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Corrosion inhibition of mild steel in acidic medium using 2-amino thiophenol and 2-cyanomethyl benzothiazole

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Abstract

The corrosion inhibition characteristics of 2-amino thiophenol (ATP) and 2-cyanomethyl benzothiazole (CNMBT) on two types of steel in 1 M HCl medium were investigated at different temperatures (25, 30, 35, 40 and 50 °C). The pitting corrosion behaviour for the same system was studied using a potentiodynamic technique. The pitting corrosion resistance of steel samples increased with increase in concentration of the ATP and CNMBT. Some samples were examined by scanning electron microscopy. The effects of the inhibitors on the general corrosion of the two samples were investigated by using gravimetric and galvanostatic polarization techniques. The inhibition efficiencies increased with increase their concentration but decreased with increase in temperature. Free energies of activation, enthalpies and entropies for the inhibition processes were determined from rate constant data measured and different temperatures at different concentrations of ATP and CNMBT. Results were compared with fits obtained from the application of the Langmuir isotherm. Results were correlated to the chemical structure of the inhibitors. The inhibition efficiency of CNMBT is higher than that of ATP.

1. Introduction

The inhibition efficiency of organic compounds is strongly dependent on the structure and chemical properties of the layer formed on the metal surface under particular experimental conditions. In acidic media, the adsorption process of the nitrogenous compounds is ascribed to the effects of the functional groups connected with aromatic rings. It has been reported that the adsorption of nitrogenous compounds occurs with aromatic rings parallel to the metal surface [1]. It has been observed that the adsorption appears to depend mainly on the electronic structure of the molecule and that the inhibition efficiency increases with increase in the number of aromatic rings [2–4]. Since aggressive acid solutions are widely used for industrial purposes, inhibitors are commonly used to reduce the corrosive attack on metallic materials. Some sulfur and/or nitrogen containing compounds were used previously [5–13] in the inhibition of the corrosion of steel in acidic medium. The available results show that most inhibitors act by adsorption on the metal surface. The strength of adsorption and hence the extent of inhibition is dependent on the nature of the organic compounds and the nature of the metal and the corrosive media. The electrochemical behaviour of the same steel samples (I and II) were studied in alkaline [14] and in neutral media [15]. The present work aims to establish the role of organic compounds such as ATP and CNMBT in the improving the passive films resistance towards general and pitting corrosion of two type of steel (samples I and II) caused by acidic medium (1 M HCl). It is also aimed to predict the thermodynamic feasibility of inhibitor via coverage of the steel surface by adsorbed ATP and CNMBT molecules. Moreover, the study throws more light on the adsorption behaviour of CNMBT and ATP on metal surfaces.

2. Experimental details

Experiments were carried out in 1 M HCl solution in the presence of different concentrations of ATP and CNMBT solutions. The CNMBT and ATP were prepared, purified, and kept as described elsewhere [16]. All solutions were prepared from doubly distilled water and A.R. chemicals. New polished electrodes were used for each run. All solutions were used under purified nitrogen gas. The Delta vanadium steel used in the present work as the working electrode was produced in the electric arc furnace of the Delta Steel Mill Company, Cairo. The composition (wt %) of sample (I) is 0.16%

C, 1.0% Mn, 0.45% S, 0.30% P, 0.20% Si and 0.08% V. The composition of the second sample (II) is 0.24% C, 1.30% Mn, 0.049% S, 0.035% P, 0.53% Si and 0.11% V and the remainder being iron. The ingots were hot rolled (at 1200–1000 °C) and then machined in the form of short rods (hot rolled electrodes), each 27 mm in length and 8 mm in diameter. The working electrode was prepared and treated following the procedure described previously [15]. A Pt sheet was used as the counter electrode. The potential was measured against a Ag/AgCl reference electrode. The influence of inhibitors on the corrosion of steel in 1 M HCl was monitored gravimetrically and electrochemically. Specimens used in gravimetric investigations were in the form of 1 cm rod with a surface area of 0.543 cm^2. The inhibition of corrosion by weight loss method described elsewhere [10]. In addition weight loss measurements were undertaken at different fixed temperatures, 25, 30, 35, 40 and 50 °C in the absence and the presence of different concentration of ATP and CNMBT in the range of 0.001–0.004 M. For the polarization study, a standard corrosion cell with a working steel electrode of cross-section 0.8 cm^2 was used. The galvanostatic and potentiodynamic measurements were run on a potentiostat (AMEL model 2094) which was controlled by a PC. The morphology of steel surface after treatment in solutions was examined by a scanning electron microscope (Jeol JSM T200).

3. Results and discussion

The effect of addition of increasing concentrations of ATP and CNMBT on the potentiodynamic behaviour of steel samples (I and II) electrodes in 1 M HCl at a scan rate 30 mV s^{-1} were studied. Figure 1 shows the potentiodynamic curves in presence of ATP for sample II. Similar curves were obtained using ATP for sample I and CNMBT for steel samples (I and II). Inspection of the curves of Figure 1 and the like indicates that an increase in the concentration of inhibitors decreases the passivation current (i_{pass}). A low passivation current density in the passive region is in agreement with the assumption that the passive film is nonporous. This result indicates that the ATP and CNMBT inhibitor molecules are adsorbed on the steel surface and form a compact passive layer (as protective layer), thus increasing the inhibition efficiency. This indicates an increased resistance to active dissolution, which depends on both the type electrode and the inhibitor. An increase of ATP and CNMBT concentrations in acidic solutions decreases the localized corrosion rate (Figures 2 and 3) and increases the breakdown potential (E_{pit}) towards the positive direction. The concentration of organic compounds required to cause a marked shift in E_{pit} in the positive direction (marked inhibition) increases in the order ATP > CNMBT. The inhibitors effectiveness, described by E_{pit} increases in the order: CNMBT > ATP. The inhibiting quality of different organic compounds may be ascribed by the variation in the adsorbability of these compounds, it can be assumed that the inhibiting effect increases with increasing molecular adsorption on the electrode. It can be seen from Figures 2 and 3 that the inhibition of the pitting corrosion caused by ATP and CNMBT is more effec-

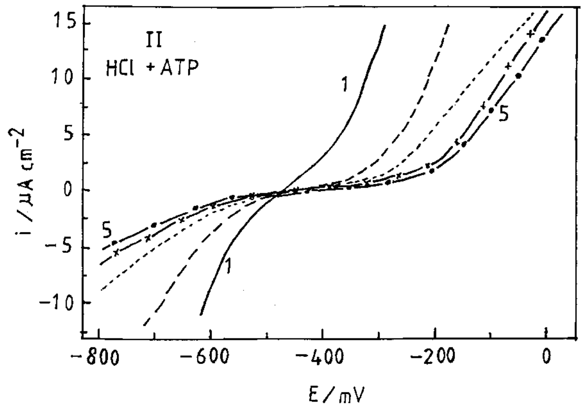

Fig. 1. Anodic potentiodynamic curves for steel anode (sample II) in 1 M HCl at scan rate 30 mV s^{-1} in presence of various concentrations of ATP: (1) 0.0, (2) 0.001, (3) 0.002, (4) 0.003 and (5) 0.004 M.

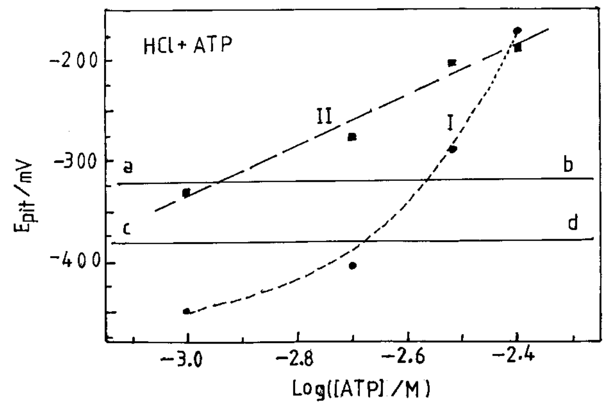

Fig. 2. Pitting potential (E_{pit}) as a function of ATP concentrations for samples I and II. The line a–b denotes the E_{pit} of sample I in 1 M HCl. The line c–d denotes the E_{pit} of sample II in 1 M HCl.

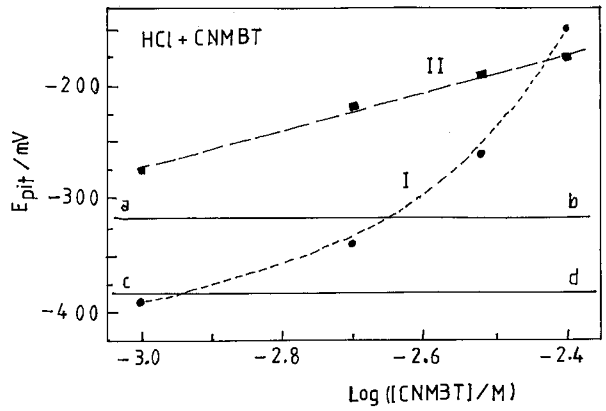

Fig. 3. Pitting potential (E_{pit}) as a function of CNMBT concentrations for samples I and II. The line a–b denotes the E_{pit} of sample I in 1 M HCl. The line c–d denotes the E_{pit} of sample II in 1 M HCl.

tiveness for sample II than for sample I. This may be interpreted by the difference of Mn and V metals content [14]. The interpretation of the effect of steel type and the difference in adsorpability of the two organic compounds will be discussed in details below.

SEM examination of steel surface potentiodynamically polarized from -1.0 to 0.0 V at 30 mV s^{-1} in 1 M HCl in presence of 0.004 M ATP (Figure 4(a)) or 0.004 M CNMBT (Figure 4(b)) solutions was carried out. In the absence of ATP or CNMBT inhibitors, the data showed that the surface was covered with a high density of pits as shown in the previous work [14, 15]. In the presence of ATP or CNMPT inhibitors, the micrographs show no evidence of pitting and formation of thick films on the steel surface. This result is due to the adsorption of inhibitor molecules around the pits in the early stages of formation (initiation and propagation). Also it can be concluded that there is a competitive adsorption between the inhibitor molecules and aggressive anions on the surface of steel.

The loss in the weight of steel samples (I and II) in 1 M HCl in the absence and presence of various concentrations of ATP or CNMBT at different temperature values were determined. The results of weight loss determinations are shown as general corrosion rate (R') (in mg cm^{-2} h^{-1}) in Figure 5, as an example. In all cases, increase in ATP or CNMBT concentrations leads to a decrease in the corrosion rate for both examined samples, indicating that the presence of ATP or CNMBT retards the general corrosion of samples I and II in 1 M HCl. This suggests that the inhibition of the steel corrosion in the presence of ATP or CNMBT occurs by adsorption at sites on the metal surface. On the other hand, an increase in temperature from 25 to 50 °C resulted in an increase in the corrosion rate, probably as a result of desorption of inhibitor molecules from the metal surface.

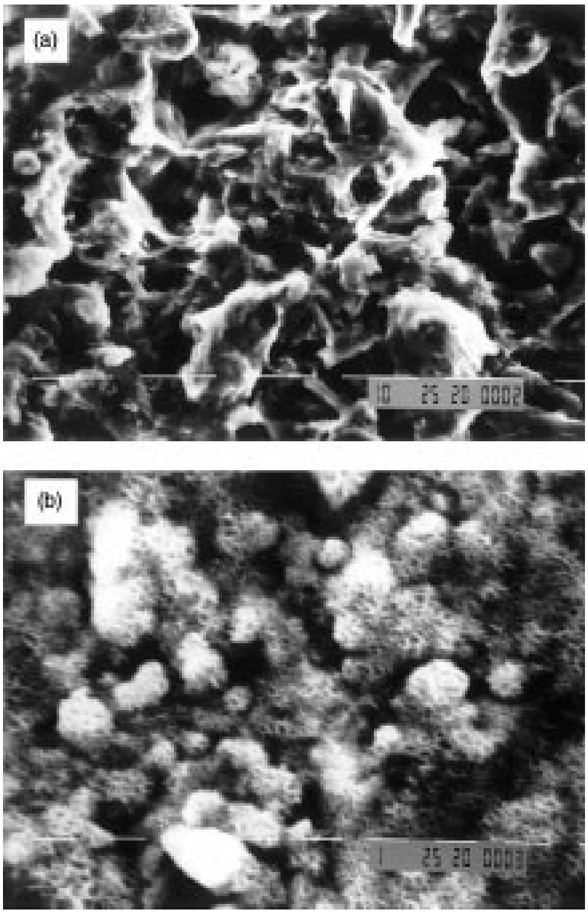

Fig. 4. Scanning electron micrograph of the steel surface after potentiodynamically treated in: (a) 1 M HCl + 0.004 M CNMBT solution X2000 and (b) 1 M HCl + 0.004 M ATP solution X10000.

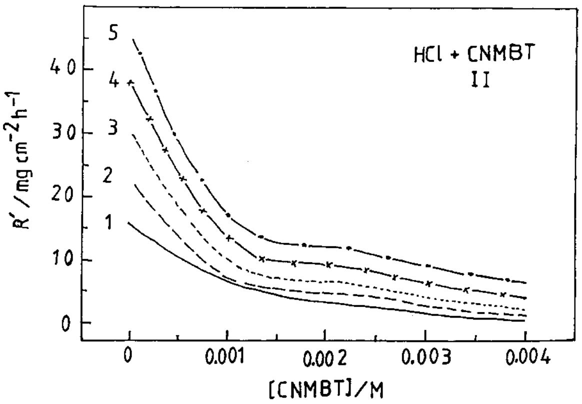

Fig. 5. Variation of corrosion rate with the concentrations of CNMBT for the steel (sample II) in 1 M HCl at different temperatures: (1) 25, (2) 30, (3) 35, (4) 40 and (5) 50 °C.

The percentage inhibition efficiency, (P), of ATP and CNMBT were calculated by applying the following equation [17]:

$$P = \frac{R'_0 - R'}{R'_0} \times 100 \tag{1}$$

where R'_0 and R' are, respectively, the corrosion rates in the absence and presence of a given inhibitor. The inhibition efficiencies calculated from the weight loss data under different experimental conditions are given in (Figure 6, as an example) and Table 1. The inhibition

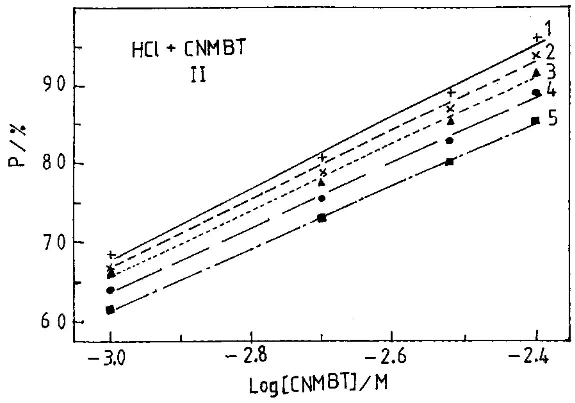

Fig. 6. Variation of percentage protection efficiency (P) with the logarithmic concentration of CNMBT for the steel (sample II) in 1 M HCl at different temperatures: (1) 25, (2) 30, (3) 35, (4) 40 and (5) 50 °C.

Table 1. Protection efficiency of ATP and CNMBT for the steel (samples I and II) in 1 M HCl, at different temperature values and different inhibitor concentrations

Inhibitor		CNMBT				ATP			
Steel type	Protection efficiency, P/%								
	Conc./M	*0.001*	*0.002*	*0.003*	*0.004*	*0.001*	*0.002*	*0.003*	*0.004*
Sample I	25 °C	51.2	69.2	82.4	91.3	45.0	61.2	72.2	82.0
	30 °C	49.5	68.0	80.4	89.6	41.0	57.3	68.4	77.3
	35 °C	47.6	66.2	79.7	88.6	38.0	54.3	65.7	75.6
	40 °C	44.5	64.8	78.0	87.5	32.6	52.1	63.7	72.6
	50 °C	42.3	61.8	75.3	86.1	28.4	49.4	61.5	71.2
Sample II	25 °C	68.4	80.8	89.1	96.3	49.3	65.6	75.1	82.5
	30 °C	67.5	78.9	87.0	93.9	48.6	61.0	69.3	75.9
	35 °C	66.4	77.5	85.2	91.6	48.0	58.6	66.0	71.4
	40 °C	64.0	75.5	82.8	89.0	47.0	56.3	63.2	68.2
	50 °C	61.5	73.0	80.0	85.3	45.8	53.5	72.2	63.7

efficiency depends on the type and concentration of inhibitor, the composition of steel and temperature. It seems that complex formation occurs between the ATP and CNMBT compounds (as ligands) and the different metal cations in the steel. These complexes can form stable passive layer on the steel surface; Thus decreasing the rate of corrosion. From Table 1, in all cases the percentage P in the presence of CNMBT is higher than that in the presence of ATP, due to the higher adsorbability of CNMBT than ATP on the steel surface. The adsorbability difference between CNMBT and ATP can be explained by the higher basicity of the thiazole ring and the lone pair of electron of sulfur in the ring of CNMBT. The inhibition efficiency of both compounds increases with increase in their concentration. The inhibition efficiencies of the inhibitors are higher for sample II than those for sample I specially at low temperatures. This result can be explained by the higher Mn and V content in sample. I than in sample II [14]. On the other hand, the inhibition efficiencies of ATP and CNMBT decrease with temperature.

The activation energy, enthalpy and entropy (E_a, $\Delta H°$ and $\Delta S°$) for the inhibition of steel samples (I and II) in 1 M HCl were calculated from (a) Arrhenius-type equation [18]:

$$\log R' = \frac{-E_a}{2.303R} + A \qquad (2)$$

where R' is the corrosion rate, E_a is the apparent activation energy and A is the pre-exponential factor and (b) from the transition-state equation [18]:

$$R' = \frac{RT}{N_A h}\exp\left(\frac{\Delta S°}{R}\right)\exp\left(\frac{-\Delta H°}{T}\right) \qquad (3)$$

where h is Planck's constant, N_A is Avogadro's number, R is the universal gas constant, $\Delta H°$ is the enthalpy of activation and $\Delta S°$ is the entropy of activation. A plot of $\log R'$ against $1/T$ for sample II gave straight lines, of slope of $E_a/2.3R$, as shown in Figure 7. E_a for the corrosion reaction in the absence and presence of the ATP and CNMBT was calculated (Table 2). The values of E_a depend on the steel composition (samples I and II), the inhibitor type and its concentration. On the other hand, the plots of $\log R'/T$ against $1/T$ (Equation 3) also gave straight lines, as shown in Figure 8. The slopes of these lines equals $-\Delta H°/2.3\ R$ and the intercept is $\log RT/N_A h + (-\Delta S°/2.3\ R)$, from which the values of $\Delta H°$ and $\Delta S°$ were calculated (Table 2). E_a and $\Delta H°$ of the inhibition processes of steel in 1 M HCl in the presence of ATP and CNMBT inhibitors are nearly the same (or slightly higher), than those in free 1 M HCl solution, indicating that no energy barrier is attained [17]. These data reveal that the inhibition of the corrosion reactions is affected without the mechanism changing. The entropy of activation in the presence and absence of the inhibitors is large and negative. This implies that the activation complex in the rate-determining step represents association rather than dissociation, indicating that a decrease in disorder takes place on going from reactants to the activated complex.

For the studied inhibitors, it was found that the experimental data fits a Langmuir type adsorption isotherm, which is given by [19]:

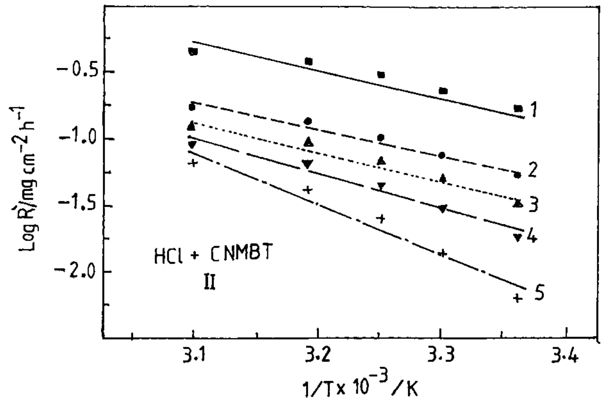

Fig. 7. Arrhenius plot of the corrosion rate for the steel (sample II) in 1 M HCl in presence of different concentrations of CNMBT: (1) 0.00, (2) 0.001, (3) 0.002, (4) 0.003 and (5) 0.004 M.

Table 2. Activation parameters for the dissolution reaction of steel (samples I and II) in the presence of ATP and CNMBT in 1 M HCl

Steel type Inhibitor	Sample I Activation parameters				Sample II		
	Conc./M	E_a/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}	E_a/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
CNMBT	0.000	40.21	37.72	−129.80	31.78	29.10	−161.02
	0.001	31.02	28.34	−165.99	31.12	29.44	−169.44
	0.002	33.89	31.40	−159.29	32.17	29.68	−171.55
	0.003	42.51	40.02	−134.97	41.55	38.87	−144.93
	0.004	68.74	66.25	−104.34	53.80	51.32	−61.25
ATP	0.000	40.21	37.72	−129.80	31.78	29.10	−161.02
	0.001	27.76.2	25.27	−173.84	33.70	31.02	−160.44
	0.002	35.04	32.36	−153.35	37.34	34.66	−150.10
	0.003	45.76	43.27	−121.19	46.14	43.66	−123.48
	0.004	58.59	55.91	−82.89	60.12	59.36	−80.78

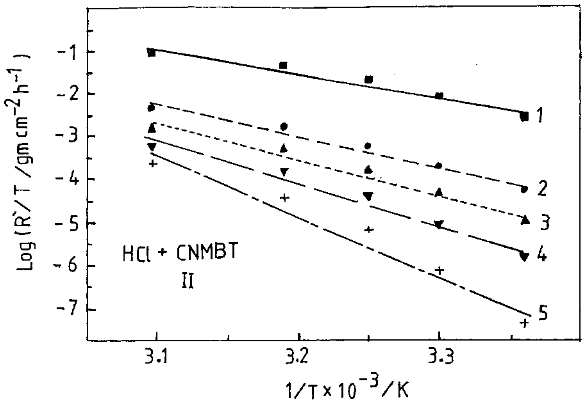

Fig. 8. Transition state plot of the corrosion rate for the steel (sample II) in 1 M HCl in presence of different concentrations of CNMBT: (1) 0.00, (2) 0.001, (3) 0.002, (4) 0.003 and (5) 0.004 M.

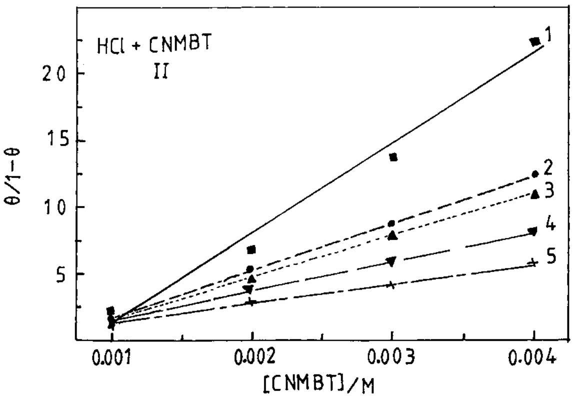

Fig. 9. Curve fitting of the corrosion data for the steel (sample II) in 1 M HCl in presence of different concentrations of CNMBT to the Langmuir isotherm at different temperatures: (1) 25, (2) 30, (3) 35, (4) 40 and (5) 50 °C.

$$\frac{\theta}{1-\theta} = KC \tag{4}$$

where θ is the degree of coverage ($\theta = P/100$), K is the equilibrium constant of the adsorption process and C is the inhibitor concentration in the bulk of solution. The data gave straight lines with slopes of K. Figure 9 (as an example) illustrates the results of a Langmuir plot for corrosion inhibition. The standard free energy of adsorption ($\Delta G^\circ_{\mathrm{ads}}$) can be calculated from the equation [11]:

$$K = \frac{1}{55.5}\exp\left(\frac{\Delta G^\circ_{\mathrm{ads}}}{RT}\right) \tag{5}$$

where 55.5 is the concentration of water in the solution in M. The thermodynamic data: $\Delta H^\circ_{\mathrm{ads}}$, $\Delta S^\circ_{\mathrm{ads}}$ and $\Delta G^\circ_{\mathrm{ads}}$ are obtained from the dependence of the equilibrium constant on temperature by the use of equations [10]:

$$\log K = \frac{-\Delta H^\circ_{\mathrm{ads}}}{2.303\,RT} + \frac{\Delta G^\circ_{\mathrm{ads}}}{2.303\,R} \tag{6}$$

$$\Delta G^\circ_{\mathrm{ads}} = \Delta H^\circ_{\mathrm{ads}} - T\Delta S^\circ_{\mathrm{ads}} \tag{7}$$

Figure 10 shows a plot of log K against $1/T$ which gives straight lines with slopes of ($-\Delta H^\circ_{\mathrm{ads}}/2.303\,R$) and intercepts of ($\Delta G^\circ_{\mathrm{ads}}/2.303\,R$) (Table 3). The $\Delta G^\circ_{\mathrm{ads}}$ values

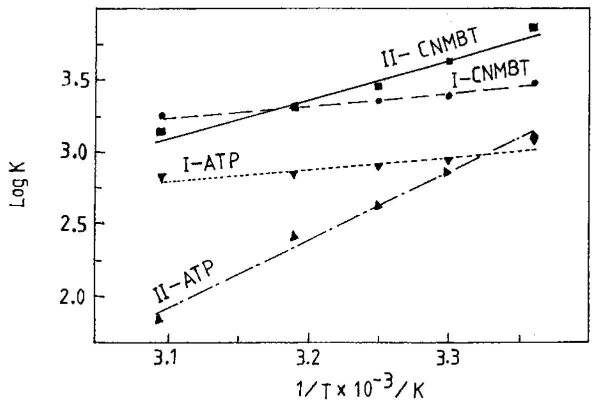

Fig. 10. Plot of log K against $1/T$ for ATP and CNMBT compounds derived from experimental adsorption isotherm for steel (samples I and II).

Table 3. Thermodynamic parameters for the adsorption of ATP and CNMBT in 1 M HCl on steel (samples I and II) surface

Inhibitor Steel type	CNMBT Thermodynamic data			ATP	
	Temp.	10^3 K/mol^{-1}	$10^3 \times (-\Delta G^\circ_{ads})$/kJ mol^{-1}	10^3 K/mol^{-1}	$10^3 \times (-\Delta G^\circ_{ads})$/kJ mol^{-1}
Sample I	25 °C	3.05	29.83	1.22	27.56
	30 °C	2.49	29.82	0.89	27.24
	35 °C	2.27	30.07	0.82	27.46
	40 °C	2.04	30.28	0.71	27.56
	50 °C	1.77	30.87	0.68	28.32
Sample II	25 °C	7.47	32.05	1.24	27.60
	30 °C	4.30	31.19	0.73	26.73
	35 °C	2.89	30.69	0.53	26.32
	40 °C	2.06	30.31	0.42	26.17
	50 °C	1.39	30.22	0.07	22.13

have a negative sign indicating that the adsorption process proceeds spontaneously. The value of ΔG°_{ads} and K are relatively small, indicating electrostatic interaction between the double layer and the adsorbing molecules (physical adsorption). The ΔG°_{ads} values for CNMBT are greater than for ATP in all cases. The equilibrium adsorption constants K follow the same trend in the sense that large values of K imply better more efficient adsorption and hence better inhibition efficiency.

The effect of the inhibitors on the anodic and cathodic galvanostatic polarization of the steel samples (I and II) in 1 M HCl solution at 25 °C was investigated. Figure 11 shows E/i curves and Table 4 collects the electrochemical parameters. The anodic polarization of the steel electrodes in the inhibitor containing 1 M HCl solution 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 overpotential and decreases the corrosion current (i_{corr}). These changes increase with increasing inhibitor concentration. This behaviour supports the inhibition function of these organic compounds. Decrease of the corrosion current (i_{corr}) was associated with an appreciable shift of corrosion potential (E_{corr}) to a less negative value. This suggests that although inhibition is of mixed type, it is predominantly anodic.

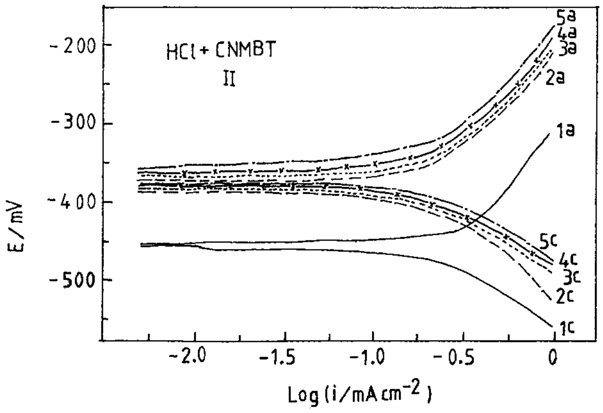

Fig. 11. Polarization curves for the steel (sample II) in 1 M HCl in presence of different concentrations of CNMBT: (1) 0.00, (2) 0.001, (3) 0.002, (4) 0.003 and (5) 0.004 M. Anode and cathode parts denoted by a and c, respectively.

The percentage inhibition efficiency (P) of these inhibitors was also determined from the polarization measurements according to the following equation [20]:

Table 4. Electrochemical parameters for steel samples (I and II) with and without CNMBT and ATP in 1 M HCl and percentage P obtained from weight loss (wt. loss) and galvanostatic polarization (η) measurements at 25 °C

Inhibitor Steel type	Electrochemical parameters		CNMBT				ATP			
	Conc./M	*0.000*	*0.001*	*0.002*	*0.003*	*0.004*	*0.001*	*0.002*	*0.003*	*0.004*
Sample I	E_{corr}/mV	−485	−435	−415	−410	−405	−445	−430	−425	−420
	I_{corr}/mA cm^{-2}	0.26	0.13	0.09	0.05	0.03	0.15	0.11	0.07	0.05
	P% (from wt. loss)	–	51.2	69.2	82.4	91.3	45.0	61.2	72.2	82.0
	P% (from η)	–	50.0	65.4	80.8	88.5	43.2	60.3	71.4	80.5
Sample II	E_{corr}/mV	−455	−385	−375	−365	−360	−420	−405	−400	−390
	I_{corr}/mA cm^{-2}	0.15	0.05	0.03	0.02	0.01	0.08	0.05	0.04	0.03
	P% (from wt. loss)	–	68.4	80.8	89.1	96.3	49.3	65.6	75.1	82.5
	P% (from η)	–	66.7	80.0	86.7	93.3	46.4	63.2	74.5	80.7

$$P = \frac{i'_{\mathrm{corr}} - i_{\mathrm{corr}}}{i'_{\mathrm{corr}}} \times 100 \quad (8)$$

where i'_{corr} and i_{corr} are the uninhibited and inhibited corrosion current density, respectively, obtained by extrapolation of the anodic and cathodic Tafel lines to the corrosion potential. The values of P are included in Table 4. The inhibition efficiency increases with increasing inhibitor concentration. The inhibition efficiency of CNMBT is higher than that obtained when using ATP. Furthermore, the inhibition efficiencies obtained from weight loss measurements are approximately consistent with those calculated from Tafel line extrapolation of.

4. Conclusions

The ATP and CNMBT compounds act as inhibitors for the pitting and general corrosion of two types of steel samples (I and II) in 1 M HCl. The pitting corrosion was investigated potentiodynamically, although the general corrosion was studied by using gravimetric and galvanostatic polarization techniques. The presence of the two organic compounds inhibits the pitting corrosion in 1 M HCl solutions. The two compounds also inhibit the general corrosion. The inhibition efficiency increases with increase in the concentration of these inhibitors but decreases with an increase in temperature. The inhibition efficiency of CNMBT is higher than that of ATP. The inhibition is due to the adsorption of the inhibitor molecules on the steel surface. The adsorption of these inhibitors on the steel surface obeys Langmuirs adsorption isotherm. The inhibitors are found to be predominantly anodic for the two steel samples (I and II) in 1 M HCl.

References

1. G. Schmitt and K. Bedbur, Proc. 9th International Congress on 'Metallic Corrosion', Toronto, Canada, (1984), p. 112.
2. S.L. Granese and B.M. Rosales, Proc. 10th International Congress on 'Metallic Corrosion', Madras, India, (1987), p. 2733.
3. S.L. Granese, *Corrosion* **44** (1988) 332.
4. S.L. Granese, C.O. Degonzalez and B. Rosales, *Quimindustria La Habana, Cuba* **88** (1988) 176.
5. B. Abd-El Nabey, E. Khamis, G. Thompson and J. Dawson, *Surf. Coat. Technol.* **28** (1986) 83.
6. F. Mansfeld, 'Corrosion Mechanism', Marcel Dekker, New York, (1987), p. 285.
7. E. Stupnisek-Lisac, K. Salajster and J. Furac, *Corros. Sci.* **28** (1988) 1189.
8. J.M. Sykes, *Br. Corros. J.* **25** (1990) 175.
9. P. Chatterjee, M.K. Banerjee and K.P. Mukherjee, *Indian J. Technol.* **29** (1991) 191.
10. S. Arab and Abd El-Nabey, *Ind. J. Chem.* **2** (1991) 23.
11. S. Arab and E.A. Noor, *Corrosion* **49**(2) (1993) 122.
12. G. Schmitt, *Br. Corros. J.* **19** (1984) 165.
13. S. Rengamani, S. Muralidharan, M. Anbu Kulandainathan and S.V.K. Iyer, *J. Appl. Electrochem.* **24** (1994) 355.
14. S.A.M. Refaey, *Appl. Surf. Sci.* (1999), submitted.
15. S.A.M. Refaey, S.S. Abe El-Rehim, F. Taha, M.B. Saleh and R.A. Ahmed, *Appl. Surf. Sci.* (1999), submitted.
16. K. Saito, S. Kambe, R. Nakano, A. Sakurai and H. Midorikowa, *Synthesis* **210** (1983).
17. K. Haladky, L. Collow and J. Dawson, *Br. Corros. J.* **15** (1980) 20.
18. I. Putilova, S. Balezin and V. Barannik, 'Metallic Corrosion Inhibitors', Pergamon, Oxford, (1960).
19. Langmuir, *J. Am. Chem. Soc.* **39** (1947) 1848.
20. A.G. Alshkel, M.M. Hefny and A.R. Ismail, *Corr. Prevent. Control* **155** (1987).