

Corrosion inhibition of mild steel by N, N'-(5,5- dimethylcyclohexane-1,3-diylidene)dianiline in acid media: Gravimetric and electrochemical evaluations

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ABSTRACT

The corrosion inhibition efficiency of the Schiff base N,N'-(5,5-dimethylcyclohexane-1,3-diylidene)dianiline (DmChDa) on mild steel in 1M HCl and 0.5M H₂SO₄ was evaluated using gravimetric, electrochemical impedance spectroscopy, potentiodynamic polarization and electrochemical noise measurement. Experimental results established that DmChDa possess relatively high corrosion inhibition capacity. Langmuir and El-Awady adsorption isotherms were obeyed by the Schiff base in 1M HCl and 0.5M H₂SO₄ respectively. SEM analysis showed that DmChDa was adsorbed on the steel surface during corrosion inhibition. The variation of metal dissolution with temperature was also examined using gravimetric study.

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1. Introduction

Mild steel plays a significant role in our day-to-day life on account of their excellent mechanical property and low price.¹⁻⁵ They are used extensively as building materials, for storage tanks, reactors, boilers, oil and gas transport pipelines and heat exchange processes. Acid solutions are used in industries for various cleaning purposes such as acid-descaling, acid-cleaning, acid-pickling, oil-well acidizing etc. During these cleaning processes, mild steel is attacked severely by the acid solution and gets corroded.⁶⁻⁹ The best method for reducing the destruction of metal during pickling is the use of inhibitors. Schiff bases which are formed by the condensation of amino acid and aldehydes/ketones has wide applications in various fields such as pharmaceuticals, catalysis, antimicrobial activity, coordination chemistry, agricultural and material science etc. They are also being utilized as a potent corrosion inhibitor for a number of reasons such as the presence of azomethine (-CH=N-) group, oxygen, nitrogen and sulphur atoms, unsaturation sites and aromatic rings.¹⁰⁻¹² The substitution of groups like OH on the benzene ring present in the ligand molecule will enhance the corrosion inhibition capacity as per our previous work.⁴ The important aspect of the Schiff base molecule that decides

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adsorption of it on the surface of the metal is a lone pair of electrons on hetero atoms. The main advantage of Schiff bases is that they can be synthesized easily from cost-effective raw material. In the present study, the corrosion inhibition nature of the Schiff base DmChDa on mild steel in 1M HCl and 0.5M H₂SO₄ were analyzed experimentally using weight loss, electrochemical impedance spectroscopy, potentiodynamic polarization and electrochemical noise measurement.

2. Results and discussion

2.1. Weight loss studies

2.1.1. Impact of inhibitor concentration

The weight loss of the MS specimen at 24 h interval in acid media in the absence and presence of various inhibitors at different concentrations were determined. The corrosion rate and inhibition efficiency were calculated, which is depicted in Table 1. The rate of corrosion of MS decreased in the presence of DmChDa. DmChDa has higher inhibition efficiency in 1M HCl than 0.5M H₂SO₄ at all concentrations. The maximal values of corrosion inhibition efficiency on the MS surface by 1mM inhibitor concentration in 1M HCl and 0.5M H₂SO₄ were found to be 92.63% and 87.52% respectively.

Table 1. The rate of corrosion of MS and corrosion inhibition efficiency of DmChDa in acid media at 28^oC for 24 h

Conc. (mM)	1M HCl		0.5M H ₂ SO ₄	
	Corrosion rate (v) (mmy ⁻¹)	%inhibition efficiency ($\eta_w\%$)	Corrosion rate (v) (mmy ⁻¹)	%inhibition efficiency ($\eta_w\%$)
0.0	7.30	-	35.20	-
0.2	1.41	80.67	24.16	31.36
0.4	1.28	82.39	10.33	70.62
0.6	1.01	86.07	6.81	80.64
0.8	0.87	88.04	4.40	87.50
1.0	0.53	92.63	4.39	87.52

2.1.2. Comparison between $\eta_w\%$ of DmChDa and its parent compounds

In order to correlate the corrosion inhibition efficiency of Schiff base DmChDa with parent compounds 5-5-dimethyl-1,3-cyclohexanedione (Dm) and aniline (An), weight loss measurements of mild steel specimens were conducted in 1M HCl and 0.5M H₂SO₄ and the efficiencies are given in Table 2. The corrosion inhibition efficiency of DmChDa was remarkably higher than the parent compounds. It is due to the involvement of C=N- group present in the inhibitor molecule during adsorption phenomena.¹³

Table 2. The corrosion inhibition efficiency of parent ketone (Dm) and amine (An) of DmChDa on MS in acid media

Conc (mM)	% inhibition efficiency ($\eta_w\%$)			
	1M HCl		0.5 M H ₂ SO ₄	
	Dm	An	Dm	An
0.2	-85.40	-70.19	29.50	28.26
0.6	-70.67	-8.46	38.68	29.70
1	-42.56	25.70	56.23	43.04

2.1.3. Determination of adsorption isotherm

The mechanism of the inhibition of corrosion of MS can be elucidated with the help of adsorption isotherms.¹⁴ Langmuir, Temkin, El-Awady, Florry-huggin, Freundlich and Frumkin adsorption

isotherms were considered, and the best suited isotherm was determined by calculating the correlation coefficient (R^2).¹⁵⁻¹⁶ The isotherms corresponding to DmChDa in 1M HCl and 0.5M H₂SO₄ medium were Langmuir and El-Awady adsorption isotherm respectively. These isotherms can be denoted as

$$\text{Langmuir isotherm} \quad \frac{C}{\theta} = \frac{1}{K} + C \quad (1)$$

$$\text{El-awady isotherm} \quad \log \frac{\theta}{(1-\theta)} = \log K + y \log C \quad (2)$$

where C , θ and K_{ads} denotes inhibitor concentration, fractional surface coverage and adsorption equilibrium constant respectively. The adsorption equilibrium constant correlates with standard free energy of adsorption ΔG_{ads}^0 as shown below¹⁷⁻¹⁸

$$\Delta G_{\text{ads}}^0 = -RT \ln(55.5 K_{\text{ads}}) \quad (3)$$

where 55.5 is the molar concentration of water, T and R represent temperature in Kelvin and universal gas constant respectively. The ΔG_{ads}^0 value upto -20 kJmol^{-1} indicates that the interaction of charged molecule and charged metal surface is electrostatic in nature (physisorption) while the value more negative than -40 kJmol^{-1} indicates the presence of co-ordinate type bond between inhibitor molecules and metal surface (chemisorption)¹⁹. The observed ΔG_{ads}^0 values of DmChDa were -34.40 and $-45.84 \text{ kJmol}^{-1}$ respectively in 1M HCl and 0.5M H₂SO₄, indicating that the adsorption behaviour involves both chemical and electrostatic interaction in 1M HCl, whereas in 0.5M H₂SO₄ the adsorption behaviour is mainly by chemical interaction. The isotherms of DmChDa on MS specimen in 1M HCl and 0.5M H₂SO₄ at 28°C is shown in Fig. 1. The mechanism of the interaction is shown in Fig. 2.

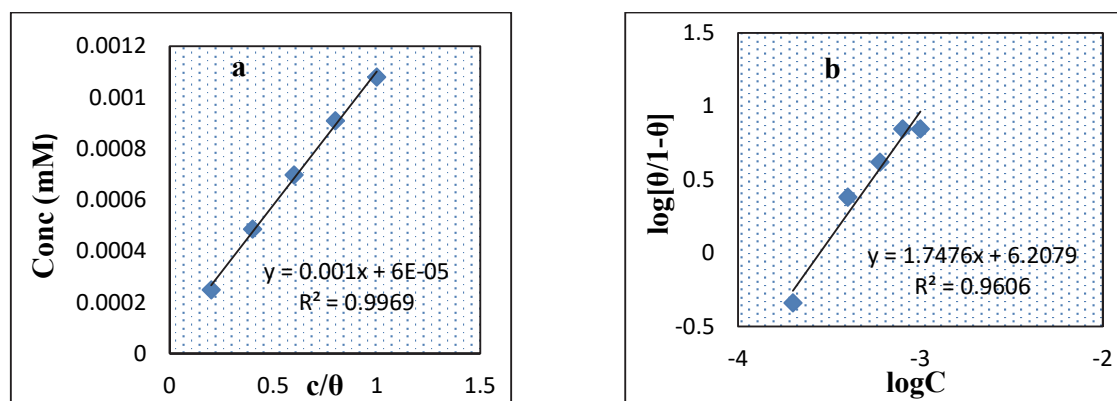


Fig. 1. (a) Langmuir adsorption isotherm of DmChDa on MS in 1M HCl at 28°C. (b) El-Awady adsorption isotherm of DmChDa on MS in 0.5 M H₂SO₄ at 28°C

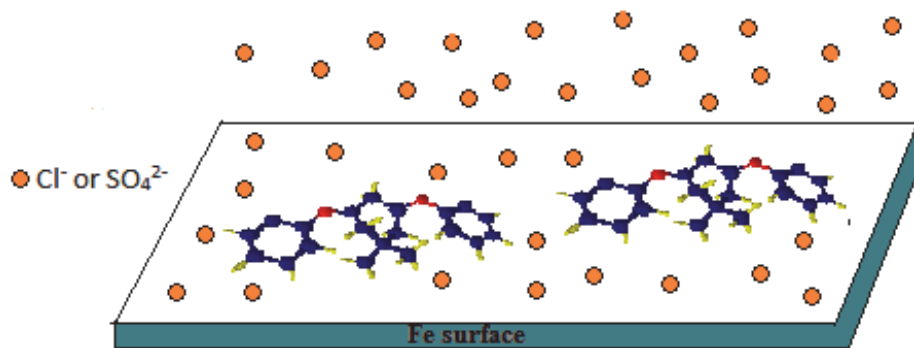


Fig. 2. Interaction of DmChDa on mild steel in acid media

2.1.4. Impact of temperature

The impact of temperature on the rate of corrosion was investigated using weight loss studies in the temperature range 30-60°C. The activation energy of metal dissolution was calculated using an Arrhenius type equation given below²⁰⁻²¹

$$K = A \exp(-E_a/RT), \quad (4)$$

where A, K, R, T and E_a denotes pre-exponential factor, corrosion rate, universal gas constant, temperature in Kelvin and activation energy respectively. The activation energy required for the dissolution of metal was obtained from the slope of the plot $\log K$ vs $1/T$ for MS specimens in acid media, with and without inhibitor molecules (Fig. 3a and 4a). Thermodynamic parameters such as enthalpy (ΔH^*) and entropy (ΔS^*) changes were evaluated using transition state theory (Eq. (9))²²

$$K = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{\Delta H^*}{RT}\right) \quad (5)$$

where h and N are Planck's constant and Avogadro number respectively. The slope, $\frac{-\Delta H^*}{2.303R}$ and intercept, $\log\left(\frac{R}{2.303Nh}\right) + \left(\frac{\Delta S^*}{2.303R}\right)$ obtained by plotting $\log K/T$ vs $1/T$ (Fig. 3b and 4b). Table 3 represents the activation energy and thermodynamic parameters such as entropy of activation (ΔS^*) and enthalpy of activation (ΔH^*). It was observed that the activation energy of metal dissolution was high in the case of an acid solution containing an inhibitor molecule²³. Also, it was found that E_a increased with inhibitor concentration, which implies that dissolution of the metal was reduced with inhibitor concentration. The positive sign of the enthalpy of activation indicates the endothermic nature of metal dissolution. The ΔH^* and ΔS^* values were found to increase along with the rise in inhibitor concentration.

2.2. Electrochemical impedance spectroscopic (EIS) studies

The corrosion inhibition behaviour of DmChDa on MS in acid media was investigated using EIS at 28°C. Fig. 5 and Fig. 6 (Nyquist and Bode plots) represent impedance spectra of mild steel in the absence and presence of DmChDa at various concentrations in 1M HCl and 0.5M H₂SO₄. The Nyquist plots of blank specimen and that treated with inhibitor were obtained to be semicircular, and the size of the semicircular plot increased upon the increasing concentration of inhibitor, which indicates the impedance enhancement of the MS with the concentration.

Table 3. Thermodynamic parameters of MS corrosion with and without DmChDa in acid media

Medium	Conc (mM)	E_a (kJ mol ⁻¹)	A	ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)
1M HCl	Blank	55.70	3.81×10^{10}	53.03	-44.26
	0.2	102.76	1.41×10^{18}	100.12	100.64
	0.4	103.55	1.68×10^{18}	100.91	102.10
	0.6	107.13	6.44×10^{18}	104.48	113.26
	0.8	109.73	1.56×10^{19}	107.09	120.65
	1.0	119.48	5.24×10^{20}	116.83	149.85
0.5M H ₂ SO ₄	Blank	33.14	2.08×10^7	30.50	-106.71
	0.2	46.10	2.46×10^9	43.46	-67.03
	0.4	69.12	1.04×10^{13}	66.48	2.38
	0.6	79.66	4.75×10^{14}	77.02	34.16
	0.8	96.33	1.96×10^{17}	93.69	84.25
	1.0	96.58	2.18×10^{17}	93.94	85.13

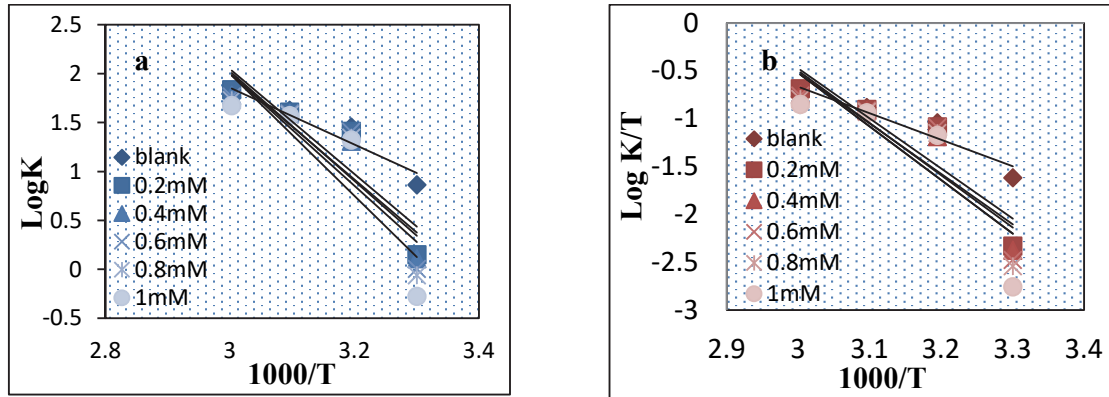


Fig. 3. Plot of a) $\log K$ vs $1000/T$ b) $\log K/T$ vs $1000/T$ with and without DmChDa in 1M HCl

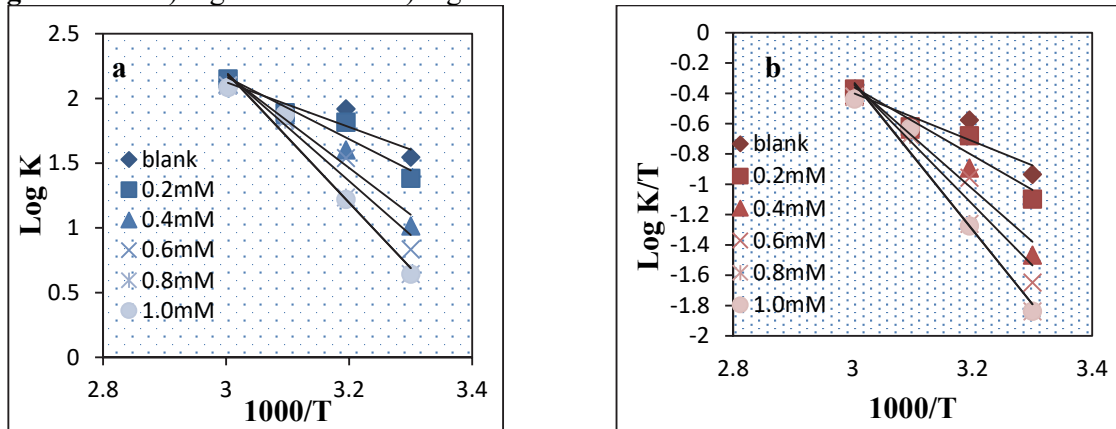


Fig. 4. Plot of a) $\log K$ vs $1000/T$ b) $\log K/T$ vs $1000/T$ with and without DmChDa in 0.5M H_2SO_4

The corrosion inhibition efficiency also increased with concentration. Randles circuit was found to be the most fit equivalent circuit for Nyquist plots (Fig. 7) which consisted of charge transfer resistance R_{ct} , double layer capacitance C_{dl} and solution resistance R_s .²⁴ Constant phase element (CPE) was inserted into the circuit in preference to pure double layer capacitance to lower the effects due to deformities on the surface of metal as shown in Fig. 8. The impedance of CPE can be expressed as²⁵

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n}, \quad (6)$$

where Y_0 , n , w and j denotes the magnitude of CPE, exponent (phase shift), angular frequency and imaginary unit respectively. Based on the values of n , CPE can be capacitance, inductance and resistance.²⁶ It was observed that the values of n were between 0.75 and 1.0, indicating the capacitance nature of CPE. The parameters CPE, R_{ct} and the percentage of corrosion inhibition efficiency ($\eta_{EIS}\%$) of DmChDa are listed in Table 4.

Table 4. Impedance data of MS specimen with and without DmChDa in acid media

Conc (mM)	1M HCl			0.5M H_2SO_4		
	R_{ct} (Ωcm^2)	C_{dl} ($\mu F cm^{-2}$)	$\eta_{EIS}\%$	R_{ct} (Ωcm^2)	C_{dl} ($\mu F cm^{-2}$)	$\eta_{EIS}\%$
0.0	29.1	105	-	7.96	113	-
0.2	181	81.8	83.92	9.10	72.6	12.53
0.4	200	81.6	85.45	12.8	66.6	37.81
0.6	232	99.4	87.45	14.3	71.6	44.33
0.8	253	92.9	88.49	14.7	62.3	45.85
1.0	308	65.4	90.55	16.7	54.6	52.33

Charge transfer resistance (R_{ct}) was increased, whereas capacitance (C_{dl}) value was reduced with inhibitor concentration in both cases. High value of charge transfer resistance was observed in 1M HCl. The decrease in C_{dl} values was attributed to the lowering of local dielectric constant and/or increase in the thickness of electrical double layer.²⁷ The maximum corrosion inhibition efficiencies of 90.55% and 52.33% were observed at 1mM concentration of DmChDa in 1M HCl and 0.5M H₂SO₄ respectively.

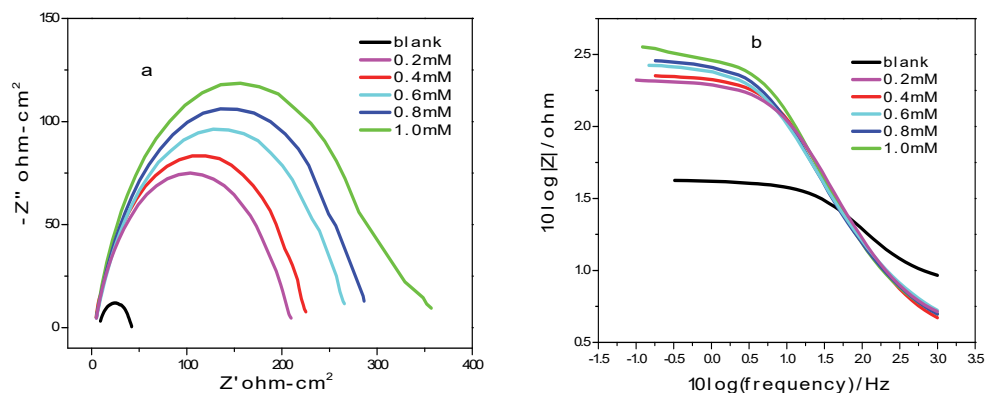


Fig. 5. Impedance spectra a) Nyquist and b) Bode plot of MS coupons with and without DmChDa in 1M HCl

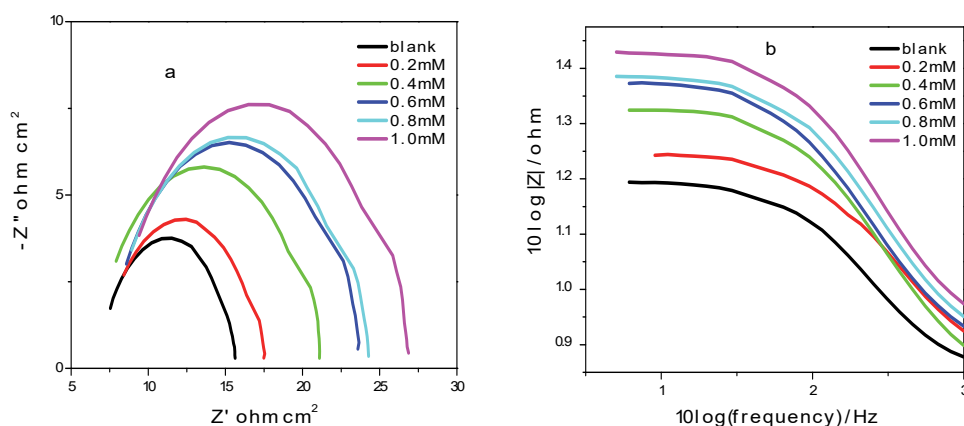


Fig. 6. Impedance spectra a) Nyquist and b) Bode plot of MS coupons with and without DmChDa in 0.5M H₂SO₄

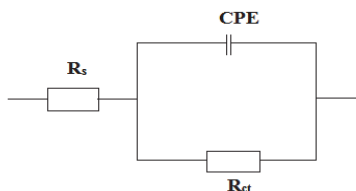


Fig. 7. Randles circuit used for EIS measurements.

2.3. Potentiodynamic polarization studies

The criteria such as corrosion current densities (I_{corr}), corrosion potential (E_{corr}), anodic slope (b_a), cathodic slope (b_c) and inhibition efficiency ($\eta_{pol}\%$) of DmChDa in 1M HCl and 0.5M H₂SO₄ are given in Table 5. Polarization curves are shown in Fig. 8. Polarization data reveals that corrosion current density decreased with the rise in concentration of DmChDa. As a result, the percentage of inhibition

efficiency also increased. A maximum inhibition efficiency of 95.59% and 44.33% were shown by DmChDa at 1mM concentration in 1M HCl and 0.5M H₂SO₄ respectively. The b_a and b_c values indicated that addition of DmChDa to acid media affected both cathodic and anodic parts of the curves and hence acted as a mixed type inhibitor.²⁸⁻²⁹

Considerable difference was noticed between the corrosion inhibition efficiency of DmChDa in gravimetric and electrochemical studies (EIS and potentiodynamic polarization) in 0.5M H₂SO₄ medium. DmChDa consists of two –C=N– linkages which are responsible for hydrolysis in acid medium. By using UV-visible spectroscopy, it was confirmed that slow hydrolysis of DmChDa is occurring in 0.5M H₂SO₄ medium. It can be supposed that appreciable degradation in the structure of DmChDa was not happening within 1-2 h. On keeping the inhibitor for a period of 24 h complete hydrolysis of the molecule takes place and the parent compounds 5-5-dimethyl-1,3-cyclohexanedione (Dm) and aniline (An) regenerated were responsible for the high inhibition efficiency. The parent compounds itself have appreciable inhibition efficiency in 0.5M H₂SO₄ (Table 2). The enhanced inhibition efficiency of DmChDa in gravimetric study than electrochemical study was attributed to the net effect of inhibition efficiency of both parent compounds formed during hydrolysis. Even though there is a probability for hydrolysis in 1M HCl medium the corrosion inhibition efficiency of DmChDa in gravimetric and electrochemical studies follows the same trend. This may be due to the higher adsorption tendency of DmChDa on Cl⁻ ion, which is strongly bind to mild steel surface instead of its hydrolysis.

2.4. Electrochemical noise studies

Electrochemical noise measurements was conducted by immersing two identical mild steel electrodes and calomel electrode (as reference electrode) in an acid medium in the presence and absence of DmChDa for a period of 1200s. Current noise for MS in the absence and presence of DmChDa (1mM) in the acid medium is shown in Figure 9. From the figure, it is clear that blank specimen exhibits higher mean value of current noise in respect of the specimen dipped in an acid medium containing inhibitor molecules, and the mean value of current noise in 0.5M H₂SO₄ was greater than in 1M HCl medium, which reflects the greater protective power of DmChDa in 1M HCl medium.³⁰

The frequency domain analysis of noise measurement gave the PSD (Power Spectral Density) of different systems, which is represented in Figure 10. On close examination of PSD plots, it is clear that at all frequencies, the values of current noise are comparatively large for blank metal specimen than for metal immersed in acid solution containing DmChDa which suggests that localised corrosion of mild steel is occurring in acid solution without an inhibitor molecule.³¹

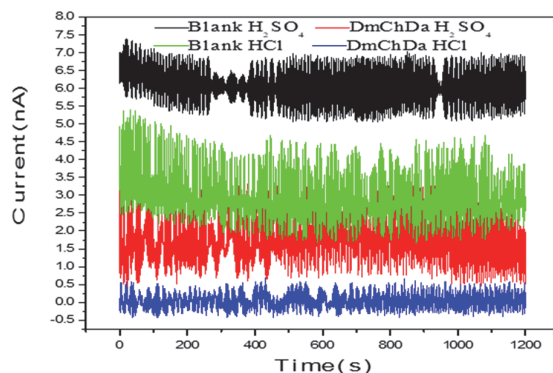
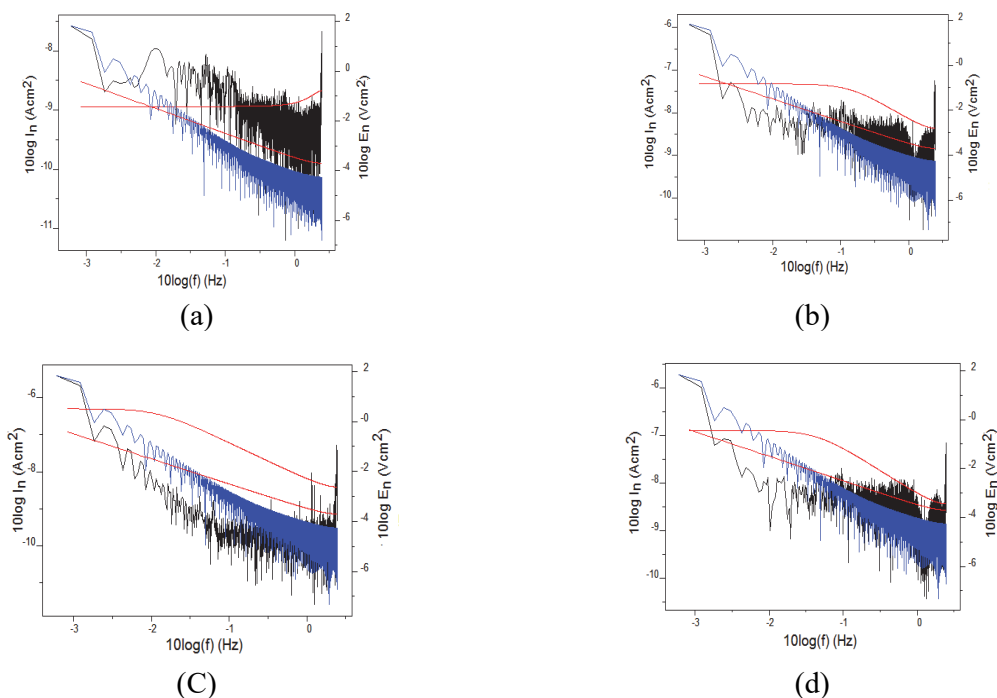
Pitting index is a measure of resisting power to localised pitting corrosion. The pitting index curves are shown in Fig. 11. The amplitude of the pitting index curve corresponding to blank metal specimen is lower than metal specimens treated with acid solution containing inhibitors. This implies that acid solution containing an inhibitor molecule has higher resistance to pitting corrosion.



Fig. 8. Tafel plots of MS coupons with and without DmChDa in a) 1M HCl and b) 0.5M H₂SO₄

Table 5. Polarization data of MS specimen with and without DmChDa in acid media

Acid	Tafel data					
	Conc (mM)	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	b_a (mV/dec)	$-b_c$ (mV/dec)	$\eta_{pol}\%$
1M HCl	0.0	-477.3	1160	172	212	
	0.2	-468.8	101	73	128	91.31
	0.4	-468.9	84.3	71	139	92.73
	0.6	-461.1	74.0	63	126	93.62
	0.8	-469.5	67.4	65	129	94.19
	1.0	-461.9	51.1	59	121	95.59
0.5M H ₂ SO ₄	0.0	-374.3	2528	241	242	
	0.2	-559.7	2329	250	236	7.87
	0.4	-556.3	1832	224	213	27.53
	0.6	-547.2	1735	220	226	31.37
	0.8	-539.1	1557	206	224	38.41
	1.0	-543.1	1408	210	212	44.33

**Fig. 9.** Current noise for MS in the absence and presence of DmChDa (1mM) in acid media**Figure 10.** Power spectral density (voltage and current) of MS a) blank 1M HCl b) in the presence of DmChDa (1mM) in 1M HCl, c) blank 0.5M H₂SO₄ and d) in the presence of DmChDa (1mM) in 0.5M H₂SO₄.

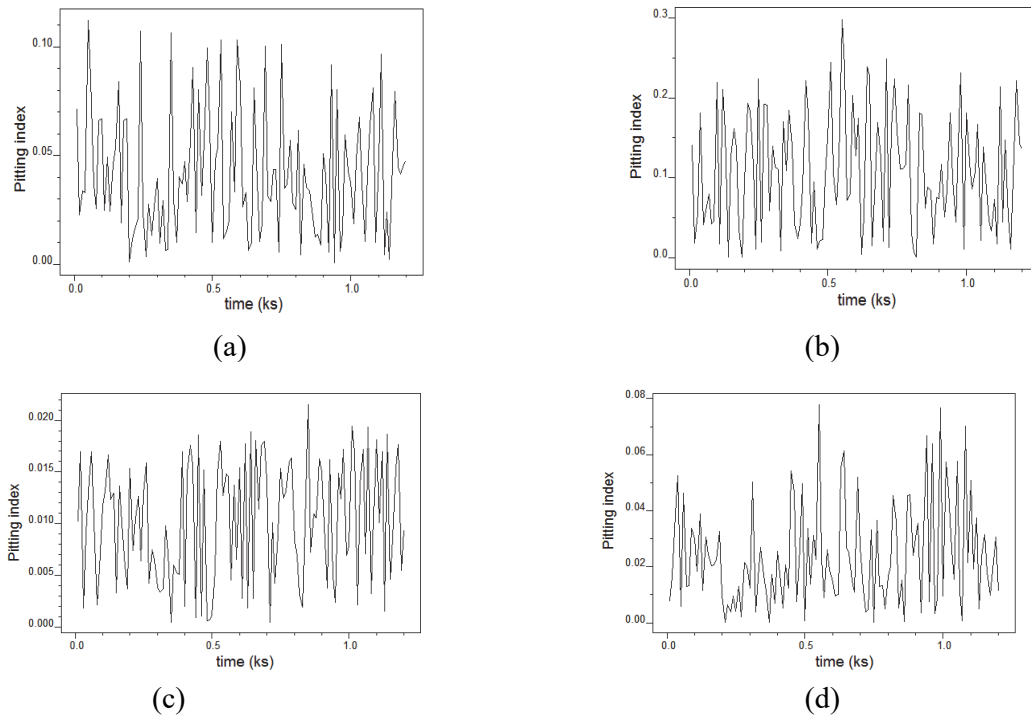


Fig. 11. Pitting index curve of MS a) blank 1M HCl b) in the presence of DmChDa (1mM) in 1M HCl c) blank 0.5M H₂SO₄ and d) in the presence of DmChDa (1mM) in 0.5M H₂SO₄

2.5. Scanning electron microscopy (SEM)

In order to determine the surface morphology of MS coupons, scanning electron microscopy was conducted. Fig. 12 (a-e) represents the SEM images of bare metal, mild steel coupon treated with 1M HCl, treated with 0.5M H₂SO₄, treated with DmChDa (1mM) in 1M HCl and treated with DmChDa (1mM) in 0.5M H₂SO₄ respectively.

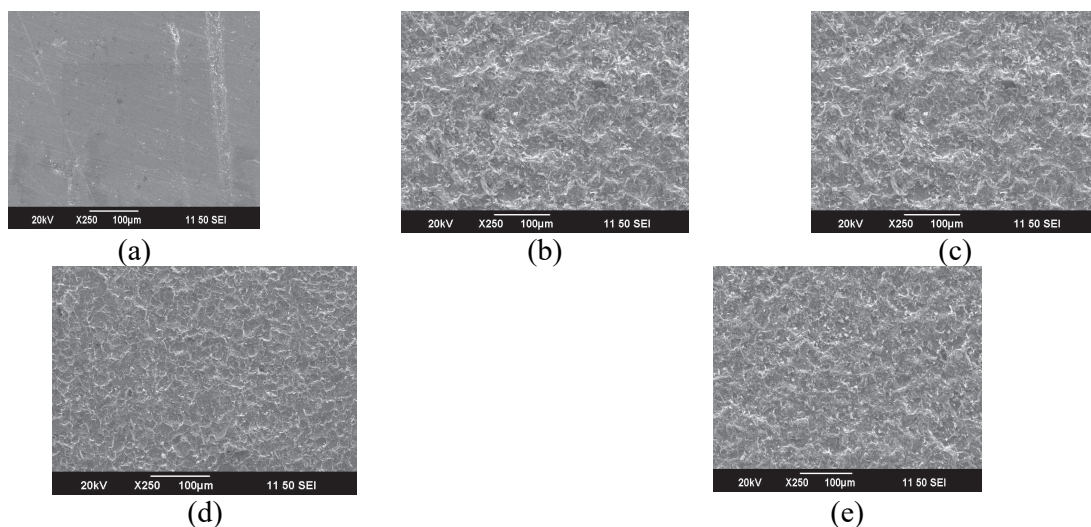


Fig. 12. SEM analysis of MS coupons before and after 24 h immersion (a) bare metal, (b) blank (1M HCl), (c) blank (0.5M H₂SO₄), (d) treated with DmChDa (1mM) in 1M HCl, (e) treated with DmChDa (1mM) in 0.5M H₂SO₄

There exists a remarkable difference between the surface of a polished mild steel specimen and the one treated with acid solution⁴. It is clear that the mild steel surface reacted with acid medium from its erratic and rough structure. A remarkable change in the surface morphology of MS was observed after adding an inhibitor molecule into an aggressive medium. In the presence of 1mM concentration of DmChDa in both acid media, the corrosion rate was found to decrease, and the surface became less corroded. This is a clear indication of the formation of a protective layer of inhibitor molecules on mild steel surface.

3. Conclusions

1. The Schiff base DmChDa is a best inhibitor of corrosion for mild steel in 1M HCl
2. The maximum inhibition potency of DmChDa in 1M HCl and 0.5M H₂SO₄ was 92.63% and 87.52% respectively according to weight loss measurements.
3. The contradiction between the corrosion inhibition efficiency of DmChDa in gravimetric and electrochemical studies is due to the complete hydrolysis of the inhibitor over a period of 24 h.
4. DmChDa exhibits high inhibition efficiency than the corresponding parent compounds.
5. The adsorption of DmChDa on a mild steel surface, in 1M HCl and 0.5M H₂SO₄ obeys Langmuir and El-Awady isotherms respectively.
6. ΔG^0_{ads} values indicate that the adsorption behaviour involves both chemical and electrostatic interaction in 1M HCl whereas in 0.5M H₂SO₄ the adsorption behaviour is mainly by chemical interaction
7. High activation energy of corrosion in the presence of inhibitor implies that dissolution of metal decreased with inhibitor concentration due to adsorption of inhibitor on mild steel surface.
8. Polarization data reveals that DmChDa acts as a mixed type inhibitor in both acid media.
9. At all frequencies, the values of current noise are comparatively large for blank metal specimen than for metal immersed in an acid solution containing DmChDa. This clearly suggests that localised corrosion of mild steel is occurring in an acid solution without an inhibitor molecule.
10. SEM analysis confirms that the inhibitor gets adsorbed on the MS surface.

Acknowledgement

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4. Materials and methods

4.1. Synthesis and characterization of DmChDa

Hot ethanolic solution of 5,5-dimethyl-1,3-cyclohexanedione (0.01mol) was added dropwise to a stirred solution containing 0.02 mol of aniline in ethanol. The mixture was refluxed for about 3 h and cooled. The yellow coloured precipitate formed was filtered, washed with distilled water and dried. Fig.13 shows the molecular structure of DmChDa and its tautomer. Anal.calcd for C₂₀H₂₂N₂: C, 82.7; H, 7.5; N, 9.6%. Found. C, 81.3; H, 6.9; N, 8.9%; IR (KBr): $\nu_{\text{C=N}}$ 1564cm⁻¹. ¹H NMR: δ_{NH} 6.1. δ_{CH_3} 1.0. ¹³C NMR: δ_{CH_3} 28.3. Mass: M⁺ peak was absent, base peak [C₁₁H₁₃N]⁺ m/z: 159. m. p. = 152 °C.

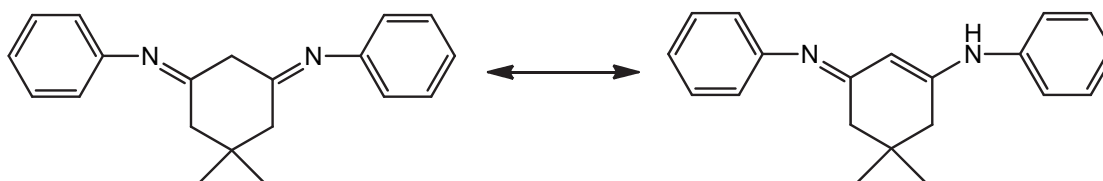


Fig. 13. Tautomeric structure of N, N'-(5,5-dimethylcyclohexane-1,3-diyldene)dianiline.

4.2. Solutions

The acid solution required for conducting corrosion monitoring techniques was prepared from analytical grade acid (Merck) by diluting it with distilled water. The inhibitor concentration employed for the study has the concentration range 0.2mM-1.0mM.

4.3. Weight loss studies

Mild steel (MS) strips having an exposed area of $1 \times 1 \times 0.096$ cm were employed for conducting weight loss studies. Prior to treatment, the strips were polished with SiC papers having grades 100, 200, 400, 600, 800, 1000, 1500 and 2000. Then washed with acetone followed by distilled water and dried. After measuring thickness and area, the MS strips were immersed in 50 ml acid solution at 28°C with the help of fishing lines. The corrosion rate (v) was calculated by measuring the weight loss of the mild steel strip after 24 h using following equation³²⁻³³.

$$v = \frac{KW}{DSt} \quad (7)$$

where $K=87600$, W , D , S and t implies average weight loss of coupon (g), density of mild steel (g cm^{-3}), total area of specimen (cm^2) and exposure time (h) respectively. The percentage of inhibition efficiency was calculated using the following equation³⁴⁻³⁵

$$\eta_w\% = \frac{v_0 - v}{v_0} \times 100, \quad (8)$$

where v_0 and v describe corrosion rate of specimens in contact with the acid solution without and with inhibitor respectively.

4.4. Electrochemical impedance spectroscopic (EIS) studies

Ivium compactstat-e electrochemical system was utilized for impedance study. The cell consists of three-electrode assembly of saturated calomel electrode (SCE), platinum electrode having 1cm^2 area and metal specimen with an exposed area of 1cm^2 as reference electrode, counter electrode and working electrode respectively. Metal specimen was immersed in electrolyte solution (acid solution) prior to each measurement for 30 minutes. EIS measurements were determined at a constant potential (OCP) in the frequency range 1 KHz- 100 MHz with an amplitude of 10 mV as excitation signal. The analysis of impedance plots gave charge transfer resistance. The corrosion inhibition efficiency was determined using the following expression³⁶⁻³⁷

$$\eta_{\text{EIS}}\% = \frac{R_{\text{ct}} - R'_{\text{ct}}}{R_{\text{ct}}} \times 100 \quad (9)$$

where R_{ct} and R'_{ct} denote charge transfer resistance of the metal specimen immersed in acid medium with and without DmChDa.

4.5. Potentiodynamic polarization studies

The MS specimens were subjected to Tafel extrapolation analysis after immersing in an acid solution with and without DmChDa for a period of 30 minutes. As mentioned in EIS studies, a three-electrode system was used in polarization studies. The analyses were carried out by changing the potential of the working electrode from -250 to +250 mV relative to the corrosion potential (E_{corr}) at a scan rate of 1mV/sec. Corrosion current density (I_{corr}) was obtained from Tafel plots from which the percentage of inhibition efficiency ($\eta_{\text{pol}}\%$) was calculated as described below³⁸⁻³⁹

$$\eta_{\text{pol}} \% = \frac{I_{\text{corr}} - I'_{\text{corr}}}{I_{\text{corr}}} \times 100 \quad (10)$$

where I_{corr} and I'_{corr} indicate corrosion current densities of the metal specimen immersed in acid medium without and with DmChDa.

4.6. Electrochemical noise studies

Electrochemical noise measurements were carried out in a three-electrode system consisting of two mild steel electrodes having 1 cm² area and a saturated calomel electrode⁴⁰. The analysis was executed with the help of Ivium Compactstat-e electrochemical system controlled by iviumsoft software. All electrochemical noise analyses were performed for a period of 1200s.

4.7. Scanning electron microscopy

Scanning electron microscope (JEOL Model JSM - 6390LV) was used to study the surface nature of the mild steel specimens after treatment with acid solution in the presence and absence of DmChDa for 24 h.

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