitors.

With respect to ΔG_{ads}^{o} values (Table 4), these values were shown to be negative for the tested compounds, and the values are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the carbon steel surface. As a general rule, ΔG_{ads}^{o} values of -20 or higher are in agreement with an electrostatic interaction between charged molecules and charged metal surface (physisorption), while values of -40 or lower are associated with charge or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond (chemisorption) [44]. In the present work, the mean value of ΔG_{ads}^{o} among the various temperatures was -32.9 for compound I and -35.2 for compound II. This implies that the adsorption of synthesized inhibitors on carbon steel surface is neither typical physisorption nor typical chemisorption but is a complex mixed type

Inhibitor	<i>T</i> (K)	$\Delta G_{\rm ads}^{\rm o}$ (kJmol ⁻¹)	$\Delta H_{\rm ads}^{\rm o}$ (kJmol ⁻¹)	$\Delta S_{ads}^{o} (Jmol^{-1} K^{-1})$
Compound I	303	-32.18	-12.2	65.2
	313	-32.26	-12.2	65.2
	323	-33.23	-12.2	65.2
	333	-34.03	-12.2	65.2
Compound II	303	-34.70	-22.2	41.1
L	313	-34.86	-22.2	41.1
	323	-35.50	-22.2	41.1
	333	-35.84	-22.2	41.1

Table 4Standard thermodynamic parameters of the adsorption of compounds I and II on carbon steelsurface in 1 M HCl

in which adsorption of inhibitor molecules on the carbon steel surface in 1 M HCl solution involves both physisorption and chemisorption.

Also, Table 4 clearly shows that temperature has an influence on the values of ΔG_{ads}^{o} , as it can be concluded that ΔG_{ads}^{o} became more negative with increased temperature, indicating that the adsorption of compounds I and II on carbon steel was favourable to the experimental temperature. Furthermore, from an adsorption point of view, compound II was more stable than compound I, as it had a higher ΔG_{ads}^{o} value than compound I in 1 M HCl solution.

Standard enthalpy and entropy of adsorption (ΔH^{o}_{ads} and ΔS^{o}_{ads})

The sequel to the thermodynamic parameters that are important in studying adsorption of organic inhibitors on metal surface, the heat of adsorption ΔH_{ads}^{o} is calculated using the Van 't Hoff equation [45]:

$$\ln K_{\rm ads} = -\frac{\Delta H_{\rm ads}^o}{\rm RT} + A \tag{10}$$

A straight line was obtained when $\ln K_{ads}$ was plotted against 1/*T*, as shown in Figs. 4b and 5b. The slope of these straight lines is equal to $(-\Delta H_{ads}^o/2.303 \text{ R})$. The heat of adsorption (ΔH_{ads}^o) can be approximately regarded as the standard heat of adsorption under experimental conditions [46]. From the basic thermodynamic equation, the standard adsorption entropy (ΔS_{ads}^o) can be deduced as follows:

$$\Delta S_{\rm ads}^{\rm o} = \frac{\Delta {\rm H}_{\rm ads}^{\rm o} - \Delta G_{\rm ads}^{\rm o}}{T} \tag{11}$$

A plot of ΔG_{ads}^{o} versus *T* gives a straight line showing good dependence of ΔG_{ads}^{o} on *T*, confirming the good correlation among thermodynamic parameters as shown in Figs. 4c and 5c. All thermodynamic parameters obtained are listed in Table 4. It is clear that values of ΔH_{ads}^{o} are negative, suggesting that the adsorption of inhibitors is an exothermic process and inhibition efficiency decreases with an increase in temperature [47]. This behaviour can be interpreted on the basis that more desorption of the adsorbed molecules from the carbon steel occurred at higher

temperatures. It is evident from Table 4 that the values of ΔS_{ads}^{o} are negative, and this is an exception, as adsorption is an exothermic process always accompanied by a decrease of entropy, suggesting that there is an association rather than dissociation in the rate-determining step.

Kinetic parameters referring to energy, enthalpy and entropy of activation $(E_a, \Delta H_a^o \text{ and } \Delta S_a^o)$

In addition to thermodynamic parameters, the kinetic model is another important tool for elucidating the mechanism of corrosion inhibition and for further clarifying the inhibitory properties of the inhibitor at different experimental temperatures.

It is generally accepted that the activation parameters for the corrosion process can be determined from the Arrhenius equation [48]:

$$\ln C_{\rm r} = -\frac{E_a}{\rm RT} + \ln A,\tag{12}$$

where E_a represents the activation energy, R is the gas constant, A is the preexponential factor, and C_r is the corrosion rate obtained from weight loss measurements. Figure 6 shows Arrhenius plots for the corrosion rate of carbon steel in 1 M HCl at different temperatures. The slope of linear regression between $\ln C_r$ and 1/T is $(-E_a/R)$, and hence the values of activation energy (E_a) were calculated for carbon steel in acidic solution at different concentrations without and with an inhibitor.

There is another formulation of the Arrhenius equation, as [49]:

$$C_{\rm r} = \frac{\rm RT}{\rm Nh} \exp\left(\frac{\Delta S_{\rm a}^{\rm o}}{R}\right) \exp\left(\frac{-\Delta H_{\rm a}^{\rm o}}{\rm RT}\right),\tag{13}$$

where *h* is Plank's constant, *N* is Avogadro's number, ΔS_a^o is the entropy of activation, and ΔH_a^o is the enthalpy of activation. Figure 7 shows a plot of ln



Fig. 6 Arrhenius plots for carbon steel corrosion in 1 M HCl in the absence and presence of different concentrations of Schiff base compounds



Fig. 7 Transition state plots for carbon steel corrosion in 1 M HCl in the absence and presence of different concentrations of Schiff base compounds

 (C_r/T) against 1/T for compounds I and II. Straight lines are obtained with a slope of $(-\Delta H_a^o/R)$ and an intercept of $(\ln R/Nh + \Delta S_a^o/R)$, from which the values of ΔH_a^o and ΔS_a^o are calculated. The important activation parameters for carbon steel in 1 M HCl without and with inhibitors at various concentrations are collected and listed in Table 5. From Table 5, it is clear that E_a values are higher in the presence than in the absence of inhibitors, indicating higher activation energies for the metal dissolution reaction; hence the process is activation-controlled. The increase in apparent activation energy with inhibitor concentration therefore indicates a more efficient inhibiting effect that can be attributed to the thickening of the electric double layer [50]. In addition, E_a and ΔH_a^o seem to vary in the same manner. The positive signs of the enthalpies (ΔH_a^o) reflect the endothermic nature of the dissolution process of carbon steel, suggesting that process is slow in the presence of inhibitors [51]. With regard to the values of activation entropies (ΔS_a^{o}), large negative values imply that the activated complex in the rate-determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place going from reactants to the activated complex [52]. However, the value of ΔS_a^o increases gradually with increasing concentrations of compounds I and II. This behaviour, which can be attributed to the adsorption of organic inhibitor molecules from the acidic solution, can be regarded as a quasi-substitution process between the inhibitor in the aqueous phase and water molecules at the electrode surface [53]. Accordingly, the adsorption of organic inhibitor is followed by desorption of water molecules from the metal surface. Consequently, the increase in entropy of activation can be attributed to the increasing solvent entropy [54].

Polarization curves

The potentiodynamic polarization method is considered the most important electrochemical tool for the study of various electrochemical phenomena that occur on metal surface. The polarization curves of carbon steel in the absence and

Inhibitor	Conc. (ppm)	$E_{\rm a} (\rm kJmol^{-1})$	$\Delta H_{\rm a}^{\rm o} ({\rm kJmol}^{-1})$	$\Delta S_{a}^{o} (\text{Jmol}^{-1} \text{ K}^{-1})$
Compound I	1 M HCl	15.85	15.85	-200.0
	100	22.03	21.91	-185.7
	300	30.35	30.27	-164.6
	600	33.51	33.36	-156.1
	900	34.34	34.28	-154.2
	1200	35.10	35.15	-152.7
Compound II	1 M HCl	15.85	13.23	-208.6
-	100	34.21	31.59	-162.9
	300	38.25	35.64	-152.6
	600	41.28	38.67	-144.7
	900	40.32	37.70	-149.5
	1200	41.50	38.89	-148.2

Table 5 Activation parameters E_a , ΔH_a^o and ΔS_a^o for carbon steel in 1 M HCl in the absence and presence of compounds I and II at different temperatures

presence of different concentrations of the synthesized inhibitors (I and II) at 303 K are depicted in Fig. 8. The important related electrochemical parameters, such as corrosion current density (I_{corr} , mA/cm²), anodic Tafel slope (β_a , mV/dec), and cathodic Tafel slope (β_c , mV/dec) were obtained by extrapolation of Tafel lines at the corrosion potential (E_{corr} , mV) and are presented in Table 6. The surface coverage (Θ) and inhibition efficiency (η_{Tafel} , %) were calculated from the following equations [55]:



Fig. 8 Potentiodynamic polarization curves (E–log I relationship) of carbon steel in 1 M HCl solution in the absence and presence of different concentrations of the inhibitors: a compound I and b compound II

Inhibitor	Conc. (ppm)	E _{corr} . (mV)	$I_{\rm corr}$ (mA/ cm ²)	$\beta_a (mV/dec)$	$\beta_{\rm c} \ ({\rm mV}/{\rm dec})$	$R_{\rm p}$ (' Ω cm ²)	$\eta_{ ext{Tafel}}$ (%)
1 M HCl	_	-605	0.3532	115	-125	78	_
Compound I	100	-575	0.1800	108	-123	163	49
	300	-576	0.0680	121	-109	476	80.7
	600	-566	0.0476	139	-158	766	87.4
	900	-575	0.0452	115	-120	784	87.3
	1200	-575	0.0414	138	-140	937	88.4
Compound II	100	-603	0.0436	125	-129	798	87.5
	300	-605	0.0354	137	-138	1080	90.1
	600	-603	0.0349	132	-145	1090	90.1
	900	-602	0.0340	133	-142	1110	90.4
	1200	-601	0.0280	130	-133	1240	92.1

Table 6Polarization parameters and corresponding inhibition efficiencies for the corrosion of carbonsteel in 1M HCl containing different concentrations of Schiff base derivatives at 303 K

$$\theta = \frac{(i_{\rm corr})_{\rm HCl} - (i_{\rm corr})_{\rm inh}}{(i_{\rm corr})_{\rm HCl}} \tag{14}$$

$$\eta_{\text{Tafel}}(\%) = \frac{(i_{\text{corr}})_{\text{HCl}} - (i_{\text{corr}})_{\text{inh}}}{(i_{\text{corr}})_{\text{HCl}}} \times 100, \tag{15}$$

where $(i_{\text{corr}})_{\text{HCl}}$ and $(i_{\text{corr}})_{\text{inh}}$ are the corrosion current densities in the absence and presence of the inhibitor, respectively.

The inhibitory action of these compounds obtained from plotting of the polarization curves was used to find the kinetic parameters of corrosion and to compare them with the kinetic parameters from the solution without inhibitor. In addition, we calculated the efficiency of the two inhibitors so that we could precisely determine which gave the best result in a given medium and at what concentration. After the results were analyzed, the following conclusions were drawn:

- 1. Table 6 shows that the corrosion current densities (i_{corr}) decreased with increasing concentrations of compounds I and II, indicating that these compounds acted as inhibitors and that their inhibition efficiencies increased. The degree of inhibition was dependent on the concentration and type of inhibitor present (the length of the hydrophobic chain).
- 2. The corrosion potential (E_{corr}) can be seen to shift slightly towards more negative and positive potential in the presence of an inhibitor, suggesting that the mechanism of inhibitor adsorption over the metal surface obeys the adsorption phenomenon that hinders both anodic and cathodic reactions. The value of E_{corr} displacement was less than 85 mV, indicating that these were mixed-type inhibitors with predominant control of the anodic reaction in the presence of compound I resulting in a shift of corrosion potential in a more noble direction compared with that obtained in the presence of an inhibitor [56].

This can be explained on the basis that inhibitor adsorption on the metal surface and the adsorption process is enhanced with increasing inhibitor concentration.

- 3. Careful analysis of Fig. 8 shows that both cathodic and anodic reactions of carbon steel electrode corrosion are suppressed with inhibitor concentrations as a result of the ability of these inhibitors to control both reactions. In addition, cathodic current–potential curves give rise to parallel Tafel lines, indicating that oxygen reduction reaction is activation-controlled and that the addition of the Schiff base compounds does not modify the mechanism of this process. Generally speaking, the inhibitor is first adsorbed onto the carbon steel surface and then impedes by merely blocking the active sites of the steel surface; as a result, the surface area available for H⁺ ions is decreased, while the actual reaction mechanism remains unaffected [57].
- 4. The order of decreased inhibition efficiency of the synthesized compounds is Compound II > Compound I, in agreement with other techniques.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was used to examine the corrosion inhibition property of Schiff base compounds (I and II) on carbon steel, including surface properties, electrode kinetics and mechanistic information. The Nyquist plots of carbon steel obtained at open-circuit potential in 1 M HCl solution in the absence and presence of various concentrations of Schiff base derivatives (compounds I and II) are shown in the Fig. 9. It is obvious from the Nyquist plots that the electrochemical response of carbon steel samples appeared in the form of depressed semicircle capacitive loops, and this can be attributed to the formation of a protective capacitive layer at the metal–acid interface.



Fig. 9 Nyquist representation plots for carbon steel in 1 M HCl in the absence and presence of different concentrations of the inhibitors at 303 K: a compound I and b compound II

It can also be noted from Fig. 9 that the impedance diagrams are larger than in the blank solution upon the addition of inhibitors to the corrosive solution, and the size of the impedance diagram (*semicircle loops*) increases as the concentration rises; hence the protection efficiency increases due to the adsorption of inhibitor molecules to the metal surface [58]. However, higher impedance against corrosion reactions was obtained for compound II than compound I. The corrosion reaction at the metal substrate/solution interface is related to the charge transfer resistance that is indicated as a measure of electron transfer across the surface and is proportional to the rate of corrosion. It is generally accepted that the depressed semicircle in the Nyquist representation is attributable to the frequency dispersion as well as inhomogeneities, roughness of the metal surface, and mass transport process [59]. Consequently, pure double-layer capacitors are better described by a transfer function with constant phase elements (CPE) to compensate for non-ideal capacitive response of the interface and to obtain a more accurate fit of the experimental data set [60]. Its impedance function is given by [61]:

$$Z_{\rm CPE} = Y_0^{-1} (j\omega)^{-n}, \tag{16}$$

where Y_{o} is a proportional factor, ω is the angular frequency, and a deviation parameter $(-1 \le n \le +1)$ has the meaning of a phase shift. While n = 0, the CPE represents a pure resistor, for n = -1 an inductor and for n = +1 a pure capacitor. The values of the double-layer capacitance (*Q*) and inhibition efficiency ($\eta_{\rm E}$) are calculated as follows:

$$Q = Y_{\rm o} \left(\omega_m^n\right)^{n-1} \tag{17}$$

$$\eta_{\rm EIS}(\%) = \frac{R_{\rm Ct} - R_{\rm Ct}^{\rm o}}{R_{\rm Ct}} \times 100, \tag{18}$$

where ω_m^n is the angular frequency at the maximum value of the imaginary part of the impedance spectrum, and R_{ct}^o and R_{ct} are the charge transfer resistance in the absence and presence of Schiff base inhibitors, respectively.

The electrochemical equivalent circuit model used to verify technical details of impedance spectra is shown in Fig. 10, and consists of R_s solution resistance, R_{ct} charge transfer resistance and CPE constant phase elements for the double layer.

The important electrochemical impedance parameters are listed in Table 7. In Table 7, it is noted that R_{ct} values increased with inhibitor concentration while C_{dl} values decreased. The increase in charger transfer resistance values can be attributed to the adsorption of the Schiff base compounds at the metal–acid interface, which effectively blocked the movement of charges across the interface, and hence corrosion inhibition was accomplished. A large charge transfer resistance is associated with a slower-corroding system, and this fact was well confirmed by the decrease in C_{dl} values, which may be attributed to the increase in the thickness of the protective layer, decrease in local dielectric constant of the film, or the occurrence of both simultaneously. This may be further explained with the help of the well-known Helmholtz model, according to the following equation [62]:

Fig. 10 Electrochemical equivalent circuit used to fit the EIS data for carbon steel in 1 M HCl



 Table 7
 Electrochemical impedance parameters for the corrosion of carbon steel in the absence and presence of different concentrations of Schiff base derivatives at 303 K

Inhibitor	Conc. (ppm)	$R_{\rm s} (\Omega {\rm cm}^2)$	$Q (\mu \mathrm{Fcm}^{-2})$	n	$R_{\rm ct} (\Omega {\rm cm}^2)$	$C_{\rm dl} (\mu {\rm Fcm}^{-2})$	η _z (%)
1 M HCl	_	5.4	6142	0.82	56	293	_
Compound I	100	4.17	300	0.82	130	147	57
	300	2.69	120	0.82	509	65	88.9
	600	5.27	90	0.78	829	43	93.2
	900	8.1	80	0.74	977	34	94.3
	1200	12.1	78	0.58	990	12	94.3
Compound II	100	3.7	104	0.82	756	60	92.5
	300	9.8	84	0.82	1093	49	94.9
	600	6.1	66	0.82	1151	38	95.1
	900	6.3	59	0.62	1149	13	95.1
	1200	9.8	35	0.72	1421	11	96.0

$$C_{\rm dl} = \frac{\varepsilon_0 \varepsilon A}{d},\tag{19}$$

where ε_{o} is the permittivity of free space (8.854 × 10⁻¹⁴ F cm⁻¹), ε is the dielectric constant of the protective layer, *A* is the electrode area, and d is the thickness of the protective layer. Accordingly, the fractional replacement of water molecules by inhibitor molecules on the carbon steel surface may change these values, also leading to a decrease in the number of active sites.

In addition, the change in the interface surface condition of the carbon steel electrode could be effectively deduced from the variation in the value of the phase shift (*n*) that can be used as an indicator for prediction of the dissolution mechanism and is related to the heterogeneity or roughness of the surface [63]. Table 7 clearly shows that the values of the phase shift (*n*) did not vary significantly, thus confirming that the charge transfer controlled the dissolution mechanism of carbon steel in 1 M HCl without and with inhibitors. Upon addition of Schiff base derivatives in the corrosive solution, *n* values (ranging from 0.58 to 0.82) remain constant or decrease compared to those obtained in inhibitor-free 1 M HCl (0.82). This indicates that there is an increase in surface inhomogeneity as a result of inhibitor adsorption. Accordingly, ideal capacitor behaviour was not shown (n < 1), which may have resulted from the

irregular surfaces of the electrode or arbitrary distribution of current on the electrode surface, causing frequency dispersion [64, 65].

Surface morphological studies by SEM

The SEM micrographs of the carbon steel surface are shown in Fig. 11. The surface of carbon steel after immersion in uninhibited 1 M HCl for 48 h shows an aggressive attack of the corrosive medium, as illustrated in Fig. 11a. Moreover, the corrosion products appear very uneven, with cube-shaped morphology, and there is a roughness on the metal surface layer. On the other hand, as shown in Fig. 11b, in the presence of the inhibitors individually, much less damage is observed on the carbon steel surface, with a more compact and pronounced layer, in the presence of compound II. These results confirm the inhibitory ability with adsorbed film on the carbon steel surface, which does not exist in Fig. 11a. Accordingly, it may be concluded that the adsorption on film can efficiently retard the corrosion of carbon steel.

Corrosion inhibition mechanism

The inhibitory action of the synthesized Schiff base cationic surfactants (SBCS) on the corrosion of carbon steel is dependent on the extent of its adsorption on the metal surface. The adsorption of SBCS molecules on the metal surface can be attributed to the presence of loosely bound electrons, lone pairs of electrons, π electron clouds and aromatic (e.g., benzene) ring systems. As we know, most organic inhibitors possess at least one functional group, regarded as the reaction centre or anchoring group. The strength of adsorption depends on the charge on this anchoring group [rather on the hetero atom (i.e., atoms other than carbon, including nitrogen and sulphur) present in the anchoring group]. The structure of the rest of the molecule influences the charge density on the anchoring group [66].

On the other hand, iron has a coordination affinity for ligands possessing heteroatoms due to its empty *d*-orbitals. In general, the potential at which there is no charge on the metal is known as the zero-charge potential (ZCP) [67, 68]. The charge on a metal surface in a given medium can be determined from the corrosion potential (E_{corr}) and zero-charge potential. When the difference ($E_{corr} - ZCP$) is negative, the metal is negatively charged and adsorption of cations is favoured. When ($E_{corr} - ZCP$) is positive, the metal is positively charged and adsorption of anions is favoured. The ZCP of iron is -530 mV versus SCE in HCl. In the present system, the obtained value of E_{corr} in 1 M HCl was -605 mV versus SCE. The steel surface charges negative in 1 M HCl solution because the value of $E_{corr} - ZCP = 0 < 0$. Consequently, adsorption occurs as a result of electrostatic forces between the electric charge on the metal and the ionic charges or dipoles on the inhibitor molecules. Also, in an acid solution, owing to the presence of neutral atoms in the (SBCS) molecules, it may become protonated as follows:

$$SBCS + xH \leftrightarrow [SBCSH_x]^{x+}$$
 (20)



Fig. 11 SEM micrographs of carbon steel surfaces after immersion for 48 h: a uninhibited 1 M HCl, and in the presence of b Compound I and c Compound II

The proposed electrostatic interactions between the protonated inhibitor molecules and the negatively charged metal surface facilitate adsorption due to the synergy created between them. Moreover, the adsorption of the protonated molecules can also occur on the carbon steel surface by direct interaction of the unshared lone pairs of electrons on the *N* atom with the vacant *d*-orbitals of Fe, leading to the formation of metal inhibitor complexes with Fe²⁺ ions resulting from the anodic dissolution of steel, according to the following equations:

$$Fe \to Fe^{2+} + 2e^- \tag{21}$$

$$[SBCSH_x]^{x+} + Fe^{2+} \leftrightarrow [SBCSH_x - Fe]^{(x+2)+}$$
(22)

Accordingly, these complexes may adsorb onto the steel surface through the van der Waals force, enhancing the inhibition of corrosion.

Conclusions

On the basis of the experimental results in the present work, the following conclusions can be deduced:

- 1. The synthesized Schiff base compounds were found to be efficient corrosion inhibitors for carbon steel in 1 M HCl, and their adsorption followed the Langmuir adsorption model.
- 2. Polarization studies indicated that these compounds are mixed-type inhibitors affecting both cathodic hydrogen reduction reactions and anodic metal dissolution, and that corrosion efficiency increased with inhibitor concentration.
- 3. The adsorption of these inhibitors involves both physical and chemical processes based on the values of $(\Delta H_{ads}^{o} \text{ and } \Delta G_{ads}^{o})$.
- 4. The experimental data of the impedance diagrams (EIS) were fitted with one equivalent structure model.
- 5. The formation of a protective inhibitor film on the carbon steel surface after 48 h of immersion in the presence of optimum inhibitor concentration in 1 M HCl was confirmed by SEM studies.

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