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Corrosion Inhibition of Carbon Steel in Acid Chloride Solution by Schiff Base of *N*-(2-chlorobenzylidene)-4-acetylaniline

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A heterocyclic Schiff base of *N*-(2-chlorobenzylidene)-4-acetylaniline (CBAA) was tested for its corrosion inhibition towards of St3S carbon steel in acidic chloride solutions using weight loss, Tafel polarization techniques, scanning electron microscopy, and quantum chemical calculations method. An inhibitory effect of *N*-(2-chlorobenzylidene)-4-acetylaniline on the corrosion carbon steel was investigated at different temperatures. The concentration of inhibitor does not influence the order anodic reaction. The adsorption of *N*-(2-chlorobenzylidene)-4-acetylaniline has been found to occur on the surface of steel according to the Langmuir isotherm at all studied temperatures. The kinetic and thermodynamic parameters for St3S corrosion and CBAA adsorption respectively were determined and discussed.

Keywords: A, Carbon steel; A, *N*-(2-chlorobenzylidene)-4-acetylaniline; C, Molecular orbital; C, Thermodynamic parameters

1. INTRODUCTION

Studying corrosion of carbon steel in acid chloride solutions is relevant for understanding the behaviour of the materials in industrial conditions where normally chloride ions are present [1-4].

The use of organic compounds to inhibit corrosion of carbon steel has assumed great significance due to their application in preventing corrosion under various corrosive environments. Corrosion inhibitors are compounds which even small concentration considerably reduce the corrosion rate. The effectiveness of any corrosion inhibitor is dependent on the type of metal and properties of the corrosive environment [5,6]. Most of the well-known organic inhibitors are heterocyclic compounds containing π-electrons, heteroatoms like N, O, or S and aromatic rings [7-8]. Specific interaction between functional groups and the metal surface and heteroatom’s play an important role in inhibition due to the free electron pairs they possess. When both these features combine increased inhibition can be observed [9-12].

Imines, which are called the Schiff bases contain in their particle the atoms of nitrogen and oxygen. Schiff bases are the condensation products of an amine and ketone or aldehyde, and have the general formula, R_1-C = N-R_2. These substances found application in many fields of biochemistry and chemistry. With this reason they are the good corrosion inhibitors of carbon steels [13-15], and other metals [16-18]. The presence of -C = N- group in Schiff base molecules enhances their adsorption ability and corrosion inhibition efficiency. The action mechanism of inhibitors with the same functional group may vary with factors such as the effect of the molecular structure on the electron density of the functional group and the size of the aromatic and aliphatic portions of molecule.

The aim of this study was the investigation of inhibition effect of *N*-(2-chlorobenzylidene)-4-acetylaniline (CBAA) (Schiff base) on the corrosion of St3S carbon steel in 1.2 M chloride solutions. Potentiodynamic polarization methods has been used for appoint corrosion parameters. The best isotherm has been selected and the effect of the temperature (25 – 60 ^{0}C) on the corrosion behavior of St3S in absence and presence CBAA have been investigated.

2. EXPERIMENTAL

2.1. Solutions

The electrolytes were prepared using of the NaCl (CHEMPUR) and HCl (POCH) analytical grade reagents. The corrosive medium 1.2 M Cl^- was prepared from a stock of NaCl and 1.0 M HCl solution (pH 1.5). The *N*-(2-chlorobenzylidene)-4-acetylaniline (CBAA) (> 98%) was purchased from ALDRICH. The structure of *N*-(2-chlorobenzylidene)-4-acetylaniline is given in Figure 1.

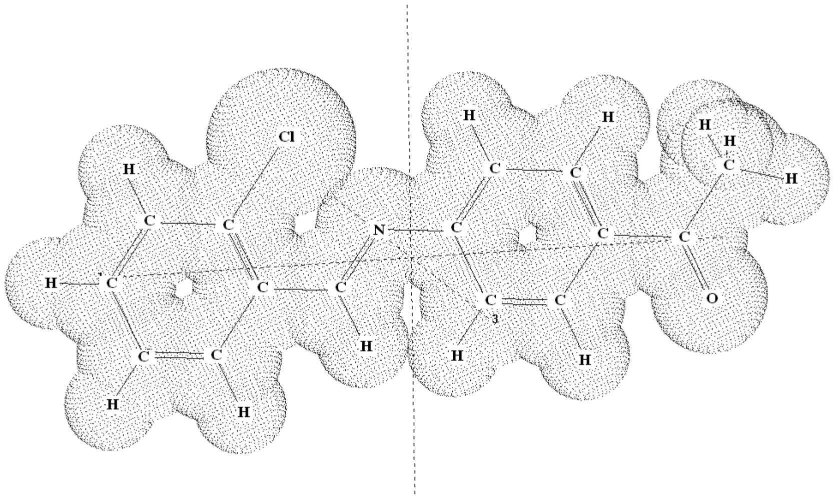

Figure 1. *N*-(2-chlorobenzylidene)-4-acetylaniline (CBAA) structure

The *N*-(2-chlorobenzylidene)-4-acetylaniline molecule is flat and it is stable in air, water and in majority organic solvents. The CBAA was dissolved at concentrations in the range of 0 - 20 mM in corrosive acid chloride solutions. All solutions were prepared from double distilled water. For each experiment a freshly made solution was used. All test have been performed in naturalny aerated electrolytes.

2.2. Weight loss measurements

The St3S carbon steel sheets of 1×3×0.3 cm were abraded with series of emery papers (800, 1200 and 2000 grade). Before immersion in experimental solutions the samples were washed with bidistilled water, ultrasonically decreased in acetone and dried at room temperature. After weighing accurately using an analytical balance (±0.1 mg) the specimen were immersed in 150 ml flat bottom which contained 100 ml the corrosive medium 1.2 M Cl^- with and without addition of different concentrations of *N*-(2-chlorobenzylidene)-4-acetylaniline. All the test solutions were open to air. After the elapsed time, the specimens were taken out, washed, dried, and weighed accurately. The average weight loss of three parallel carbon steel specimens were obtained. Chemical composition of carbon steel is listed in Table 1.

Table 1. Chemical composition of St3S carbon steel

Element	C	S	P	Si	Mn	Cr	Ni	Cu
Weight (%)	<0.22	<0.050	<0.050	0.10 – 0.35	<1.10	0.301	<0.30	<0.30

The inhibition efficiency was determined by using the equation:

$$IE(\%) = \frac{w_0 - w}{w_0} \times 100 \tag{1}$$

where w_0 and w are the weight loss value in presence and absence of inhibitor, respectively. The corrosion rate of steel was calculated using the relation:

$$C_r\left(mm\ year^{-1}\right) = \frac{87.6\ w}{S\ t\ \rho} \tag{2}$$

where w is the corrosion weight loss of steel, S is the area of the sample, t is the exposure time, and ρ is the density of carbon steel.

2.3. Electrodes

The working electrode was prepared from St3S carbon steel. The geometric electrode area was 2 cm^2. The electrode was mechanically abraded with a series of emery papers (800, 1200 and 2000 grade). Than it was rinsed in acetone and double distilled water before their immersion in experimental solution.

Electrode potentials were measured and reported against the external saturated calomel electrode (SCE) connected with solution via a Luggin probe. The capillary tip was opposite to the end of the working electrode about 3 mm from it. A platinum wire (99,99% Pt) was used as an auxiliary electrode.

2.4. Apparatus

All voltammetric experiments were performed using a potentiostat/galvanostat PGSTAT 128N, AutoLab, Netherlands with NOVA 1.7 software the same firm. Moreover, experiments were carried out at suitably well-chosen temperature (±0.5 ^{0}C) in an air thermostat with the forced air circulation.

2.5. Electrochemical experiments

The electrochemical studies were made using a three-electrode glass cell with a 200 cm^3 capacity. Prior to the electrochemical measurement a stabilization period of 30 min was allowed. The electrochemical behavior of St3S carbon steel sample in uninhibited and inhibited solution were studied by recording cathodic and anodic potentiodynamic polarization curves. The electrode potential was changed in range from -1200 to +200 mV vs. SCE at a scan rate of 1 mV s^{-1}. The linear Tafel segments of cathodic and anodic curves were extrapolated to corrosion potential (E_{corr}) to obtain corrosion current densities (j_{corr}) and the Tafel slopes the cathodic (b_{c}) and anodic (b_{a}).

The degree of surface coverage and the corrosion inhibition efficiency were calculated using the relationships:

$$IE(\%) = \frac{j_{corr}^{0} - j_{corr}}{j_{corr}^{0}} \times 100 \qquad (3)$$

where j_{corr} is the corrosion current density at a particular the inhibitor concentration, and j^0_{corr} is the corrosion current density in the absence of inhibitor in the solution.

2.6. Quantum chemical calculation

HyperChem version 7.5 a quantum–mechanical program from Hypercube Inc (Gainesville, Florida, USA) was used for molecular modeling. The calculation was based on Parametric Method (PM3) *ab* initio semi-empirical method with 3-21G* basis set. Moreover, quantum chemical parameters such as the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), energy gap ($\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$), and dipole moment ($\mu$) were considered.

2.7. Scanning electron microscopy

The surface morphology of the formed layers on the specimens surface of St3S after its immersion in 1.2 M Cl^- solution in the absence and presence of 20 mM of *N*-(2-chlorobenzylidene)-4-acetylaniline for 360 hours, and were tested on a JSM-5400 scanning electron microscope (SEM). The accelerating voltage was 20 kV.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

Corrosion inhibition performance of inhibitors can be evaluated by using weight loss method. The Figure 2 present weight loss of St3S carbon steel sheets in the absence and presence of different concentrations of *N*-(2-chlorobenzylidene)-4-acetylaniline. The inhibition efficiency and corrosion rate of St3S were determined by using equations (1) and (2). The corrosion parameters obtained by conducting weight loss measurements are tabulated in Table 2.

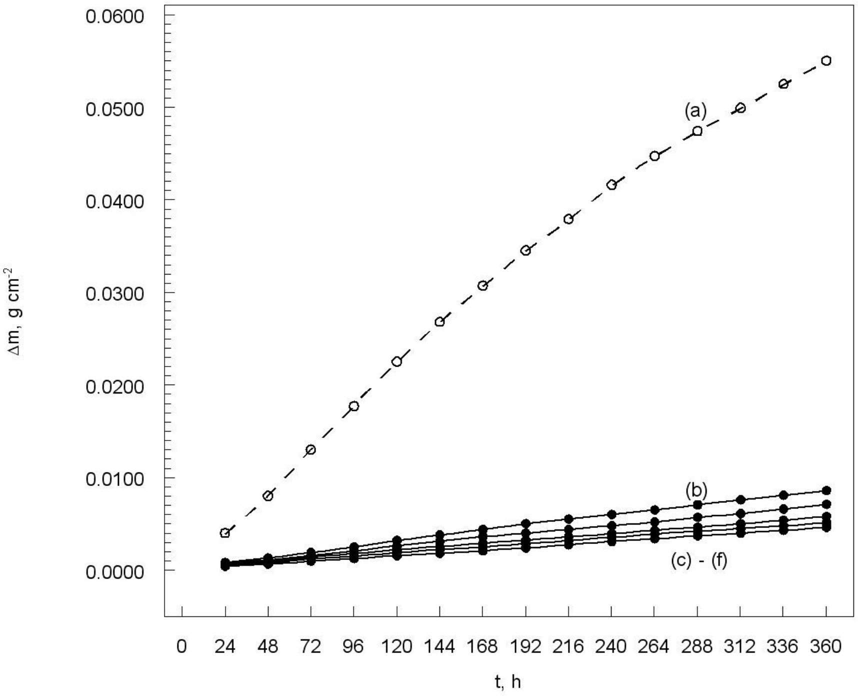

Figure 2. Weight loss of St3S carbon steel with immersion time. Solution containing 1.2 M Cl^- as well as: (a) 0, (b) 1, (c) 5, (d) 10, (e) 15 and (f) 20 mM of *N*-(2-chlorobenzylidene)-4-acetylaniline, at temperature 25 ^{0}C

From the Table 2 arises that inhibition efficiency increased and corrosion rate values get decreased with concentration of inhibitor. This is due to the fact that the adsorption coverage of inhibitor on St3S carbon steel surface increases with CBAA concentration.

Table 2. Inhibition efficiency, corrosion rate, correlation coefficients, and rate laws for St3S carbon steel in 1.2 M Cl^- in the absence and presence of *N*-(2-chlorobenzylidene)-4-acetylaniline, at temperature 25 ^{0}C

c_{inh} mM	IE %	C_r mm $year^{-1}$	R^2	Rate law (for curves (a)-(f))
0	---	1.699	0.9936	$W_a = 6.5\, k_a + 2.96$
1	85	0.266	0.9991	$W_b = 42.7\, k_b + 0.32$
5	88	0.219	0.9994	$W_c = 53.0\, k_c + 0.29$
10	90	0.179	0.9996	$W_d = 65.7\, k_d + 0.30$
15	91	0.157	0.9997	$W_e = 72.3\, k_e + 0.19$
20	93	0.142	0.9996	$W_f = 78.9\, k_f + 0.03$

The kinetics of the St3S carbon steel corrosion in the Cl^- solution in the absence and presence of *N*-(2-chlorobenzylidene)-4-acetylaniline was studied by fitting the corrosion data into different rate lows. The rate laws considered were [19,20]:

Zero-order: $W_t = kt$ (4)

First-order: $\ln W_t = t + \ln W_0$ (5)

Second-order: $1/W_t = kt + 1/W_0$ (6)

where W_0 is the initial weight, and W_t is the weight loss of St3S carbon steel at time t, and k is the rate constant.

The best results were obtained for zero-order kinetics and the plot the weight loss of steel (W_t) against time (t) is as shown Figure 2. The received plots were linear with good correlation coefficients ($R^2 > 0.99$) which rate laws were attributed, and are listed in Table 2. The linearity of the curves in the absence and presence of *N*-(2-chlorobenzylidene)-4-acetylaniline suggests that its occurrence does not change the kinetics of the corrosion reaction though it significantly reduces its rate. This indicates that the corrosion reaction of St3S carbon steel in 1.2 M Cl^- in the absence and presence of *N*-(2-chlorobenzylidene)-4-acetylaniline follows zero-order kinetics. This results suggests that of CBAA does not influence the order of anodic reaction.

3.2. Polarization measurements

The electrochemical behaviour of St3S carbon steel in chloride acid solutions without of *N*-(2-chlorobenzylidene)-4-acetylaniline at 25 ^{0}C is shown in Figure 3 as curve (a).

In chloride acid solution the following mechanism is propose for the corrosion of St3S carbon steel [21].

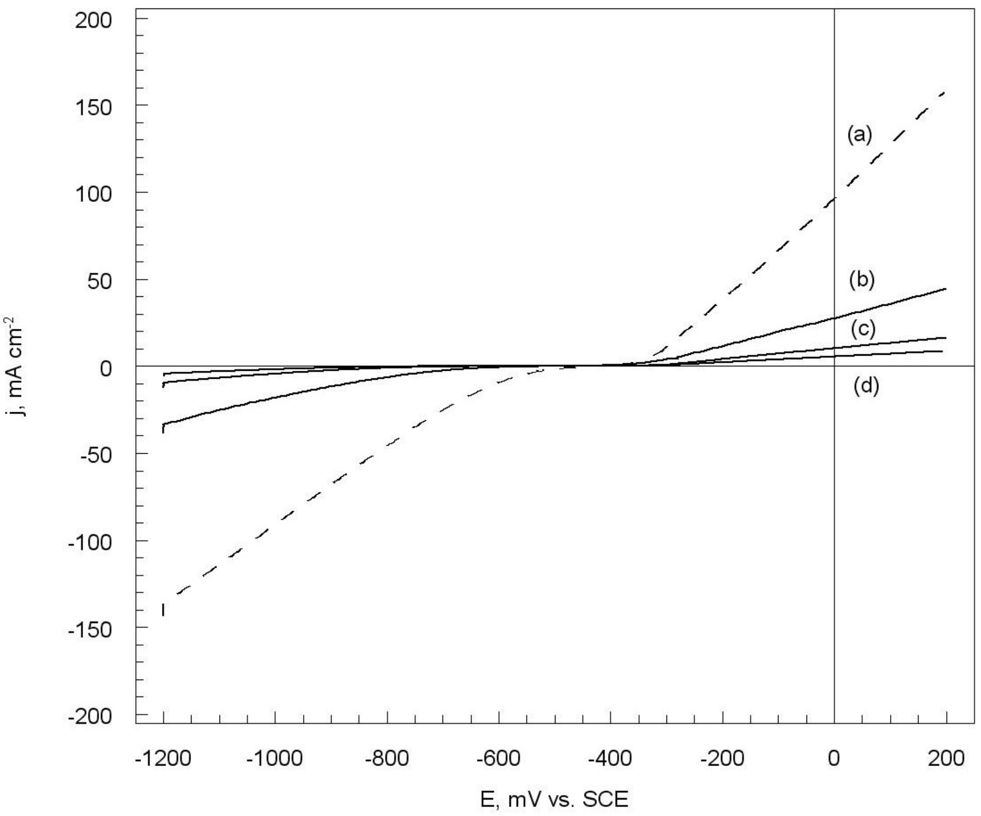

Figure 3. Polarization curves for St3S carbon steel. Solution containing 1.2 M Cl^- as well as: (a) 0, (b) 1, (c) 5, (d) 10, (e) 15 and (f) 20 mM of *N*-(2-chlorobenzylidene)-4-acetylaniline, dE/dt 1 mV s^{-1}, at temperature 25 ^{0}C

The cathodic hydrogen evolution mechanism is:

$Fe + H^+ = (FeH^+)_{ads}$, (7)

$(FeH^+)_{ads} + e^- = (FeH)_{ads}$, (8)

$(FeH)_{ads} + H^+ + e^- = Fe + H_2$. (9)

The kinetics of dissolution of steel in an acidic environment depending on the thickness of the adsorbed layer of $Fe(OH)_{ads}$, which is formed by the reaction [22]:

$Fe + H_2O = Fe(H_2O)_{ads}$, (10)

$Fe(H_2O)_{ads} = Fe(OH^-)_{ads} + H^+$, (11)

$Fe(OH^-)_{ads} = Fe(OH)_{ads} + e^-$, (12)

$Fe(OH)_{ads} = Fe(OH)^+ + e^-$, (13)

$Fe(OH)^+ + H^+ = Fe^{2+} + H_2O$. (14)

In acidic chloride solutions, the Cl^- ions may be adsorbed on the surface of the steel according to the mechanism:

$Fe + Cl^- = (FeCl^-)_{ads}$, (15)

$(FeCl^-)_{ads} = (FeCl)_{ads} + e^-$. (16)

The $(FeCl)_{ads}$ is adsorbed on the steel surface. In the more positive potential the adsorbed intermediate (reaction (12)) is dissolved [21]:

$(FeCl)_{ads} = (FeCl^+)_{ads} + e^-$, (17)

$$(FeCl^{+})_{ads} = Fe^{2+} + Cl^{-}. \qquad (18)$$

However, adsorbed intermediate as $(FeCl)_{ads}$ doesn't protect prior to oxidation the carbon steel surface.

The polarization curves for St3S carbon steel in 1.20 M Cl^- in presence of *N*-(2-chlorobenzylidene)-4-acetylaniline are shown in Figure 3 as curves (b) – (d). Both the cathodic and anodic reactions were suppressed with the addition of *N*-(2-chlorobenzylidene)-4-acetylaniline which suggested that the CBAA reduced the hydrogen evaluation, and also retarded anodic dissolution of carbon steel. This proves that investigated compound is a mixed type inhibitor because both cathodic and anodic reactions are inhibited.

Electrochemical corrosion kinetics parameters i.e. corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c) and (b_a), and corrosion current density (j_{corr}) are given in Table 3.

Table 3. Corrosion parameters of St3S carbon steel in 1.2 M Cl^- solutions in the absence and presence *N*-(2-chlorobenzylidene)-4-acetylaniline, at temperature 25 °C

Concentration CBAA mM	E_{corr} mV	$-b_c$	b_a	j_{corr} mA/cm^2
		mV/j.log		
0	-424	70	40	0.890
1	-474	60	38	0.500
10	-468	50	35	0.019
20	-477	30	25	0.006

It should be noted that E_{corr} shifted towards more negative values with an increase the concentration of CBAA. The corrosion current density (j_{corr}) decreased with an increase the concentration of *N*-(2-chlorobenzylidene)-4-acetylaniline (Table 3). This indicates the inhibiting effect of Schiff base. Moreover, a decrease both cathodic (b_c) and anodic (b_a) Tafel slopes indicated a mixed effect of the inhibition corrosion mechanism.

3.3. Effect of temperature

The effect of temperature was evaluated by polarization curves test at different temperatures in range from 30 to 60 ^{0}C in presence of 20 mM CBAA, Figure 4 as Tafel plots. For comparison on the Figure 4 is shown curve (a) for a temperature of 25 ^{0}C. Similar polarization curves were obtained for different concentrations of Schiff base.

The increase in temperature causes a shift of the corrosion potential (E_{corr}) towards more negative values. The corrosion current density (j_{corr}) increase when the temperature is higher. The corrosion current density was used to calculate the inhibition efficiency (*IE*) (Equation (3)).

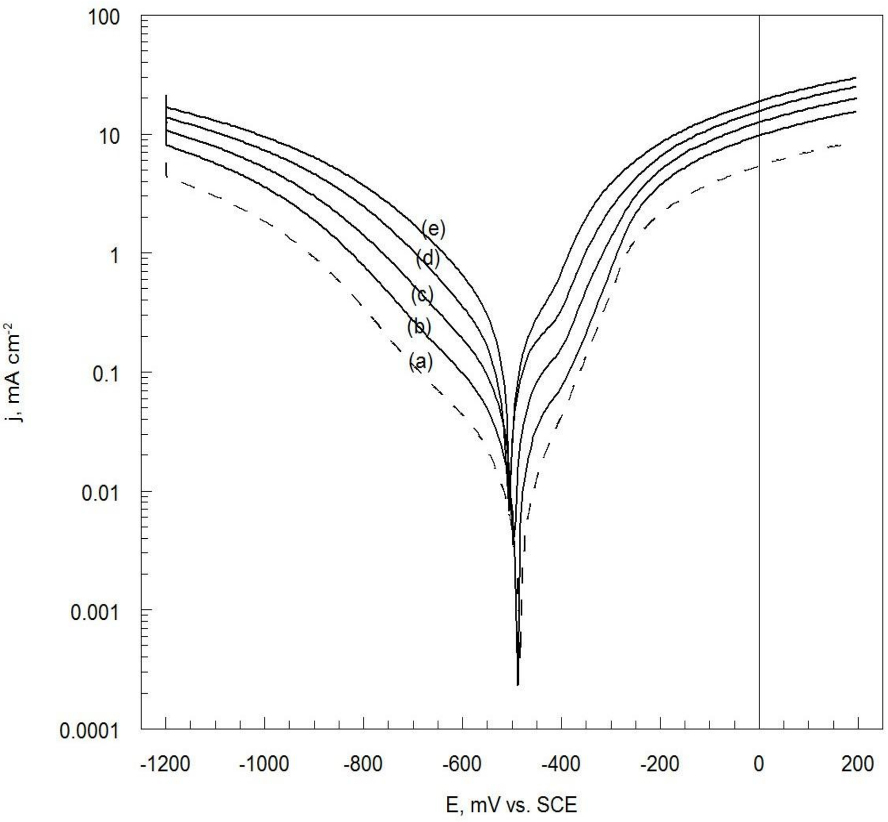

Figure 4. Tafel plots for St3S carbon steel. Solution containing 1.2 M Cl^- and 20 mM of *N*-(2-chlorobenzylidene)-4-acetylaniline, at temperatures: (a) 25, (b) 30, (c) 40, (d) 50, and (e) 60 ^{0}C, dE/dt 1 mV s^{-1}

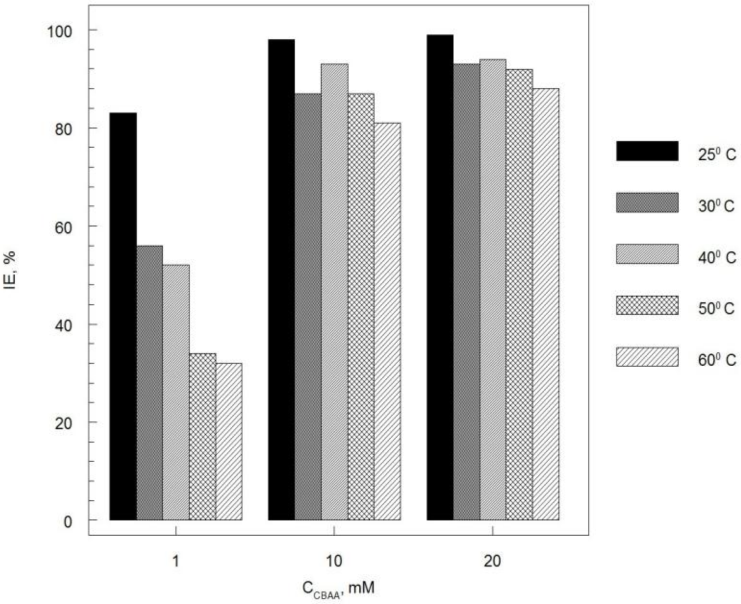

Figure 5. Corrosion inhibition efficiency of St3S carbon steel. Solution containing 1.2 M Cl^- and of *N*-(2-chlorobenzylidene)-4-acetylaniline, at temperatures: 25, 30, 40, 50 and 60 ^{0}C

The values of corrosion inhibition efficiency are presented in Figure 5. The increase in the concentration of *N*-(2-chlorobenzylidene)-4-acetylaniline causes increase the inhibition efficiency values for the same temperature. However, the increase temperature effects decrease of *IE* values for the same concentration of CBAA. Moreover, for 20 mM of CBAA and temperatures range of 30 – 60^0 C inhibition efficiency was change from 93 to 88%. This means that CBAA doesn't interact strongly with the surface of St3S carbon steel [7].

3.4. Adsorption parameters

The efficiency of organic molecules as good corrosion inhibitors mainly depends on their adsorption ability on the metal surface. The adsorption isotherms can provide important information about the nature of metal-inhibitor interaction. For determine the mechanism of adsorption of *N*-(2-chlorobenzylidene)-4-acetylaniline on the surface of St3S carbon steel in acidic solutions, the adsorption isotherms were determined at temperatures ranging from 25 to 60 °C, Figure 6. In the coordinate system, $c / \Theta = \mathrm{f}\,(c_{\mathrm{inh}})$ were obtained a straight lines, which compliant with the Langmuir isotherm [23-27] described by:

$$C_{\mathrm{inh}} / \Theta = 1/ K_{\mathrm{ads}} + C_{\mathrm{inh}} \qquad (19)$$

where C_{inh} is the inhibitor concentration, K_{ads} is the equilibrium constant for the adsorption/desorption process.

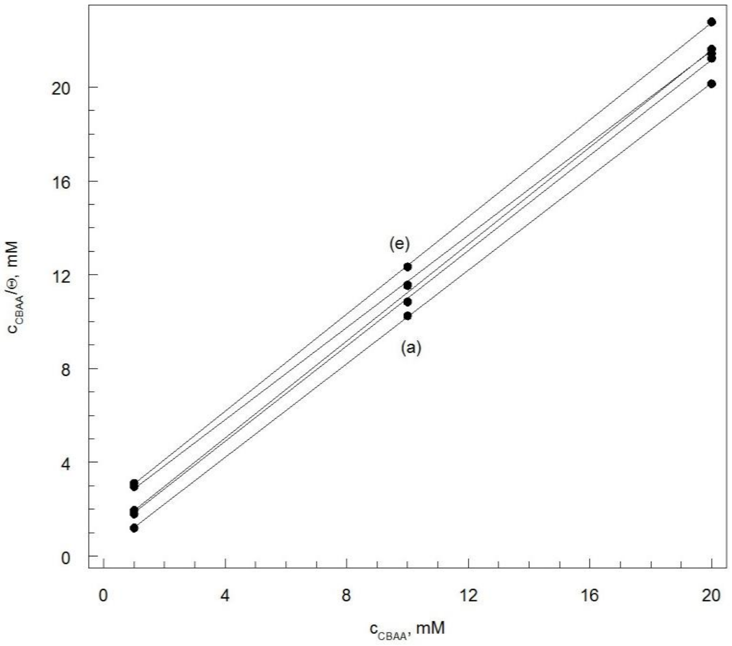

Figure 6. Adsorption isotherms of *N*-(2-chlorobenzylidene)-4-acetylaniline on the St3S carbon steel surface. Solution containing 1.2 M Cl^-, at temperatures: (a) 25, (b) 30, (c) 40, (d) 50, and (e) 60 ^{0}C

Isotherms shown in Figure 6 were used to determine the equilibrium constants for adsorption / desorption of inhibitor molecules to the steel surface:

$$K_{ads} = A \exp(-\Delta G^{\circ}_{ads} / RT) \qquad (20)$$

and the standard free energy of adsorption:

$$\Delta G^{\circ}_{ads} = -RT \ln(55{,}5 \times K_{ads}) \qquad (21)$$

where A is the inverse of the concentration of solvent (water in this case), ΔG°_{ads} - standard free energy of adsorption, K_{ads} – adsorption equilibrium constant, R – gas constant, T – temperature.

Obtained of K_{ads} and ΔG°_{ads} results are presented in Table 4.

Table 4. Linear correlation coefficient, equilibrium constant adsorption/desorption and standard free: energy, enthalpy, and entropy of the adsorption for St3S carbon steel in 1.2 M Cl^- solution in the presence of *N*-(2-chlorobenzylidene)-4-acetylaniline, at different temperatures

Temperature °C	R^2	$K_{ads} \times 10^2$ M^{-1}	ΔG^0_{ads} kJ/mol	ΔH^o_{ads} kJ/mol	ΔS^o_{ads} kJ/mol
25	1.0000	50.0	-31.1	-45.14	-47.11
30	0.9993	10.0	-27.5		-58.22
40	0.9998	10.0	-28.4		-53.48
50	0.9998	5.3	-27.6		-54.30
60	1.0000	5.0	-28.3		-50.57

According to the assumptions Langmuir's isotherm, the adsorption of the inhibitor on the surface of metal will occur on active centers, according to the mechanism:

$$CBAA_{sol} + H_2O_{ads} = CBAA_{sol} + H_2O_{sol}. \qquad (22)$$

Generally the standard free energy of adsorption values of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged metal surface (physical adsorption), those of -40 kJ mol^{-1} or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [22-26]. The values presented in Table 4 (especially ΔG^0_{ads}) indicate interaction of *N*-(2-chlorobenzylidene)-4-acetylaniline with the metal surface. The negative values of ΔG^0_{ads} indicate spontaneous adsorption of *N*-(2-chlorobenzylidene)-4-acetylaniline on the carbon steel. However, the standard free energy of adsorption values around -31 kJ mol^{-1} at 25 ^{0}C indicating that the adsorption mechanism of CBAA on St3S surface in chloride acid solution is probably physical character. With increasing temperature both of the values K_{ads} and ΔG^0_{ads} decreasing. However, the CBAA does not form strong bonds with the surface of St3S carbon steel, and rise in temperature causes them to remove.

Thermodynamically, ΔG^0_{ads} is related to the standard enthalpy, ΔH^0_{ads} and entropy, ΔS^0_{ads} of the adsorption process according equation [27]:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T \Delta S^{\circ}_{ads} \tag{23}$$

and the standard enthalpy of adsorption can be calculated on basis the Van't Hoff formula:

$$\ln K_{ads} = -\frac{\Delta H^0_{ads}}{RT} + const \tag{24}$$

A plot of *ln* K_{ads} vs. 1 / T gives straight line, as shown in Figure 7.

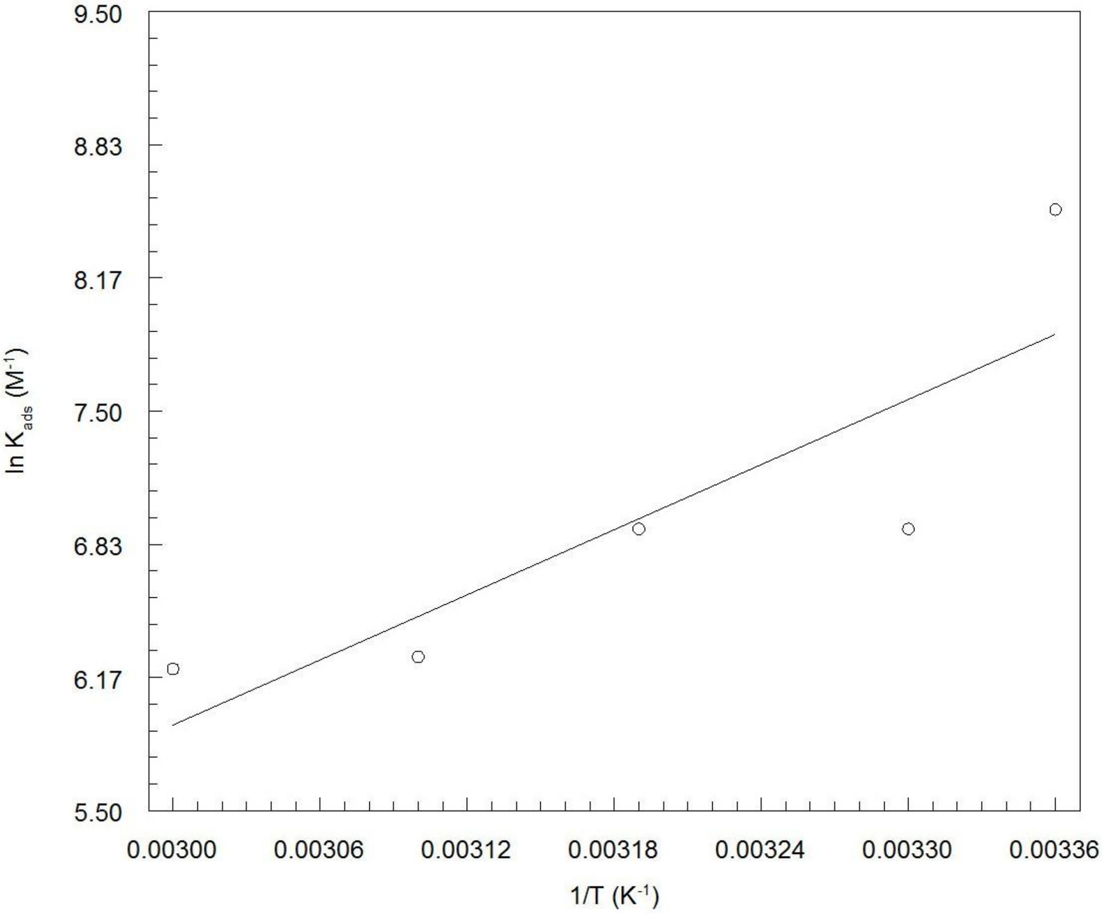

Figure 7. Dependence of ln K_{ads} on 1/ T for steel/inhibitor systems in a 1.2 M Cl^- solution

The slope of the straight line is $-\Delta H^0_{ads}/R$. The value of standard free enthalpy of the adsorption is given in Table 4. Since the ΔH^0_{ads} value is negative the adsorption of *N*-(2-chlorobenzylidene)-4-acetylaniline molecules onto the carbon steel surface is an exothermic process which involves the reaction of substitution of the water molecules of inhibitor molecules (reaction (22)). Since the ΔH^0_{ads} value is negative the adsorption of inhibitor molecules onto metal surface is an exothermic process. In a exothermic process chemisorption is distinguished from physisorption by considering the absolute value of ΔH^0_{ads} for the chemisorption process it approaches 100 kJ/mol while for the physisorption process it is less than 40 kJ/mol [25,28]. In the present study (Table 4) the ΔH^0_{ads} value is slightly larger than the common physical adsorption heat once again implying that physical adsorption of CBAA is taking place.

The standard entropy adsorption, ΔS^0_{ads} of inhibitor can be calculated from:

$$\Delta S^0_{ads} = \frac{\Delta H^0_{ads} - \Delta G^0_{ads}}{T} \quad (25)$$

The values of ΔS^0_{ads} are recorded in Table 4. Negative values ΔS^0_{ads} indicate on free and chaotic movement of the molecules inhibitor in the bulk solution (are chaotic) before adsorption on the St3S steel surface, while as adsorption progresses the CBAA molecules adsorbed onto the St3S steel surface become more orderly resulting in a decrease in entropy [29]. The increase temperature causes a decrease entropy and ordered adsorption organic compounds on surface steel [30].

3.5. Quantum chemical study

It is well known that molecular structure of the inhibitor plays a vital role in determining its mode of adsorption on the corroded surface. To investigate the correlation between molecular structure of *N*-(2-chlorobenzylidene)-4-acetylaniline and its inhibition effect, quantum chemical parameters has been performed.

Protection efficiency of inhibitors depends on the electronic properties of the corrosion inhibitors such as: highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO). It has been reported [31-33] that the higher the HOMO energy of the inhibitor the greater the trend of offering electrons to unoccupied *d* orbital of the metal, and the higher the corrosion efficiency. In addition, the lower the LUMO energy the easier the acceptance of electrons from metal surface [34]. The frontier molecular orbital density distributions of HOMO and LUMO for CBAA were shown in Figure 8. The calculated quantum chemical parameters for *N*-(2-chlorobenzylidene)-4-acetylaniline were listed in Table 5. The higher value of E_{HOMO} suggests that the CBAA molecule offering electrons to unoccupied *d* orbital of the metal atom creating strong bond St3S–CBAA. Attentively observing to the Figure 8 it is understandable that *N*-(2-chlorobenzylidene)-4-acetylaniline also could accept the *d*-orbital electrons of iron by LUMO on the benzene ring. Consequently, this electron acceptance could help to form more stable bond between inhibitor molecule and iron surface. Moreover, the results obtained show that of *N*-(2-chlorobenzylidene)-4-acetylaniline has the low value of energy gap and the high value of dipole moment (Table 5) which will favor the enhancement of corrosion inhibition by the adsorption of *N*-(2-chlorobenzylidene)-4-acetylaniline on the St3S carbon steel surface.

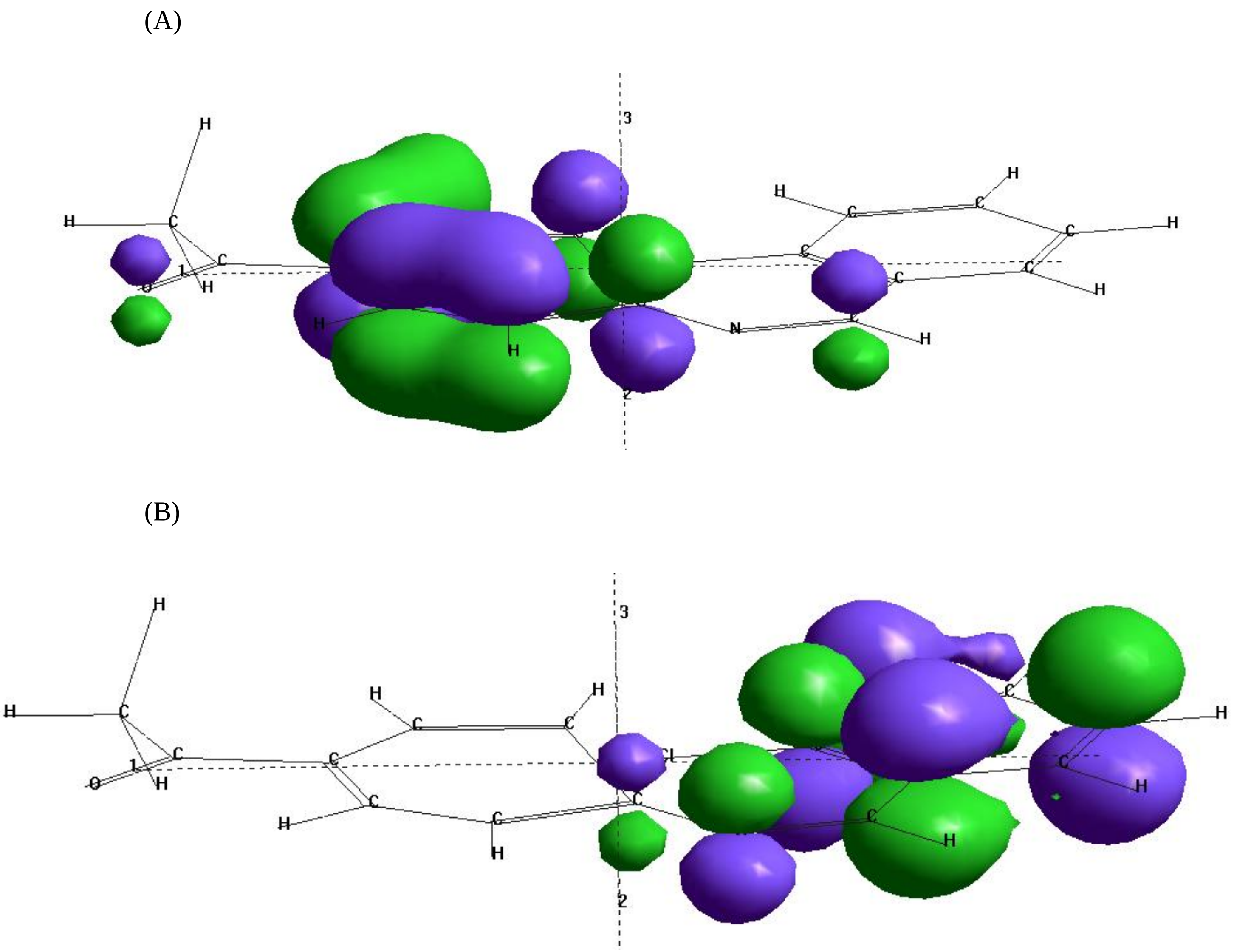

Figure 8. The frontier molecular orbital density distribution for *N*-(2-chlorobenzylidene)-4-acetylaniline: (A) HOMO, (B) LUMO

Table 5. The calculated quantum chemical parameters for *N*-(2-chlorobenzylidene)-4-acetylaniline

Inhibitor	E_{HOMO} eV	E_{LUMO} eV	ΔE eV	μ D	I eV	A eV	χ eV	η eV	ΔN
CBAA	-8.556	-2.244	6.312	9.393	8.556	2.244	5.400	3.156	0.253

The energies of the HOMO and the LUMO orbital's of the inhibitor molecule are related to the ionization potential, $I = -E_{HOMO}$, and electron affinity, $A = -E_{LUMO}$ of the studied molecule [35], are placed in Table 5. The values of I and A were considered for the calculation of the electronegativity (χ) and the global hardness (η) using the following relations:

$$\chi = \frac{I + A}{2} \tag{26}$$

and:

$$\eta = \frac{I - A}{2} \tag{27}$$

The calculated parameters are listed in Table 5.

The number of transferred electrons (ΔN) from the inhibitor molecule to the iron atom was calculated according to formula:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \tag{28}$$

where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and the molecule, respectively.

The idea behind this is that in the reaction of two systems with different electronegativity as a metallic surface and an inhibitor molecule the following mechanism will take place: the electron flow will move from the molecule with the low electronegativity towards that of a higher value until the chemical potentials are the same.

The theoretical values of χ_{Fe} and η_{Fe} are 7.0 and 0 eV mol^{-1}, respectively [35]. The fraction of electrons transferred from *N*-(2-chlorobenzylidene)-4-acetylaniline to the metal molecule was calculated (Table 5). The value of ΔN showed inhibition effect of CBAA resulted from electron donation. However, the *N*-(2-chlorobenzylidene)-4-acetylaniline was the donators of electrons while the St3S was acceptor. However, atoms: *N*, *O*, and *Cl* have the most probability to form coordinating bond. The *N*-(2-chlorobenzylidene)-4-acetylaniline was bound to the St3S carbon steel surface and thus formed inhibition adsorption layer against corrosion.

3.6. Scanning electron microscopy studies

The surface morphology of St3S carbon steel samples immersed in 1.2 M Cl^- solution in the absence and in the presence of *N*-(2-chlorobenzylidene)-4-acetylaniline were show in Figure 9. The photograph 9(a) revels that the surface was strongly damaged in absence of the inhibitor. Chloride ions, oxygen and water penetrate the surface through pores, flaws or other weak spots what results in the further corrosion of investigated steel. There are wide and deep pits on the surface which indicate the main characteristic of pitting corrosion. Figure 9(b) show SEM image of St3S carbon steel surface after immersion (for the same time interval) in corrosive solution containing additionally 20 mM of CBAA. The surface is more uniform in the inhibited solution than the surface in the absence of *N*-(2-chlorobenzylidene)-4-acetylaniline except some hallows structures which most probably due to polishing lines. The image clearly demonstrate the high inhibition efficiency of CBAA. The inhibitor molecules were adsorbed on the active sites and protected the carbon steel against corrosion.

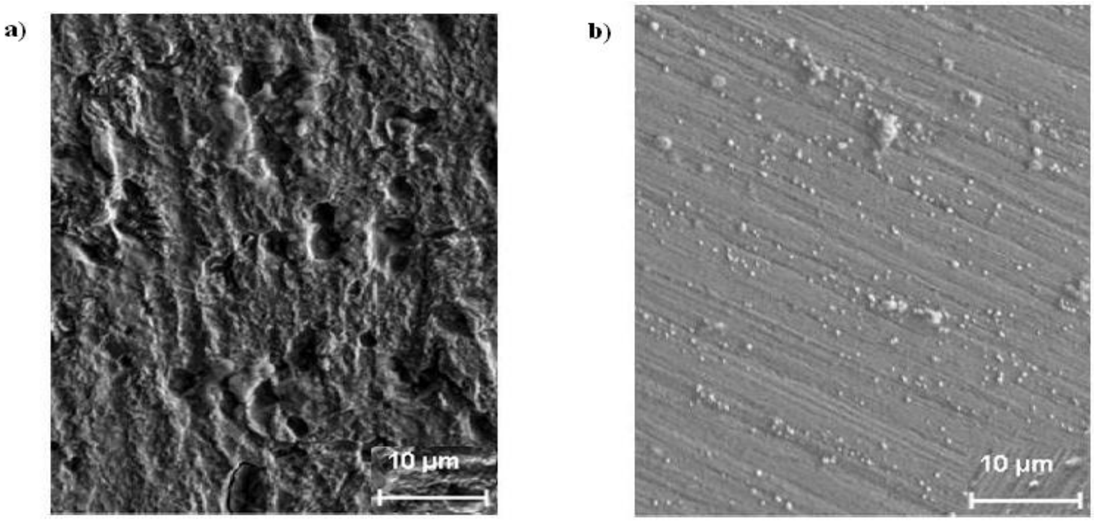

Figure 9. SEM images of St3S carbon steel surface after expose 360 hours to 1.2 M Cl^- solution: a) without, b) with the addition of 20 mM *N*-(2-chlorobenzylidene)-4-acetylaniline. Magnification 500×

4. MECHANISM OF INHIBITION

The corrosion inhibition mechanism in acid medium the most often depends on the adsorption of an inhibitor onto the metal surface. The inhibitive action of inhibitors depends on the electron densities around the adsorption centers. The higher the electron density at the centre, the more efficient is the inhibitor. The adsorption of the inhibitor on metal surface is the first step in the action mechanism of inhibition. Physical adsorption requires presence of both electrically charged surface of the metal and charged species in the bulk of the solution. Moreover, chemical adsorption requires in the presence of a metal to have a vacant low-energy electron orbital, and an inhibitor with molecules having relatively loosely bond electrons or heteroatom with lone pair electrons.

The studied of *N*-(2-chlorobenzylidene)-4-acetylaniline as an inhibitor is organic compound (Schiff base) which contains of an imine group (─CH=N─) (Fig. 1). The imine group determines propriety of this kind of compounds. The addition of acid or a base to the aqueous solution of any of these inhibitor will transform the neutral molecule into a cation or an anion. In acid solution the CBAA molecule was protonated according to the reaction:

$$\text{CBAA} + H^+ \leftrightarrow \text{CBAAH}^+, \quad (29)$$

thus they become cation, existing in equilibrium with the corresponding molecular form. The molecular and cation both forms played separate role in the adsorption of inhibitor on the metal surface. The protective layer has been formed according to:

$$(\text{Fe} - \text{Cl})_{\text{ads}} + \text{CBAAH}^+ \leftrightarrow (\text{Fe} - \text{CBAA})_{\text{ads}} + H^+ + Cl^-. \quad (30)$$

The inhibiting effect of CBAA can be regarded as an adsorption of inhibitor and the formation compound protective film onto steel surface, whose proposal of model is presented in Figure 10.

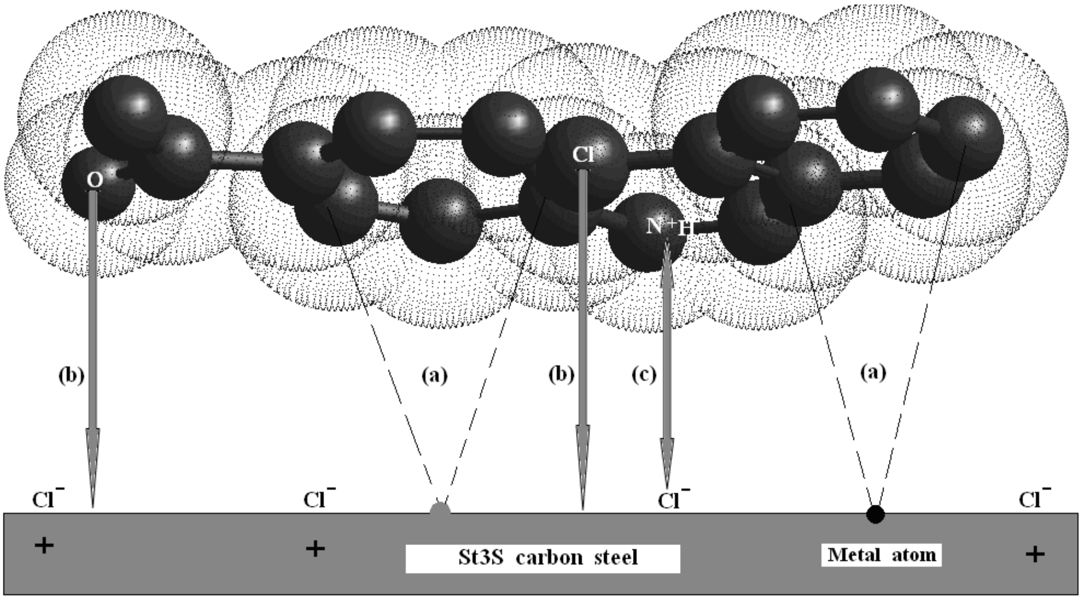

Figure 10. Proposal of model of protective layer of *N*-(2-chlorobenzylidene)-4-acetylaniline on St3S carbon steel surface in a 1.2 M Cl^- solution: (a) chemisorptions, (b) feedback bond, and (c) electrostatic interaction (physisorption)

Therefore, it may be assumed that of *N*-(2-chlorobenzylidene)-4-acetylaniline adsorption can also occur via electrostatic interaction (physisorption) with the surface of the electrode. The adsorption of *N*-(2-chlorobenzylidene)-4-acetylaniline onto the St3S surface makes a barrier for mass and charge transfers. This situation leads to the protection of carbon steel surface from the attack of aggressive anions, Cl^- of the solution.

5. CONCLUSION

The inhibition effect of *N*-(2-chlorobenzylidene)-4-acetylaniline on the corrosion of St3S carbon steel in chloride acidic solutions was studied. From the data obtained the following points can be emphasized:

(1) The corrosion of St3S carbon steel in a 1.2 M Cl^- solution is significantly inhibited by of *N*-(2-chlorobenzylidene)-4-acetylaniline.

(2) The corrosion reaction of St3S in the absence and presence of *N*-(2-chlorobenzylidene)-4-acetylaniline follows zero-order kinetics.

(3) The CBAA behaves as mixed type corrosion inhibitor.

(4) The inhibition efficiency corrosion of St3S increases with increase of concentration of CBAA for the same temperature of solution. The increase temperature effects decrease of *IE* values for the same concentration of inhibitor.

(5) Adsorption and thermodynamic study showed that the adsorption of *N*-(2-chlorobenzylidene)-4-acetylaniline molecule on steel surface follow Langmuir adsorption isotherm.

(6) Thermodynamic adsorption parameters show that of CBAA was adsorbed by spontaneous, exothermic process which is unequivocally to physical adsorption of inhibitor.

(7) Quantum chemical method shows that of *N*-(2-chlorobenzylidene)-4-acetylaniline molecule can be directly adsorbed at the steel surface on the basis of donor-acceptor interactions.

(8) SEM micrographs showed that the CBAA molecules form a protective film on the steel surface.

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