SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY SOUTH. BRAZ. J. CHEM., Vol. 11, Nº 12, 2003

A STUDY OF THE CORROSION INHIBITION OF CARBON STEEL IN AMMONIACAL MEDIA DILUTED BY N-CYCLOHEXYL BENZOTHIAZOLE SULPHEN AMIDE

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ABSTRACT

The inhibition effect of N-cyclohexyl benzothiazole sulphen amide (NCBSA) was studied on the corrosion of carbon steel in diluted ammoniacal solution at temperatures of 25 °C and 30°C.

The effects of the inhibitor on the corrosion were investigated and determined by using electrochemical measurements (curves of intensity - voltage). The efficiency of NCBSA increased with increase in concentration, but decreased with increase in temperature. Free energy of activation was determined from Arrhenius type equation. Experimental data fitted on adsorption isotherm of Langmuir type, while the results were correlated to the chemical structure of the inhibitor.

RESUMO

A inibição da corrosão do aço carbono por N-ciclohexil benzotiazol amida (NCBSA) em solução amoniacal diluída foi estudada á 25 e 30 °C. Os efeitos do inibidor foram estudados e determinados usando medidas eletroquímicas (curvas de intensidade-voltagem). A eficiência do inibidor (NCBSA) aumentou com a concentração e diminuiu com o aumento na temperatura. A energia de ativação foi determinada usando a equação de Arrhenius. Os resultados expereimentais seguem o isoterma de adsorção de Langmuir e foram relacionados com a estrutura do inibidor.

KEYWORDS: carbon steel, ammoniacal media, inhibitor, N-cyclohexyl benzothiazole sulphen amide

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INTRODUCTION

Before 1960, the treatment of the carbon steel corrosion in the systems of water cooling was based on inorganic inhibitors such as chromates, nitrates, polyphosphates and zinc salts.¹⁻³ The use of chromates is restricted because of their toxicity, while the nitrates are efficient in concentrations that economically disadvantageous, being also easily decomposed by bacteria.³

Particular attention has been given lately to the use of polyphosphates and their derivates.⁴ The advantageous use of these compounds consists in the lack of toxicity. Moreover, only a concentration of a few ppm is necessary for the protection of great systems of water supply. Yet they can be media favourable for the development of microorganisms.

Ever since 1960 more advanced treatments based on organic compounds^{5,6} have been proposed to improve protection against corrosion.

The efficiency of the corrosion inhibition by the organic compounds is closely related to the structure and the properties of the layer formed on the metal surface under experimental conditions. The process of the adsorption of the organic compounds is attributed to the effects of the functional groups grafted on aromatic nuclei.^{7,8}

It appeared that the adsorption depended especially on the electronic structure of the molecule and that the inhibiting effect increased with the number of aromatic nuclei.

The organic compounds containing sulphur and nitrogen have been utilized for the corrosion inhibition of carbon steel in acid media, the results showing that the most inhibitors act through adsorption at the metal surface.⁹⁻¹⁰ The power of adsorption and consequently the strength of the inhibiting effect are dependent on the nature of the organic compounds, on the nature of the metal and of corrosive medium.

The current investigation establish the role of NCBSA in improving the passive films resistance towards general corrosion of the carbon steel in diluted ammoniacal solution of 10^{-3} N concentration.

EXPERIMENTAL DETAILS

The sample chosen for investigation is carbon steel LC 35 having the following composition: C = 0.35%, Mn = 0.65%, Si = 0.25%, S = 0.035% and iron up to 100%. For all experiments the carbon steel samples were polished with sand paper, cleaned in water, degreased in ethilic alcohol and dried in warm air.

The corrosion medium was the ammoniacal solution of 10^{-3} N concentration in contact with air at a temperature of 25°C and 30°C.

The tested inhibitor was N-cyclohexyl benzthiazole sulphen amide (NCBSA) and the measurements were made for its concentrations of 10^{-4} M, 2×10^{-4} M, 3×10^{-4} M and 4×10^{-4} M.

The electrochemical measurements were made using a standard corrosion cell. The working electrode was a carbon steel plate with an area of 4 cm^2 . A calomel-saturated electrode was used as a reference electrode and the auxiliary electrode was a platinum plate. Data were computerized.

RESULTS AND DISCUSSION

The polarization curves are presented in figure 1. As compared to the non-inhibited solution, the corrosion potential shifted towards positive values. The presence of NCBSA

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increases the anodic over-voltage and leads to a decrease in the corrosion current. Up to current densities of 5 mA dm⁻² the anodic potentials present a slight increase towards higher positive values. At current densities higher than 5 mA dm⁻² the increase in potentials is significant, which supposes the inhibitor desorption on electrode surface. The decrease in the corrosion current was associated with a significant shifting of the corrosion potential towards higher values. This suggests that when the inhibition is mixed type it is preponderently anodic. The Tafel segments in the curves of cathodic polarization have small slopes being in the vicinity of the cathodic current limit. The nature of this limit is probably determined by the total transfer of all the cathodic-reduced compounds such as: O_2 , NH_4^+ , H_3O^+ . The retardation of the metal ionization by inhibitors is stronger than the stimulation of the cathodic process, the free corrosion potential of carbon steel significantly increasing with the increase in NCBSA concentration.



Figure 1. The polarization curves for carbon steel in ammoniacal solution 10^{-3} N in the presence of NCBSA at different concentrations: (1) 0.0; (2) 10^{-4} M; (3) 2 x 10^{-4} M; (4) 3 x 10^{-4} M; (5) 4 x 10^{-4} M.

In inhibitor solutions the steel remains active and behaves as an anode and dissolves after a Tafel-type slope b_a at 36±3 mV (figure 2)





Figure 2. Graphical representation of $\eta = f(\lg I)$ for carbon steel in ammoniacal solution $10^3 M$ in the presence of NCBSA at different concentration: (1) $10^{-4} M$; (2) $2 \times 10^{-4} M$; (3) $3 \times 10^{-4} M$; (4) $4 \times 10^{-4} M$.

The corrosion current can be calculated from Tafel-type equation with potentials far apart from the corrosion potential for a theoretical slope b_a equal to 2,3RT/zF α mV, as follows:

$lg I_{cor} = 2.06$	- 0.026(ŋ ₂ -	η_1)
$lg I_{cor} = 2.12$	$-0.025(n_2 -$	η_1

(1), for the temperature of 25°C;
(2), for temperature of 30°C,

where:

 I_{cor} = corrosion current in the presence of inhibitor;

 η_1 = galvanostatic over-voltage for non-inhibiting solution;

 η_2 = galvanostatic over-voltage for inhibiting solution.

The efficiency of inhibition represented by the rate was calculated from the formula:

$$P = \frac{i_{cor_1} - i_{cor_2}}{i_{cor_1}}$$
(3)

where: $i_{corl} = corrosion$ current for non-inhibiting solution

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 i_{cor2} = corrosion current for inhibiting solution The results are presented in Table:

Table 1. The electrochemical parameters for carbon steel in ammoniacal solutions 10^3 N in the presence or absence of NCSBA, the percent P obtained from the galvanostatic polarization η and the corrosion rate at 25°C and 30°C.

C _{NCBSA}	25°C				30°C					
	0	10-4	2x10 ⁻⁴	3x10 ⁻⁴	4x10 ⁻⁴	0	10-4	2x10 ⁻⁴	3x10 ⁻⁴	4x10 ⁻⁴
E _{cor} (mV)	159	267	272	278	284	153	260	265	270	277
$I_A (mA dm^{-2})$	8.75	8.75	8.75	8.75	8.75	8.75	8.75	8.75	8.75	8.75
η (mV)	67	107	111.7	118.6	132	64	102.5	107.5	111.6	119
I_{cor} (µA dm ⁻²)	116	10.5	7.9	5.3	2.3	132	14.5	10.8	8.5	5.9
P (%)	-	90.9	93.2	95.4	98	-	89	91.8	93.5	94.6
$K_{a} (mg m^{-2} h^{-1})$	8.1	0.74	0.56	0.37	0.16	9.3	1.02	0.76	0.6	0.42

The variation of the corrosion rate with an inhibitor concentration is presented in Figure 3. The corrosion rate decreases with the increase in the inhibitor concentration and increases with the increase in temperature, which indicates a stronger desorption of the inhibitor on the electrode surface. It is known from a previous work,¹¹ where the electrochemical measurements were associated with Mössbauer spectroscopy measurements, that in absence of the inhibitors the carbon steel surface is covered with a nonstoichiometric iron oxide layer.



Figure 3. The variation of the corrosion rate with NCBSA concentration: (1) $25^{\circ}C$; (2) $30^{\circ}C$.

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The investigation of the inhibition led to the conclusion that the experimental data fit an adsorption isotherm of Langmuir-type expressed by the relation:

$$\frac{\theta}{1-\theta} = \mathrm{Kc} \tag{4}$$

where: $\theta = P/100$

K = the equilibrium constant of the adsorption process; c = the inhibitor concentration in the solution mass





Data are presented in Table 2. Figure 4 illustrates the results of a Langmuir-type diagram. The standard free energy of adsorption was calculated from the formula:

$$\Delta G_{ads}^{0} = -345.6 \cdot 10^{3} \lg \frac{K_{1}}{K_{2}}$$
(5)

The values of K are relatively high indicating an electrostatic interaction between the double layer and the adsorbed molecules. The equilibrium constants of adsorption imply a more efficient adsorption at the temperature of 25°C than at 30°C. The values of ΔG_{ads}^{0} are

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negative, which shows the adsorption process takes place spontaneously. The activation energy characteristic to the corrosion inhibition was mathematically calculated from Arrhenius-type equation for tow different temperatures.

$$E_{\rm a} = -345.6 \cdot 10^3 \, \lg \frac{k_{\rm g_1}}{k_{\rm g_2}} \tag{6}$$

Table 2. The activation energy, the equilibrium constant and the standard free energy of adsorption for the carbon steel sample in ammoniacal solution 10^{-3} N in presence of NCBSA.

C _{NCSBA} E _a (mol L ⁻¹) (kJ mol ⁻¹)	25°C		30°C		ΔG_{ads}^{0}	
	θ/(1-θ)	K (mol ⁻¹)	θ/(1-θ)	K (mol ⁻¹)	(kJ/mol)	
0	21.5	-		0		and the second secon
10-4	48.6	9.98		7		
2 x 10 ⁻⁴	45.8	13.7	53.6×10^3	9.75	3.7×10^3	-52.81
3 x 10 ⁻⁴	72.5	20.7		12.7		
4 x 10 ⁻⁴	144.8	49		18.6		

The values of the activation energy depend on the nature and concentration of the inhibitor.

CONCLUSIONS

Concurrently with the increase in the current density the anodic potentials of the steel electrodes in ammoniacal solution 10^{-3} N containing NCBSA are shifted towards higher values, while the cathodic potentials are shifted towards lower values. The presence of NCBSA in the corrosion medium increases the anodic and cathodic over-voltage and decreases the corrosion current. These changes increase with the increase in NCBSA concentration.

The decrease in the corrosion current was associated to a significant shift of the corrosion potential towards higher values. This suggests that when the inhibition is of mixed-type it is predominantly anodic.

NCBSA behaves as an inhibitor of generalized corrosion. The efficiency of inhibition increases with the increase in the NCBSA concentration, but decreases with the temperature increase.

Inhibition was associated with the NCBSA adsorption on the steel surface. Due to its great efficiency, it appeared that a complex was formed between NCBSA and different metallic cations in steel composition. These complexes can form passivating layers that are stable at the steel surface, thus decreasing the corrosion rate. The adsorption of these inhibitors on the steel surface fits the conditions of Langmuir-type isotherm of adsorption.

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The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM. http://www.sbjchem.com.

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