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ORIGINAL PAPER

Inhibiting effects of 4-amino-antipyrine based schiff base derivatives on the corrosion of mild steel in hydrochloric acid

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Abstract The inhibiting action of 4-amino-antipyrine (AAP) and its schiff bases 4-[(benzylidene)-amino]-antipyrine (BAAP), 4-[(4-hydroxy benzylidene)-amino]-antipyrine (SAAP) and 4-[(4-methoxy benzylidene)-amino]-antipyrine (AAAP) which are derived from 4-amino-antipyrine with benzaldehyde, salicylaldehyde and anisaldehyde, toward the corrosion behavior of mild steel in 1 M HCl solution was studied using weight loss, potentiodynamic polarization, electrochemical impedance and FT-IR spectroscopic techniques. Although AAP was found to retard the corrosion rate of mild steel, the synthesized schiff base compounds were seen to retard the corrosion rate very effectively. The inhibitor efficiencies calculated from all the applied methods were in good agreement and were found to be in the order: AAAP > SAAP > BAAP > AAP.

Keywords Antipyrine · Mild steel · Inhibitor · Corrosion · Potentiodynamic polarization

1 Introduction

Mild steel is widely used in many applications, this intensified the research in corrosion resistance in various aggressive environments [1, 2]. In order to mitigate electrochemical corrosion, the primary strategy adopted is to isolate the metal from corrosive agents. Among the various methods available, the use of inhibitors is one of the most reliable methods for protection against corrosion especially in acidic media [3–5]. Heterocyclic organic compounds containing nitrogen, sulphur or oxygen atoms are often used to protect metals from corrosion. For the past few years, azoles have been intensively investigated as effective corrosion inhibitors [6–10] for various environments.

Hydrochloric acid (HCl) is normally used in the acid pickling of steel and ferrous alloys, acid cleaning, acid descaling, oil well cleaning, petrochemical industry, and various electrochemical systems. Hence, the corrosion inhibitors are needed to pay much attention to reduce the corrosion rates of metallic materials. There are few reports about the successful use of some polydentate schiff base compounds containing aminic nitrogen as corrosion inhibitors for mild steel and copper in acidic media [11–19]. It is found that the inhibition efficiencies of schiff bases depend on the type and the nature of the substituents present in the molecule. El Rehim et al. [20] have studied the inhibition of 4-(2-amino-5-methylphenylazo) antipyrine on the corrosion of mild steel in HCl medium. In a similar way the effect of schiff base compound from phenazone and vanillin on the corrosion of mild steel have also been reported by Emregu et al. [11]. These observations have prompted us to investigate the inhibiting effects of some schiff bases derived from 4-amino antipyrine (AAP).

In the present work, a systematic study has been undertaken to understand the corrosion behavior of mild steel and the inhibiting effects of synthesized schiff bases (BAAP, SAAP and AAAP) derived from 4-amino antipyrine in 1 M HCl environment. Electrochemical techniques such as potentiodynamic polarization and electrochemical

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impedance have been employed to study the corrosion rate and inhibition efficiency. Also it was found that the adsorbed inhibitor on the mild steel surface may account for protecting the metal from the corrosive medium and modifying the electrode reactions in favor of corrosion protection of the metal.

2 Experimental

2.1 Synthesis of schiff base derivatives of 4-amino-antipyrine

In this paper, schiff bases having structures as shown in Fig. 1 were synthesized [21, 22]. The inhibitors, BAAP, SAAP and AAAP were prepared by condensation of 4-amino-antipyrine with benzaldehyde, salicylaldehyde and anisaldehyde, respectively. All the chemicals chosen for our study were of analytical grade and double distilled water was used throughout the experiment. Further, the inhibitor solutions were prepared using 1 M HCl.

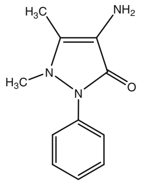
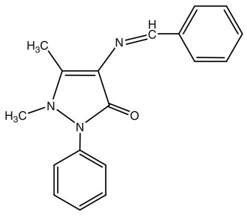
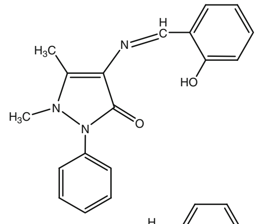
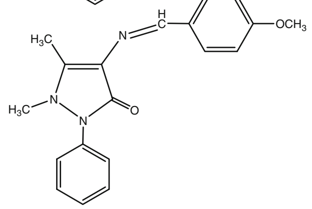
2.2 Specimen preparation

The mild steel specimen with the composition C—0.13%, P—0.032%, Si—0.014%, S—0.025%, Mn—0.48% and balance Fe were used in this study. For weight loss measurements the metal specimen were mechanically cut into 4.0 cm × 2.0 cm × 0.3 cm dimension and polished with SiC abrasive papers (from grits 120–1,200), for further use. For the electrochemical studies, specimen of size 1.0 cm × 1.0 cm × 0.3 cm was cut, which is embedded in the epoxy resin, also polished finally rinsed with double distilled water and dried.

2.3 Weight loss measurements

Mild steel specimen in triplicate was immersed in 1 M HCl for 2 h at room temperature (28 ± 2 °C) for each inhibitor concentration. Then the specimen was removed, rinsed in double distilled water, acetone and the loss in weight was determined. From this the inhibition efficiency (IE%) was calculated using the formula,

Fig. 1 Names and structures of the inhibitors

Name of the inhibitor	**Abbreviation**	**Structure of the inhibitors**
4-Amino antipyrine	AAP	
4-Benzalidine amino antipyrine	BAAP	
4-Salisilidine amino antipyrine	SAAP	
4-Anisalidine amino antipyrine	AAAP	

$$\mathrm{IE}(\%) = \frac{W_0 - W_i}{W_0} \times 100 \quad (1)$$

where, W_0 and W_i (in g) are the weight loss observed in the absence and presence of inhibitors.

2.4 Electrochemical studies

All the electrochemical measurements were performed using the Electrochemical Workstation (Model No: CHI 760, CH Instruments, USA) and a constant temperature of 28 ± 2 °C is maintained with 1 M HCl as an electrolyte. A platinum electrode and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively, while the working electrode comprised of mild steel specimen with 1 cm^2 exposed area. The tip of the reference electrode was carefully positioned very close to the surface of the working electrode by the use of a fine Luggin capillary in order to minimize the ohmic potential drop. The remaining uncompensated resistance was also reduced by the electrochemical workstation. Potentiodynamic polarization studies were carried out at a scan rate of 0.01 $\mathrm{mV\ s^{-1}}$ and at a potential range of −800 to −200 mV for various concentrations of inhibitors. The electrochemical impedance studies were carried out in the same setup as that of potentiodynamic polarization studies and the applied ac perturbation signal was about 10 mV within the frequency range 1 Hz to 1 kHz. All the electrochemical impedance measurements were carried out at open circuit potential.

The percentage of inhibition efficiency is calculated from the values of the corrosion current density (i_{corr}) with the aid of following formula,

$$\mathrm{IE}(\%) = \frac{\left(i_{\mathrm{corr}} - i'_{\mathrm{corr}}\right)}{i_{\mathrm{corr}}} \times 100 \quad (2)$$

where, i_{corr} and i'_{corr} are the values of corrosion current density of uninhibited and inhibited specimen, respectively.

2.5 Surface examination

The mild steel specimen was immersed in 1 M HCl containing the inhibitor AAAP (0.008 M) for 2 h after which it was taken out dried and scraped the film using non-metallic scrapper. The FT-IR spectra of the scraped film were recorded using a Nicolet 380 FT-IR spectrophotometer.

3 Results and discussion

3.1 Weight loss measurements

The corrosion of mild steel in 1 M HCl medium containing various concentrations of AAP and its Schiff bases BAAP, SAAP and AAAP (0.001, 0.002, 0.004, 0.006 and 0.008 M) were studied by weight loss measurements. Figure 2 summarizes the inhibition efficiencies of the studied AAP and its schiff bases at different concentrations. It is obvious from the figures that all these compounds inhibit the corrosion of mild steel in 1 M HCl solution at all concentrations used in this study. The inhibition efficiency was seen to increase with increasing additive concentration up to the optimum level after which there is no remarkable change in the inhibition efficiency. The studied inhibitors were found to attain the maximum inhibition efficiency at 0.008 M concentration. Thus, we deduce that these schiff base compounds are good inhibitor for the mild steel corrosion and the inhibition efficiency was found to be in the following order: AAAP > SAAP > BAAP > AAP. The difference in their inhibitive action can be explained on the basis of the type of functional group present in the benzene ring. In order to have better understanding of the inhibition mechanism of schiff bases, a detailed study on corrosion inhibition of these compounds was carried out using potentiodynamic polarization and electrochemical impedance spectroscopy.

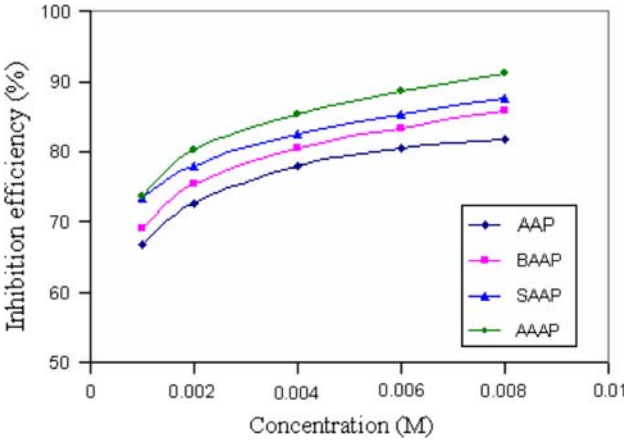


Fig. 2 Inhibition efficiency of AAP, BAAP, SAAP and AAAP at various concentrations by weight loss measurement in 1 M HCl

3.2 Potentiodynamic polarization studies

Potentiodynamic polarization results obtained for the inhibitory effect of AAP and its schiff bases BAAP, SAAP and AAAP on mild steel corrosion in 1 M HCl are depicted clearly in Figs. 3, 4, 5, 6 and 7. The associated corrosion parameters such as corrosion potential (E_{corr}), cathodic and anodic Tafel slops ($\mathrm{b_c}$, $\mathrm{b_a}$), and corrosion current density (i_{corr}) are listed in Table 1.

As shown in Fig. 3 the i_{corr} values obtained for the solution containing AAP seems to appreciably decrease with the increase in AAP concentration up to 0.008 M, after which no significant change in the i_{corr} value is noted.

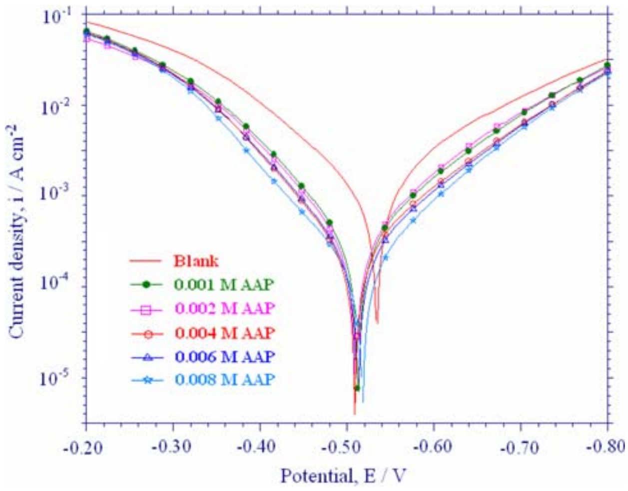


Fig. 3 Potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of various concentration of AAP

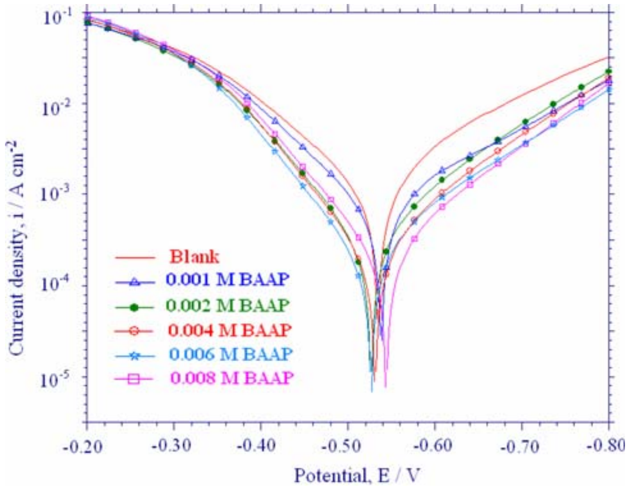


Fig. 4 Potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of various concentration of BAAP

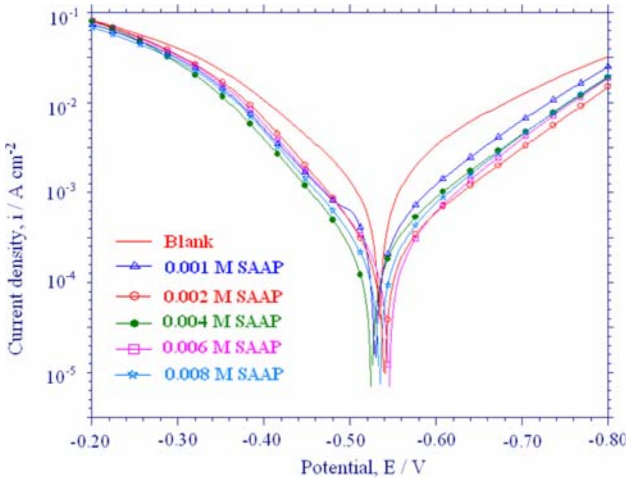


Fig. 5 Potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of various concentration of SAAP

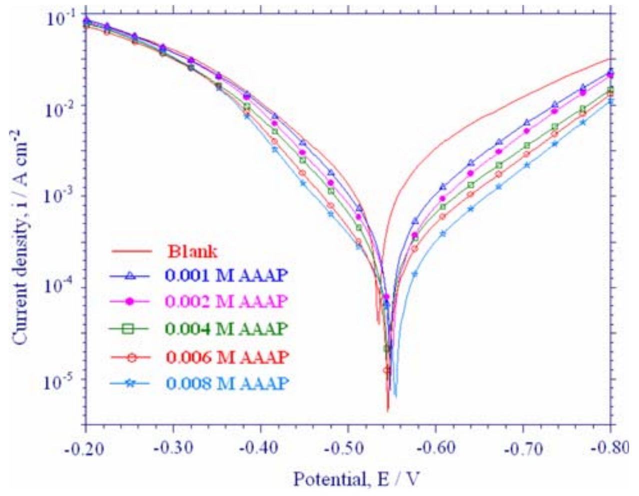


Fig. 6 Potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of various concentration of AAAP

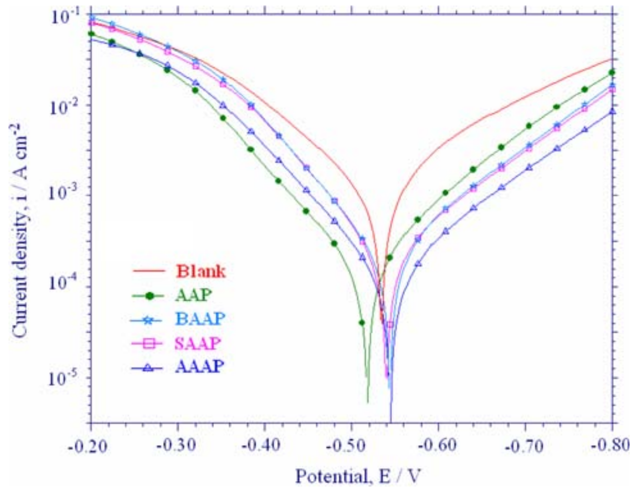


Fig. 7 Potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of AAP, BAAP, SAAP and AAAP

Further, it can be also seen that both cathodic and anodic reactions of mild steel electrode were inhibited with the increase in AAP concentration in 1 M HCl acid, although slightly higher inhibition was observed on the anodic reaction. The addition of AAP decreases the i_{corr} values significantly for all the studied concentrations may be due to the increase in adsorption of schiff base on the electrode surface and blocking the active sites. It is also evident from this study that the inhibition of the mild steel corrosion is under both cathodic and anodic control, while the control of later is marginally higher than the former one. Therefore, AAP can be classified as a mixed-type inhibitor.

Potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of various concentrations of BAAP, SAAP and AAAP are shown in Figs. 4, 5 and 6, and the corresponding Tafel parameters are summarized in

Table 1 Potentiodynamic polarization parameters of mild steel in 1 M HCl in the absence and presence of various concentrations of AAP, BAAP, SAAP and AAAP

Inhibitor	Conc. of inhibitor (M)	b_c (V dec^{-1})	b_a (V dec^{-1})	E_{corr} (V)	i_{corr} (mA)	Rate (mpy)	IE (%)
Blank	–	0.15	0.14	−0.525	125.86	574.8	–
AAP	0.001	0.13	0.10	−0.507	40.12	183.2	68.12
	0.002	0.12	0.10	−0.509	32.05	146.4	74.56
	0.004	0.13	0.09	−0.507	27.30	124.7	78.31
	0.006	0.13	0.09	−0.502	24.78	113.2	80.31
	0.008	0.12	0.10	−0.510	22.05	100.7	82.48
BAAP	0.001	0.17	0.11	−0.5321	38.90	177.7	69.10
	0.002	0.15	0.10	−0.5171	31.11	142.1	75.27
	0.004	0.13	0.10	−0.5310	26.24	119.8	79.15
	0.006	0.14	0.10	−0.5262	20.50	93.6	83.71
	0.008	0.13	0.10	−0.5544	18.20	83.1	85.53
SAAP	0.001	0.13	0.11	−0.5287	34.27	156.5	72.77
	0.002	0.12	0.10	−0.5247	27.17	124.1	78.41
	0.004	0.13	0.10	−0.5339	22.31	101.9	82.27
	0.006	0.12	0.10	−0.5447	19.22	87.8	84.73
	0.008	0.14	0.10	−0.5399	15.85	72.4	87.40
AAAP	0.001	0.13	0.11	−0.5498	33.16	151.4	73.65
	0.002	0.14	0.10	−0.5459	25.75	117.6	79.54
	0.004	0.14	0.10	−0.5449	20.82	95.0	83.45
	0.006	0.13	0.10	−0.5538	15.38	70.2	87.78
	0.008	0.13	0.10	−0.5442	11.74	53.6	90.83

Table 1. Figure 4 shows the influence of various concentrations of BAAP on the polarization behavior of the mild steel in 1 M HCl. It should be noted that with the addition of the BAAP both the anodic and cathodic current densities appreciably decrease and therefore it acts as a mixed type inhibitor. In fact the other two inhibitors (SAAP and AAAP) were also found to act as a mixed type inhibitors because the i_{corr} values for mild steel in their presence decreased up to 0.008 M concentration and after which there is no significant change (Figs. 5 and 6). In the presence of studied schiff bases the anodic and cathodic current densities are seen to decrease. In particular the cathodic decrease being greater for AAAP when compared AAP and its other schiff bases. Hence the AAAP is classified as a mixed type inhibitor with a slight leading control of cathodic reaction. The potentiodynamic polarization curves in the absence and presence of AAP, BAAP, SAAP and AAAP at their optimum concentration is shown in Fig. 7. From the potentiodynamic polarization studies, AAAP shows the maximum inhibition efficiency (90.83%) among all the other studied compounds due to the higher electrostatic attraction of AAAP and metal surface by the high electron density of the nitrogen atom in the molecule. The inhibition efficiency follows the order AAAP > SAAP > BAAP > AAP.

The schiff bases strongly affect the cathodic and anodic reaction may due to its tendency to adsorption and hence they are classified as mixed type inhibitors. This result suggests that the addition of inhibitors retards the hydrogen evolution reaction [23]. The behavior of AAP at anodic potentials may be the result of significant dissolution of the steel surface, leading to desorption of the adsorbed AAP inhibitor from the electrode surface.

One can conclude that the ability of the molecule to adsorb on the iron surface is dependent on the nature and position of the nitrogen atom on the pyrine ring. Also the presence of an electron-releasing group (–OCH$_3$) in the AAAP compound seems to increase the inhibiting effect by high electron density.

3.3 Electrochemical impedance spectroscopy (EIS)

The corrosion of mild steel in 1 M HCl solution in the absence and presence of AAP and its schiff bases BAAP, SAAP and AAAP were investigated by EIS at the open circuit potential condition. Nyquist plots for mild steel obtained at the interface in the absence and presence of optimum concentration of inhibitors is given in Fig. 8. The Nyquist diagram obtained with 1 M HCl shows only one capacitive loop and the diameter of the semicircle increases on increasing the electrostatic attraction of the inhibitor suggesting that the formed inhibitive film was strengthened

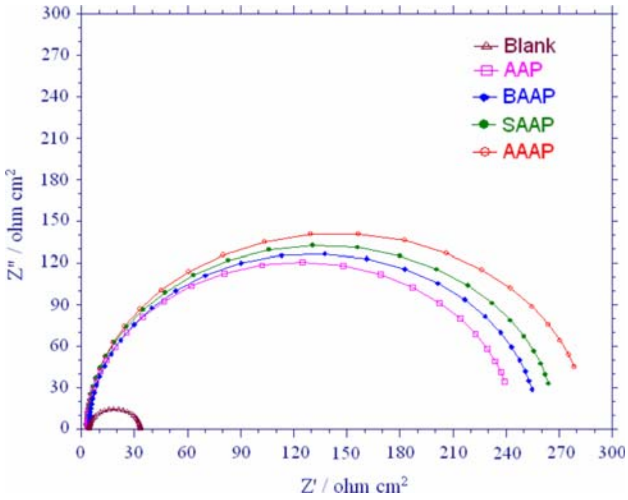


Fig. 8 Nyquist plots of mild steel in 1 M HCl in the absence and presence of AAP, BAAP, SAAP and AAAP

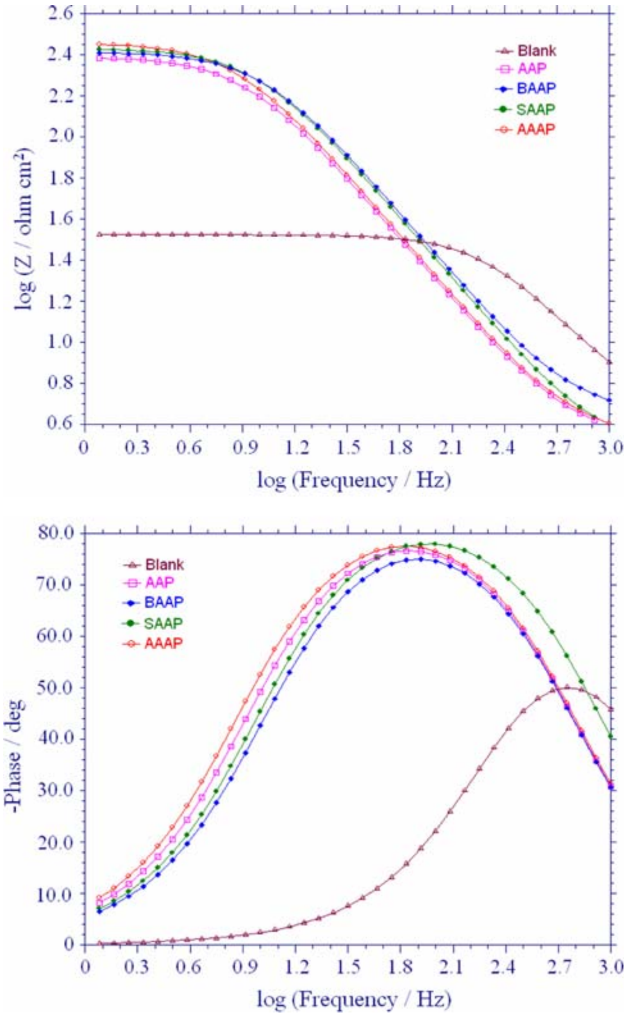


Fig. 9 Bode plots of mild steel in 1 M HCl in the absence and presence of AAP, BAAP, SAAP and AAAP

Table 2 Electrochemical impedance parameters obtained for mild steel in 1 M HCl in the absence and presence of AAP, BAAP, SAAP and AAAP

System	R_s (Ω)	R_P (Ω)	C_{dl} (μF cm^{-2})
Blank	4.45	28.9	0.791
AAP	2.55	233.7	0.137
BAAP	2.30	245.0	0.120
SAAP	1.97	262.5	0.117
AAAP	1.35	280.5	0.103

by the addition of such inhibitors. All the obtained plots show only one semicircle and they were fitted using one time constant equivalent model (Randle's model) with capacitance (C) and charge transfer resistance (R_{ct}). The corresponding Bode plots are shown in Fig. 9 and all the main parameters deduced from the impedance technique are given in Table 2.

The lower capacitance (C_{dl}) value for 1 M HCl medium indicates that the inhomogeneity of surface of the metal roughened due to corrosion. The C_{dl} values decreases on increasing the inhibitor concentration and reaches very low value for the optimum concentrations of all the studied systems indicating that the reduction of charges accumulated in the double layer due to formation of adsorbed inhibitor layer [24]. The charge transfer resistance of double layer increases on increasing the concentration of the inhibitors up to the optimum level indicating the decreased corrosion rate (i.e., increased corrosion inhibition). The impedance results follow the same trend as the polarization results.

The increase in the inhibiting efficiencies with the increase in the concentrations of the studied schiff bases shows that the inhibitory actions may be due to the adsorption of the inhibitors on steel surface. Among the compounds investigated in the present study, AAAP has been found to give an excellent inhibition due to the presence the electron donating group (–OCH_3) on the schiff base structure which increases the electron density on the nitrogen of the C=N group. This leads to the strong electrostatic attraction of AAAP on the metal surface thereby resulting in the high inhibition efficiency.

Generally on the metal side, electrons control the charge distribution whereas on the solution side it is controlled by ions. Since ions are much larger than the electrons, the equivalent ions to the charge on the metal will occupy quite a large volume on the solution side of the double layer [25]. It can be obtained from Table 2 that, the capacitance of electrical double layer (C_{dl}) decreases in the presence of inhibitors. Decrease in the C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that

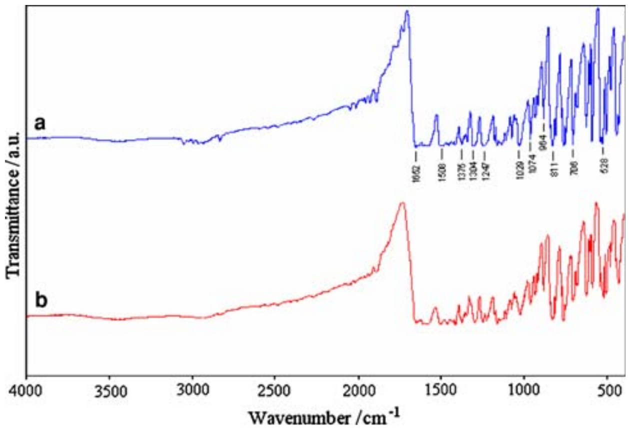


Fig. 10 FT-IR spectra of **a** AAAP and **b** mild steel immersed in 1 M HCl containing optimum concentration of AAAP

the inhibitor molecules may act by adsorption at the metal/solution interface [26].

3.4 FT-IR spectral studies

Transmission FT-IR spectra of AAAP and the film formed on the mild steel specimen immersed in 1 M HCl containing the inhibitor AAAP (0.008 M) is depicted in Fig. 10a and b. From these spectra the pure AAAP and the film formed on the mild steel shows the same peak positions. A peak at the region of 1,500–1,450 cm^{-1} indicates the presence of the C=N bond of the formed schiff base and the appearance of a peak in the region of 1,650 cm^{-1} corresponds to the absorption of C=O stretching vibration of the pyrazole ring. The presence of C–N stretching frequency is clearly manifested in the region 1,250–1,020 cm^{-1}. Further peaks at 1,415–1,375 cm^{-1} can be attributed to the N–N group present in the ring and the peaks for C–N stretching modes can be assigned in the region around 1,250–1,120 cm^{-1}. C–H and C=C out of plane bending peaks appear in the region 811–528 cm^{-1}. Moreover there is no additional peaks identified for the formation of Fe-inhibitor complex and this reveals that there is only a physical adsorption occurred on the surface of the metal.

4 Conclusions

1. All the examined 4-amino antipyrine and its schiff bases as a corrosion inhibitor for mild steel in 1 M HCl solution showed good inhibition efficiency, which follows in the order: AAAP > SAAP > BAAP > AAP.
2. The percentage inhibition efficiency is seen to increase with increasing additive concentration upto the optimum level (0.008 M).
3. AAAP exhibit highest inhibition efficiency of 90.83% at 0.008 M concentration.
4. Polarization measurements demonstrate the compounds under investigation (AAP, BAAP, SAAP, and AAAP) inhibit both anodic and cathodic reaction and hence act as mixed type inhibitors.
5. Impedance measurements indicate that, the presence of electron donating group on the schiff base is increasing the charge transfer resistance and decreasing the double layer capacitance. The type of the substituents group and the type of the functional atoms of the inhibitor molecule are found to play an important role in the inhibition process.
6. Results obtained from weight loss measurements and electrochemical measurements are in good agreement.

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