Ragi K “ Structural, corrosion inhibition, chelation, biological and in silico studies of schiff bases.” Thesis. Research and Postgraduate Department of Chemistry, St. Thomas’ college (autonomous), University of Calicut, 2020.

CHAPTER 5

CORROSION INHIBITION STUDIES OF SCHIFF BASES IN 0.5 M H_2SO_4 MEDIUM

Corrosion inhibition efficiency of the Schiff bases 2,2’-(5,5-dimethyl cyclohexane-1,3-diylidene)bis(azanylylidene))diphenol (DMCHDP), N,N’-(5,5-dimethylcyclohexane-1,3-diylidene)dianiline (DMCHDA), 2,2’-(5,5-dimethylcyclo hexane-1,3-diylidene)bis(hydrazinecarboxamide) (DMCHHC), 2-((2hydroxy benzylidene)amino)phenol (2HBAP), 2-(cyclohexylideneamino)phenol (2CHAP) on mild steel were also conducted 0.5 M H_2SO_4. 0.2-1.0 mM concentration of Schiff bases was used for the study. Gravimetric (weight loss) and electrochemical studies such as electrochemical impedance spectroscopy, potentiodynamic polarization studies and electrochemical noise measurements were employed for monitoring corrosion inhibition efficiency. Adsorption isotherm, impact of temperature and surface morphology were also evaluated in this chapter.

Weight loss studies

The weight loss of the MS specimen at 24 h interval in 0.5 M H_2SO_4 in the absence and presence of Schiff bases (DMCHDP, DMCHDA, DMCHHC, 2HBAP and 2CHAP) at different concentrations were determined. Corrosion rate and inhibition efficiency were calculated, which is depicted in Table 5.1 and 5.2 respectively.

On close examination of the results, it is found that the rate of corrosion of MS specimen immersed in 0.5 M H_2SO_4 was higher (35.20 mmy^{-1}) than that immersed in acid solution containing Schiff base molecules. Also the corrosion rate was found to be decreased with concentration of Schiff base molecules. Comparison of corrosion rate of mild steel at different concentrations of the Schiff bases DMCHDP, DMCHDA, DMCHHC, 2HBAP and 2CHAP in 0.5 M H_2SO_4 are shown in Fig. 5.1. Corrosion inhibition efficiency of the Schiff bases increased with rise in concentration of Schiff base molecules. Inhibition efficiency of the Schiff bases except 2HBAP was lower in 0.5 M H_2SO_4 compared to the inhibition efficiency in 1.0 M HCl at all concentrations. This may be attributed to the aggressive nature of 0.5 M H_2SO_4.

Table 5.1 Rate of corrosion of MS in mmy^{-1} with and without Schiff bases DMCHDP, DMCHDA, DMCHHC, 2HBAP and 2CHAP in 0.5 M H_2SO_4

Conc	Schiff base				
(mM)	DMCHDP	DMCHDA	DMCHHC	2HBAP	2CHAP
0.0	35.20	35.20	35.20	35.20	35.20
0.2	19.80	24.16	28.77	22.66	26.82
0.4	7.87	10.33	26.55	22.48	18.82
0.6	7.49	6.81	20.04	21.88	18.15
0.8	2.97	4.39	18.29	17.06	11.66
1.0	2.65	4.40	16.96	15.66	9.77

Table 5.2 Corrosion inhibition efficiency (η_w%) of Schiff bases DMCHDP, DMCHDA, DMCHHC, 2HBAP and 2CHAP on MS specimen in 0.5 M H_2SO_4

Conc (mM)	Schiff base				
	DMCHDP	DMCHDA	DMCHHC	2HBAP	2CHAP
0.2	43.73	31.36	18.25	35.61	23.79
0.4	77.63	70.62	24.55	36.13	46.50
0.6	78.70	80.64	43.05	37.81	48.41
0.8	91.54	87.50	48.03	51.52	66.85
1.0	92.46	87.52	51.81	55.49	72.23

Corrosion inhibition efficiency of DMCHDP and DMCHDA were higher compared to other three Schiff bases. This may be due to the presence of azomethine groups, aromatic rings and hetero atoms. The maximal values of corrosion inhibition efficiency on the MS surface by 1 mM concentration of DMCHDP and DMCHDA were found to be 92.46% and 87.52% respectively. Comparison of corrosion inhibition efficiency of the Schiff bases DMCHDP, DMCHDA, DMCHHC, 2HBAP and 2CHAP on MS in 0.5 M H_2SO_4 were shown in Fig. 5.2.

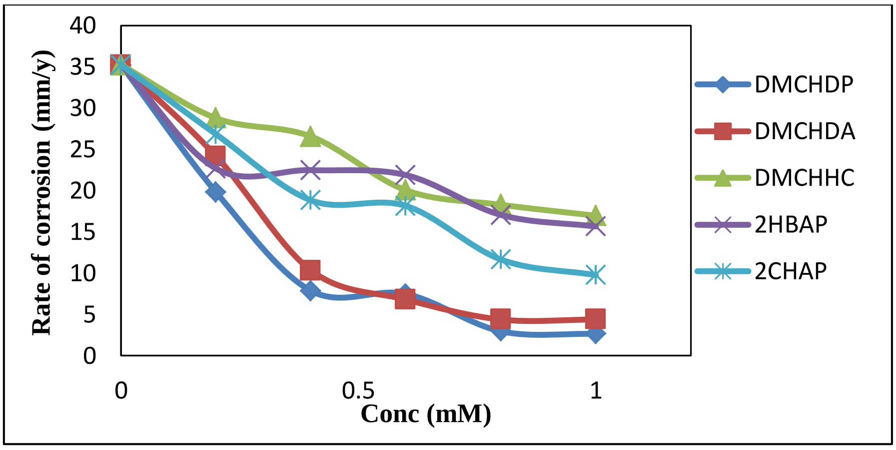

Fig. 5.1 Comparison of corrosion rate of mild steel at different concentrations of the Schiff bases DMCHDP, DMCHDA, DMCHHC, 2HBAP and 2CHAP in 0.5 M H_2SO_4

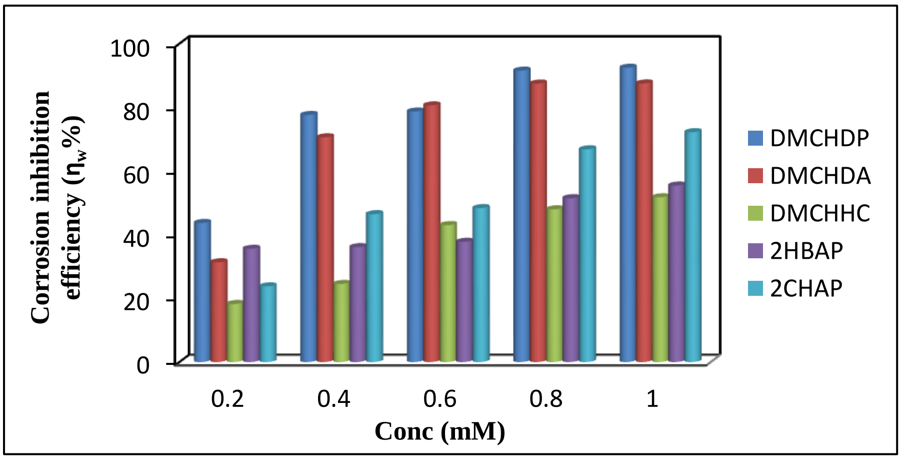

Fig. 5.2 Comparison of corrosion inhibition efficiency (η_w%) of the Schiff bases DMCHDP, DMCHDA, DMCHHC, 2HBAP and 2CHAP on MS in 0.5 M H_2SO_4

Comparison between η_w% of Schiff bases with its parent compounds

In order to correlate the corrosion inhibition efficiency of Schiff bases with parent compounds such as salicylaldehyde (SAY), 5,5-dimethyl-1,3-cyclohexanedione (DM), cyclohexanone (CH), 2-aminophenol (2AP), aniline (AN) and semicarbazide (SZ), weight loss measurements of mild steel specimens were conducted in 0.5 M H_2SO_4 and the efficiencies are given in Table 5.3. Corrosion inhibition efficiency of Schiff bases was higher than the parent compounds. It is due to the involvement of >C=N- group present in the Schiff base molecule during adsorption phenomena. Comparison of corrosion inhibition efficiencies of Schiff bases and their parent compounds on MS in 0.5 M H_2SO_4 are shown in Fig. 5.3.

Table 5.3 Corrosion inhibition efficiency of Schiff bases and their parent compounds on MS in 0.5 M H_2SO_4

Compounds	Conc (mM)		
	0.2	0.6	1.0
DM	29.50	38.68	56.23
2AP	21.14	25.22	29.86
AN	28.26	29.70	43.04
SZ	-9.42	-8.32	-5.39
SAY	6.10	10.41	20.66
CH	0.83	1.57	6.57
DMCHDP	43.73	78.70	92.46
DMCHDA	31.36	80.64	87.50
DMCHHC	18.25	43.05	51.81
2HBAP	35.61	37.81	55.49
2CHAP	23.79	18.15	9.77

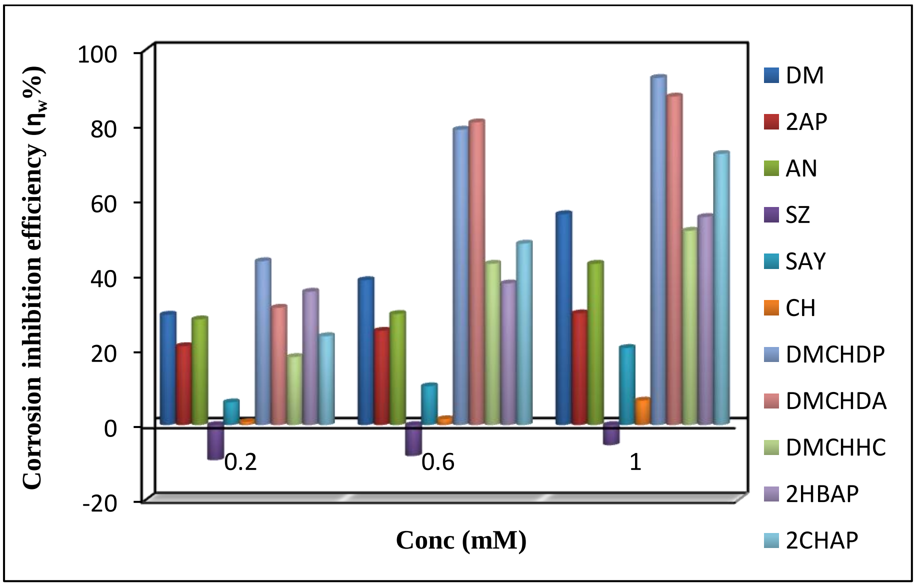

Fig. 5.3 Comparison of corrosion inhibition efficiency (η_w%) of Schiff bases and their parent compounds on MS in 0.5 M H_2SO_4

Adsorption studies

Mechanism of the inhibition of corrosion of MS in 0.5 M H_2SO_4 can be elucidated with the help of adsorption isotherms. 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). Correlation coefficients obtained for the Schiff bases in various isotherms are given in Table 5.4. Thermodynamic parameters obtained from the study are free energy of adsorption (ΔG^0_{ads}) and adsorption equilibrium constant (K_{ads}). From the results it is clear that Langmiur isotherm was obeyed by the Schiff bases DMCHDP and 2CHAP whereas El-Awady isotherm was obeyed by DMCHDA. None of the isotherms considered to study the mechanism of inhibition was obeyed by DMCHHC and 2HBAP. Thermodynamic parameters obtained from the analysis of isotherms are given in Table 5.5 and the adsorption isotherms of Schiff base molecule on MS surface in 0.5 M H_2SO_4 medium are described in Fig. 5.4.

Table 5.4 Correlation coefficients of the Schiff bases derived from various isotherms

Isotherm	Correlation coefficient (R^2)				
	DMCHDP	DMCHDA	DMCHHC	2HBAP	2CHAP
Langmiur	0.9728	0.8592	0.3781	0.8464	0.9997
Freunlich	0.7949	0.7556	0.5881	0.8008	0.6217
Frumkin	0.8801	0.8449	0.2995	0.6101	0.9136
Temkin	0.9233	0.9189	0.5882	0.6441	0.8163
El-Awady	0.9485	0.9606	0.6046	0.6454	0.8986
Florry Huggin	0.8345	0.5999	0.0073	0.3808	0.8812

Table 5.5 Thermodynamic parameters for the adsorption of DMCHDP, DMCHDA, DMCHHC, 2HBAP and 2CHAP on MS in 0.5 M H_2SO_4

Parameter	Schiff base		
	DMCHDP	DMCHDA	2CHAP
Correlation coefficient	0.9728	0.9606	0.9997
K_{ads}	3333.33	1613968.88	33333.33
ΔG^0_{ads} (kJmol^{-1})	-30.37	-45.84	-36.13

Negative values of ΔG^0_{ads} in all case indicate spontaneity of the process. The value of ΔG^0_{ads} for DMCHDP and 2CHAP were -30.37 and -36.13 kJmol^{-1} respectively. This indicates that the adsorption behaviour of these molecules involves both physisorption and chemisorption. In the case of DMCHDA ΔG^0_{ads} value was -45.84kJmol^{-1}, which indicates the presence of co-ordinate type bond between DMCHDA and metal surface (chemical interaction).

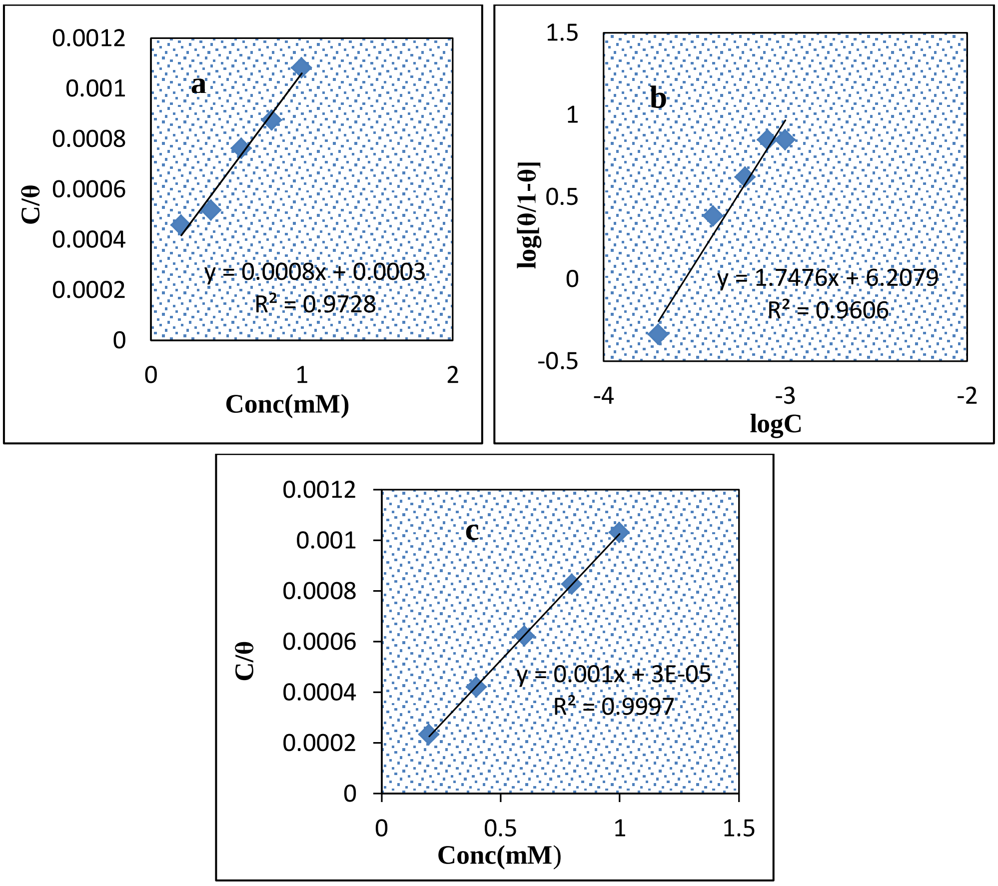

Fig. 5.4 a) Langmuir adsorption isotherm of DMCHDP b) El-Awady adsorption isotherm of DMCHDA and c) Langmuir adsorption isotherm of 2CHAP on MS in 0.5 M H_2SO_4 at 28^0C

Temparature studies

Impact of temperature on the rate of corrosion was investigated using weight loss studies at temperatures 301 K, 313 K, 323 K and 333 K. The activation energy of metal dissolution was calculated using an Arrhenius type equation given below

$$\mathrm{K} = \mathrm{A} \exp(-\mathrm{E_a}/\mathrm{RT}) \qquad (1)$$

where A, K, R, T and E_a denote pre-exponential factor, corrosion rate, universal gas constant, temperature in Kelvin and activation energy respectively. 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 Schiff base molecules (Fig. 5.5-5.9a). Thermodynamic parameters such as enthalpy (ΔH^*) and entropy (ΔS^*) changes were evaluated using transition state theory (equation 2)

$$K = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \qquad (2)$$

where h and N are Planck's constant and Avogadro number respectively. The slope, $\frac{-\Delta H^*}{2.303R}$ and intercept, $\log\left(\frac{R}{2.303Nh}\right) + \left(\frac{\Delta S^*}{2.303R}\right)$ were obtained by plotting log K/T vs 1/T (Fig. 5.5-5.9b). Table 5.6 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 acid solution containing Schiff base molecules. Also, it was found that E_a increased with concentration of Schiff base, which implies that dissolution of the metal was reduced with respect to the rise in Schiff base concentration. Activation energy of corrosion in 0.5 M H_2SO_4 is less compared to that in 1.0 M HCl. This indicates that the corrosion is more pronounced in 0.5 M H_2SO_4 due to its high aggressive nature. Positive sign of the enthalpy of activation indicates the endothermic nature of metal dissolution. ΔH^* and ΔS^* values were found to increase along with rise in concentration of Schiff bases.

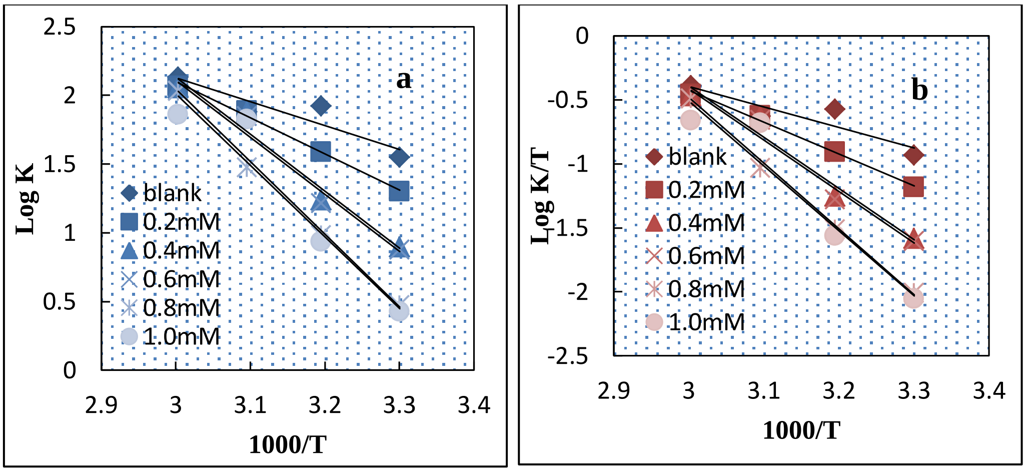

Fig. 5.5 Plot of a) log K vs 1000/T b) log K/T vs 1000/T with and without DMCHDP on MS in 0.5 M H_2SO_4

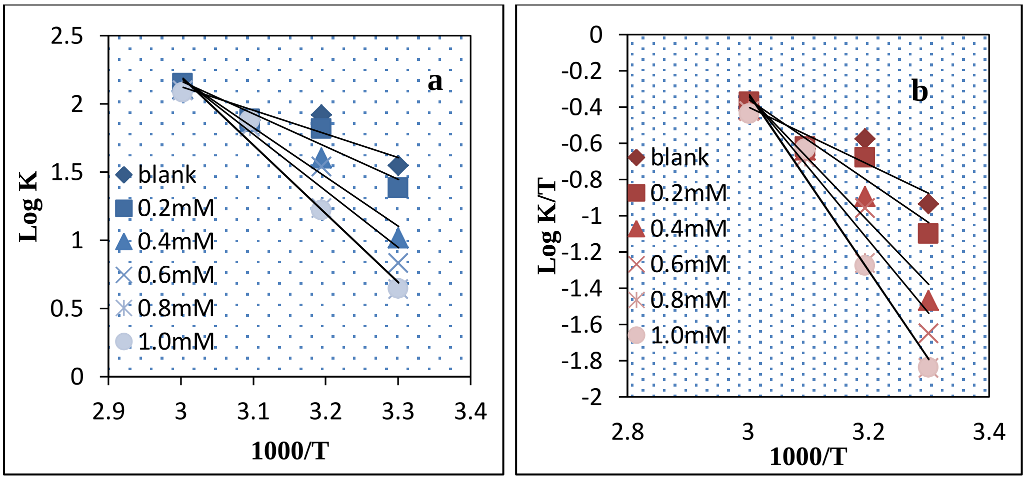

Fig. 5.6 Plot of a) log K vs 1000/T b) log K/T vs 1000/T with and without DMCHDA on MS in 0.5 M H_2SO_4

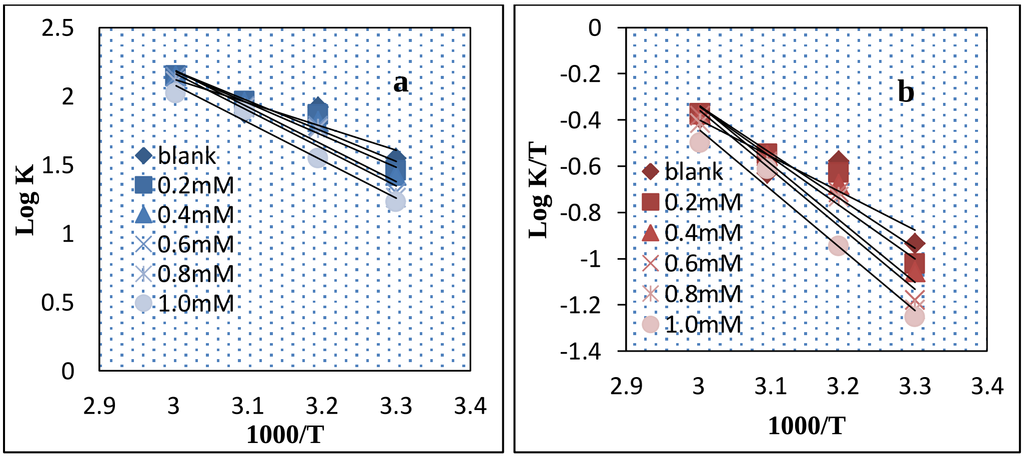

Fig. 5.7 Plot of a) log K vs 1000/T b) log K/T vs 1000/T with and without DMCHHC on MS in 0.5 M H_2SO_4

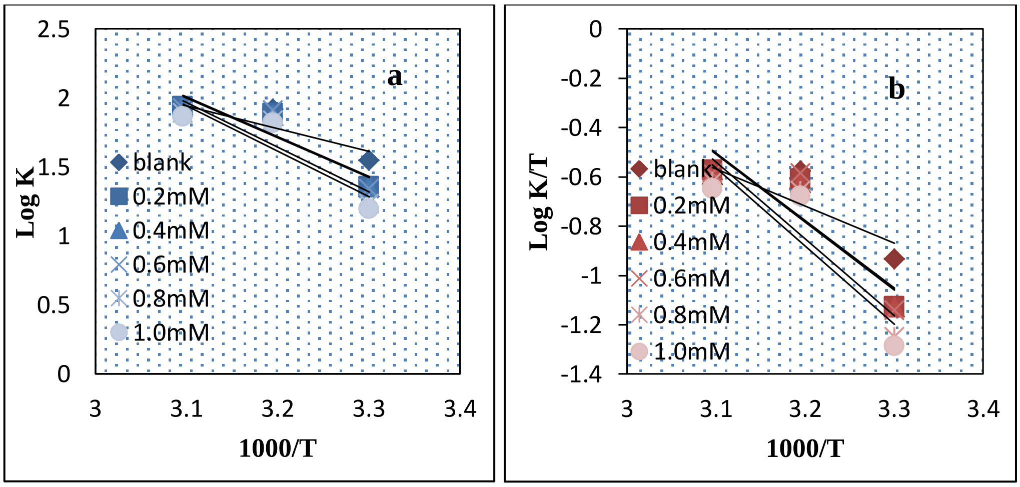

Fig. 5.8 Plot of a) log K vs 1000/T b) log K/T vs 1000/ with and without 2HBAP on MS in 0.5 M H_2SO_4

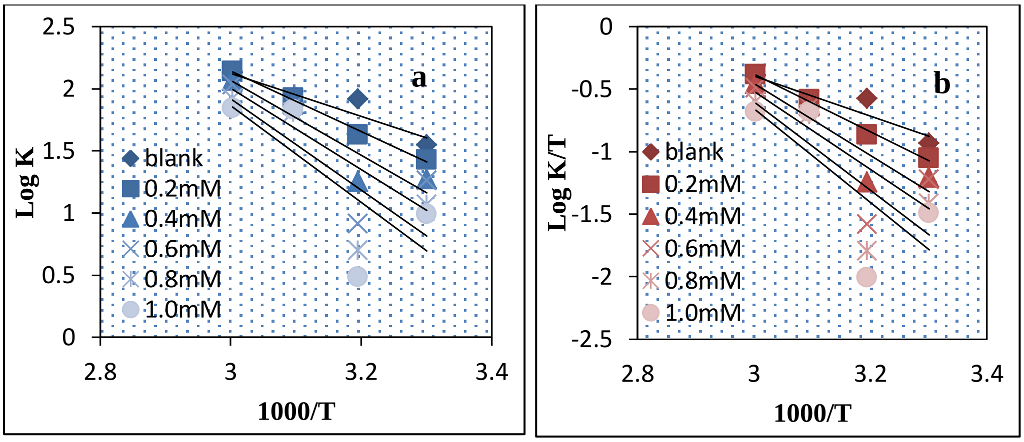

Fig. 5.9 Plot of a) log K vs 1000/T b) log K/T vs 1000/T with and without 2CHAP on MS in 0.5 M H_2SO_4

Table 5.6 Thermodynamic parameters of corrosion of MS with and without Schiff bases in 0.5 M H_2SO_4

Schiff base	Conc (mM)	E_a (kJ mol^{-1})	A	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1}K^{-1})
DMCHDP	Blank	33.1	2.08×10^{7}	30.5	-106.71
	0.2	50.24	9.31×10^{9}	47.60	-55.97
	0.4	79.40	3.73×10^{14}	76.76	32.15
	0.6	79.43	3.58×10^{14}	76.79	31.81
	0.8	99.57	4.09×10^{17}	96.93	90.36
	1.0	100.93	7.21×10^{17}	98.29	95.07
DMCHDA	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
DMCHHC	0.2	42.23	6.38×10^{8}	39.59	-78.26
	0.4	44.90	1.67×10^{9}	42.26	-70.29
	0.6	51.81	2.04×10^{10}	49.17	-49.44
	0.8	52.43	2.43×10^{10}	49.79	-48.01
	1.0	52.92	2.39×10^{10}	50.28	-48.15
2HBAP	0.2	54.99	8.09×10^{10}	52.39	-37.86
	0.4	55.21	8.69×10^{10}	52.61	-37.27
	0.6	55.22	8.83×10^{10}	52.62	-37.14
	0.8	62.13	1.07×10^{12}	59.53	-16.42
	1.0	63.05	1.43×10^{12}	60.45	-14.02
2CHAP	0.2	46.77	2.96×10^{9}	44.13	-65.50
	0.4	57.67	1.26×10^{11}	55.03	-34.28
	0.6	62.45	6.14×10^{11}	59.81	-21.14
	0.8	70.22	8.36×10^{12}	67.58	0.56
	1.0	74.59	3.57×10^{13}	71.95	12.64

Electrochemical impedance spectroscopy

Ivium compactstat-e electrochemical system associated with a new version of iviumsoft software was utilized for the electrochemical measurements. A three electrode system, consisting of platinum electrode having 1 cm^2 area as counter electrode, saturated calomel electrode (SCE) as the reference electrode, metal specimen with an exposed area of 1cm^2 as working electrode, were used for the studies. Impedance spectra (Nyquist and Bode plots) of MS in the absence and presence of Schiff bases at various concentrations in 0.5 M H_2SO_4 are shown in Fig. 5.10, 5.11, 5.12, 5.13 and 5.14.

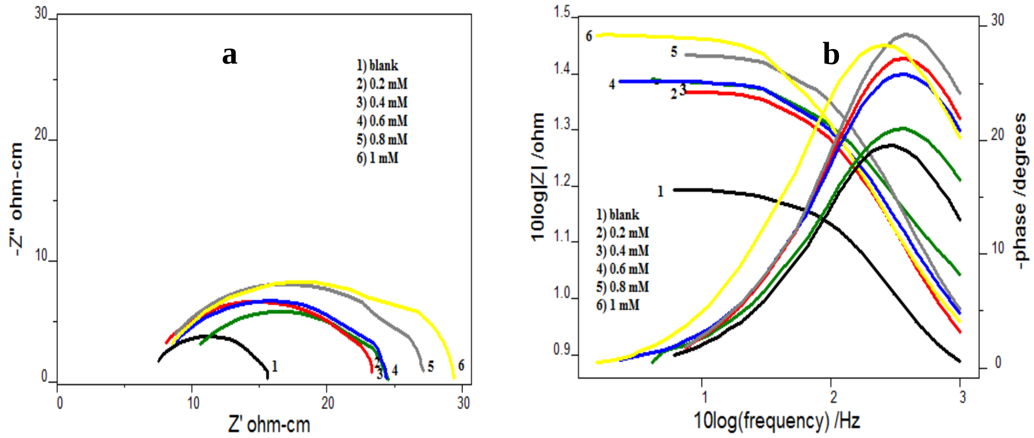

Fig. 5.10 a) Nyquist and b) Bode plots of MS coupons with and without DMCHDP in 0.5 M H_2SO_4

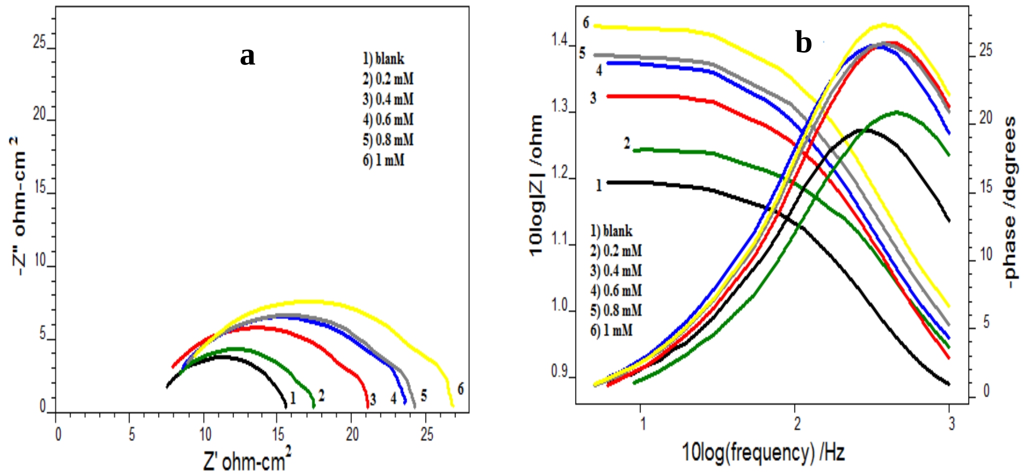

Fig. 5.11 a) Nyquist and b) Bode plots of MS coupons with and without DMCHDA in 0.5 M H_2SO_4

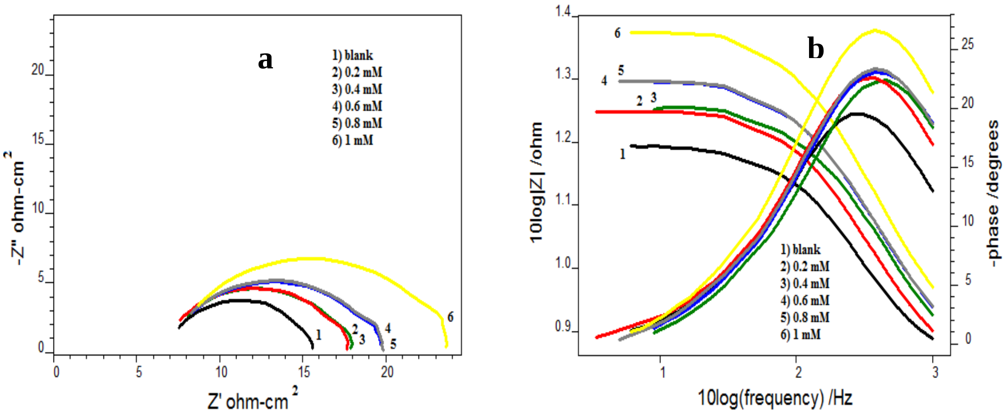

Fig. 5.12 a) Nyquist and b) Bode plots of MS coupons with and without DMCHHC in 0.5 M H_2SO_4

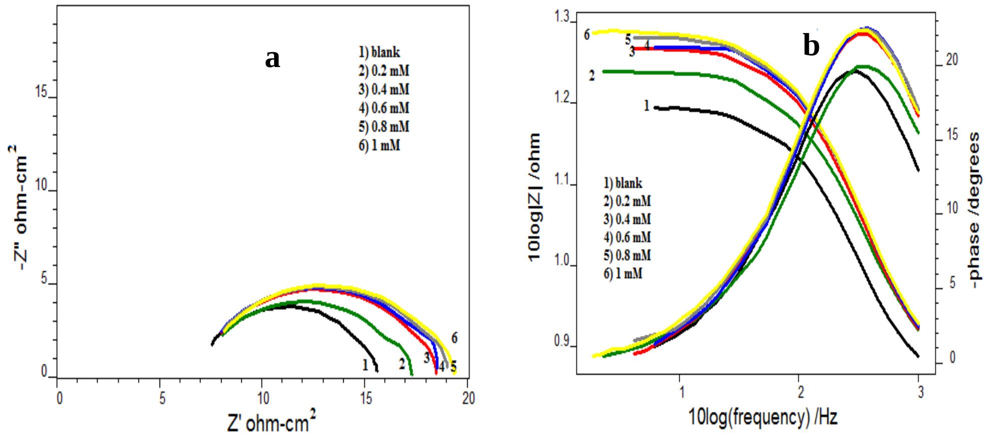

Fig. 5.13 a) Nyquist and b) Bode plots of MS coupons with and without 2HBAP in 0.5 M H_2SO_4

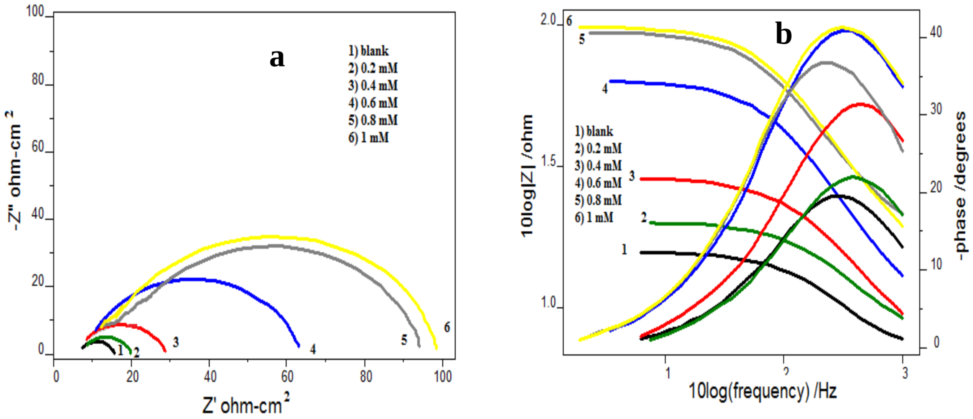

Fig. 5.14 a) Nyquist and b) Bode plots of MS coupons with and without 2CHAP in 0.5 M H_2SO_4

Electrochemical impedance data such as $R_{ct,}$ C_{dl} and the percentage of inhibition efficiency (η_{EIS}%) of the Schiff bases are listed in Table 5.7. From the data it is established that charge transfer resistance of the blank solution (7.96 Ωcm^2) is less than that of the solution containing Schiff base molecule. Also charge transfer resistance (R_{ct}) was found to increase and capacitance (C_{dl}) was reduced with increase in concentration of Schiff bases. As a result corrosion inhibition efficiency (η_{EIS}%) was also increased with concentration.

Table 5.7 Impedance data of MS coupons with and without Schiff bases in 0.5 M H_2SO_4

Schiff base	Conc (mM)	C_{dl} (μFcm^{-2})	R_{ct} (Ωcm^2)	η_{EIS}%
Blank	0.0	113	7.9	-
DMCHDP	0.2	72.8	13.1	39.23
	0.4	66.5	14.6	45.48
	0.6	67.7	14.9	46.57
	0.8	53.2	17.5	54.51
	1.0	83.9	19.3	58.76
DMCHDA	0.2	72.6	9.10	12.53
	0.4	66.6	12.8	37.81
	0.6	71.6	14.3	44.33
	0.8	62.3	14.7	45.85
	1.0	54.6	16.7	52.33
DMCHHC	0.2	72.0	9.86	19.26
	0.4	85.7	9.91	19.68
	0.6	71.4	11.1	28.28
	0.8	72.0	11.2	28.93
	1.0	60.4	14.6	45.48
2HBAP	0.2	94.5	8.88	10.36
	0.4	86.1	10.2	21.96
	0.6	80.9	10.3	22.71
	0.8	83.1	10.5	24.19
	1.0	87.3	10.8	26.29
2CHAP	0.2	72.8	10.9	26.97
	0.4	49.4	19.1	58.32
	0.6	33.2	48.8	83.69
	0.8	27.1	70.2	88.66
	1.0	23.2	77.1	89.67

Maximum inhibition efficiencies of about 58.76%, 52.33%, 45.48%, 26.29% and 89.67% were exhibited by the Schiff bases DMCHDP, DMCHDA, DMCHHC, 2HBAP and 2CHAP respectively at 1 mM concentration. Inhibition efficiency of all the Schiff bases is lower compared to the EIS measurements in 1.0 M HCl medium. Minimum efficiency of about 26.97% was exhibited by 2CHAP at 0.2 mM concentration while at

1.0 mM concentration, maximum efficienty of 89.67% was achieved. According to gravimetric analysis DMCHDP and DMCHDA have appreciable corrosion inhibition efficiency. In contrary to this observation, the inhibition efficiency is low at all concentrations according to EIS measurements. Comparison of corrosion inhibition efficiency (η_{EIS}%) of the Schiff bases on MS in 0.5 M H_2SO_4 was shown in Fig. 5.15.

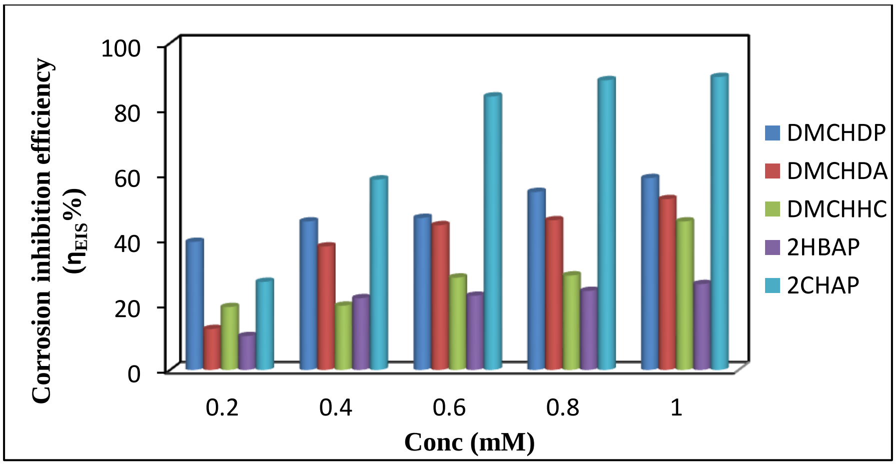

Fig. 5.15 Comparison of corrosion inhibition efficiency (η_{EIS}%) of the Schiff bases on MS in 0.5 M H_2SO_4

Potentiodynamic polarization studies

Tafel and linear polarization studies were carried out to understand the effect of Schiff bases towards polarization of metal specimens. Polarization parameters such as corrosion current density (I_{corr}) and polarization resistance (R_p) were measured using this technique and then inhibition efficiency (η_{pol}% and η_{Rp}%) was calculated using these parameters. Tafel and linear polarization plots of the Schiff bases are shown in Fig. 5.16, 5.17, 5.18, 5.19 and 5.20. Polarization data such as corrosion potential (E_{corr}), corrosion current densities (I_{corr}), cathodic slope (b_c), anodic slope (b_a), polarization resistance (R_p) and inhibition efficiency (η_{pol}% and η_{Rp}%) of the Schiff bases in 0.5 M H_2SO_4 are listed in Table 5.8.

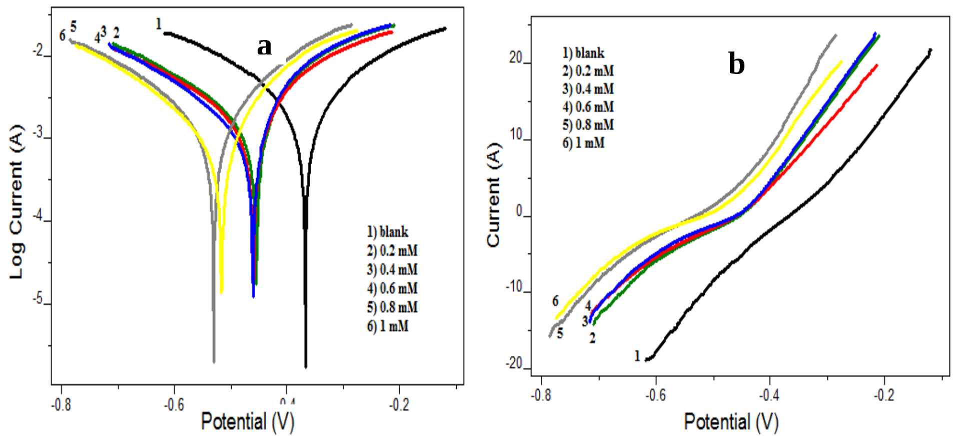

Fig. 5.16 a) Tafel and b) linear polarization plots of MS coupons with and without DMCHDP in 0.5 M H_2SO_4

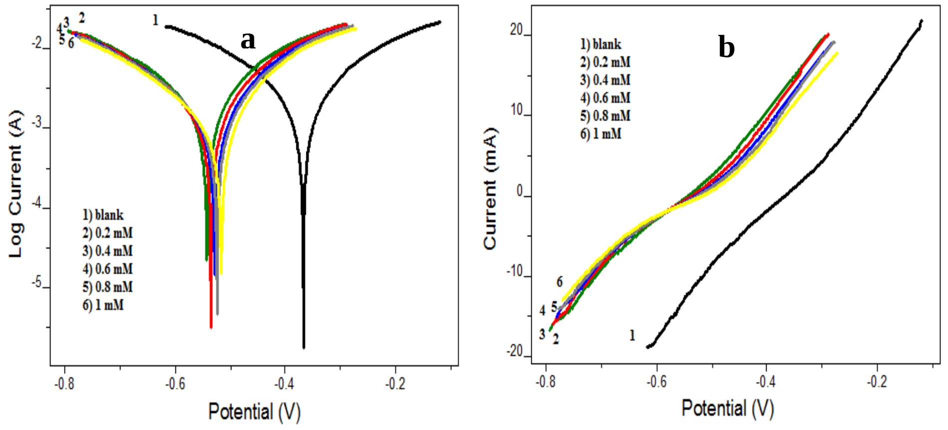

Fig. 5.17 a) Tafel and b) linear polarization plots of MS coupons with and without DMCHDA in 0.5 M H_2SO_4

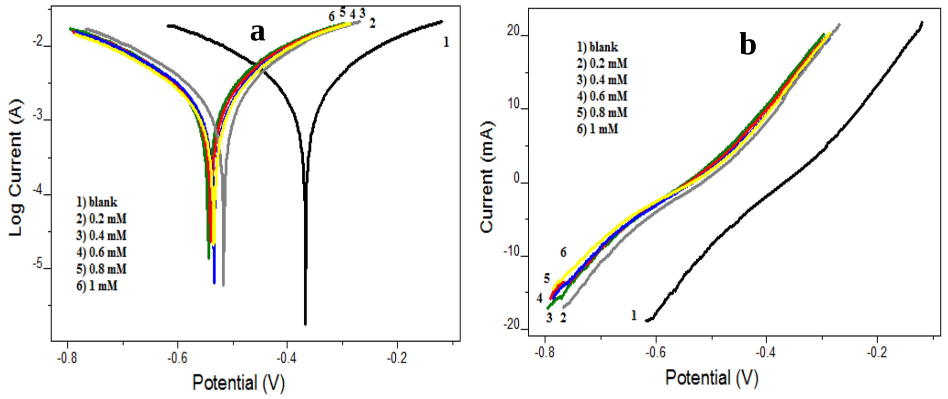

Fig. 5.18 a) Tafel and b) linear polarization plots of MS coupons with and without DMCHHC in 0.5 M H_2SO_4

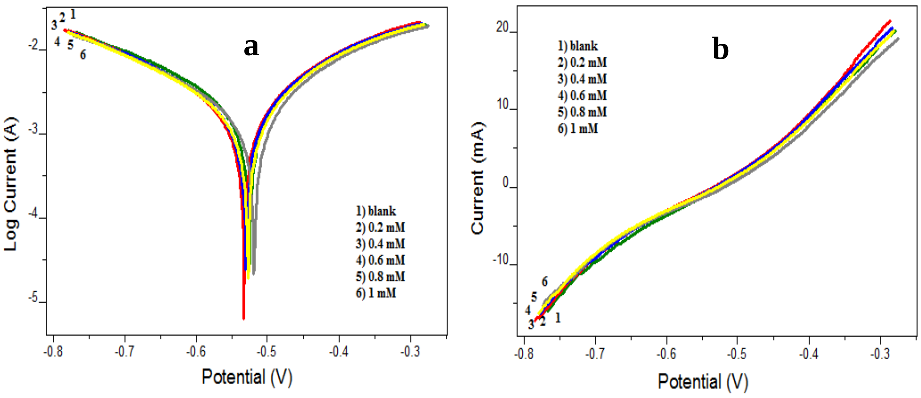

Fig. 5.19 a) Tafel and b) linear polarization plots of MS coupons with and without 2HBAP in 0.5 M H_2SO_4

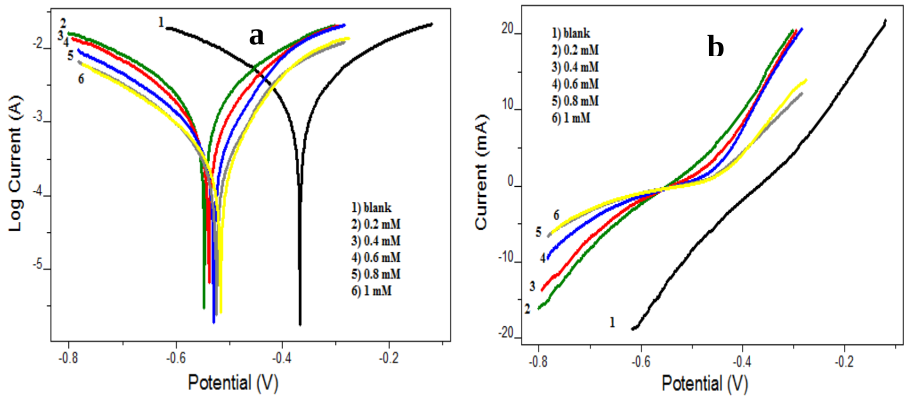

Fig. 5.20 a) Tafel and b) linear polarization plots of MS coupons with and without 2CHAP in 0.5 M H_2SO_4

Polarization data reveals that corrosion current density increased and polarization resistance decreased with the rise in concentration of Schiff bases. As a result, the percentage of inhibition efficiency also increased. A maximum inhibition efficiency (η_{pol}%) of 50.79%, 44.33%, 28.4%, 24.32% and 81.41% were shown by DMCHDP, DMCHDA, DMCHHC, 2HBAP and 2CHAP respectively at 1 mM concentration. The b_a and b_c values indicated that addition of Schiff bases to acid media affected both cathodic and anodic parts of the curves and hence acted as a mixed type inhibitor. Comparison of corrosion inhibition efficiency (η_{pol}%) of the Schiff bases on MS in 0.5 M H_2SO_4 were shown in Fig. 5.21. Impedance and polarization data are in good agreement. Considerable difference was noticed between the corrosion inhibition efficiency of DMCHDP and

DMCHDA in gravimetric and electrochemical studies (EIS and potentiodynamic polarization) in 0.5 M H_2SO_4 medium.

Table 5.8 Polarization data of MS coupons with and without Schiff bases in 0.5 M H_2SO_4

Schiff base	Tafel data						Polarization data	
	Conc (mM)	E_{corr} (mV)	I_{corr} (μA/cm^2)	b_a (mV/dec)	$-b_c$ (mV/dec)	η_{pol}%	R_p (Ω)	η_{Rp}%
Blank	0	-374.3	2528	241	242	-	20.74	-
DMCHDP	0.2	-500.5	2282	253	243	9.73	23.61	12.16
	0.4	-496.3	2058	257	251	18.47	25.59	18.95
	0.6	-514.5	1957	244	219	22.59	26.76	22.49
	0.8	-538.3	1563	185	222	38.17	28.04	26.03
	1	-539.9	1244	185	205	50.79	33.91	38.83
DMCHDA	0.2	-559.7	2329	250	236	7.87	22.63	8.35
	0.4	-556.3	1832	224	213	27.53	25.87	19.83
	0.6	-547.2	1735	220	226	31.37	27.93	25.74
	0.8	-539.1	1557	206	224	38.41	29.9	30.64
	1	-543.1	1408	210	212	44.33	32.52	36.22
DMCHHC	0.2	-556.1	2348	244	243	7.12	22.54	7.98
	0.4	-557.1	2145	240	229	15.15	23.52	11.82
	0.6	-549.8	2127	240	243	15.86	23.76	12.71
	0.8	-529.4	2102	220	233	16.85	24.63	15.79
	1	-551.3	1810	219	231	28.4	27.02	23.24
2HBAP	0.2	-525.9	2269	250	238	10.24	23.35	11.18
	0.4	-544.4	2010	221	237	20.49	24.71	16.07
	0.6	-543.3	2002	223	237	20.8	24.89	16.67
	0.8	-537.7	1914	229	244	24.29	26.16	20.72
	1	-545.8	1913	228	233	24.32	26.79	22.58
2CHAP	0.2	-552.3	1909	217	233	24.49	25.55	18.83
	0.4	-539.6	1233	173	215	51.23	33.74	38.53
	0.6	-536.5	754	142	209	70.17	48.77	57.47
	0.8	-536.4	530	155	205	79.03	72.28	71.31
	1	-532.2	470	143	201	81.41	77.29	73.16

Evaluated corrosion inhibition efficiency of these two Schiff bases according to gravimetric studies in H_2SO_4 medium was higher than that of EIS and potentiodynamic polarization investigations. By using UV-visible spectroscopy, it was confirmed that slow hydrolysis of DMCHDP and DMCHDA is occurring in 0.5 M H_2SO_4 medium.

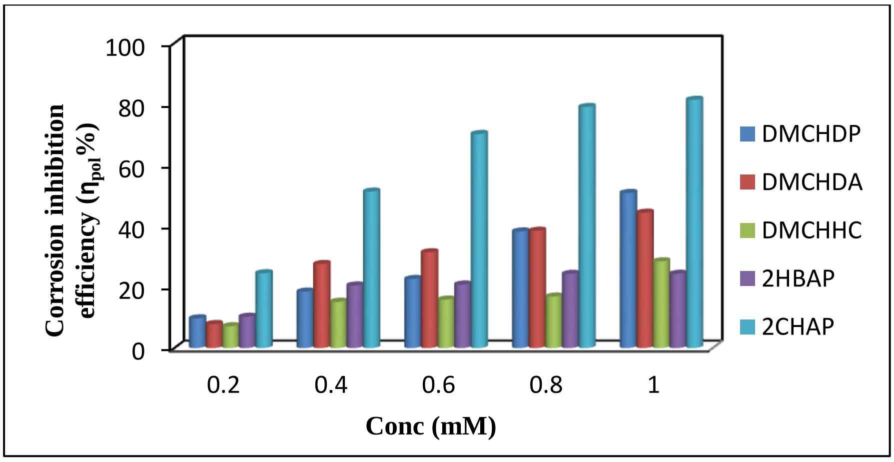

Fig. 5.21 Comparison of corrosion inhibition efficiency (η_{pol}%) of the Schiff bases on MS in 0.5 M H_2SO_4

Fig. 5.22 represents the UV-Vis spectra of DMCHDP and its corresponding parent compounds in 0.5 M H_2SO_4. In the figure 5-5-dimethyl-1,3-cyclohexanedione and 2-aminophenol exhibited peaks at 259 nm and 268 nm respectively. The peak at 290 nm due to DMCHDP is shifted to 265 nm when UV-Vis spectrum of DMCHDP was taken after immersion time of 24 h. This indicates the formation of 2-aminophenol molecule. It can be assumed that large number of Schiff bases didn’t undergo appreciable structural degradation for 1-2 h and thus exhibit poor corrosion inhibition potency on MS according to electrochemical studies. On keeping DMCHDP for a period of 24 h it can be imagined that partial hydrolysis takes place (for one C=N linkage only). This structural degradation of DMCHDP may be highly beneficial to interact effectively on the MS surface, since the bulky nature of the molecule is appreciably lowered. Electron rich aromatic ring and the C=N linkage now can make coordinate type bonds with the surface metal atoms easily. Thus after a period of 24 h, DMCHDP molecule showed much enhanced corrosion inhibition efficiency on MS surface.

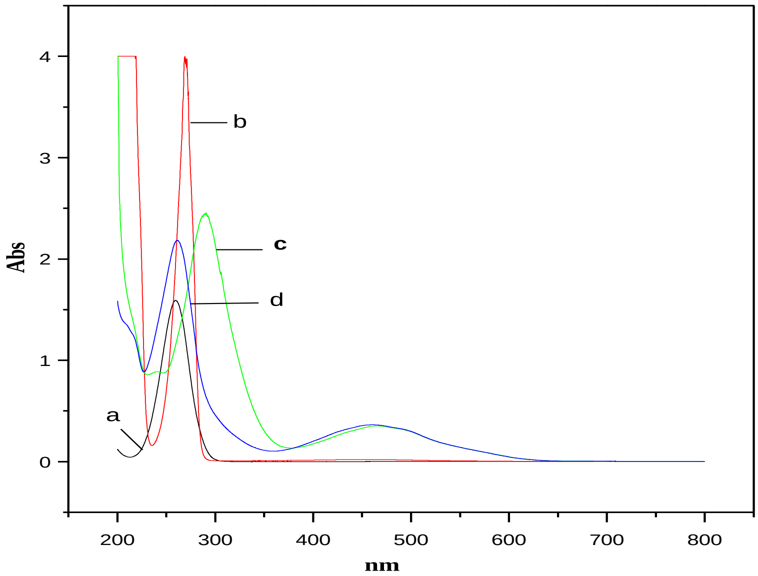

Fig. 5.22 UV-Vis spectra of a) 5,5-dimethyl-1,3-cyclohexanedione b) 2-aminophenol c) DMCHDP at 0 h and d) DMCHDP at 24 h in 0.5 M H_2SO_4

Fig. 5.23 represents the UV-Vis spectra of DMCHDA and its corresponding parent compounds in 0.5 M H_2SO_4. In the case of DMCHDA 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 peak of 5-5-dimethyl-1,3-cyclohexanedione at 259 nm is observed in the UV-Vis spectrum of DMCHDA after immersion time of 24 h in 0.5 M H_2SO_4. Peak due to aniline at 252 nm may be merged. Parent compounds itself have appreciable inhibition efficiency in 0.5 M H_2SO_4 (Table 5.3). 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 1.0 M HCl medium the corrosion inhibition efficiency of DMCHDP and DMCHDA in gravimetric and electrochemical studies follows the same trend. This may be due to the higher adsorption tendency of these Schiff bases on Cl^- ion, which is strongly bind to mild steel surface instead of its hydrolysis.

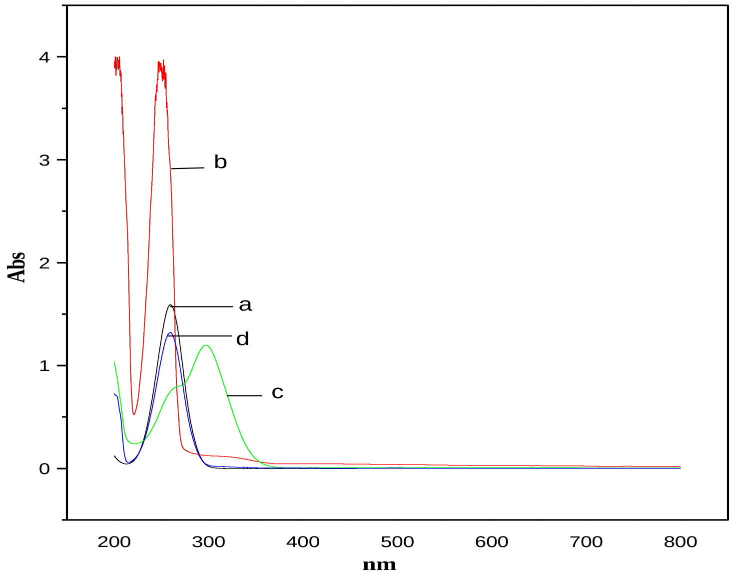

Fig. 5.23 UV-Vis spectra of a) 5,5-dimethyl-1,3-cyclohexanedione b) aniline c) DMCHDA at 0 h and d) DMCHDA at 24 h in 0.5 M H_2SO_4

Electrochemical noise measurements

The parameters mean value of current noise and pitting index were measured from noise plots. Mean value of current noise gives information regarding protective power of sample against corrosion and pitting index value helps to quantify localized pitting corrosion. Current noise for MS in the absence and presence of Schiff bases (1 mM) in 0.5 M H_2SO_4 is shown in Fig. 5.24.

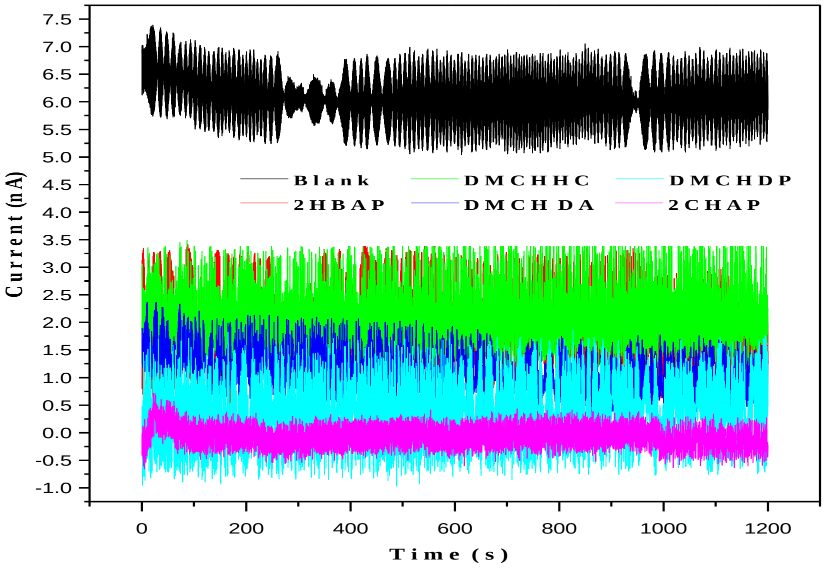

Fig. 5.24 Current noise for MS in the absence and presence of Schiff bases (1 mM) in 0.5 M H_2SO_4

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 Schiff base molecules, and the mean value of current noise in 0.5 M H_2SO_4 was greater than in 1.0 M HCl medium, which reflects the greater protective power of Schiff bases in 1.0 M HCl medium. PSD plot is shown in Fig 5.25.

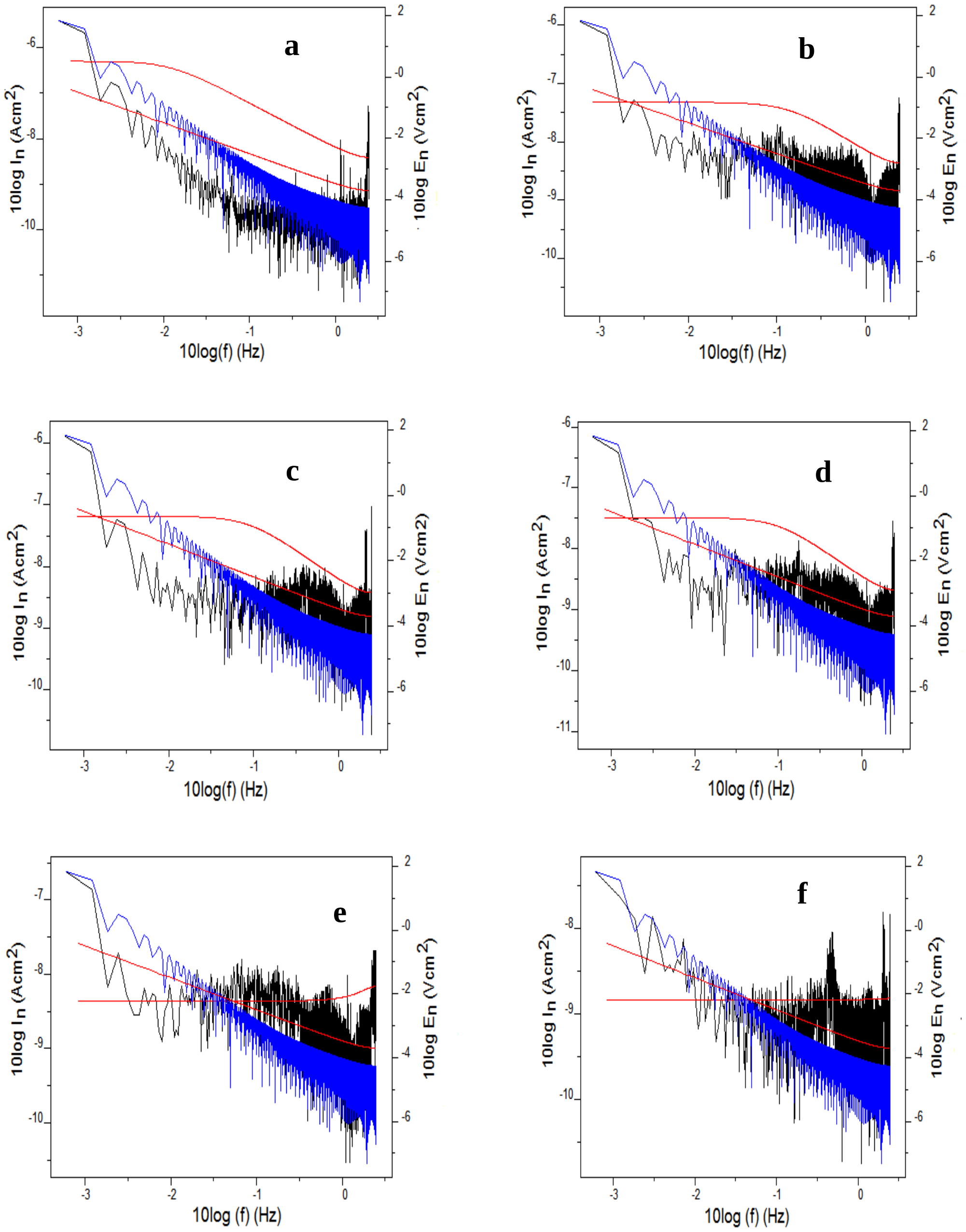

Fig. 5.25 Power spectral density (voltage and current) plots of MS in 0.5 M H_2SO_4 in the presence of a) blank b) 2HBAP c) DMCHHC d) DMCHDA e) DMCHDP and f) 2CHAP

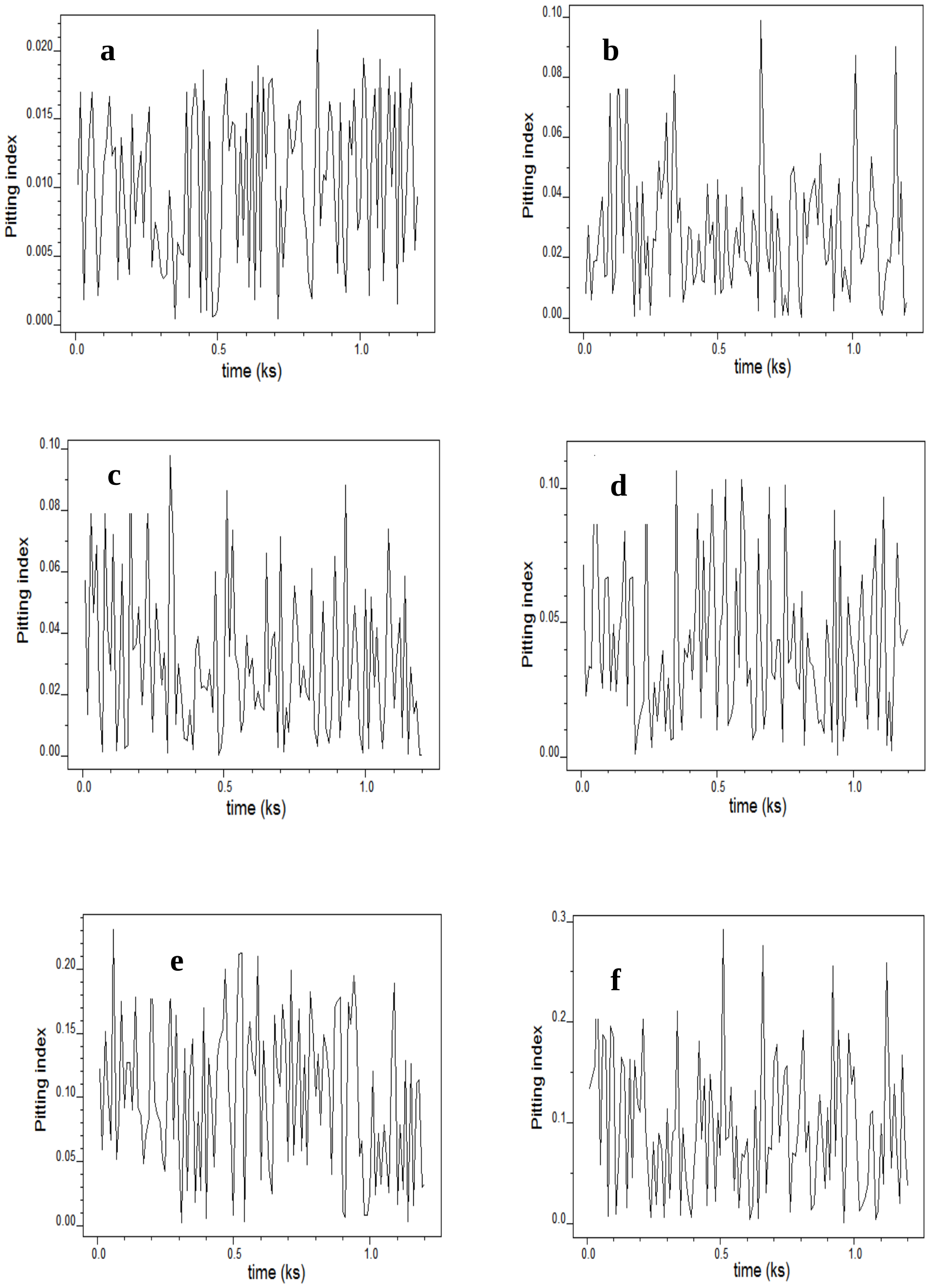

Fig. 5.26 Pitting index curves of MS in 0.5 M H_2SO_4 in the presence of a) blank b) 2HBAP c) DMCHHC d) DMCHDA e) DMCHDP and f) 2CHAP

The values of current noise are comparatively large for blank metal specimen than for metal immersed in acid solution containing Schiff base molecules at all frequencies. Thus localised corrosion is happening in the absence of Schiff base molecule. Pitting index curves are shown in Fig. 5.26. Amplitude of the pitting index curve corresponding to blank metal specimen is lower than metal specimens treated with acid solution containing Schiff bases. Thus the acid solution containing Schiff base molecule has high resistance to corrosion.

Surface morphological studies

In order to determine the surface morphology of MS coupons, scanning electron microscopy was conducted. Fig. 5.27(a-d) represents the SEM images of bare metal, mild steel coupon in 0.5 M H_2SO_4, MS treated with DMCHDP (1 mM) and MS treated with DMCHDA (1 mM) respectively.

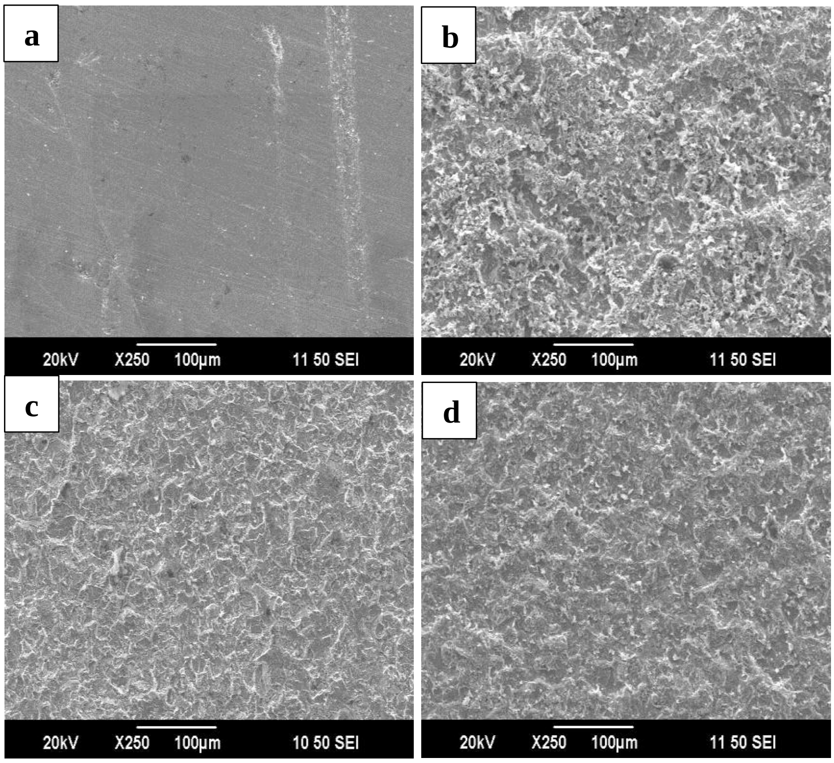

Fig. 5.27 SEM images of MS coupons before and after 24 h immersion a) bare b) blank (0.5 M H_2SO_4) c) treated with DMCHDP (1 mM) in 0.5 M H_2SO_4 and d) treated with DMCHDA(1 mM) in 0.5 M H_2SO_4

There exists a remarkable difference between the surface of a polished mild steel specimen and the one treated with acid solution. It is clear that the mild steel surface reacted with acid medium is erratic and rough in nature. A remarkable change in the surface morphology of MS was observed after adding Schiff base molecule into 0.5 M H_2SO_4 medium. In the presence of 1 mM concentration of DMCHDP and DMCHDA 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 Schiff base molecules on mild steel surface.

SUMMARY

In this part synthesis and characterization of the Schiff bases such as 2,2’-(5,5-dimethylcyclohexane-1,3-diylidene)bis(azanylylidene))diphenol (DMCHDP), N,N’-(5,5-dimethylcyclohexane-1,3-diylidene)dianiline (DMCHDA), 2,2’-(5,5-dimethylcyclo hexane-1,3-diylidene)bis(hydrazinecarboxamide) (DMCHHC), 2-((2hydroxy benzylidene)amino) phenol (2HBAP) and 2-(cyclohexylideneamino)phenol (2CHAP) were carried out. Elemental analysis, spectral studies such as FTIR, UV-visible, NMR (^{1}H and ^{13}C) and mass spectroscopy and cyclic voltammetric studies were employed for the structural elucidation.

Corrosion inhibition efficiency of these Schiff bases on mild steel was also investigated in 1.0 M HCl and 0.5 M H_2SO_4. The concentration of the Schiff bases used for the study lies in the range of 0.2-1.0 mM. Corrosion inhibition efficiency of the synthesized Schiff bases was evaluated using gravimetric method and electrochemical methods such as electrochemical impedance spectroscopy (EIS), potentiodynamic polarization studies and electrochemical noise measurements. Evaluation of adsorption phenomenon on the mild steel surface was carried out using various adsorption isotherms to verify the mechanism of inhibition and surface morphological studies were performed to confirm the adsorption behaviour. Effect of temperature on the corrosion inhibition efficiency as well as quantum chemical calculations was also done.

Data revealed that corrosion inhibition capacity of the Schiff bases derived from 5,5-dimethylcyclohexane-1,3-dione such as DMCHDP, DMCHDA and DMCHHC was high compared to that of 2HBAP and 2CHAP in 1.0 M HCl. Also the inhibition efficiency of these three inhibitors is greater than 90% at 1 mM concentration according to weight loss studies. Azomethine, hydroxyl group and presence of hetero atoms present in these Schiff bases are responsible for their higher efficiency. In the case of all Schiff

bases except 2HBAP, rate of corrosion is less than that of blank specimen and is found to be decreasing with rise in concentration, which established the antagonistic nature of 2HBAP on corrosion. Adsorption study revealed that the Schiff bases DMCHDP, DMCHDA and DMCHHC obey Langmuir adsorption isotherm whereas 2HBAP and 2CHAP follow Frumkin adsorption isotherm on mild steel in 1.0 M HCl. According to impedance and polarization studies all the Schiff bases have appreciable inhibition efficiency, and act as mixed type inhibitors towards mild steel corrosion.

In 0.5 M H_2SO_4 the corrosion inhibition efficiency of all the Schiff bases except 2HBAP are less compared to that in 1.0 M HCl according to weight loss study. This can be attributed to the aggressive nature of sulphuric acid medium. The inhibition efficiency of DMCHDP and DMCHDA was high than other Schiff bases according to weight loss study. Also it was observed that the inhibition efficiency of these two Schiff bases reduced considerably in impedance and potentiodynamic polarization measurements. Comparatively high efficiency observed in weight loss measurement may be attributed to hydrolysis of DMCHDP and DMCHDA in sulphuric acid medium. DMCHDP undergo partial hydrolysis whereas DMCHDA undergo complete hydrolysis which was clearly observed in UV-visible spectra taken after 24 h immersion of mild steel specimen in inhibitor solutions. High inhibition efficiency upon hydrolysis can be explained by the lowering of steric nature in the case of DMCHDP whereas it may be because of the formation of parent compounds having appreciable inhibition efficiency, in the case of DMCHDA. Schiff bases DMCHDP and 2CHAP obeyed Langmuir adsorption isotherm whereas DMCHDA followed El-Awady isotherm. In sulphuric acid medium also all the Schiff bases acted as mixed type inhibitors, towards the mild steel corrosion.

Temperature-dependent gravimetric analysis showed that the activation energy of corrosion was high in both acid solutions containing Schiff base molecules. Also it was observed that activation energy increased with rise in concentration of Schiff bases. Positive value of enthalpy of corrosion reflects the endothermic nature of corrosion. Surface morphological study established the protective nature of Schiff bases on mild steel surface. Electrochemical noise measurement was also carried out to examine the inhibition capacity.

REFERENCES

1. Z. Tao, S. Zhang, W. Li and B. Hou, *Ind. Eng. Chem. Res.* 49, 2593-2599 (2010).
2. S. John and A. Joseph, *Mater. Chem. Phys*. 133, 1083-1091 (2012).
3. S. Deng, X. Li and H. Fu, *Corros. Sci*. 53, 3596-3602 (2011).
4. K. R. Ansari and M. A. Quraishi, *Corros. Sci*. 95, 62-70 (2015).
5. I. Ahamad, R. Prasad and M. A. Quraishi, *J. Solid State Electrochem*. 14, 2095-2105 (2010).
6. K. C. Emregül and O. Atakol, *Mater. Chem. Phys*. 83, 373-379(2004).
7. D. Gopi, K. M. Govindaraju and L. Kavitha, *J. Appl. Electrochem*. 40, 1349-1356 (2010).
8. X. Wang, H. Yang and F. Wang, *Corros. Sci*. 53, 113-121 (2011).
9. M. P. Chakravarthy and K. N. Mohana, *ISRN Corrosion*. 2014, 1-13 (2014).
10. A. K. Singh, S. K. Shukla, M. Singh and M. A. Quraishi, *Mater. Chem. Phys*. 129, 68-76 (2011).
11. K. Ramya, R. Mohan, K. K. Anupama and A. Joseph, *Mater. Chem. Phys*. 149, 632-647 (2015).
12. A. K. Singh, S. K. Shukla, M. A. Quraishi and E. E. Ebenso, *J. Taiwan Inst. Chem. Eng*. 43, 463-472 (2012).
13. X. Wang, Y. Wang, Q. Wang, Y. Wan, X. Huang and C. Jing, *Int. J. Electrochem. Sci*. 13, 5228-5242 (2018).
14. N. G. Thompson, M. Yunovich and D. Dunmire, *Corros. Rev*. 25, 247-261 (2007).
15. O. S. I. Fayomi, I. G. Akande and S. Odigie, *J. Phys.: Conf. Ser*. 1378, 1-8 (2019).

16. K. S. Jacob and G. Parameswaran, *Corros. Sci*. 52, 224-228(2010).
17. K. S. Shaju, K. J. Thomas and V. P. Raphael, *Orient. J. Chem.* 30, 807-813 (2014).
18. R. Solmaza, E. Altunbas and G. Kardas, *Mater. Chem. Phys*. 125, 796-801 (2011).
19. H. Keles, M. Keles, I. Dehri, and O. Serindag, *Mater. Chem. Phys*. 112, 173-179 (2008).
20. P. Lowmunkhong, D. Ungthararak and P. Sutthivaiyakit, *Corros. Sci*. 52, 30-36 (2010).
21. M. Paulson Binsi, K. Thomas Joby, K. Ragi, C. Varghese Sini and J. Reeja, *Curr. Chem. Lett.* 9, 1-12 (2019).
22. K. Mallaiya, R. Subramaniam, S. S. Srikandan, S. Gowri, N. Rajasekaran and A. Selvaraj, *Electrochim. Acta*. 56, 3857-3863 (2011).
23. K. R. Ansari, M. A. Quraishi and A. Singh, *Corros. Sci*. 79, 5-15 (2014).
24. N. Soltani, M. Behpour, S. M. Ghoreishi and H. Naeimi, *Corros. Sci*. 52, 1351-1361 (2010).
25. E. E. Oguzie, *Mater. Lett.* 59, 1076-1079 (2005).
26. H. Schiff, *Justus Liebigs Ann. Chem*. 131, 118-119 (1864).
27. D. N. Dhar and C. L. Taploo, *J. Sci. Ind. Res*. 41, 501-506 (1982).
28. E. Bayer, *Angew. Chem. Int. Ed*. 3, 325-332 (1964).
29. F. Feigl, *Spot Tests in Organic Analysis*, Elsevier, New York, NY, USA, 2, (1958).
30. P. Przybylski, A. Huczynski, K. Pyta, B. Brzezinski and F. Bartl, *Curr. Org. Chem*. 13, 124-148 (2009).
31. P. Singh, R. L. Goel and B. P. Singh, *J. Indian Chem. Soc*. 52, 958-959 (1975).

32. Elmali, M. Kabak and Y. Elerman, *J. Mol. Struct*. 477, 151-158 (2000).
33. A. Chawla, K. Kuldeep, P. Chawla and R. K. Dhawan, *J. Res. Appl. Nat. Soc. Sci*. 1, 85-92 (2015).
34. A. Fattah-alhosseini and M. Noori, *Measurement*. 94, 787-793 (2016).
35. M. N. Ibrahim and S. E. A. Sharif, *E-J. Chem.* 4, 531-535 (2007).
36. M. Colak, T. Aral, H. Hosgoren and N. Demirel, *Tetrahedron: Asymmetr.* 18, 1129–1133 (2007).
37. S. Kumar, D. N. Dhar, and P. N. Saxena, *J. Sci. Ind. Res*. 68, 181-187 (2009).
38. M. S. Karthikeyan, D. J. Prasad, B. Poojary, K. S. Bhat, B. S. Holla and N. S. Kumari, *Bioorg. Med. Chem*. 14, 482-489 (2006).
39. L. Heinisch, E. Roemer, P. Jutten, W. Haas, W. Werner and U. Mollmann, *J. Antibiot*. 52, 1029-1041 (1999).
40. W. Rehman, M. K. Baloch, B. Muhammad, A. Badshah and K. M. Khan, *Chin. Sci. Bull*. 49, 119-122 (2004).
41. M. S. Alam, J. –H. Choi and D. –U. Lee, *Bioorg. Med. Chem.* 20, 4103-4108 (2012).
42. D. Sriram, P. Yogeeswari, N. S. Myneedu and V. Saraswat, *Bioorg. Med. Chem. Lett*. 16, 2127-2129 (2006).
43. A. K. Chaubey and S. N. Pandeya, *Int. J. Pharmtech. Res.* 4, 590-598 (2012).
44. Y. -F. Li and Z. -Q. Liu, *Eur. J. Pharm. Sci*. 44, 158-163 (2011).
45. Dr. A. Xavier and N. Srividhya, *IOSR J. Appl. Chem*. 7, 6-15 (2014).
46. W. Qin, S. Long, M. Panunzio and B. Stefano, *Molecules*. 18, 12264-12289 (2013).
47. P. Rathelot, P. Vanelle, M. Gasquet, F. Delmas, M. P. Crozet, P. Timon-David and J. Maldonado, *Eur. J. Med. Chem*. 30, 503-508 (1995).

48. B. Witkop and T. W. Beiler, *J. Am. Chem. Soc.* 76, 5589-5597 (1954).
49. M. S. Novikov, A. F. Khlebnikov, O. V. Besedin and R. R. Kostikov, *Tetrahedron Lett.* 42, 533-535 (2001).
50. I. N. Booysen, S. Maikoo, M. P. Akerman and B. Xulu, *Polyhedron*. 79, 250-257 (2014).
51. N. K. Chaudhary and P. Mishra, *Bioinorg. Chem. Appl*. 2017, 1-13 (2017).
52. B. K. Singh, A. Prakash, H. K. Rajour, N. Bhojak and D. Adhikari, *Spectrochim. Acta A*. 76, 376-383 (2010).
53. M. El-Behery and H. El-Twigry, *Spectrochim. Acta A*. 66, 28-36 (2007).
54. S. Li, S. Chen, S. Lei, H. Ma, R. Yu and D. Liu, *Corros. Sci.* 41, 1273-1287 (1999).
55. S. John, B. Joseph, K. K. Aravindakshan and A. Joseph, *Mater. Chem. Phys*. 122, 374-379 (2010).
56. A. Yurt, A. Balaban, S. Ustün Kandemir, G. Bereket and B. Erk, *Mater. Chem. Phys*. 85, 420-426 (2004).
57. W. Li, Q. He, S. Zhang, C. Pei and B. Hou, *J. Appl. Electrochem.* 38, 289-295 (2008).
58. K. M. Govindaraju, D. Gopi and L. Kavitha, *J. Appl. Electrochem.* 39, 2345-2352 (2009).
59. N. Kuriakose, J. T. Kakkassery, V. P. Raphael and S. K. Shanmughan, *Indian J. Mater. S.* 2014, 1-6 (2014).
60. M. G. Hosseini, M. Ehteshamzadeh and T. Shahrabi, *Electrochim. Acta*. 52, 3680-3685 (2007).
61. I. Ahamad, C. Gupta, R. Prasad and M. A. Quraishi, *J. Appl. Electrochem*. 40, 2171-2183 (2010).

62. K. R. Ansari and M. A. Quraishi, *J. Ind. Eng. Chem.* 20, 2819-2829 (2014).
63. K. S. Shaju, K. J. Thomas, V. P. Raphael and A. Paul, *ISRN Corrosion*. 2012, 1-8 (2012).
64. M. A. Quraishi and D. Jamal, *Mater. Chem. Phys*. 78, 608–613 (2003).
65. N. K. Gupta, C. Verma, M. A. Quraishi and A. K. Mukherjee, *J. Mol. Liq.* 215, 47-57 (2016).
66. A. M. Abdel-Gaber, M. S. Masoud, E. A. Khalil and E. E. Shehata, *Corros. Sci*. 51, 3021-3024 (2009).
67. M. Balaji, N. Chandrasekar, G. Sharmila and R. Manivannan, *Int. J. Res. Eng. Technol*. 4, 51-64 (2016).
68. S. P. Fakrudeen, H. C. Ananda murthy and V. B. Raju, *J. Chil. Chem. Soc.* 57, 1364-1371 (2012).
69. P. Karuppasamy, M. Ragu, J. Thiruppathy, M. Ganesan, T. Rajendran and V. K. Sivasubramanian, *Int. J. Multidiscip. Res. Dev.* 1, 14-24 (2014).
70. A. Barbosa da Silva, E. D. Elia and J. Antonio da Cunha Ponciano Gomes, *Corros. Sci*. 52, 788-793 (2010).
71. R. Menaka and S. Subhashini, *J. Adhes. Sci. Technol.* 30, 1622-1640 (2016).
72. R. Solmaza, E. Altunbas and G. Kardas, *Mater. Chem. Phys*. 125, 796-801 (2011).
73. A. S. Fouda and S. A. EL-Sayyad, *Anti-Corros. Method M*. 58, 63-69 (2011).
74. K. Veni, A. D. Karthik, K. Geetha and D. Shakila, *IOSR J. Pharm*. 2, 62-68 (2017).
75. M. Q. Mohammed, *J. Basrah Researches*. 37, 116-130 (2011).
76. Y. B. Zemede, D. Nithyakalyani and S. Ananda Kumar, *Int. J. Med. Res*. 2, 128-141 (2016).

77. S. K. Saha, A. Dutta, P. Ghosh, D. Sukulc and P. Banerjee, *Phys. Chem. Chem. Phys.* 17, 5679-5690 (2015).
78. P. Silku, S. Ozkinali, Z. Ozturk, A. Asan and D. A. Kose, *J. Mol. Struct.* 1116, 72-83 (2016).
79. R. K. Upadhyay, S. Anthony and S. P. Mathur, *Russ. J. Electrochem*. 43, 238-241 (2007).
80. D. Daoud, T. Douadi, S. Issaadi and S. Chafaa, *Corros. Sci*. 79, 50-58 (2014).
81. M. Farsak, H. Keles and M. Keles, *Corros. Sci*. 98, 223-232 (2015).
82. B. M. Mistry and S. Jauhari, *Res. Chem. Intermed.* 41, 6289-6307 (2014).
83. V. P. Raphael, K. J. Thomas, K. S. Shaju and A. Paul, *Res. Chem. Intermed*. 40, 2689-2701 (2013).
84. T. S. Franklin Rajesh, A. Sheik Mideen, J. Karthikeyan and S. Anitha, *Int. J. Appl. Bioeng.* 6, 2810-2815 (2012).
85. C. M. Goulart, A. Esteves-Souza, C. A. Martinez-Huitle, C. J. F. Rodrigues, M. A. M. Maciel and A. Echevarria, *Corros. Sci*. 67, 281-291 (2013).
86. V. P. Raphael, J. T. Kakkassery, K. S. Shaju and S. Varghese, *Int. J. Ind. Chem*. 8, 49-60 (2016).
87. P. C. Okafor, E. E. Oguzie, G. E. Iniama, M. E. Ikpi and U. J. Ekpe, *Global J. Pure Appl. Sci.*14, 89-95 (2008).
88. Dr. L. Ravikumar, Dr .G. Rathika and R. Punitha, *Int. J. Adv. Res. Technol.* 2, 3137-3143 (2013).
89. N. Raman, S. Ravichandran, and C. Thangaraja, *J. Chem. Sci*. 116, 215-219 (2004).
90. Y. Meng, W. Ning, B. Xu, W. Yang, K. Zhang, Y. Chen, L. Li, X. Liu, J. Zheng and Y. Zhang, *RSC Adv*. 7, 43014-43029 (2017).

91. A. Dandia, S. L. Gupta, M. A. Quraishi, and P. Singh, *ACS Sustain. Chem. Eng.* 1, 1303-1310 (2013).
92. A. A. Farag, M. A. Migahed and A. M. Al-Sabagh, *Egypt. J. Pet.* 24, 307-315 (2015).
93. S. Issaadi, T. Douadi, A. Zouaoui, S. Chafaa, M. A. Khan and G. Bouet, *Corros. Sci*. 53, 1484-1488 (2011).
94. X. Li, S. Deng, H. Fu and T. Li, *Electrochim. Acta.* 54, 4089–4098 (2009).
95. A. Ghanbari, M. M. Attar and M. Mahdavian, *Mater. Chem. Phys*. 124, 1205-1209 (2010).
96. S. A. Umoren, *J. Appl. Polym. Sci*. 119, 2072-2084 (2011).
97. H. Ashassi-Sorkhabi, B. Shaabani and D. Seifzadeh, *Electrochim. Acta.* 50, 3446-3452 (2005).
98. G. E. Badr, *Corros. Sci*. 51, 2529-2536 (2009).
99. D. K. Yadav, M. A. Quraishi and B. Maiti, *Corros. Sci*. 55, 254-266 (2012).
100. Z. Tao, W. He, S. Wang, S. Zhang and G. Zhou, *Corros. Sci*. 60, 205-213 (2012).
101. P. Singh, V. Srivastava and M. A. Quraishi, *J. Mol. Liq*. 216, 164-173 (2016).
102. Y. Tang, X. Yang, W. Yang, R. Wana, Y. Chen and X. Yin, *Corros. Sci*. 52, 1801-1808 (2010).
103. A. R. Sathiya Priya, V. S. Muralidharan and A. Subramania, *Corrosion*. 64, 541-552 (2008).
104. C. Verma, M. A. Quraishi, E. E. Ebenso, I. B. Obot and A. El Assyry, *J. Mol. Liq*. 219, 647-660 (2016).
105. E. E. Elemike, D. C. Onwudiwe, H. U. Nwankwo and E. C. Hosten, *J. Mol. Struct*. 1136, 253-262 (2017).

106. N. K. Gupta, M. A. Quraishi, C. Verma and A. K. Mukherjee, *RSC Adv*. 6, 102076-102087 (2016).

107. A. Y. Musa, A. B. Mohamad, A. A. H. Kadhum, M. S. Takriff and L. T. Tien, *Corros. Sci*. 53, 3672-3677 (2011).

108. L. Li, Q. Qu, W. Bai, F. Yang, Y. Chen, S. Zhang and Z. Ding, *Corros. Sci*. 59, 249-257 (2012).

109. R. Baboian, "*Corrosion Tests and Standards: Application and Interpretation"*, ASTM stock NO: MNL-20, 2nd edn. (1998).

110. C. Wagner and W. Z. Traud, *Z. Elektrochem*. 44, 391 (1938).

111. T. Badea, M. Nicola, I. D. Vaireanu, I. Maior and A. Cojocaru, "*Electrochimie si Coroziune, Matrixrom, Bucuresti*", 150 (2005).

112. A. Pandey, B. Singh, C. Verma and E. E. Ebenso, *RSC Adv*. 7, 47148-47163 (2017).

113. P. P. Kumari, S. A. Rao and P. Shetty, *Procedia Mater. Sci.* 5, 499-507 (2014).

114. M. Dekker, "*Electrochemical Techniques in Corrosion, Science and Engineering*", New York (2003).

115. I. Ahamad, R. Prasad and M. A. Quraishi, *Mater. Chem. Phys*. 124, 1155-1165 (2010).

116. Y. J. Tan, S. Bailey and B. Kinsella, *Corros. Sci*. 38, 1681-1695 (1996).

117. F. Mansfeld, Z. Sun, C. H. Hsu and A. Nagiub, *Corros. Sci*. 43, 341-352 (2001).

118. J. Smulko, K. Darowicki and A. Zieliński, *Electrochem. Commun*. 4, 388-391 (2002).

119. S. Abd El Wanees, A. Abd and M. Abdel Azzem, *Int. J. Electrochem. Sci*. 3, 104-117 (2008).

120. J. F. Chen and W. F. Bogaerts, *Corros. Sci*. 37, 1839-1842 (1995).

121. H. Ashassi-Sorkhabi, D. Seifzadeh and M. Raghibi-Boroujeni, *Arab. J. Chem*. 9, S1320–S1327 (2016).
122. A. M. Homborg, R. A. Cottis and J. M. C. Mol, *Electrochim. Acta*. 222, 627-640 (2016).
123. A. M. Homborg, E. P. M. van Westing, T. Tinga, X. Zhang, P. J. Oonincx, G. M. Ferrari, J. H. W. de Wit and J. M. C. Mol, *Corros. Sci*. 66, 97-110 (2013).
124. S. F. Burch, S. F. Gull and J. Skilling, *Comput. Vision, Graph. Image Processing*. 23, 113-128 (1983).
125. K. F. Al-Azawi, S. B. Al-Baghdadi, A. Z. Mohamed, A. A. Al-Amiery, T. K. Abed, S. A. Mohammed, A. A. H. Kadhum and A. B. Mohamad, *Chem. Cent. J.* 10, 1-9 (2016).
126. T. Arslan, F. Kandemirli, E. E. Ebenso, I. Love and H. Alemu, *Corros. Sci*. 51, 35-47 (2009).
127. E. E. Ebenso, D. A. Isabirye and N. O. Eddy, *Int. J. Mol. Sci*. 11, 2473-2498 (2010).
128. P. M. Nouri and M. M. Attar, *Bull. Mater. Sci*. 38, 499-509 (2015).
129. M. M. Kabanda, L. C. Murulana, M. Ozcan, F. Karadag, I. Dehri, I. B. Obot and E. E. Ebenso, *Int. J. Electrochem. Sci*. 7, 5035-5056 (2012).