The Study of the Process of Corrosion Inhibition of Carbon Steel in a Solution of Ammonium Chloride by using N-Cyclohexylbenzothiazolsulphen-amida

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Abstract

The inhibiting effect of N-Cyclohexylbenzothiazolsulphen-amida (NCBSA) on the corrosion of carbon steel in a solution of NH_4Cl $10^{-1}M$ (pH = 5,5) at temperatures of 25º C, 35º C, 45º C and 55º C has been studied by using weight loss measurements and electrochemical measurements. The morphology of carbon-steel surface in the absence and in the presence of NCBSA was examined under the microscope. The activation energy (E_a) was determined from Arrhenius equation. The activation enthalpy ($\Delta H°$) and the activation entropy ($\Delta S°$) were calculated from the diagram of the critical complex. The experimental data characterize an adsorption isotherm of type Langmuir.

Key words: carbon steel, corrosion, inhibition, NCBSA, ammonium chloride

Introduction

Treatments with organic compounds [1-9] have been proposed in order to improve anti-corrosion protection. The efficiency of the corrosion inhibition by organic compounds is closely related to the structure and properties of the film formed on the metal surface. For the carbon-steel corrosion inhibition in different mediums, there have been used organic compounds that contain sulphur and nitrogen, the results showing that several inhibitors act through adsorption on the metal surface [10-19]. It has been observed that the adsorption depends especially on the electronic structure of the molecule and that the inhibiting effect increases with the increase in the number of the aromatic nuclei. The adsorption process is also influenced by the metal nature and surface, by the electrolyte nature and the interactions between the organic molecules and the metal surface, and by temperature [20-33].

The action mechanisms of the organic inhibitors as well as the factors influencing the adsorption depend on the strength of the bond inhibitor-metal [34-39].

The present study aims to determine the role of NCBSA in improving the protective film in case of generalized corrosion of carbon steel in a low acid medium (pH = 5,5) that contains NH_4Cl $10^{-1}M$, by determining the parameters of activation of the dissolving reaction and the thermodynamic parameters of adsorption of the inhibitor on the metal surface.

Experimental

Weight loss measurements

The experimental determinations follow the calculation of the corrosion rate of carbon steel in a solution of NH_4Cl $10^{-1}M$ in the absence and presence of NCBSA by

using the gravimetric method. The utilized carbon steel has the following composition: C=0,1%, Si=0,035%, Mn=0,4%, Cr=0,3%, Ni=0,3% and the rest up to 100% Fe.

For the gravimetrical determinations, the metal samples with a surface of 4 cm^2 were mechanically polished with sand-paper of different sizes, decapped with a solution of 5% HCl, washed in double distilled water, degreased in ethylic alcohol and dried in warm air. To avoid the change of the solution concentration on through water evaporation, the experiments were effected in a closed system.

The corrosion rates of carbon steel were determined in a solution of NH$_4$Cl 10^{-1}M in the absence and presence of some variable concentrations of NCBSA: 50 ppm, 100 ppm, 150 ppm, 200 ppm and respectively, $1,89^.10^{-4}$M, $3,78^.10^{-4}$M, $5,68^.10^{-4}$M, $7,56^.10^{-4}$M. The immersion time of the plates in the respective media were 3 hours at temperatures of 25º C, 35º C, 45º C and 55º C. Before being introduced in corrosive media, the plates were exactly weighed on analytical scales. The corrosion products were removed once the samples were taken out of the corrosive mediums, by washing them in a warm solution of HCl 5%, after which they were degreased in ethilic alcohol, dried in warm air and weighed again on the analytical scales.

The mass variation is conditioned by the composition; the nature of medium and work temperature

Electrochemical measurements

For the study of polarization a standard corrosion cell was used, with a working electrode made of carbon-steel with an active surface of 4 cm^2. The saturated calomel electrode (SCE) was used as a reference electrode. The auxiliary electrode was a carbon-steel plate identical to the one used as the working electrode. The carbon steel

electrodes were made of the same material as the plates used for weight loss measurements.

The electrochemical measurements were carried out using a Keithley 2420 3A Source Meter, and the data were computerized. The morphology of steel's surface before and after being treated with NCBSA was examined with a STEM LEO 911 OMEGA microscope

Results and discussion

Weight loss measurements

For the carbon steel samples the weight losses were determined in a solution of NH_4Cl $10^{-1}M$, in the absence and presence of several variable concentrations of NCBSA: 50 ppm, 100 ppm, 150 ppm, 200 ppm at different temperatures: 25º C, 35º C, 45º C, 55º C.

The corrosion rate was expressed by the gravimetric indices (k_g) determined according to relation 1.

$$k_g = \frac{\Delta G}{S \cdot t} \tag{1}$$

where: ΔG = mass loss due to corrosion (g), S = the corroded surface (m^2), t = action time for corrosive processes.

The variation of the corrosion rate with the concentration of NCBSA at different temperatures is presented in Figure 1.

The increase in concentration of NCBSA leads to a decrease in the corrosion rate. This suggests that the inhibition of carbon steel corrosion in the presence of NCBSA is due to the adsorption of the latter on the metal surface. On the other hand, an increase in temperature from 25º C to 50º C leads to an increase in the corrosion rate,

the probable cause being the desorbtion of the inhibitor molecules from the metal
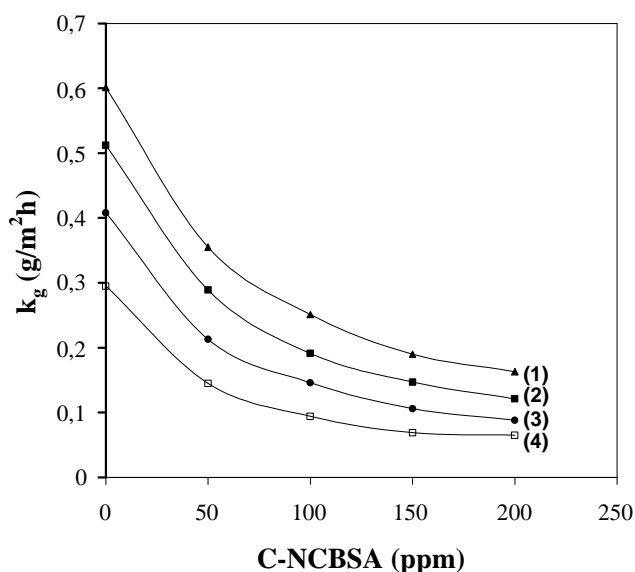
surface.

Figure 1. The variation of the corrosion rate for carbon steel corroded in a solution of

NH_4Cl $10^{-1}M$ at different temperatures: (1) 55^0C; (2) 45^0C; (3) 35^0C; (4) 25^0C.

The efficiency of inhibition expressed in percentage (P) for NCBSA was

calculated using the relation 2.

$$P = \frac{k_{g0} - k_g}{k_{g0}} \cdot 100 \qquad (2)$$

where: k_{g0} = the corrosion rate in the absence of inhibitor, k_g = the corrosion rate in the

presence of inhibitor.

The inhibition efficiency determined under experimental conditions is presented

in Figure 2.

The inhibition efficiency depends on the inhibitor concentration and on

temperature. It is observed that at a concentration of NCBSA of 200 ppm ($7,56^. 10^{-4}M$)

and a temperature of 25º C, the practically determined efficiency is of 81%. There is a

possible formation of some complexes between NCBSA (as a binder) and different

metallic cations that are found in the steel composition. These complexes can form permanent stable films on the steel surface, thus decreasing the corrosion rate. The good adsorbability of NCBSA can be related to the basicity of the thiazolic nucleus and to the pair of non-participant electrons from the sulphur atom in the thiazolic cycle.
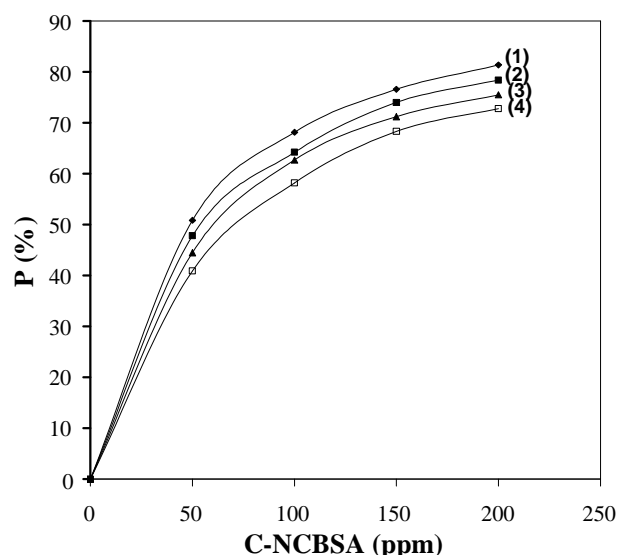

Figure 2. The variation of the inhibition efficiency expressed in percentage (P) with the concentration of NCBSA for carbon steel corroded in a solution of NH_4Cl $10^{-1}M$ at different temperatures. (1) 25^0C;(2) 35^0C;(3) 45^0C;(4) 55^0C.

It can be also presupposed that the adsorbability of the NCBSA molecules around the corrosion spots in incipient stages (initiation and propagation) is due to the non-participant electrons from the sulphur atom and nitrogen from the lateral chain of the thiazolic cycle, or that this chain contributes to the increase in the thickness of the adsorption layer.

It can be said that a competitive adsorption takes place between the inhibitor molecules and the Cl^- anion on the steel surface.

The activation energy that characterizes the corrosion inhibition of carbon steel in a solution of NH_4Cl $10^{-1}M$ in the absence and presence of NCBSA was determined from the logarithmic equation of Arrhenius:

$$\log k_g = \frac{-E_a}{2{,}303 \cdot RT} + \log A \qquad (3)$$

where: k_g = corrosion rate, E_a = apparent activation energy, A = pre-exponential factor, R = gas constant, T = temperature

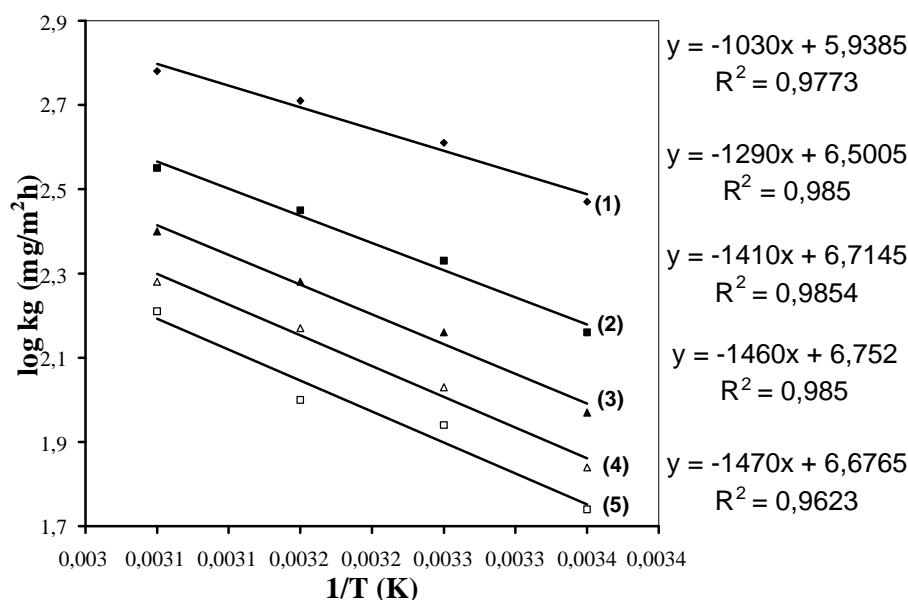By graphically representing $\log k_g$ = f (1/T) straight lines can be obtained with slopes $E_a/2{,}303R$ (Figure 3).

Figure 3. The Arrhenius diagram for the corrosion rate of the carbon steel sample in NH_4Cl $10^{-1}M$ in the absence and presence of different concentrations of NCBSA. (1) 0; (2) $1{,}89 \cdot 10^{-4}$ M; (3) $3{,}78 \cdot 10^{-4}$ M; (4) $5{,}68 \cdot 10^{-4}$ M; (5) $7{,}56 \cdot 10^{-4}M$.

The enthalpy and entropy that characterize the processes of corrosion and inhibition were determined from the relation 4:

$$k_g = \frac{RT}{N_a h} \exp\left(\frac{\Delta S^0}{R}\right) \exp\left(-\frac{\Delta H^0}{RT}\right) \qquad (4)$$

where: h = the Planck constant, N_a = Avogadro's number, R = gas universal constant, ΔH^o = activation enthalpy, ΔS^o = activation entropy.

By graphically representing $\log(k_g/T)$ function of $(1/T)$ straight lines are obtained, as it can be observed in Figure 4. The slopes of these straight lines are equal to $\Delta H^o/2{,}303R$, the intersection with the ordinate representing $\log \dfrac{R}{N_a h} + \left(\dfrac{\Delta S^0}{2{,}303R} \right)$, out of which the values ΔH^o and ΔS^o were calculated.

y = -887,2x + 2,9859
R^2 = 0,9693

y = -1143x + 3,5363
R^2 = 0,983

y = -1256x + 3,7292
R^2 = 0,9807
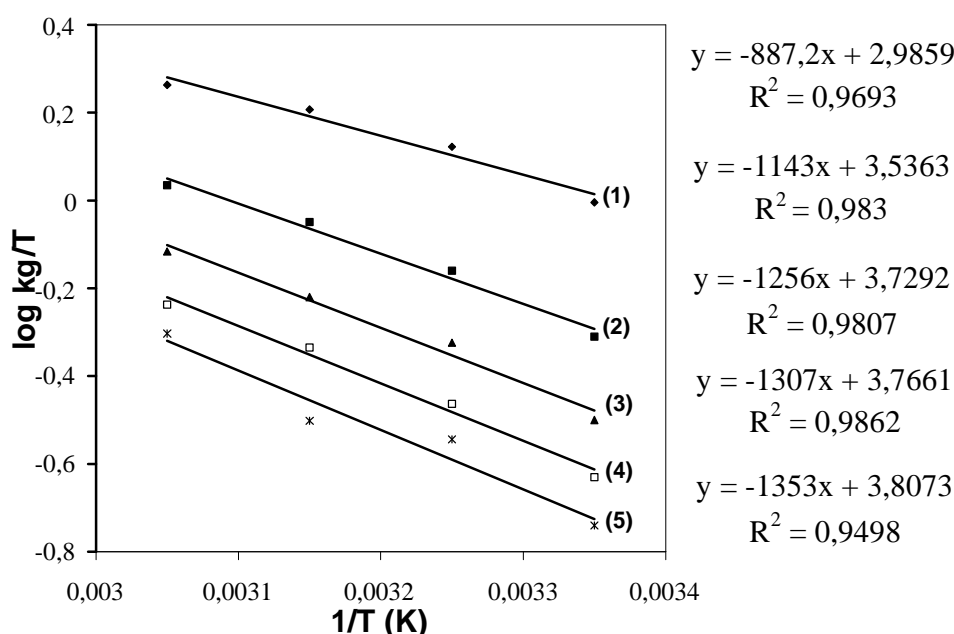
y = -1307x + 3,7661
R^2 = 0,9862

y = -1353x + 3,8073
R^2 = 0,9498

Figure 4. The diagram of the critical complex for the corrosion rate of carbon steel in a solution of NH_4Cl $10^{-1}M$ in the absence and presence of different concentrations of NCBSA. (1) 0;(2) $1{,}89 \cdot 10^{-4}M$;(3) $3{,}78 \cdot 10^{-4}M$;(4) $5{,}68 \cdot 10^{-4}M$;(5)$7{,}56 \cdot 10^{-4}$ M.

The values obtained for E_a, ΔH^o and ΔS^o are presented in Table 1.

E_a and ΔH^o that characterize the inhibition process of carbon steel corrosion in a solution of NH_4Cl $10^{-1}M$, in the presence of NCBSA as an inhibitor have values relatively close to those that characterize the corrosive process in the absence of the inhibitor. This proves that no energetic barrier is reached. The results show that the

reaction of corrosion inhibition is affected, but without any modification of the mechanism being produced.

Table 1. The parameters of activation for the dissolving reaction of carbon steel in a solution of NH_4Cl $10^{-1}M$ in the absence and presence of NCBSA.

NCBSA concentration (M)	E_a (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/K·mol)
0	19,7	16,77	-142,15
$1,89 \cdot 10^{-4}$	24,67	21,86	-131,62
$3,78 \cdot 10^{-4}$	26,97	24,03	-127,93
$5,58 \cdot 10^{-4}$	27,92	25	-127,22
$7,56 \cdot 10^{-4}$	28,12	25,88	-126,44

This implies that at the stage determining the rate, the activation complex represents rather an association than a dissociation.

On studying the inhibitor we have reached the conclusion that the experimental data characterize an adsorption isotherm of Langmuir type expressed by the relation 5.

$$\frac{\theta}{1-\theta} = Kc \qquad (5)$$

where: θ = degree of covering, K = the equilibrium constant of the adsorption-desorption process, c = concentration of the inhibitor

By graphically representing $\dfrac{\theta}{1-\theta}$ function of the NCBSA concentration, straight lines are obtained with the slope K (Figure 5).
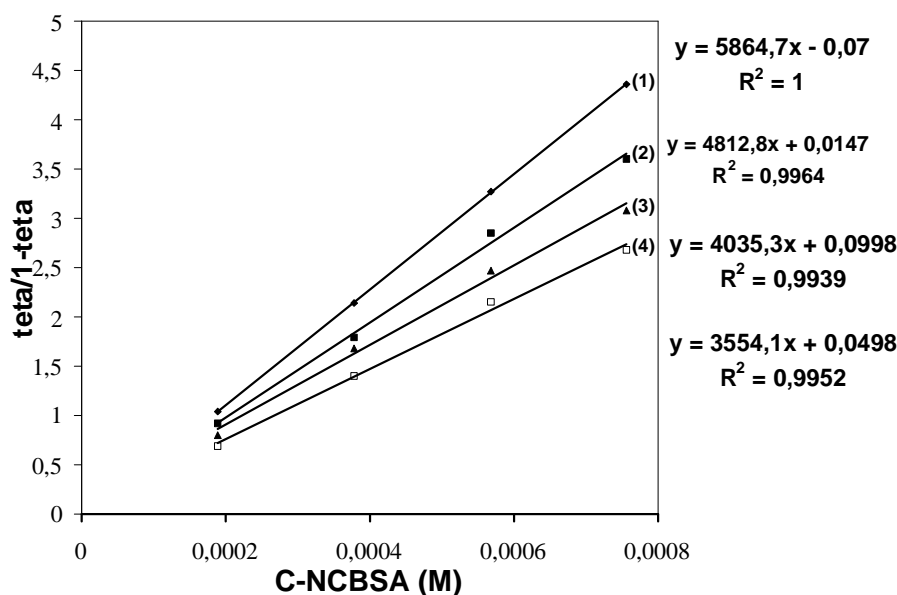
Figure 5. The results of a Langmuir diagram in case of corrosion inhibition of carbon steel in a solution of NH$_4$Cl 10^{-1}M with NCBSA at different temperatures. (1) 25^{0}C; (2) 35^{0}C; (3) 45^{0}C; (4) 55^{0}C.

The thermodynamic parameters of adsorption ΔH^o_{ads} and ΔS^o_{ads} were obtained from the dependence relation of the equilibrium constant (K) of temperature.

$$\log K = \frac{-\Delta H^0_{ads}}{2,303RT} + \frac{\Delta S^0_{ads}}{2,303R} + \log\frac{1}{55,5} \qquad (6)$$

By graphically representing logK function of 1/T a straight line is obtained whose slope is equal to $\dfrac{\Delta H^0_{ads}}{2,303RT}$, while the intersection with the ordinate axis is

$\dfrac{\Delta S^0_{ads}}{2,303R} + \log\dfrac{1}{55,5}$ (Figure 6).

The free standard energy of adsorption (ΔG^o_{ads}) was calculated with relation 7:

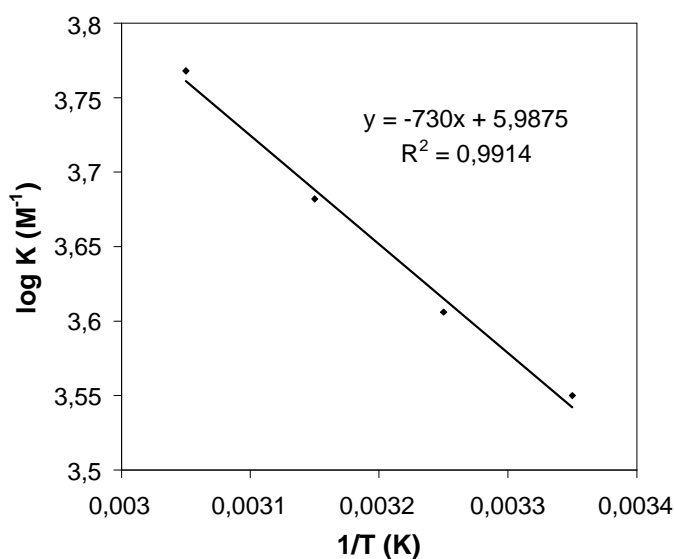$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \qquad (7)$$

Figure 6. The graphical representation of logk function of 1/T for NCBSA derived from

the experimental adsorption isotherm of carbon steel.

The results are presented in Table 2.

Table 2. The thermodynamic parameters for the NCBSA adsorption on the carbon steel

surface in a solution of NH_4Cl $10^{-1}M$.

Temperature	25^0C	35^0C	45^0C	55^0C
K (mol^{-1})	5864,7	4812,8	4035,3	3554,1
ΔG_{ads}^0 (kJ/mol)	-40,28	-42,1	-43,92	-45,73

The values of $\Delta G°$ are negative, which shows that the process of adsorption is

spontaneous. The equilibrium constants K vary towards the same direction, in the sense

that higher values of K imply a better adsorption, which leads to an increase in the

inhibition efficiency.

Electrochemical measurements

The effect of the inhibitor has been studied by the anodic and cathodic

galvanostatic polarization of the carbon-steel sample in a NH_4Cl $10^{-1}M$, both in the

presence and absence of NCBSA. The anodic and cathodic polarization curves are
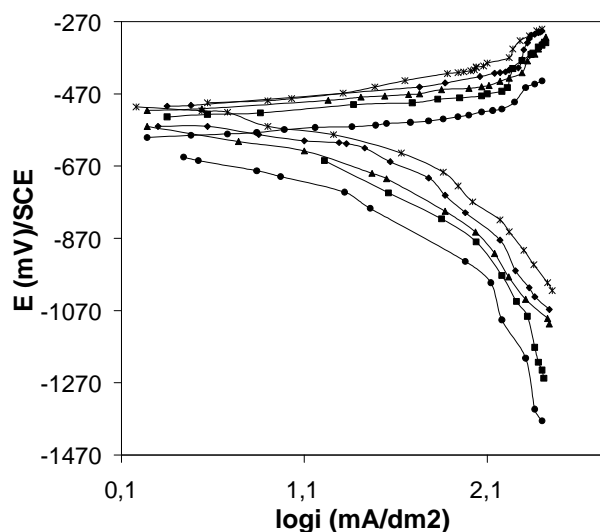
presented in figure 7.

Figure 7. The polarization curves for carbon steel in a solution of NH_4Cl 0,1M, in the

presence of different concentrations of NCBSA: (——●——)0; (——■——)50ppm; (——▲——) 100ppm;

(——◆——)150ppm; (——✳——)200ppm

Five determinations were made for each solution, taking into consideration the

most reproducible responses for the same current densities. In this study, the minimum

recorded current was 10µA. Thus E_{cor} was defined as the potential from which a current

larger than 10µA was observed.

The anodic polarization of steel electrodes in the inhibitor containing NH_4Cl

$10^{-1}M$ is shifted to less negative values, while the cathodic polarization shifts to more

negative values with increasing current density. The presence of organic inhibitors in

the corrosive medium increases the anodic and cathodic overpotentials and decreases

the corrosion current (i_{cor}). These changes increase with increasing inhibitor

concentration. This behaviour supports the inhibition function of these organic

compounds. Decrease of the corrosion current (i_{cor}) was associated with an appreciable

shift of corrosion potential (E_{cor}) to a less negative value. This suggests that although inhibition is of mixed type, it is predominantly anodic.

The percentage inhibition efficiency (P) of these inhibitors was also determined from the polarization measurements according to the equation:

$$P = \frac{i'_{cor} - i_{cor}}{i'_{cor}} \cdot 100 \qquad (8)$$

where i'_{cor} and i_{cor} are the uninhibited and inhibited corrosion current density, respectively, obtained by extrapolation of the anodic and cathodic Tafel lines to the corrosion potential. In the presence of the inhibitor, the steel is active and dissolves by a Tafel slope of 85 ± 5 mV. The cathodic process is determined by the cathodic reduction of all the components, namely, O_2, NH_4^+. The reduction of water molecules is probably an additional cathodic process. Metal ionization is suppressed by the inhibitor more strongly (Figure 7) than the cathodic process is stimulated, and the free corrosion potential of steel becomes significantly higher with an increase in C-NCBSA The results are presented in table 3.

Table 3. The electrochemical parameters for carbon steel in the presence and absence of NCBSA and the percentage P obtained by galvanostatic polarization.

NCBSA concentration (ppm)	E_{cor} (mV)	b_a (mV)	i_{cor} (mA/dm^2)	P (%)
0	-596	85	99,7	0
50	-545	83	52,8	47
100	-538	87	33,7	66,2
150	-520	84	22,4	77,5
200	-511	87	16,3	83,6

It can be observed that the inhibition efficiency calculated from the weight loss measurements is close to that calculated from electrochemical measurements, especially at high concentrations of inhibitor.

The surface analysis of the corroded samples was effected under a microscope STEM LEO 912 omega. In the absence of the inhibitor (Figure 8.1) the experiments show that the surface was covered with a great number of corrosion spots. In the presence of NCBSA the corrosion spots decrease in intensity at the same time with the increase in inhibitor concentration 200 ppm (Figure 8.2). This demonstrates that the metal surface is covered by a superficial layer that offers it a good protection.
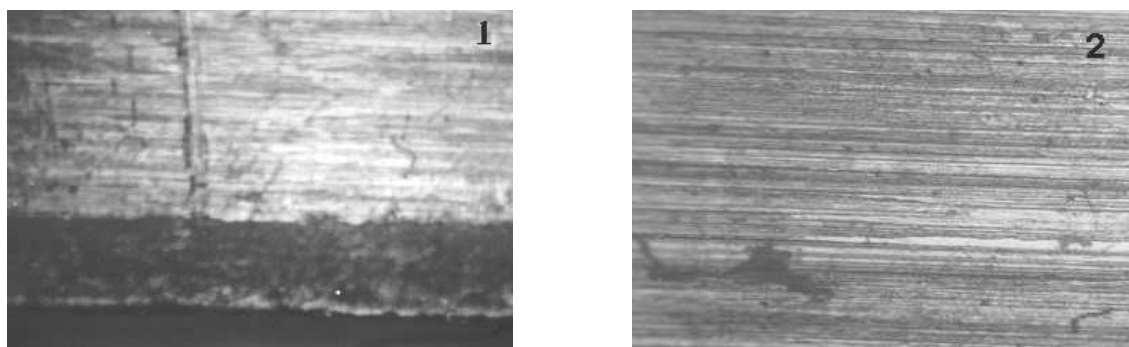

Figure 8. The microscopic analysis of the metal surface after the corrosion of carbon steel in a solution of NH_4Cl $10^{-1}M$ in the absence or presence of NCBSA (x1000).

Conclusions

NCBSA is an inhibitor for the corrosion of carbon steel in a solution of NH_4Cl $10^{-1}M$ at a concentration of 200 ppm ($7,56.10^{-4}M$) in the corrosive medium it has an efficiency of 81% obtained by weight loss measurements respectively 83.6% by electrochemical measurements. NCBSA acts through adsorption on the metal surface.

On studying the inhibitor it has been found that the experimental data observe the Langmuir adsorption isotherm. ΔG^o_{ads} is negative, which shows that the adsorption process of NCBSA on the metal surface is spontaneous.

By the microscopic analysis of the carbon-steel surface it has been found that the corrosion spots decrease in intensity in the presence of the inhibitor . This demonstrates the formation of a superficial layer that ensures a good protection to the metal.

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