The impact of naphthalimide derivative on the mitigation of mild steel corrosion in sulfamic acid medium: experimental and theoretical insights

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Abstract

The deterioration of iron-based alloys, especially mild steel (MS) is one amongst the most challenging problems faced in various chemical industries. The present work focuses on the potential activity of a naphthalimide derivative namely 2-(2-hydroxyethyl)benzo[de]isoquinoline-1,3-dione (HBIQ) as corrosion inhibitor for MS in sulfamic acid (SA) medium in the temperature range from 303 to 323 K. Potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) were employed in the experimental measurement and HBIQ exhibited 89% inhibition at its optimum concentration. HBIQ demonstrated electrostatic interactions with MS surface and behaved as a mixed type of inhibitor by obeying Langmuir's isotherm model. Surface characterization of uninhibited and inhibited MS specimens combined with elemental analysis data provided clear evidences for the formation of a protective adsorption layer of HBIQ on MS surface. Spectral analysis such as Ultraviolet visible and Fourier Transform Infra-red spectral analyses were carried out in order to confirm the adsorption of HBIQ on to the metal surface. The density functional theory calculations supported the experimental results and indicated the contribution of delocalized π -electrons in the naphthalimide unit and the lone-pair electrons of oxygen in the carbonyl and hydroxyl group for improved adsorption of HBIQ onto MS surface, thereby reducing the corrosion of the alloy in SA environment.

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Graphic abstract

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List of symbols

IE	Inhibition efficiency (%)
CR	Corrosion rate (mmpy)
i_{corr}	Corrosion current density (mA cm^{-2})
E_{corr}	Corrosion potential (V/SCE)
β_c	Cathodic slope (mV dec^{-1})
T	Temperature (K)
β_a	Anodic slope (mV dec^{-1})
E_a	Energy of activation (kJ/mol)
$\Delta H^\#$	Enthalpy of activation (kJ/mol)
$\Delta S^\#$	Entropy of activation ($\text{J mol}^{-1} \text{K}^{-1}$)
R_{ct}	Charge transfer resistance (ohm cm^2)
C_{dl}	Double layer capacitance ($\mu\text{F cm}^{-2}$)
$\Delta G^\circ_{\text{ads}}$	Change in free energy (KJ mol^{-1})

Introduction

Among the iron-based alloys, mild steel (MS) has drawn significant attention due to not only its higher mechanical strength, ductility, machinability and weldability compared to other alloys, but also easy availability and exceptionally low cost (Ahmed et al. 2019). Wide usage of MS is observed in various construction systems, gas storage tanks, pipelines for oil and gas distribution, heat exchangers, boilers and engineering machineries (Shukla and Ebenso 2011).

However, the alloy can undergo electrochemical oxidation on interaction with the environment resulting in adverse effects on its properties, which can later weaken the equipment. Hence, protection of MS and thereby conservation of economic resources in technology has gained wide attention. In most of the chemical industries, the deposition of scale on the metal surface of heat exchangers, evaporators and boilers, considerably reduces the rate of heat transfer, lowering the efficiency of the equipment. Thus, in order to ensure and maintain trouble-free functioning of these plants, descaling is essential. Different acid solutions are largely employed for the removal of unwanted scale and deposits from the metal surface, which causes metal dissolution. The destruction of MS in acid environment needs to be addressed as huge amount of material loss occurs due to acid wash every year worldwide.

Among the commercially available acids, Sulfamic acid (SA) or mono amido sulfuric acid ($\text{H}_2\text{NSO}_3\text{H}$) is one of the most frequently used acid for pickling, cleaning and descaling process (Fouda and Ibrahim 2018; Morad 2008). Though SA is a stable solid compound, it can easily undergo hydrolysis in aqueous solutions resulting in the formation of sulfamate of ammonium and ammonium hydrogen sulfate (Motamedi et al. 2014). The SA features many attractive properties including non-volatile, non-hygroscopic, odorless, stable and ability to act as strong acid in aqueous

solution with significantly less corrosion to the metals exposed. These unique characteristics allow its usage in many chemical industries for dissolving hard iron oxide and variety of water-formed scales and deposits from the metal surface without any causing any chloride-induced stress corrosion cracking (SCC) (Fouda et al. 2014). It is widely used as a cleaning agent in a variety of industrial applications including cooling tower systems, desalination plants, heat exchangers and flash evaporators. Moreover, SA is extensively used in sugar industry for scale removal, because it is non-toxic and easily solubilizes hard scales without promoting pitting corrosion. But, tremendous metal loss occurs during such descaling processes (Motamedi et al. 2013). Hence, the addition of corrosion inhibitors to the corrosive medium is one of the most effective means to combat MS corrosion and thereby conserve the alloy.

The ability of an organic molecule to inhibit the metal deterioration mainly depends on its structural framework, the interaction with the metal surface, the mode of adsorption and the corrosive medium. Moreover, there are various conditions that aid in the selection of a suitable inhibitor substance including the cost and amount of the inhibitor required, ability to treat the corroded surfaces, stability in the environments and long-term toxicological effects on the environment. Though there are numerous organic molecules reported as potential inhibitors for MS, to the best of our knowledge, there are no literature evidences on heterocyclic 1,8-naphthalimide derivatives investigated for their potential to mitigate MS corrosion. Naphthalimides are one of the important classes of polycyclic imides consisting of a flat structure with hetero aromatic system. The widespread biological applications of naphthalimide and their derivative products including antitumor activity against both murine and human tumor cells (kamal et al. 2002) antitrypanosomal (Muth et al. 2007) antiviral (Clark et al. 1993), local anesthetics (Berque-Bestel et al. 2003), analgesic (Duke et al. 2010) and many more makes them potential class of organic compounds. Furthermore, naphthalimide derivatives have also been used as optical brighteners (Dorlars et al. 1975), sensors (Wolfbeis 2005), fluorescent probes (Xu et al. 2010), etc.

There are only a few reports available on the use of corrosion inhibitors for MS in SA medium (Fouda and Ibrahim 2018; Morad 2008; Fouda et al. 2014; Motamedi et al. 2011; Motamedi et al. 2013, Motamedi et al., 2014); Abd El Rehim et al. 2016; Abdel-Fatah et al. 2016; Abdel-Fatah et al. 2017; Quraishi and Jamal 2001). 1,8-Naphthalimide derivatives can be easily prepared by imidation of 1,8-naphthalic anhydrides with suitable amines, to achieve various functionalized derivatives of imide nitrogen. In this study, 2-(2-hydroxyethyl)benzo[de] isoquinoline-1,3-dione (HBIQ) that carry hetero atoms like N and O as well as conjugated π -electrons was prepared to probe the inhibition of MS

corrosion in 1 M SA medium through electrochemical approaches. The activation and thermodynamic parameters of the corrosion inhibition process, surface characterization and spectroscopic investigations were performed to arrive at the mechanism of corrosion inhibition using HBIQ. In addition, the quantum chemical calculations were performed to give basic insights into the mode of HBIQ action, as well as to validate the experimental results.

Experimental

Material, medium and inhibitor preparation

Test coupons of MS with composition (%weight) of Fe (98.51), C (0.432), Si (0.187), Mn (0.77), P (0.0085), S (0.011), Cr (0.011), Ni (0.0063), Mo (0.019), Al (0.039) and Cu (0.0015) were employed for the present study. Acenaphthene was oxidized in presence of potassium dichromate in glacial acetic acid and the formed 1,8-naphthalic anhydride product was allowed to undergo imidation using ethanalamine to obtain HBIQ (Huang et al. 2019) which was characterized by Infrared spectrophotometry (Schimadzu FTIR 8400S Spectrophotometer). The synthetic method for the preparation of HBIQ is presented in Supplementary Figure (SF.1), respectively.

2-(2-Hydroxyethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (HBIQ): Off white solid; yield: 78%; m.p.: 178–180 °C; FT-IR (cm^{-1}): 3473, 2961, 2873, 1695, 1684, 1622 (SF.2); ^1H NMR (400 MHz, DMSO- d_6 , ppm): 3.606–3.654 (q, 2H, CH_2), 4.149–4.182 (t, 2H, CH_2), 4.804–4.834 (t, OH), 7.860–8.513 (6. Ar.H) (SF.3); MS of $\text{C}_{14}\text{H}_{11}\text{NO}_3$: 241 (SF.4).

The corrosive electrolyte (sulfamic acid) of 1 M concentration was prepared by dissolving 97.5 g SA in 1000 mL of double distilled water.

Electrochemical measurements

CH Instrument (USA Model 604D) with conventional three-electrode thermostated cell assembly was used to carry out the electrochemical measurements. A Hg-Hg $_2$ Cl $_2$ (calomel) was used as reference electrode, platinum as counter electrode and MS coupons as working electrode. Prior to each test, the MS test coupon was dipped in SA solution and steady-state open-circuit potential (OCP) was allowed to establish at the end of 30 min. In EIS technique, small amplitude ac signal of 10 mV was applied to the electrochemical system in the frequency range of 10 kHz to 0.01 Hz at the OCP, and the response to the input signal was recorded in the form of Nyquist plots. In PP method the potential of the MS specimen was ramped ± 0.25 V with respect to OCP and the anodic and cathodic curves were obtained at a scan

rate of 1 mVS^{-1} . The corrosion current density (i_{corr}) values were calculated by the extrapolation of the anodic and cathodic slopes in the presence and absence of HBIQ, which were further used to calculate corrosion rate (CR), surface coverage (θ) and inhibition efficiency (IE).

Computational study

Gaussian maestro material science software with the basic set (B3LYP) and 631 +G was used to acquire the DFT calculations. The optimized structure of HBIQ molecule with HOMO and LUMO levels were obtained by 2D and 3D molecule builders. The energies of the highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) molecular orbitals were then used to evaluate other quantum chemical parameters.

Spectral analysis of HBIQ adsorption

Ultraviolet–Visible (UV/Vis) spectral studies

Shimadzu 1800 UV-Visible spectrophotometer was used to record the UV/visible spectra of 1 M SA containing HBIQ ($1 \times 10^{-4} \text{ M}$). The absorption spectrum of the same solution was further recorded after immersing MS specimen for 3 h.

Fourier transform Infra-red spectral analyses

Shimadzu IR spirit spectrophotometer was used to record the FTIR spectrum of HBIQ molecule and the scraped out product of the adsorbed protective layer formed on the MS surface exposed to $7.5 \times 10^{-4} \text{ M}$ HBIQ in 1 M SA acid solution.

Surface characterization

Freshly polished MS metal coupons were introduced in 1 M SA solution in the absence and presence of HBIQ to carry out surface morphological studies using JEOL JSM–6380L scanning electron microscope (SEM) and 1B342 Innova atomic force microscope (AFM).

Results and discussion

Potentiodynamic polarization (PP) method

The influence of different concentrations of HBIQ on MS corrosion inhibition was monitored by PP technique. Tafel plots of MS in 1 M SA solution, both in the absence and the presence of HBIQ, are shown in Fig. 1a. The parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic (β_c) and anodic Tafel slope (β_a) were obtained from the plot. The i_{corr} values were then used to calculate the corrosion rate (CR) and inhibition efficiency (IE) using Eqs. 1 and 2, respectively, and are presented in Table 1

$$\text{CR}(\text{mmY}^{-1}) = \frac{3270 \times \text{EW} \times i_{\text{corr}}}{d} \quad (1)$$

where 3270 is a constant that defines the unit for the CR, d expressed in g/cm^3 and EW are the density and the equivalent weight of corroding metal, respectively (Kumari et al. 2017a, b; Kumari et al. 2020a, b)

Fig. 1 **a** Tafel plots for the corrosion of MS in 1 M SA at 313 K in the absence and presence of HBIQ and **b** the 3D plots for the variation of %IE with varying concentrations of HBIQ at different temperatures

Table 1 Results of PP experiments for the corrosion of MS in 1 M SA in the absence and presence of HBIQ at different temperatures

Temp (K)	Conc. Of HBIQ (M)	E_{corr} (V/ SCE)	$-\beta_c$ (mV dec $^{-1}$)	β_a (mV dec $^{-1}$)	i_{corr} ($\times 10^{-3}$ mA cm $^{-2}$)	CR (mpy)	% IE
303	0	−0.535	52.86	49.74	4.724	1095	–
	1×10^{-4}	−0.524	53.41	55.96	2.555	592.4	45.91
	1.5×10^{-4}	−0.507	78.67	62.65	1.711	396.7	63.78
	2.5×10^{-4}	−0.511	67.13	79.97	1.300	290.4	72.48
	5×10^{-4}	−0.518	68.15	80.64	0.621	144.1	85.0
	7.5×10^{-4}	−0.518	72.32	89.03	0.459	89.36	89.0
313	0	−0.523	51.22	49.68	5.963	1382	–
	1×10^{-4}	−0.514	52.31	54.95	3.902	927.1	34.56
	1.5×10^{-4}	−0.499	57.31	61.44	2.925	566.6	50.54
	2.5×10^{-4}	−0.510	56.36	66.12	2.112	512.9	62.90
	5×10^{-4}	−0.510	61.31	66.94	1.778	412.2	70.18
	7.5×10^{-4}	−0.512	69.32	88.43	0.668	155.2	88.7
323	0	−0.523	55.04	50.63	7.452	1728	–
	1×10^{-4}	−0.526	53.08	50.61	5.750	1371	22.83
	1.5×10^{-4}	−0.509	51.38	54.46	4.911	1139	34.09
	2.5×10^{-4}	−0.513	54.71	58.33	3.421	920	55.30
	5×10^{-4}	−0.503	56.49	63.34	2.974	553.9	60.00
	7.5×10^{-4}	−0.503	61.76	77.35	1.577	365.5	78.83

$$\text{IE}(\%) = \frac{i_{\text{corr}} - i_{\text{corr(inh)}}}{i_{\text{corr}}} \times 100 \quad (2)$$

where, i_{corr} and $i_{\text{corr(inh)}}$ signify the current density values for the corrosion process in the absence and presence of HBIQ, respectively (Yadav et al. 2016).

Tafel plots confirmed that the addition of HBIQ to SA solution leads to a substantial reduction in the CR, i.e., shifts the cathodic and anodic current curves toward the lower current densities. HBIQ exerted a concentration-dependent IE with a maximum of 89% at 7.5×10^{-4} M. The decrease in i_{corr} and CR values with increase in HBIQ concentration indicated the role of HBIQ in delaying the anodic and cathodic reactions that occur during the course of acid corrosion. Further, the increase in IE is essentially attributed to the formation of protective HBIQ passive films on the MS surface, thereby blocking the cathodic and anodic reaction sites (Kumari et al. 2015). Thus, the HBIQ molecules adsorbed on to the reactive sites of the metal surface play an important role in reducing the corrosion process. It is also observed that both cathodic (β_c) and anodic (β_a) Tafel lines are parallel and there is no significant variation in the slope values in the inhibited solution compared to uninhibited. This suggested that the corrosion inhibition is through simple adsorption without affecting the inhibition mechanism (Li et al. 2007).

Further, the effect of temperature on the i_{corr} , CR and IE was investigated. The i_{corr} and CR values increased with increase in temperature in the absence of HBIQ owing to the increase in the conductance of SA medium resulting

in increased hydrogen evolution reaction at the cathodic region (Wang et al. 2010). However, the addition of HBIQ to the medium showed not only a remarkable decrease in i_{corr} and CR values, but also increase in the IE values at each temperature. However, for a specific concentration of HBIQ, the % IE decreased with increase in temperature. At lower temperature, the adsorption of HBIQ completely shielded the MS surface, thereby exhibiting good IE, whereas at higher temperature the % IE slightly decreased. This behavior is attributed to the desorption of adsorbed HBIQ molecules from the MS surface, further exposing the fresh surface to the corrosive medium (Pinto et al. 2011). The variation of % IE with varying concentrations of HBIQ at various temperatures is presented in Fig. 1b.

The influence of temperature on the corrosion rate is also one of the most important factors that affects the kinetic parameters such as energy of activation (E_a), enthalpy of activation ($\Delta H^\ddagger$), and entropy of activation ($\Delta S^\ddagger$). E_a was calculated using Arrhenius Eq. 3 (Kumari et al. 2020a, b).

$$\ln(\text{CR}) = B - \frac{E_a}{RT} \quad (3)$$

where R is the gas constant in kJmol $^{-1}$ and T is the temperature in Kelvin. The Arrhenius plot for the corrosion of mild steel at different concentration of HBIQ in 1 M SA is shown in Fig. 2a. The slope of the straight line plots gives

Fig. 2 **a** Arrhenius plot, **b** Plots of $\ln (CR/T)$ versus $1/T$ for corrosion MS in 1 M SA at different concentration of HBIQ

Table 2 Activation parameters for the corrosion of MS in 1 M SA having different inhibitor concentration

Conc. of HBIQ (M)	E_a (kJmol ⁻¹)	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)
0	18.59	15.96	-164.7
1×10^{-4}	34.15	31.55	-118.3
1.5×10^{-4}	42.75	40.15	-93.81
2.5×10^{-4}	46.96	44.29	-82.31
5×10^{-4}	55.09	52.49	-60.03
7.5×10^{-4}	57.16	54.56	-58.62

$(-E_a/R)$, from which E_a was calculated. The obtained E_a values along with the enthalpy and entropy of activation values are listed in Table 2.

The E_a values increased with rise in HBIQ concentration, which suggested that at larger HBIQ concentration, the corrosion reaction will be pushed to the surface sites with higher E_a values. This indicated the formation of a barrier layer through the inhibitor adsorption on the MS surface, which can hinder metal dissolution process. The larger values of E_a compared to the blank also pointed towards the reduced adsorption tendency of HBIQ with rise in temperature leading to the electrostatic interaction between the MS surface and HBIQ molecules (Rbaa et al 2020).

The entropy ($\Delta S^\ddagger$) and enthalpy ($\Delta H^\ddagger$) of activation for dissolution of metal was determined using the transition state Eq. 4 (Kumari et al. 2014)

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^\ddagger}{RT}\right) \exp\left(\frac{-\Delta H^\ddagger}{RT}\right) \quad (4)$$

where h is Planck's constant and N is Avogadro's number. The plot of $\ln (CR/T)$ versus $1/T$ for MS in 1 M

SA in different concentrations of HBIQ (Fig. 2b) with slope = $\Delta H^\ddagger/R$ and intercept = $\ln (R/Nh) + (\Delta S^\ddagger/R)$ was used to calculate changes in entropy ($\Delta S^\ddagger$) and enthalpy ($\Delta H^\ddagger$). The $\Delta S^\ddagger$ values were found to be large and negative, which suggested towards increased order in the system when the reactants were associated to form activated complex in the rate determining step (Fouda et al.2017).

Electrochemical impedance spectroscopy (EIS)

EIS technique provides not only more insight into the corrosion mechanism, but also kinetic evidence for the electrochemical system under investigation. The Nyquist plots obtained for the corrosion of MS in 1 M SA at 303 K is displayed in Fig. 3a. Similar plots were attained at 313 and 323 K also. The shape of the Nyquist plots remained the same, both in the absence and presence of HBIQ, which indicated that its presence increases the impedance towards corrosion process without affecting any other aspects of the corrosion behavior (Khaled 2008). The Nyquist plots contained a single depressed semicircle loop at the high frequency region with a remarkable deviation from an ideal semicircle. The depressed feature is due to the surface inhomogeneity that arises when the corrosion product is deposited on the MS surface (Charita and Rao 2017). The electrical capacity is decreased due to the adsorption of the HBIQ molecules by replacing the initially adsorbed water molecules from the metal surface. This change widens the diameter of the capacitive loop with increase in the HBIQ concentration, which pointed towards the increased resistance of the metal towards the charge transfer process (Amin et al. 2007). This can be ascribed to the formation of protective film of HBIQ on the MS surface that creates a barrier for mass and charge-transfer.

Fig. 3 **a** Nyquist plot of MS in 1 M SA at different concentrations of HBIQ at 303 K, **b** Equivalent circuit used to analyze the impedance data, and **c** Bode plots MS in 1 M SA at different concentrations of HBIQ at 303 K

In order to evaluate the mathematical simulations of the impedance plot, the Nyquist plots were fitted with the equivalent circuit. A simple Randle's equivalent circuit (RQR) as shown in Fig. 3b was used to analyze the data. The circuit composed of two resistances R_s and R_{ct} offered by the solution and charge transfer process, respectively, and one constant phase element (Q). The results are presented in Table 3.

From Table 3 it is found that R_{ct} values increased with increase in HBIQ concentration, which indicated that charge transfer process mainly controls the corrosion process. The HBIQ molecules adsorbed on to the metal surface form a protective layer and decrease the corrosion process. The R_{ct} values were further used to calculate the percentage inhibition efficiency using Eq. 5, (Ahmed et al. 2018)

$$\%IE = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \quad (5)$$

where R_{ct} and $R_{ct(inh)}$ represent the resistance of polarization for the uninhibited and inhibited solutions, respectively. The constant phase element, Q was introduced in the circuit instead of a pure double layer capacitor to provide more accurate fit for Nyquist plot. The Q impedance (Z_Q) was calculated using Eq. 6, (Kumari et al 2017a, b).

$$Z_Q = Q^{-1} (i\omega_{max})^{-n} \quad (6)$$

where, Q is the proportionality coefficient, ω_{max} is the angular frequency, i is the imaginary number and n is the exponent related to the phase shift. The values of phase shift

Table 3 Results of EIS measurements in 1 M SA at different concentrations of HBIQ at different temperature for corrosion of MS

Temp (K)	Conc. of HBIQ (M)	R_{ct} (ohm cm ²)	chi-squared values	C_{dl} (μF cm ⁻²)	% IE
303	0	10.20	9.093×10^{-4}	10,634	—
	1×10^{-4}	18.18	2.300×10^{-4}	1221	43.89
	1.5×10^{-4}	30.5	4.794×10^{-4}	491.1	66.56
	2.5×10^{-4}	42.11	5.155×10^{-4}	254.8	75.78
	5×10^{-4}	69.3	5.064×10^{-4}	104.2	85.28
	7.5×10^{-4}	97.29	3.809×10^{-4}	62.92	89.52
313	0	6.2	9.011×10^{-4}	23,980	—
	1×10^{-4}	8.97	8.842×10^{-4}	6204	30.88
	1.5×10^{-4}	12.66	3.284×10^{-4}	2507	51.03
	2.5×10^{-4}	19.29	9.722×10^{-4}	1150	67.83
	5×10^{-4}	23.92	3.162×10^{-4}	731.9	74.08
	7.5×10^{-4}	42.93	3.284×10^{-4}	231.2	85.56
323	0	3.50	7.669×10^{-4}	80,666	—
	1×10^{-4}	4.56	9.328×10^{-4}	26,394	23.25
	1.5×10^{-4}	5.51	2.987×10^{-4}	12,548	36.48
	2.5×10^{-4}	8.10	3.862×10^{-4}	5444	56.79
	5×10^{-4}	11.15	1.043×10^{-4}	3249	68.61
	7.5×10^{-4}	20.75	9.619×10^{-5}	1016	83.13

(n) lies between 0 and 1 ($0 \leq n \leq 1$). If $n = 1$, then Q behaves as ideal capacitive behavior. The correction in the capacitance to its real value (C_{dl}) was calculated using Eq. 7 (El-Haddad and Elattar 2015).

$$C_{dl} = \frac{1}{2\pi f_{\max} R_{ct}} \quad (7)$$

where $f_{\max}$ is the frequency at which the imaginary constituent of impedance is maximum. C_{dl} decreased with increase in HBIQ concentration. The capacitance values are inversely proportional to the thickness of the electrical double layer formed at the metal solution interface. The thickness of the double layer increased due to the adsorption of larger inhibitor molecules by replacing the initially adsorbed water molecules from the metal surface (Lebrini et al. 2011).

The Bode plots for the corrosion MS in 1 M SA solution are shown in Fig. 3c. The plots phase angle versus frequency shows one peak measured at the absence of HBIQ maximum at around -10° , further the subsequent peaks moved slightly to lower frequencies and increased the maximum phase angle with increase in the HBIQ concentration, up to around -50° . The plots modulus of impedance $|Z|$ versus frequency displayed the presence of two plateaus: one at high frequency and the other at low frequency, and one negative slope along the spectra that was associated with the semicircles shown in the Nyquist plot. The plateaus observed at high frequency are related to the solution resistance of the system, R_s and that of low frequency plateaus are associated to the charge transfer resistance (Bhuvneshvari et al. 2020). Moreover, the shapes of the Nyquist and Bode plots are similar in the absence and presence of inhibitor, which indicated that HBIQ does not influence on the corrosion mechanism.

Adsorption isotherm

Generally, there are three possible ways of adsorption of inhibitor molecules on to the metal surface; physisorption, chemisorption and mixed adsorption. The adsorption phenomenon of any inhibitor can be defined by studying the adsorption isotherms. For HBIQ, various adsorption isotherm models such as Frumkin, Temkin, Freundlich and Langmuir were attempted to fit the values of surface coverage (θ), which was calculated using Eq. 8 (Al-Azawi, et al. 2018).

$$\theta = \%IE/100 \quad (8)$$

The plots of C_{inh}/θ versus C_{inh} depicted in Fig. 4 showed a straight line with slope and correlation coefficient R^2 values nearly equal to one, which specified that the adsorption of HBIQ on to the MS surface obeyed Langmuir's isotherm model (Boudjellal et al 2020) as given by Eq. 9.

Fig. 4 Langmuir adsorption isotherm for mild steel in 1 M SA using different inhibitor concentration

Table 4 Thermodynamic parameters for adsorption of HBIQ on MS in 1 M SA at different temperature

Temp (K)	K_{ads} (M^{-1})	Slope	R^2	ΔG°_{ads} ($KJ\ mol^{-1}$)
303	5444.3	0.978	0.989	-32.83
313	3181.5	0.973	0.993	-32.44
323	9730.2	0.980	0.999	-33.25

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \quad (9)$$

where, K and C_{inh} represent the adsorptive equilibrium constant and the concentration of inhibitor, respectively. The K_{ads} values are related to standard free energy of adsorption (ΔG°_{ads}) as given by Eq. 10 and recorded in Table 4.

$$K = \frac{1}{55.5} \exp \left(\frac{-\Delta G^\circ_{ads}}{RT} \right) \quad (10)$$

where T , R , ΔG°_{ads} and 55.5 represent the absolute temperature, the universal gas constant, free energy of adsorption and the concentration of water in solution in $mol\ dm^{-3}$, respectively (Mistry and Jauhari 2013). Generally, if ΔG°_{ads} values are less negative than $-20\ kJ\ mol^{-1}$, then physical adsorption is favored between the charged inhibitor molecule and charged metal surface, whereas chemical adsorption occurs if the ΔG°_{ads} values are more negative than $-40\ kJ\ mol^{-1}$ (Saliyan and Adhikari 2008). The ΔG°_{ads} values for HBIQ in 1 M SA solution at the three studied temperatures were found to be between -20 and $-40\ kJ\ mol^{-1}$, which indicated mixed adsorption mode,

with predominant physisorption? (Mistry and Jauhari 2015). The HBIQ molecules could be directly adsorbed on the MS surface through the electrostatic interactions between the negatively charged metal surface and the protonated HBIQ molecules. Besides, the adsorption of the HBIQ molecules through donor acceptor interactions between free electron pairs of N, O atoms and π electrons of multiple bonds and vacant d orbitals of iron are also possible.

Corrosion inhibition mechanism

The corrosion mechanism is a surface phenomenon that depends on various factors like molecular size of inhibitor, charge density and number of active sites on metal surface (Martinez and Stern 2002). The interaction between metal and inhibitor plays a very important role in protecting metal from corrosion. The HBIQ molecules get adsorbed on to the MS surface to reduce the corrosion rate. As the thermodynamic parameters revealed mixed type of adsorption mode, HBIQ molecules can interact either through electron transfer or by electrostatic interaction with the MS surface (Abdallah et al 2018; Abdel-Fatah et al. 2017).

The electrostatic interaction can take place through the following steps; (i) in SA medium the MS surface attains positive charge due to its dissolution, (ii) the sulfamate ions (H_2NSO_3^-) formed are attracted towards the positively charged MS surface to form an electrical double layer and (iii) the double layer then favors the adsorption of protonated HBIQ molecules from the acidic solution through electrostatic interaction to form a protective film. Similarly, HBIQ molecules can also get adsorbed by donor acceptor

interactions. The unshared electrons pairs of the heteroatoms and double bonds of HBIQ can form a chemical bond with the empty d-orbitals of the iron atom on MS surface leading to chemisorption (Popova et al 2003). The schematic representation for the electron pair transfer and electrostatic interaction is shown in Fig. 5.

Theoretical calculations using DFT

Studies using density functional theories can be applied to corrosion systems to acquire more information on various factors such as frontier molecular orbital electron density and charge distribution, which can be co-related to the adsorption tendency and inhibition efficiency of organic molecules. The computational studies provide theoretical framework for effective inhibition mechanism depending on the structure of inhibitor molecule and predict its adsorption mechanism on the metal surface. Frontier orbital theory (MOT) is very useful for predicting the adsorption capacity of an inhibitor molecule. The optimized structure, HOMO, LUMO, and Mulliken charges on HBIQ are depicted in Fig. 6. The geometry of inhibitor structure was fully optimized and the electronic parameters such as highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) molecular orbitals energies and the energy gap between them (ΔE) were obtained. These values were used to compute other quantum chemical parameters which enable to relate the effect of structure of molecule on the inhibition activity (Aoufir et al. 2017).

The high E_{HOMO} values represent greater electron contribution capabilities of HBIQ to the d-orbitals of Fe in MS, whereas the low E_{LUMO} values denote stronger electron acceptance tendencies from the metal (Obot et al 2015; Sastri and Perumareddi 1997). Thus high HOMO and low LUMO values enabled adsorption of HBIQ on to the metal surface (Sneha et al 2020). ΔE value was low in case of HBIQ, which suggested its highly reactive

Fig. 5 Schematic representation of **a** physical and **b** chemical mode of adsorption for the HBIQ molecule on the MS surface

Fig. 6 **a** Optimized geometry **b** Mulliken charges, **c** HOMO and **d** LUMO levels of HBIQ

tendency (Wang et al. 2007). The ionization potential (I) value, which is the amount of energy required to remove an electron from a molecule (Obot et al. 2015) is related to energies of molecular orbitals according to the Koopmans theorem and is obtained from $I = -E_{\text{LUMO}}$. The low I value of HBIQ suggested easy removal of electron and hence high inhibition efficiency (Pearson 1986).

The other quantum chemical parameters could be used to describe the reactivity of HBIQ molecule such as absolute electronegativity (χ), chemical hardness (η), softness (σ), and the fraction of electron transfer (ΔN) calculated by applying Eqs. 11–14, respectively, and are presented in Table 5 together with Mulliken charges on the HBIQ (Abd El Rehim. et al. 2001)

$$\chi = \frac{1}{2}(I + A) \quad (11)$$

$$\eta = \frac{1}{2}(I - A) \quad (12)$$

$$\sigma = \frac{1}{\eta} \quad (13)$$

$$\Delta N = \frac{\phi_{\text{Fe}} - \chi_{\text{inh}}}{2\eta_{\text{inh}}} \quad (14)$$

where ϕ values indicates the work function. Chemical hardness and softness parameters are related to the description of the hard and soft acid/base as per the acid–base theory. A hard molecule has the least tendency to react, while a soft molecule has high tendency to react and hence soft molecules are expected to have the highest inhibition efficiency (Kikalj 2010). The tendency of the inhibitor molecule to donate the electrons to the metal surface is described based

Table 5 DFT parameters and Mulliken charges on the atoms of HBIQ

DFT parameters		Mulliken charges on atom			
Property	Value	Atoms	Mulliken charges	Atoms	Mulliken charge
E_{HOMO}	−6.5198 eV	C1	−0.0604	C10	0.0005
E_{LUMO}	−2.4509 eV	C2	−0.1029	C11	0.5849
Band gap (E_g)	4.0689 eV	C3	−0.0833	N12	−0.5548
Ionization potential (I)	6.5198	C4	0.0708	C13	0.5848
Electron affinity (A)	2.4509	C5	−0.1391	O14	−0.5020
Electronegativity (χ)	4.4853	C6	0.0015	O15	−0.5014
Global hardness (η)	2.0345	C7	−0.0830	C16	−0.0607
Global softness (σ)	0.4915	C8	−0.1030	C17	0.0585
Fractions of electron transferred (ΔN)	0.0822	C9	−0.0605	O18	−0.5411

Bold values indicate the hetero atoms with more negative Mulliken charge

on the fraction of electron transferred (ΔN). The ΔN value of HBIQ being 0.0822 ($\Delta N > 0$), clearly suggested that the electron transfer occurs from the inhibitor to the metal surface (Kovačević and Kokalj 2011).

Mulliken charges on the atoms play vital role in predicting the adsorption spots of the inhibitor molecule and also the electron accepting and donating tendency between the metal surface and the inhibitor. It is reported (Gao and Liang 2007) that the hetero atoms with more negative Mulliken charge are considered as active sites for the adsorption process. As depicted in Table 5, the oxygen (O14, O15 and O18) and nitrogen (N12) atoms with more negative charge are found to be effective adsorption sites for the HBIQ molecule, thus preventing the corrosion of MS in SA solution.

Spectral analysis of inhibitor adsorption

UV-visible spectra were used to study the adsorption of HBIQ molecules on the metal surface as presented in Fig. 7a. Initially, absorption spectrum of 1 M SA containing 1×10^{-4} M HBIQ was recorded at room temperature, which displayed bands at 237, 265 and 340 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Later the absorption spectrum of the test solution containing the same concentration of HBIQ in 1 M SA was recorded after immersing MS coupon for about 1 h. The spectrum showed a comparatively reduced absorption intensity, confirming the adsorption of some HBIQ molecules on MS surface.

FTIR measurements support in functional group identification and offer a qualitative idea about the adsorption of inhibitor molecules on the metal surface. FTIR spectra of HBIQ alone and the protective layer scraped out from the surface of MS specimen exposed to 7.5×10^{-4} M HBIQ in 1 M SA solution are depicted in Fig. 7b. A shift in the

OH absorption was observed from 3473 cm^{-1} of inhibitor to 3478 cm^{-1} of corroded product. In addition, the aliphatic and aromatic C-H stretching absorptions detected at 2873 cm^{-1} and 3067 cm^{-1} in the inhibitor were displaced to 2877 cm^{-1} and 3174 cm^{-1} in the corrosion product. These shifts in the IR frequencies of the functional groups present in inhibitor before and after adsorption to MS might be due to the metal–inhibitor interactions through functional groups.

Surface morphology studies

Scanning electron microscopy (SEM), atomic force microscopy (AFM) and elemental analysis

MS specimen was immersed in 1 M SA medium for 3 h in the absence and presence of inhibitor for surface topography analysis and the respective SEM and AFM images are depicted in Fig. 8. The uninhibited specimen (Fig. 8a) showed uneven surface with large number of pits due to the metal dissolution and deposition of corrosion product. However, the SEM image obtained in the presence of HBIQ inhibitor (Fig. 8b) displayed a smooth surface without any pits and cracks. This is due to the formation of protective layer of HBIQ on the metal surface, which could adsorb on almost all the pits and cavities, thereby reducing the corrosion rate. The three-dimensional AFM image (Fig. 8d) of specimen exposed to HBIQ in 1 M SA exhibited a smooth metal surface, when compared to that introduced in acid medium alone (Fig. 8c). The decrease in average surface roughness (R_a) and root-mean-square roughness (R_q) in the presence of inhibited solution when compared to uninhibited confirm the adsorption of HBIQ on to the metal surface. The R_a and R_q values are given in the table presented in Fig. 8.

Fig. 7 **a** Overlay of absorption spectra of 1×10^{-4} M HBIQ solution without and with MS coupon immersed in 1 M SA solution and **b** Overlay of the IR spectra of HBIQ and adsorption product formed on MS in 7.5×10^{-4} M HBIQ in 1 M SA solution

Fig. 8 SEM images of MS material **a** immersed in 1 M SA **b** immersed in 1 M SA + HBIQ. AFM image of MS material **c** immersed in 1 M SA **d** immersed in 1 M SA + HBIQ. The table

represents surface roughness values in the absence and presence of HBIQ. EDX spectrum of MS surface **e** immersed in 1 M SA **f** immersed in 1 M SA + HBIQ

The EDX profile of MS surface after its immersion in 1 M SA solution along with atomic percentage of the elements in the absence and presence of HBIQ is depicted in Fig. 8e and f correspondingly. From the data table it can be observed that for the corroded sample the percentage of sulfur, nitrogen and oxygen is 0.23, 0.35 and 7.85%, respectively, which confirms the adsorption of sulfamate ions (H_2NSO_3^-) from the acid solution on to the metal surface. Further, the increase in the carbon percentage (3.47–6.24) and decrease in the oxygen percentage (17.85–5.38) in the presence of HBIQ endorse its adsorption on to the MS surface.

Conclusions

A naphthalimide derivative HBIQ was prepared by easy synthetic protocol from acenaphthene and following inferences are drawn from the various investigations performed to study its corrosion inhibition capability.

- Potentiodynamic studies validated HBIQ as a mixed-type corrosion inhibitor for mild steel corrosion in 1 M Sulfamic acid, and exhibited a concentration-dependent rise in the inhibition efficiency.
- HBIQ molecules adsorbed on to the metal surface, obeying Langmuir isotherm to form a protective film that hinders the metal corrosion.

- Activation energy and thermodynamic parameters established physisorption of HBIQ on metal surface.
- SEM and AFM images supported by EDX analyses demonstrated the protective film formation of HBIQ on MS surface which acts as a barrier to the sulfamic acid medium.
- Theoretical studies supplemented the experimental data and showed that the high HOMO and low LUMO values enabled adsorption of HBIQ on to the metal and the N and O atoms and the π -electron centers aid in strong interactions with Fe to bind to the metal surface.

Hence, the naphthalimide derivative HBIQ can be potential inhibitor to combat the corrosion of MS in sulfamic acid environment.

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Declarations

Conflicts of interest The authors do not have any conflict of interest.

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