

Electrochemical investigation of hydrazide derivative as corrosion inhibitor for mild steel in hydrochloric acid medium

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Inhibition effect of (2*E*)-2-(3-hydroxy-2-methoxybenzylidene) hydrazinecarbothioamide (HMBHC) on the corrosion of mild steel in 0.5 M HCl solution has been investigated using potentiostatic polarization and electrochemical impedance spectroscopic techniques. The inhibition efficiency increases with increase in inhibitor concentration and with increase in temperature. The polarization study show that the HMBHC acted as mixed type of inhibitor. The kinetic and thermodynamic parameters have been calculated and discussed in detail. The adsorption of inhibitor on the metal surface is found to be through chemisorption and followed Langmuir's adsorption isotherm. The surface morphology of the specimen has been studied by scanning electron microscopy study.

Keywords: Mild steel, Tafel polarization, EIS, Adsorption, Chemisorption, SEM

Corrosion of metals and alloys is the common problem in many industries and it has received a considerable amount of attention by many researchers¹. Mild steel the most widely used among them, finds various applications in chemical and petrochemical industries. It has been widely employed as construction materials for pipe work in the oil and gas production such as down hole tubular, flow lines and transmission pipelines due to its excellent mechanical property and low cost^{2,3}. Acid solutions are widely used for removal of undesirable scale and rust in many industrial processes. Among the commercially available acids the most frequently used one is hydrochloric acid, especially during pickling and acidization of oil process^{1,4,5}. However mild steel exhibit poor corrosion resistance in presence of hydrochloric acid and involves tremendous metal loss due to its corrosion⁶. One of the most popular combating methods for the corrosion of metals in acid solution is the use of corrosion inhibitors^{1,7}. It is well-known that the most effective acidic corrosion inhibitors for many metals and alloys are organic compounds containing electronegative atoms (nitrogen, sulphur, oxygen, phosphor etc.) and unsaturated bonds (such as double or triple bonds)^{7,8}. The compounds with imine group (-RC = NR-) and π electron system also found to be potential inhibitors

for mild steel in acid medium^{7,9}. Aromatic hydrazide derivatives offer special affinity to inhibit corrosion of metals in acid solutions⁹⁻¹¹. The inhibition property of these compounds is attributed to their molecular structure, the planarity and the lone pairs of electrons in the hetero atoms are the important features that determine the adsorption of these molecules on the metallic surface. They can be readily adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion rate¹².

The aim of the present work is to study the inhibitive properties of (2*E*)-2-(3-hydroxy-2-methoxybenzylidene) hydrazinecarbothioamide (HMBHC) on the corrosion behaviour of mild steel in 0.5 M hydrochloric acid using Tafel polarization and EIS methods. Further the study is also intended to understand the corrosion inhibition mechanism by evaluating the adsorption isotherms, activation and thermodynamic parameters.

Experimental Section

Synthesis of HMBHC

(2*E*)-2-(3-hydroxy-2-methoxybenzylidene) hydrazinecarbothioamide (HMBHC) was prepared as per the reported literature¹³. An equimolar mixture of ethanolic solution of 3-hydroxy-2-methoxybenzaldehyde (vaniline) (0.01 mol) and

thiosemicarbazide (0.01 mol) was refluxed on a hot water bath for about 2 h. The precipitated product was filtered, dried and recrystallized from ethanol. The characterization of the compound was done by Infrared spectroscopy (Shimadzu FTIR 8400S spectrophotometer) and Mass spectroscopy (Agilent Technologies 1200 series) techniques. Figure 1 represents the structure of HMBHC.

Medium

Standard solution of 0.5 M hydrochloric acid was prepared by diluting AR grade hydrochloric acid with double distilled water. Inhibitive action of HMBHC on the corrosion of mild steel in 0.5 M HCl solution was studied by adding different concentrations of the inhibitor. The experiments were carried out at temperatures 30, 40, 50 and 60°C ($\pm 0.5^\circ\text{C}$), in a calibrated thermostat.

Material

The material employed in the present work is mild steel with composition of (% wt) C (0.159), Si (0.157), Mn (0.496), P (0.060), S (0.062), Cr (0.047), Ni (0.06), Mo (0.029), Al (0.0043), Cu (0.116) and balance was iron. The specimen was taken in the form of a cylindrical rod embedded in epoxy resin, by leaving one end of the rod with an open surface area of 0.95 cm². It was abraded using emery papers of different grades (400-1500) and subsequently on polishing wheel using levigated alumina. The abraded specimen was cleaned with acetone, followed with double distilled water and finally dried.

Electrochemical measurements

Electrochemical measurements were carried out using an electrochemical work station (CH Instrument USA Model 604D). The electrochemical cell consists of conventional three-electrode Pyrex glass cell with platinum as counter electrode, saturated calomel electrode (SCE) as reference electrode and mild steel as working electrode.

Finely abraded mild steel specimen was exposed to the corrosive medium of 0.5 M hydrochloric acid solution in the presence and absence of the inhibitor at different temperatures (30-60°C). The study state

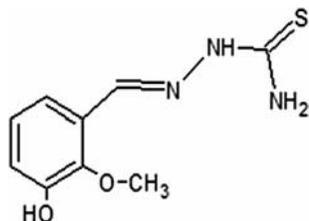


Fig. 1 — Chemical structure of HMBHC molecule

open circuit potential (OCP) with respect to saturated calomel electrode was noted at the end of 25-30 min. The potentiodynamic current versus potential curves were recorded by polarizing the specimen to -250 mV cathodically and +250 mV anodically with respect to the OCP at a scan rate of 1 mV s⁻¹. The impedance experiments were carried out in the frequency range of 100 kHz to 0.01 Hz, at the OCP by applying small amplitude AC signal of 10 mV.

Scanning Electron Microscopy (SEM)

The surface morphology of the mild steel specimen immersed in 0.5 M hydrochloric acid solution in the presence and absence of optimal concentration of HMBHC were compared by recording the SEM images of the specimen using scanning electron microscopy (EVO 18-5-57 model).

Results and Discussion

Characterization of HMBHC

Crystalline white solid (95%); m.p. 216-218°C; IR (KBr) [cm⁻¹]: 1596 (C=N str.), 1296 (C=S str.), 1580 (Ar. C=C str.), 2823, 3031 (CH str.), 3147 (NH str.), 3433, 3278 (NH₂ str.), 3525(OH); MS (m/z): 225 (M⁺). Elemental analysis: Found (Calcd): C, 48.91 (49); H, 5.54(5.6); N, 15.5(15.6) %; C₉H₁₁N₃O₂S.

Tafel polarization measurement

The results of Tafel polarization measurement for the inhibition behaviour of HMBHC on the corrosion of mild steel in 0.5 M hydrochloric acid solution at different temperatures were tabulated in Table 1. Figure 2 shows the Tafel polarization curves for the

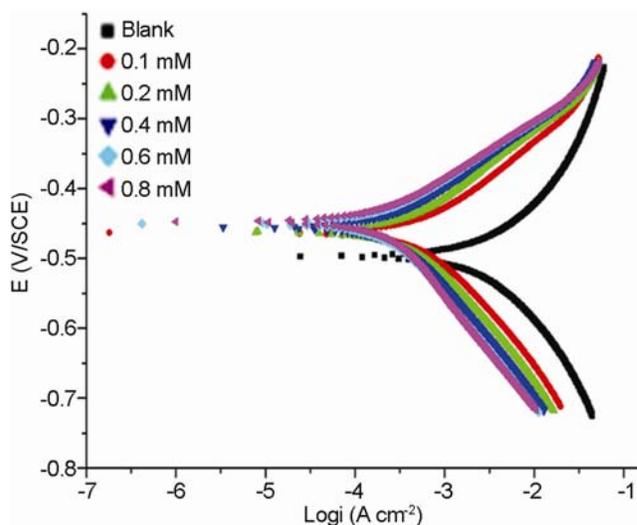


Fig. 2 — Tafel polarization curves for the mild steel specimen in 0.5 M HCl with various concentrations of HMBHC at 30°C

Table 1 — Tafel polarization results for the corrosion of mild steel in 0.5 M HCl in the absence and presence of inhibitor at different temperatures

Temp. (°C)	Conc. of Inhibitor (mM)	E_{corr} (mV)	$-b_c$ (mVdec ⁻¹)	b_a (mVdec ⁻¹)	i_{corr} (mAcm ⁻²)	CR (mmpy)	IE (%)
30	0	-480	77.11	78.87	1.405	8.71	-
	0.1	-467	78.77	90.21	0.457	2.52	67.4
	0.2	-461	64.10	103.8	0.281	1.75	79.9
	0.4	-462	57.11	124.0	0.222	1.38	84.1
	0.6	-459	55.32	133.7	0.206	1.28	85.3
	0.8	-460	50.52	138.9	0.188	1.17	86.6
40	0	-474	69.89	68.76	3.001	18.59	-
	0.1	-461	74.12	98.45	0.602	3.73	79.9
	0.2	-467	72.54	99.45	0.414	2.57	86.1
	0.4	-468	68.81	106.0	0.315	1.95	89.7
	0.6	-469	63.44	117.7	0.236	1.46	92.1
	0.8	-467	59.13	120.4	0.224	1.39	92.5
50	0	-476	61.38	67.32	5.887	36.49	-
	0.1	-471	74.52	79.56	1.025	6.21	82.5
	0.2	-474	75.73	82.31	0.756	4.69	87.2
	0.4	-473	76.28	89.92	0.559	3.69	90.5
	0.6	-476	76.78	100.9	0.423	2.62	92.8
	0.8	-479	77.01	107.2	0.349	2.04	94.0
60	0	-476	65.96	64.06	11.35	70.38	-
	0.1	-477	69.78	76.92	1.944	12.05	82.8
	0.2	-480	69.80	73.01	1.434	10.13	87.3
	0.4	-481	73.69	84.62	1.051	6.64	90.7
	0.6	-483	75.96	94.57	0.855	5.55	92.5
	0.8	-481	75.18	98.74	0.678	4.45	94.1

dissolution of mild steel in 0.5 M hydrochloric acid solution at 30°C in the absence and presence of HMBHC. It can be observed from the experimental results and Tafel plots, that there is no remarkable shift in the corrosion potential (E_{corr}) with reference to the blank. This indicates the inhibitor shows its inhibitory action by influencing both anodic metal dissolution and cathodic hydrogen evolution reaction¹⁴. According to the reported literature¹⁵, if the shift in corrosion potential exceeds ± 85 mV with respect to corrosion potential of the uninhibited solution, then the inhibitor considered as either anodic or cathodic type. However in the present case the maximum displacement in E_{corr} was found to be within +20 mV, which indicates that HMBHC acts as mixed type inhibitor.

The corrosion rate (CR) can be calculated using equation 1.

$$CR(mmpy) = \frac{3270 \times M \times i_{corr}}{p \times Z} \quad \dots (1)$$

where, the constant, 3270 represents the unit of corrosion rate, i_{corr} = corrosion current density in A cm⁻²,

ρ = density of the corroding material (7.74 g cm⁻³), M = Atomic mass of the metal (55.85), and Z = Number of electrons transferred per metal atom.

The surface coverage (θ) and the percentage inhibition efficiency (% IE) were calculated using equation 2 and 3 respectively¹⁶.

$$\theta = \frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \quad \dots (2)$$

where, i_{corr} and $i_{corr(inh)}$ represents the corrosion current densities in the presence of uninhibited and inhibited solution respectively.

$$\% IE = \theta \times 100 \quad \dots (3)$$

It can be seen from the Table 1 that the addition of inhibitor resulted in significant decrease in corrosion current density (i_{corr}) followed by decrease in corrosion rate (CR). The inhibition efficiency increases with increase in inhibitor concentrations and increases with increase in temperatures. The increase in %IE with increase in inhibitor concentrations is due to the blocking effect of the metal surface by adsorption and film formation. Further it is observed that the values of

cathodic slope (b_c) and anodic slope (b_a) does not vary significantly with increase in HMBHC concentration, which indicates that the presence of inhibitor does not alter the inhibition mechanism¹⁷.

Electrochemical impedance spectroscopy

The experimental results of EIS measurement obtained for the corrosion of mild steel in 0.5 M hydrochloric acid solution with and without inhibitor are summarized in Table 2. Nyquist plots for the corrosion of mild steel in the absence and in the presence of various concentrations of the HMBHC were shown in Figure 3. It is observed that the Nyquist plots obtained with depressed semicircles instead of ideal semicircles in the absence as well presence of HMBHC. The depressed behaviour of the Nyquist plots is often attributed to the surface roughness, in homogeneity of the solid surface and adsorption of the inhibitor on the metal surface¹⁸. The diameter of the semicircles increased with increase in inhibitor concentrations, which indicates that the impedance of the inhibited substrate increases with the increase in inhibitor concentration. The impedance

Table 2 — Impedance results for the corrosion of mild steel in 0.5 M HCl in the absence and presence of inhibitor at different temperatures

Temp. (°C)	Conc. of Inhibitor (mM)	R_{ct} (ohm cm ²)	C_{dl} (μF cm ²)	IE (%)
30	0	16.75	1279	-
	0.1	42.14	308.2	60.2
	0.2	69.97	137.6	76.0
	0.4	94.53	82.89	82.2
	0.6	120.8	56.07	86.1
	0.8	185.6	26.87	90.9
40	0	10.01	2945	-
	0.1	35.00	328.70	71.4
	0.2	42.75	258.12	76.1
	0.4	60.60	148.79	83.4
	0.6	80.53	95.29	87.6
	0.8	81.82	88.34	87.7
50	0	5.7	10615	-
	0.1	27.00	710.55	81.5
	0.2	30.32	561.09	83.5
	0.4	33.65	487.84	85.1
	0.6	44.75	270.80	88.8
	0.8	52.93	205.35	90.6
60	0	2.331	45560	-
	0.1	16.25	1749.8	85.6
	0.2	17.92	1548.0	86.9
	0.4	24.57	911.51	90.5
	0.6	26.64	763.38	91.3
	0.8	30.53	600.19	92.4

parameters were analysed by fitting suitable equivalent circuit to the Nyquist plots using ZSimpWin software version 3.21. Figure 4a shows the equivalent circuit model used to simulate the impedance parameters in the absence of HMBHC. This equivalent circuit involved solution resistance (R_s), charge transfer resistance (R_{ct}) and constant phase element (CPE). A constant phase element was introduced instead of pure double layer capacitance (C_{dl}) to give the more accurate fit¹⁹. The Nyquist plots for the corrosion inhibition of mild steel in the presence of HMBHC comprised of one distorted capacitive loop at higher frequency due to charge transfer reaction and the time constant of the electric double layer²⁰. The suitable equivalent circuit was used to simulate the impedance data in presence of HMBHC as shown in Fig. 4b. Similar circuits were used to model steel acid interface in the presence of inhibitor²¹. It involved the solution resistance (R_s), charge transfer process (R_{ct}), time constant of the

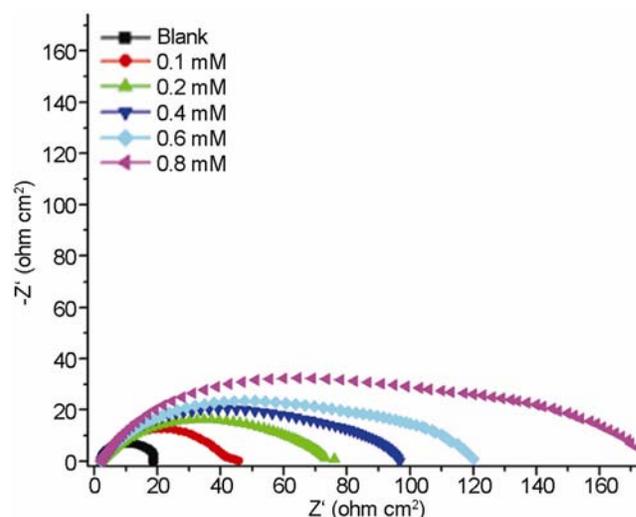


Fig. 3 — Nyquist plots for mild steel specimen in 0.5 M HCl acid containing different concentrations of HMBHC at 30°C

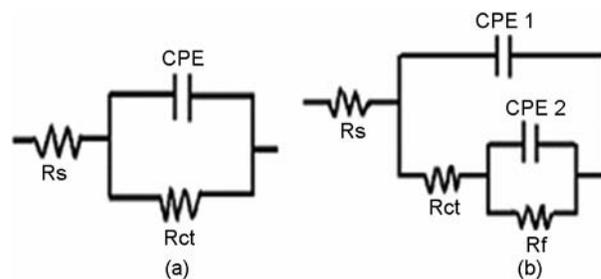


Fig. 4 — Equivalent circuits used to fit experimental EIS data for the corrosion of mild steel specimen in 0.5 M HCl medium (a) in the absence of HMBHC and (b) in the presence of HMBHC

electric double layer (CPE_1), the capacitance of the surface film (CPE_2) and the film resistance (R_f). The impedance parameters obtained are reported in Table 2.

The CPE impedance was calculated using the equation²²,

$$Z = Q^{-1} (i\omega)^{-n} \quad \dots (4)$$

where, Q is the proportionality coefficient, ω is the angular frequency, i is the imaginary number and n is the exponent related to the phase shift. If the value of $n=1$, the CPE behaves like an ideal double layer capacitor. The correction in the capacitance to its real value was calculated using the following equation²³.

$$C_{dl} = Q (W_{max})^{n-1} \quad \dots (5)$$

It was observed from the Table 2 that the values of C_{dl} decreased with increase in inhibitor concentration at all studied temperatures. The decrease in C_{dl} is due to the increase in the electrical double layer at the metal solution interface and also by the gradual replacement of water molecules by the adsorbed inhibitor molecules on the metal surface²⁴. The charge transfer resistance (R_{ct}) increased with increase in the inhibitor concentrations, which indicated that the charge transfer process was mainly controlling the corrosion of mild steel²⁵. The resultant R_{ct} values were used to calculate the percentage inhibition efficiency (% IE) using equation 6.

$$\% IE = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad \dots (6)$$

where, R_{ct} and R_{ct}^0 indicate the charge transfer resistance in the presence and absence of HMBHC respectively.

Effect of temperature

It was evident from the Table 1 that the corrosion current density (i_{corr}) as well as corrosion rate (CR) increased with increase in temperatures. This was attributed to the fact that the rate of chemical reaction increases with increase in temperature. The rise in temperature increases the conductivity of aqueous medium and thereby increasing the diffusion rate of hydrogen ions towards the metal surface and hence the corrosion progresses at higher temperature²⁶. Further the inhibition efficiency increased with increase in temperatures. The high protection efficiency of HMBHC was mainly due to its bonding interaction with the metal surface. The strong bonding is generally attributed to higher electron densities at

active functional groups, imine group and π electrons present in the adsorbate molecules²⁷.

The activation energy (E_a) for the corrosion process was calculated from Arrhenius equation²⁸.

$$\ln(CR) = B - \frac{E_a}{RT} \quad \dots (7)$$

where, B is the Arrhenius pre-exponential constant, and R is the universal gas constant. A plot of $\ln CR$ versus $1/T$ gives a straight line (Fig. 5) with a slope equal to $-E_a/R$ and hence, the values of E_a were obtained. The enthalpy and entropy of activation for the metal dissolution process were determined using the transition state equation²⁹,

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(\frac{-\Delta H^\ddagger}{RT}\right) \quad \dots (8)$$

where, h is Plank's constant, and N is Avagadro's number.

The plot of $\ln(CR/T)$ versus $1/T$, gives a straight line with slope equal to $-1/T$ and intercept equal to $\ln(R/Nh) + \Delta H^\ddagger/RT$. The activation parameters obtained are recorded in Table 3.

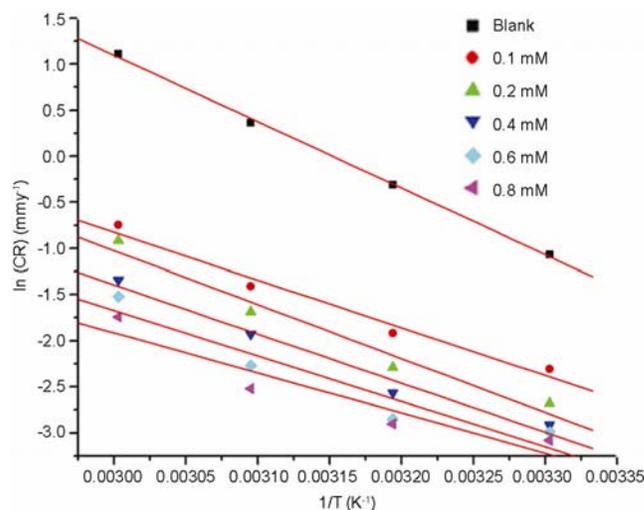


Fig. 5 — Arrhenius plots of $\ln(CR)$ versus $1/T$ for mild steel in 0.5 M HCl with different concentrations of HMBHC

Table 3 — Activation parameters for the corrosion of mild steel in 0.5 M HCl acid containing different concentrations of HMBHC

Conc. of Inhibitor (mM)	E_a (kJmol ⁻¹)	ΔH^\ddagger (kJmol ⁻¹)	ΔS^\ddagger (Jmol ⁻¹ K ⁻¹)
0	59.94	57.33	- 64.7
0.1	51.28	48.67	- 114.98
0.2	48.59	45.98	- 116.40
0.4	43.31	41.69	- 132.33
0.6	41.01	38.38	- 144.57
0.8	36.14	33.52	- 161.17

It was evident from the Table 3 that the values of E_a for the corrosion of mild steel in the presence of HMBHC lower than those in the absence of inhibitor was attributed to chemical adsorption of inhibitor molecules on the metal surface³⁰. The adsorption of the inhibitor on the metal surface leads to the formation of a physical barrier between the metal surface and the corrosive medium, blocking the charge transfer, and there by controlling the corrosion process³¹.

Adsorption isotherm

The study of adsorption isotherms provides basic information regarding the interaction between the inhibitor molecule and the metal surface. Two main types of interaction can describe the adsorption of the organic compound: physical adsorption and chemisorption. These are influenced by the chemical structure of the inhibitor, the type of the electrolyte, the charge and nature of the metal. The values of surface coverage (θ) used to explain the best isotherm to determine the adsorption process. In the present study, various adsorption isotherms are tested and it is found that the adsorption of HMBHC on the mild steel surface in hydrochloric acid medium follows the Langmuir adsorption isotherm which is given by the expression³²,

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \quad \dots (9)$$

where, C_{inh} is inhibitor concentration, θ is the degree of surface coverage and K_{ads} is the adsorption equilibrium constant. The value of K_{ads} , determined from the plot of C_{inh}/θ versus C_{inh} (Fig. 6) is used to calculate the value of the standard free energy of adsorption (ΔG°_{ads}) using the expression³³,

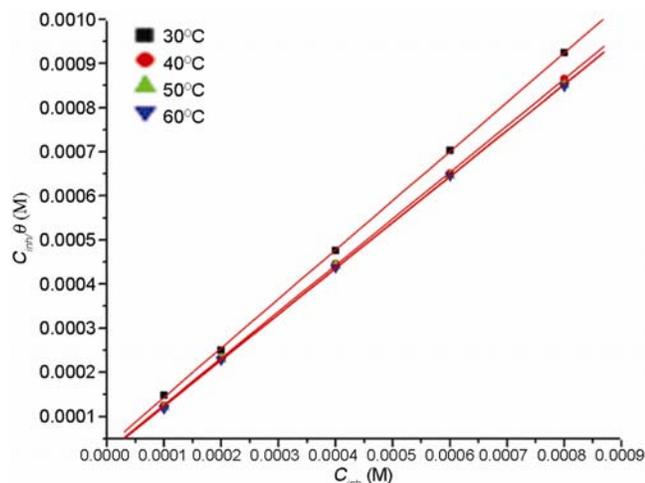


Fig. 6 — Langmuir's adsorption isotherm of HMBHC on mild steel in 0.5 M HCl at different temperatures

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

where, K is the equilibrium constant, R is the universal gas constant and T is absolute temperature and 55.5 is the concentration of water in solution in mol/dm³. The standard enthalpy of adsorption (ΔH°_{ads}) and the standard entropy of adsorption (ΔS°_{ads}) are computed from the slope and intercept of the straight line obtained by plotting ΔG°_{ads} versus T , as per the thermodynamic equation,

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \quad \dots (11)$$

The calculated values of ΔG°_{ads} , ΔH°_{ads} and ΔS°_{ads} are tabulated in Table 4. In general, the values of ΔG°_{ads} up to -20 kJ mol⁻¹ or less than -20 kJ mol⁻¹ imply the electrostatic interactions exist between the charged molecules and the charged metal surface^{34,35}. The values greater than -40 kJ mol⁻¹ imply the formation of the chemical bond between the inhibitor molecule and the metal surface through charge sharing or charge transfer³⁶. In this case ΔG°_{ads} values corresponding to lower temperature (30-50°C) indicates the mixed adsorption of HMBHC, predominately with chemisorption at higher temperature³⁷.

The positive sign of ΔH°_{ads} indicated that the adsorption of inhibitor molecule is an endothermic process. In general, an endothermic process is attributed to chemisorption while an exothermic adsorption process signifies either physisorption or chemisorption³⁸. In the present study, the calculated value of ΔH°_{ads} with positive sign (5.006 kJ mol⁻¹) indicates the chemisorption of inhibitor. The large and negative ΔS°_{ads} value indicates that decrease in disorder takes place on going from reactant to the metal activated complex³⁹.

Inhibition mechanism

Corrosion inhibition action of HMBHC on mild steel in 0.5 M hydrochloric acid solution is due to the adsorption of inhibitor molecule on the metal surface.

Table 4 — Thermodynamic parameters for the adsorption of HMBHC on mild steel surface in 0.5 M HCl acid at different temperatures

Temp. (°C)	$-\Delta G^{\circ}_{ads}$ (kJ mol ⁻¹)	R ²	Slope	ΔH°_{ads} (kJ mol ⁻¹)	ΔS°_{ads} (J mol ⁻¹ K ⁻¹)
30	36.18	0.999	1.014	5.066	-139.1
40	38.46	0.999	1.054		
50	39.77	0.999	1.041		
60	41.32	0.999	1.042		

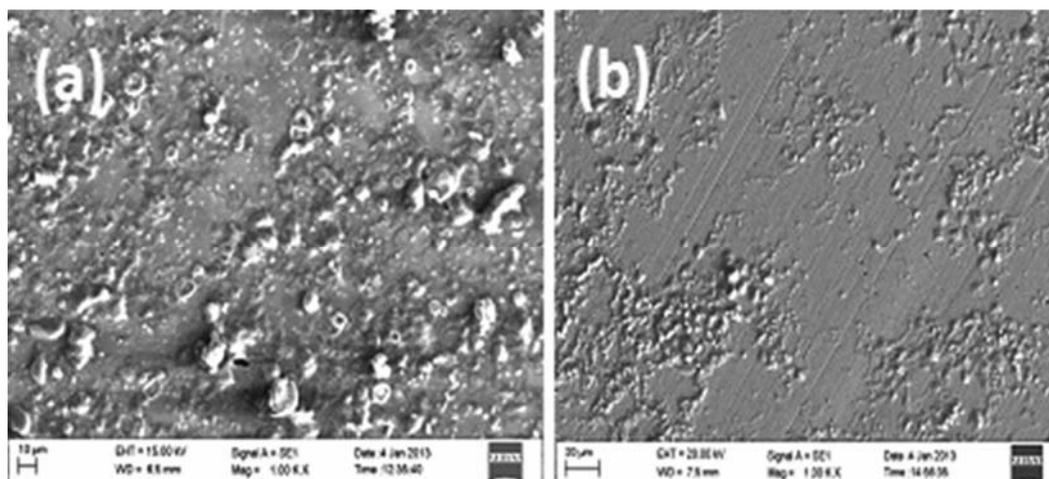


Fig. 7 — SEM images of the mild steel (a) Exposed to 0.5 M HCl solution and (b) Exposed to 0.5 M HCl containing 0.8 mM of HMBHC

The mode of adsorption of HMBHC molecule on the mild steel surface can be explained as follows: In a highly acidic solution, the HMBHC molecule can undergo protonation at its amino groups and can exist as a protonated positive species. Further, the metal surface is also gets positive charge in the presence of acidic medium. This would cause the negatively charged chloride ions to become adsorbed on the metal surface, making the metal surface negatively charged. The positively charged protonated HMBHC molecules then interact electrostatically with the negatively charged chloride ions adsorbed on the metal surface resulting in physisorption particularly at lower temperature⁴⁰.

The maximum inhibition efficiency attained at higher temperature (60°C) is due to the adsorption HMBHC molecule on the surface of metal via chemisorption process. This is due the displacement of the initially occupied water molecules from the surface of the metal leading to the sharing of electrons between the hetero atoms (O, S and N) and the metal. In addition, the horizontal orientation of the entire molecule with respect to the metal surface can also lead to donor-acceptor interaction of π -electrons of the aromatic ring with those vacant d orbitals of the metal surface resulting in chemisorption. The presence of imine group ($-\text{CH}=\text{N}-$) and electron donating groups ($-\text{OH}$ and $-\text{OCH}_3$) in HMBHC makes it more effective and potential corrosion inhibitor for mild steel⁴¹.

Scanning electron microscopy

SEM investigations were carried out to differentiate between the surface morphology of

the metal surface after its immersion in 0.5 M hydrochloric acid for three hours in the absence and presence of HMBHC. Figures 7a and 7b shows the surface images of mild steel sample in the absence and presence of HMBHC respectively. The closed observation of Fig. 7a shows the formation of rough surface including pits due to the corrosion, whereas smooth sample surface was obtained in the presence of HMBHC as shown in Fig. 7b. This confirms the adsorption of HMBHC on the mild steel surface through the formation of protective film.

Conclusion

The conclusions drawn from the present study are,

- HMBHC is found to be potential inhibitor for the corrosion control of mild steel in 0.5 M hydrochloric acid solution.
- Percentage inhibition efficiency increases with increase in HMBHC concentrations and increases with increase in the temperature.
- The adsorption of HMBHC on the mild steel surface obeys Langmuir adsorption isotherm.
- Tafel polarization measurements indicate HMBHC acts as mixed type inhibitor.
- Activation and thermodynamic parameters indicates the adsorption of HMBHC is through mixed type adsorption, with predominately chemisorption.

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References

- 1 Matjazn F & Jennifer J, *Corros Sci*, 86 (2014) 17.
- 2 Singh A K & Quraishi M A, *Int J Electrochem Sci*, 7 (2012) 3222.
- 3 Ostovari A, Hosseini S M, Pei Kari M, Shadzadeh S R & Hashemi S J, *Corros Sci*, 51 (2009) 1935.
- 4 Li X H, Deng S D & Fu H, *J Appl Electrochem*, 40 (2010) 1641.
- 5 Singh A, Ebenso E E & Quraishi M A, *Int J Corros*, 2012 (2012) Article ID 897430.
- 6 John S, Joseph B, Balakrishna K V, Aravindakshan K K & Joseph A, *Mater Chem Phys*, 123 (2010) 218.
- 7 John S & Abraham J, *Indian J Chem Technol*, 19 (2012) 195.
- 8 Ahamad I & Quraishi M A, *Corros Sci*, 51 (2009) 2006.
- 9 Fouda A S, Mohamed M T & Soltan M R, *J Electrochem Sci Technol*, 4 (2013) 61.
- 10 Mohan P, Arunsunai K, Paruthimal K G & Muralidharan V S, *Asian J Chem*, 24 (2012) 5821.
- 11 Shanbhag A V, Venkatesha T V, Prabhu R, Kalkhambkar R G & Kulkarni G M, *J Appl Electrochem*, 38 (2008) 279.
- 12 Yesim K, Seda G & AsliE, *Prot Met Phys Chem Surf*, 48 (2012) 710 h.
- 13 Renata B O, Elaine M S F, Rodrigo P P S, Anderson A A, Antoniana U K & Carlos L Z, *Eur J Med Chem*, 43 (2008) 1984.
- 14 Sangeetha M, Rajendran S, Sathiyabama J, Krishnaveni A, Shanthi P, Manimaran N & Shyamaladevi B, *Port Electrochim Acta*, 29 (2011) 429.
- 15 Li W, He Q, Zhang S, Pei C & Hou B, *J Appl Electrochem*, 38 (2008) 289.
- 16 Sanat kumar B S, Nayak J & Shetty A N, *J Coat Technol Res*, 4 (2011) 1.
- 17 E I Kadher A, M E I Warraky J & Abd el Aziz A M, *Br Corros J*, 33 (1998) 139.
- 18 Barsoukov E & Macdonald J R, *Impedance Spectroscopy, Theory, Experiment and Applications*, 2nd Edn, (John Wiley & Sons, Hoboken, New Jersey) 2005, 13.
- 19 McCafferty E, *Corros Sci*, 39 (1997) 243.
- 20 Singh A K & Quraishi M A, *Corros Sci*, 52 (2010) 152.
- 21 Lowmunkhong P, Ungthararak D & Sutthivaiyakit P, *Corros Sci*, 52 (2010) 30.
- 22 Ahamad I, Prasad R & Quraishi M A, *Corros Sci*, 52 (2010) 933.
- 23 Hsu C H & Mansfeld F, *Corrosion*, 57 (2011) 747.
- 24 Machnikova E, Whitmire K H & Hackerman N, *Electrochim Acta*, 53 (2008) 6024.
- 25 Khaled K F, *Mater Chem Phys*, 112 (2008) 290.
- 26 Rafique M Z A, Saxena N, Khan S & Quarashi M A, *Indian J Chem Technol*, 14 (2007) 576.
- 27 Poornima T, Nayak J & Shetty A N, *J Appl Electrochem*, 41 (2011) 223.
- 28 Yahalom J, *Corros Sci*, 12 (1972) 867.
- 29 Abdel Rehim S S, Magdy A M & Ibrahim K F, *J Appl Electrochem*, 29 (1999) 593.
- 30 Fouda A S, Heikal F E & Radwan M S, *J Appl Electrochem*, 39 (2009) 391.
- 31 Mansfeld F, *Corrosion Mechanism*, (Marcel Dekkar, New York) 1987, 119.
- 32 Ashassi-Sorkhabi H, Majidi M R & Seyyedi K, *Appl Surf Sci*, 225 (2004) 176.
- 33 Kliskic M, Radosevic J, Gudic S & Katalinic V, *J Appl Electrochem*, 30 (2000) 823.
- 34 Ma H, Chen S, Yin B, Zhao S & Liu X, *Corros Sci*, 45 (2003) 867.
- 35 Yurt A, Bereket G, Kivrak A, Balaban A & Erk B, *J Appl Electrochem*, 35 (2005) 1025.
- 36 Saliyan R V & Adhikari A V, *Corros Sci*, 50 (2008) 55.
- 37 Behpour M, Ghoreishi S M, Gandomi-Niasar A, Soltani N & Salavati-Niasari M, *J Mater Sci*, 44 (2009) 2444.
- 38 Durnie W, Marco R D, Jefferson A & Kinsella B, *J Electrochem Soc*, 146 (1999) 17.
- 39 Martinez S & Stern I, *Appl Surf Sci*, 199 (2002) 83.
- 40 Popova A, Sokolova E, Raicheva S & Christov M, *Corros Sci*, 45 (2003) 33.
- 41 Emregul K C, Duzgun E & Atakol O, *Corros Sci*, 48 (2006) 3243.