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Electrochemical and thermodynamical investigation of Schiff's bases of Glycine and Aldehydes on Corrosion inhibition behavior of Mild steel in 1M hydrochloric acid medium

Lakhan khandelwal, Chandra Bhan Verma, M.A. Quraishi*
Department of Applied Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi-221005, India

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**E-mail:* maquraishi.apc@itbhu.ac.in,maquraishi@rediffmail.com

Abstract

Three Schiff's bases (SBs) namely 2-(2-hydroxybenzylidene amino) acetic acid (HBAA), 2-(4-(dimethylamino) benzylidene amino) acetic acid (DMBA), and 2-(2-hydroxy-4-methyxybenzylidene amino) acetic acid (HMBA) were synthesized and their effects on the electrochemical behavior of mild steel in 1 M HCl was investigated using gravimetric measurements, Tafel extrapolation technique, linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) methods. Tafel polarization measurements revealed that these Schiff's bases act as mixed-type inhibitors. Among the studied SBs, HMBA exhibited the best inhibition efficiency of 95% at 400 ppm concentration. Some thermodynamic parameters were also determined to investigate the mechanism of adsorption. The results obtained from weight loss and electrochemical methods are in good agreement.

Keywords: Acid corrosion, Mild steel, Thermodynamic parameter, EIS

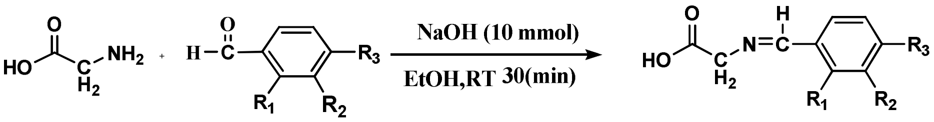
1. Introduction

Acidic solutions are used extensively in several industrial processes such as acid pickling, acid cleaning, acid descaling and oil wet cleaning, etc. [1].The use of inhibitor is one of the most practical methods for protection against corrosion specially in acidic media [2-3]. In an effort to mitigate the corrosion of mild steel in acid solutions, the strategy is to isolate the metal from corrosive agents. During past few years, a variety of N-heterocyclic compounds have been reported to be effective as corrosion inhibitors for mild steel in acid solutions [4-7]. The choices of these compounds are based on the consideration that these compounds contain a better π electron conjugation and hetero atoms (N, O) enhancing a better coordination and adsorption property. Inhibition occurs via adsorption of these heterocyclic molecules on metal surface following some known adsorption isotherms with the polar groups acting as adsorptive centers. Various heterocyclic SBs have been recently studied in considerable detail as effective corrosion inhibitors for mild steel in acidic media by our research group [8-12].The present study was undertaken toSynthesize and investigate the corrosion inhibition of mild steel in 1 M HCl by three SBs of Glycine and aldehydes. The study was conducted by weight-loss, potentiodynamic polarization, linear polarization and electrochemical impedance spectroscopy methods.

2. Experimental section

2.1 Inhibitors synthesis

All Schiff's bases were synthesized according to scheme given in Scheme 1 [13]. This synthesis also achieved by ultrasonicting above reaction mixture for 10 minutes. The purity of the products determined by thin-layer chromatography with a mixture of ethyl acetate/n-hexane (4:6) using the SiliaPlate TLC Plates Aluminum (Al) Silica. The melting points and relative flow (R_f) values of synthesized Schiff's bases is given in Table 1.The IR-spectroscopic data for Schiff's bases of Glycine and Salicylaldehyde also in favors of this synthesis. IR-(KBr, cm^{-1}): *v* 3400, 2942, 2850, 2660, 1754, 1650, 1485, 1230, 1158, 890, 824,798, 735,690, 665.



Glycine **Aldehyde** **Shiffs base**

Scheme 1: Synthetic scheme of Schiff's bases

Table 1: Melting points and relative flow of three synthesized Schiff's bases with nature of $–R_1$, $-R_2$ and $–R_3$ in three Schiff's bases

Schiff's Base	$-R_1$	$-R_2$	$-R_3$	*Molecular weight*	*M.P (^0C)*	*$-R_f$*
HBAA	-OH	-H	-H	179.17	195^0	51.51
HBAA	-H	-H	$-N(CH3)_2$	206.24	178^0	63.50
HMBA	-H	-OH	$-OCH_3$	209.20	185^0	48.10

2.2 Materials:

Corrosion tests were performed on mild steel specimens of following composition (wt %): C = 0.076, Mn = 0.192, P = 0.012, Si = 0.026, Cr =0.050, Al = 0.023, and remainder Fe. Mild steel specimens used in gravimetric and electrochemical experiments were mechanically cut into 2.5 × 2 × 0.025 cm^3 and 7.5 × 1 × 0.025 cm^3 dimensions with exposed area of 1.0 × 1.0 cm^2 and remaining portion were covered with epoxy resin, and then abraded with SiC abrasive papers of grades 600, 800, 1000, and 1200, respectively, washed with acetone, dried and stored in moisture-free desiccators before use in corrosion studies. The aggressive solution, 1M HCl was prepared by dilution of analytical grade 37% HCl with double distilled water.

2.3 Test Solution:

The test solutions of inhibitor were made by dissolving Schiff's bases in 1M HCl and for dilution double distilled water was used.

2.4. Weight loss method:

The weight loss measurements were carried out by standard method as described earlier [14].The inhibition efficiency (η %) and surface coverage (θ) was calculated by using the following equations:

$$\eta\% = \frac{C_R - C_{R(i)}}{C_R} \times 100 \tag{1}$$

$$\theta = \frac{C_R - C_{R(i)}}{C_R} \tag{2}$$

where $C_R$and $C_{R(i)}$ are the corrosion rate values in absence and presence of inhibitor respectively. The corrosion rate (C_R) of mild steel in acidic medium was calculated by using following equation:

$$C_R = \frac{W}{A\ t} \tag{3}$$

where, *W* is weight loss of mild steel specimens (mg), *A* is the area of the specimen (cm^2) and *t* is the exposure time (*h*).

2.4. Electrochemical measurements

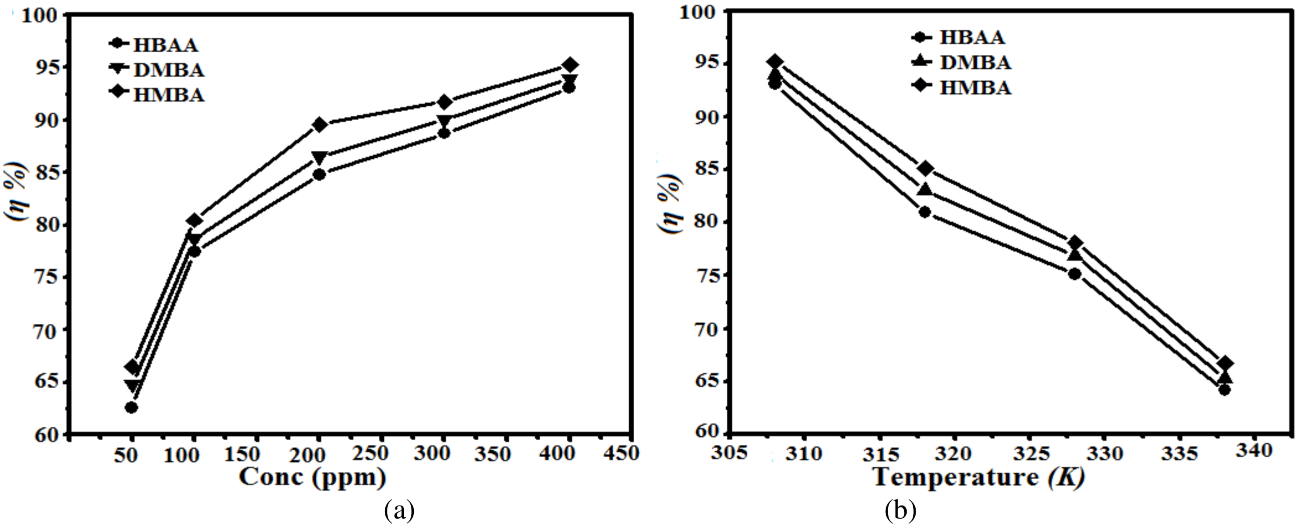
The electrochemical measurements were carried out by standard method as described earlier [14].

3. Result and discussion:

3.1 Weight loss studies:

3.1.1 Effect of inhibitor concentration

The mild steel specimens were exposed to naturally aerated 1 M HCl for 3 hours. It has been found that inhibition efficiency of all the all three Schiff's bases increases with increase in concentration. The maximum inhibition efficiency for each inhibitor was found at 400 ppm concentration and no appreciable increases were observed on further increase in concentration of SBs. The variation of inhibition efficiency with increases the SBs concentration from 50 ppm to 400 ppm shown in Figure 2 (a, b). It is clear that on increasing SBs concentration inhibition efficiency increases. The values of percentage inhibition efficiency (η%) , corrosion rate (*C*R), Surface coverage (θ) and corresponding efficiency obtained from weight loss method at different concentrations are summarized in Table 2.



(a) (b)

Figure 1(a-b): (a) Inhibition efficiency of SBs at different concentration, (b) Inhibition efficiency of SBs at different temperatures

3.1.2. Effect of Temperature:

The effect of the temperature on inhibition efficiency was studied by weight loss measurement from 303 to 338 K in absence and presence of optimum concentration of Schiff's bases for three hours immersion time. From Figure 1(c) it is cleared that corrosion rate is temperature dependent and generally increases with increasing the temperature. This decrease in inhibition is due to desorption of inhibitors from metal surface [15].Thus, at higher temperature , more desorption of inhibitor molecules takes place and larger surface area of metal come in contact with acid, resulting in an increase in corrosion rate [16].

Table 2*:* Corrosion rate (C_R), Surface coverage (θ) and inhibition ($\eta\,\%$) for mild steel in 1M HCl in absence and in presence of different concentrations of SBs from weight loss measurements at 308 K.

Inhibitor	Conc (ppm)	Weight loss (mg)	Surface coverage (θ)	Inhibition efficiency ($\eta\%$)	Corrosion rate (mm/y)
Blank	-	230	-	-	85.3
HBAA	50	86	0.626	62.6	31.09
	100	52	0.773	77.3	19.29
	200	35	0.847	84.7	12.98
	300	26	0.886	88.6	9.64
	400	16	0.930	93.0	5.93
DMBA	50	81	0.647	64.7	30.03
	100	49	0.786	78.6	18.18
	200	31	0.865	86.5	11.5
	300	23	0.900	90.0	8.53
	400	14	0.939	93.9	5.19
HMBA	50	77	0.665	66.5	28.50
	100	45	0.804	80.4	16.69
	200	24	0.895	89.5	8.90
	300	19	0.917	91.7	7.04
	400	11	0.952	95.2	4.08

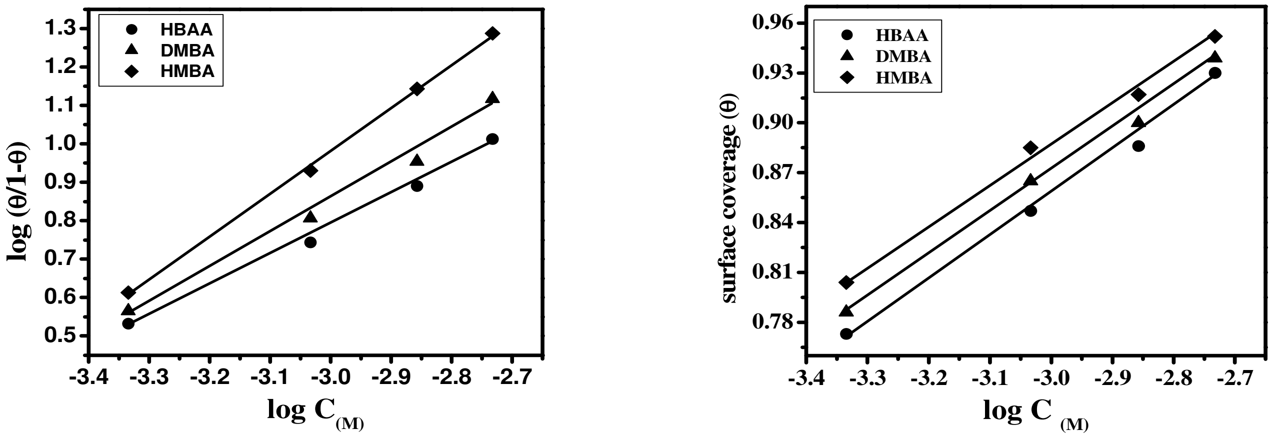
3.1.3 Thermodynamically parameters and Adsorption isotherms:

The mechanism of corrosion inhibition may be explained on basis of adsorption behavior [17]. Several adsorption isotherms were tested to describe the adsorption behavior of all the compounds used in study. The Langmuir adsorption isotherm can be expressed by following equation.

$$\frac{C_{(\text{inh})}}{\theta} = \frac{1}{K_{(\text{ads})}} + C_{(\text{inh})} \quad (4)$$

where, $C_{(\text{inh})}$ is SBs concentration and K_{ads} is equilibrium constant for adsorption-desorption process.

The degree of surface coverage (θ) for different concentrations of SBs in 1N HCl at 35-65 *°C* for 3 h of immersion time has been evaluated from weight loss values. The data were tested graphically by fitting tovarious isotherms. The Langmuir and Temkin isotherm were also tested and given in Figure 3(a-b).



(a) (b)

Figure 2:(a): Langmuir adsorption isotherm (b): Temkin adsorption isotherm

The value of heat of adsorption was determined from the slope *(-ΔG_{ads}/2.303RT)* of the graph. K_{ads}related to standard energy of adsorption (ΔG_{ads}) by following equation [18]:

$$\Delta G^{\text{o}}_{\text{ads}} = -RT\ln(55.5K_{\text{ads}}) \quad (5)$$

$$\ln K_{\text{ads}} = \frac{-\Delta H^{\text{o}}_{\text{ads}}}{RT} + \text{constant} \quad (6)$$

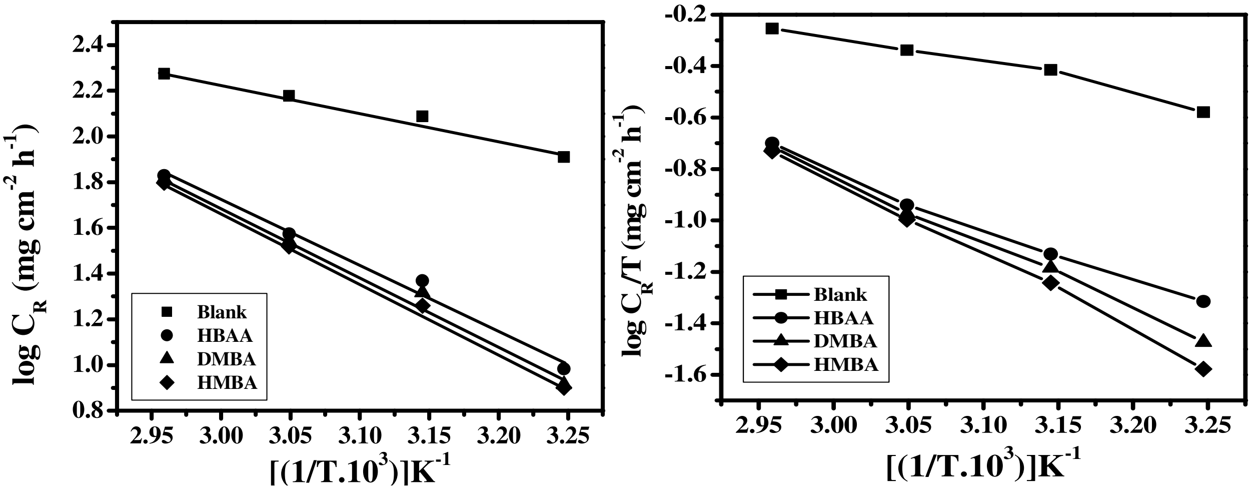
The calculated value of heat of adsorption and adsorption constant are given in Table 2. Since the values of heat of adsorption for the all three Schiff's base are less that *-40 KJmol^{-1}* suggests physical adsorption on mild steel surface [19, 20].

Corrosion rate depend upon temperature and this dependency on temperature can be express by Arrhenius and Transition state equations:

$$\log(C_{\text{R}}) = \frac{-E_{\text{a}}}{2.303RT} + \log\lambda \quad (7)$$

$$C_{\text{R}} = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \quad (8)$$

where E_{a} apparent activation energy, λ is the pre-exponential factor, *T* is absolute temperature, $\Delta H^*$is the apparent enthalpy of activation, ΔS^* the apparent entropy of activation, *h* Planck's constant and *N is* the Avogadro number. A linear plot between log(*CR*) vs 1/*T* and log(*CR/T*) vs. 1/*T* (Figure 4 a-b), with a slope of ($-\Delta H^*/2.303\,R$) and an intercept of [log(*R/Nh*) + ($\Delta S^*/2.303R$)], from which the values of ΔS^* and ΔH^* were calculated and listed in Table 2. The data shows that thermodynamic activation functions (*Ea)* of the corrosion in mild steel in 1N HCl solution in the presence of the SBs is lower than those in free acid solution this show that corrosion rate of mild steel is mainly controlled by activation energy [21]. The negative values of ΔS^* indicates that the process of adsorption is spontaneous [22, 23].



(a) (b)

Figure 3: (a) Arrhenius plot of log *CR* vs. 1/*T* (b) Transition state plot of log *CR/T* vs. 1/*T*

Table 3: Thermodynamicparameter for mild steel in 1M HCl in absence and presence of optimum concentration of Schiff's bases

Inhibitor Blank	E_a (kJ mol^{-1})	-ΔG (kJ mol^{-1})				K_{ads} (M-1 10^3)				ΔH* (kJ mol^{-1})	ΔS* (JK^{-1}mol^{-1})
		308	318	328	338	308	318	328	338		
Blank	23.48	-	-	-	-	-	-	-	-	21.04	-178.9
HBAA	44.69	-35.07	-33.19	-33.30	-32.85	15.94	5.08	3.66	2.14	64.35	-19.73
DMBA	44.74	-35.45	-33.56	-33.54	-32.96	18.47	5.86	3.97	2.24	69.92	-9.25
HMBA	46.13	-36.10	-33.98	-33.7	-33.2	23.80	6.85	4.25	2.39	73.87	8.24

3.2 Electrochemical measurements

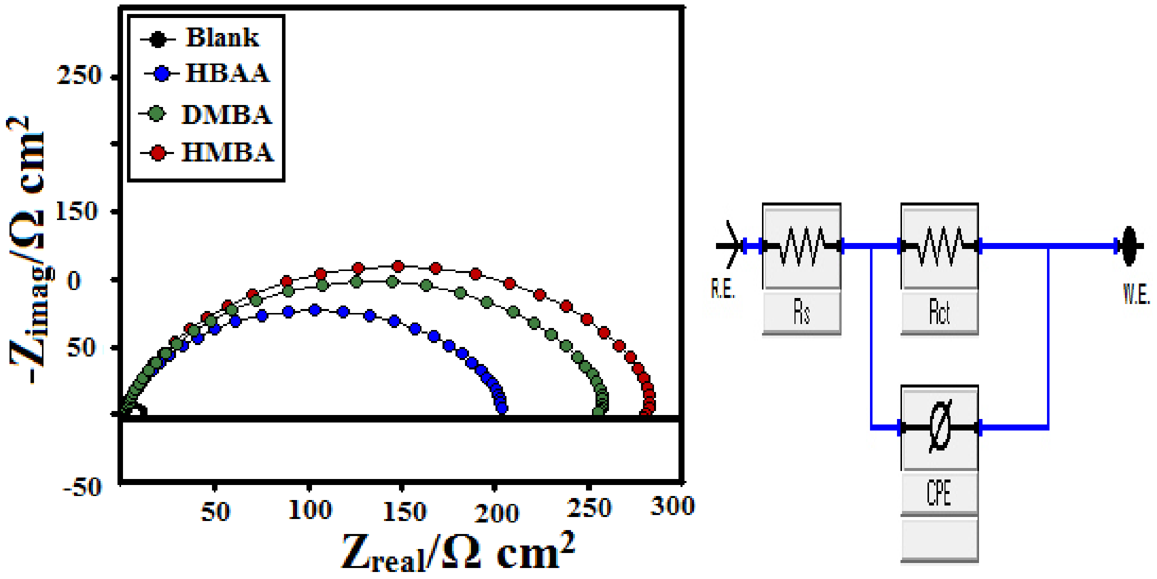
3.2.1: Electrochemical impedance spectroscopy:

Impedance method provides information about the kinetics of the electrode processes and simultaneously about the surface properties of the investigated systems.Electrochemical impedance spectra of mild steel in presence of optimum concentration of *HBAA*, *DMBA* and *HMBA* in 1M HCl are depicted in Figure 4. (Nyquist plots).

It is observed that Nyquist plots are semicircle and the diameter of semicircle increase with increasing the concentration of SBs, the increase in the impedance results into increase in inhibition efficiency [24]. For corrosion reactions which are strictly charge transfer controlled, impedance behavior can be explained with the help of a simple and commonly used equivalent circuit [Figure 4 (b)] composed of a double layer capacitance, charge transfer resistance (R_{ct}) and solution resistance (R_s). The double layer capacitance (C_{dl}) was calculated by using following equation [25]:

$$C_{dl} = Y^0(\omega_{max})^{n-1} \quad (9)$$

where Y^0*is CPE* coefficient, n is *CPE* exponent (phase shift), ω is the angular frequency. The ω_{max} represents the frequency at which the imaginary component reaches a maximum. Various impedance parameters such as R_{ct}, R_s, Y^0 and C_{dl} were calculated and given in table 4.: From Table it is observed that C_{dl} values decreases, which normally results from a decrease in the dielectric constant and/or increase in double layer thickness, can be attributed to the adsorption of organic inhibitors on metal surface, thereby protecting the metal from corrosive attack [26].



(a) (b)

Figure 4. (a) Nyquist plots in absence and presence of optimum concentration of SBs
(b) Equivalent circuit used to fit the impedance data

Table 4: The Electrochemical Impedance parameters and corresponding efficiencies of three Schiff's bases in 1 M HCl at optimum concentration.

Inhibitor	**Conc (ppm)**	**R_s (Ω cm^2)**	**R_{ct}(Ω cm^2)**	**Y^0 (μF cm^{-2})**	**n**	**C_{dl} (μF cm^{-2})**	*η%*
Blank	-	1.11	11.8	249.6	0.827	85.05	-
HBAA	400	0.823	187.6	141.5	0.842	50.12	93.47
DMBA	400	1.12	250.2	121.0	0.821	43.3	95.08
HMBA	400	1.32	254.1	112.1	0.823	31.8	95.16

3.2.2 Potentiodynamic polarization measurements:

Potentiodynamic polarization experiments were undertaken to distinguish effect of SBs on anodic dissolution of mild steel and cathodic hydrogen reduction. Typical potentiodynamic polarization curves for mild steel in 1M HCl in absence and presence of optimum concentration of SBs is shown in Figure 5. While electrochemical parameters derived from the polarization curves are summarized in Table 4. Addition of the SBs seems to affect anodic as well as cathodic partial reaction. The decrease in I_{corr}value indicates the adsorption of SBs molecules on metal surfaces [27]. It is also observed that addition of SBs the corrosion potential (E_{corr}) value shifted slightly this indicates that all the studied SBs acted as mixed type inhibitors in 1M HCl [28-31].

Table 5. The potentiodynamic polarization and Linear polarization parameters and corresponding efficiencies of Schiff's bases in 1 M HCl at optimum concentration.

Inhibitor	**Conc (ppm)**	**Tafel Polarization**					**Linear Polarization**	
		E_{corr} (mV vs. SCE)	**I_{corr} (μAcm^{-2})**	**$β_a$ (mV/dec)**	**$β_c$ (mV/dec)**	*η%*	**R_P (Ω cm^2)**	*η%*
Blank	-	-495	1320	90.0	152.0	-	11.81	-
HBAA	400	-500	113	72.3	177.5	89.72	132.5	91.09
DMBA	400	-498	100	77.4	187.7	90.90	141.6	91.66
HMBA	400	-522	66.5	76.3	166.4	93.95	198	94.09

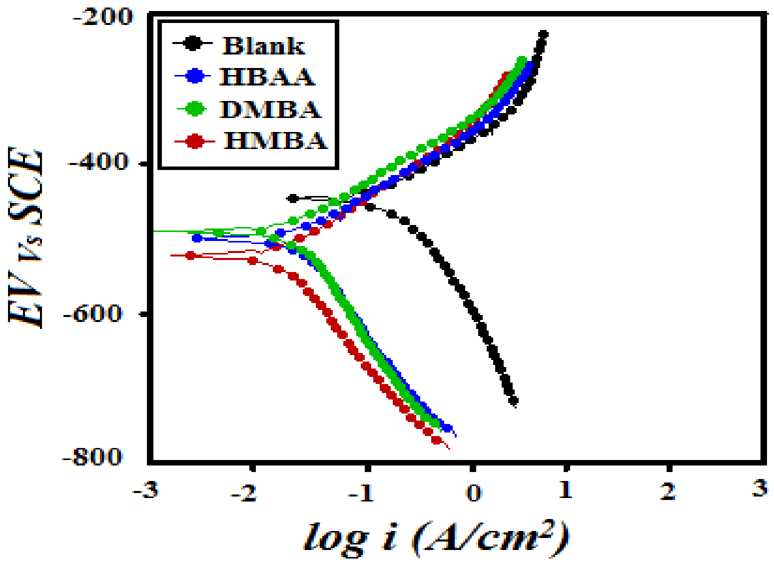


Figure 5: Potentiodynamic polarization plots in absence and presence of optimum concentration of SBs

3.2.3. Linear polarization method.

The inhibition efficiencies and polarization resistance (R_p) parameters are presented in Table 4. The increase in the $R_p$value depicted the higher efficiency as the concentration of SBs increases from 100 to 400 ppm. The values calculated by Tafel polarization and *EIS* data shows good agreement with the results obtained from linear polarization resistance

4. Mechanism of Inhibition:

From the results of different electrochemical and weight loss measurements, it was concluded that all the SBs inhibit the corrosion of mild steel in 1 M HCl by adsorption at mild steel/solution interface. It is general assumption that the adsorption of organic inhibitors at metal surface interface is the first step in the mechanism of the inhibitor action. Organic molecules may be adsorbed on the metal surface in four ways namely,

(i) Electrostatic interaction between the charged molecules andthe charged metal,
(ii) Interaction of unshared electron pairs in the molecule with the metal,
(iii) Interaction of π-electrons with the metal and
(iv) A combination of types (i–iii) [32–33]

The efficiency order of all these SBs is as follows:
HBAA< DMBA < HMBA

In acid solution mild steel surface bears positive charge; it is difficult for the protonated molecules to approach the positively charged mild steel surface (H_3O^+/metal interface) due to the electrostatic repulsion. Since chloride ions have a smaller degree of hydration, they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged inhibitor molecules, the protonated inhibitors adsorb through electrostatic interactions between the positively charged molecules and the negatively charged Cl^- ions. Thus, there is a synergism between the adsorbed Cl^- ions and protonated inhibitors. Hence, we can assume that the inhibition of mild steel corrosion in 1 M HCl is due to the adsorption of SBs on the mild steel surface.

Conclusions

(1) The SBs are good corrosion inhibitors for mild steel corrosion in 1 M HCl solution.
(2) The Potentiodynamic polarization study revealed that SBs act as mixed-type inhibitors.
(3) The inhibition efficiency order of all three SBs increases with increase in concentration and maximum efficiency was observed at 400ppm concentration.
(4) The order of inhibition efficiency was as follows HMBA > DMBA > HBAA
(5) The adsorption SBs on mild steel surface obeys the Langmuir adsorption isotherm.
(6) The highest inhibition efficiency was 93.9%, 95.1% and 95.4% at concentration of 400 ppm for HBAA, DMBA and HMBA respectively.

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