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# Contribution to the synergistic effect of triazole derivatives on corrosion inhibition of Cu-30Ni alloy in aerated NaCl 3% in presence of ammonia

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#### ABSTRACT

The electrochemical behavior of Cu-30Ni alloy was investigated in aerated NaCl 3% in presence of ammonia solutions containing 3-amino-1,2,4-triazole (ATA) and 3-4'-bitriazole -1,2,4 (BiTA), separately and mixed. For the ca-thodic processes, the addition of ATA, BiTA and mixture slows down markedly the reduction reaction of dissolved oxygen, and the cathodic processes is controlled merely by the hydrogen evolution. For the anodic processes, the addition of ATA, BiTA and mixture suppressed completely the current peak observed at the active–passive transition revealed in their absence, and the passive current plateau is observed directly from the corrosion potential. Therefore, the addition of ATA, BiTA and mixture reduces both the anodic and the cathodic partial currents of the corrosion process. The inhibiting efficiency of mixture is high, more than 98%, and even enhanced in presence of ammoniac. It was found also that this inhibiting effect increased with the immersion period. © 2014 Trade Science Inc. - INDIA

#### INTRODUCTION

Copper and its alloys are largely used in industrial applications because of their high electrical and thermal conductivities, and also because of their relatively good resistance against the corrosion. In fact, the ionization potential of copper is more anodic than the hydrogen evolution process, and in presence of oxygen and in neutral medium, a stable oxide will cover the surface of these alloys. However, in presence of some pollutants such as chlorine, sulphide or ammoniac in chloride medium, these materials may suffer a severe corrosion.

#### **KEYWORDS**

Electrochemical impedance spectroscopy; Triazole; Polarization curve; Inhibiting efficiency; Cupro-nickel.

Organic inhibitors are largely used, with success, to protect copper and copper alloys from the corrosion. Many papers reported that organic compounds containing nitrogen and their derivatives such as amines<sup>[1-9]</sup>, amino acids<sup>[10,11]</sup>, containing sulphur<sup>[12,13]</sup>, and many others showed inhibition effect for the corrosion of Cu and Cu alloys in different media. Unfortunately, most of these compounds are synthetic chemicals which may be very expensive, toxic and hazardous to living creatures and environment e.g. benzotriazole (BTAH)<sup>[14]</sup> and its derivatives are excellent corrosion inhibitors for Cu and its alloys but these are toxic<sup>[15-17]</sup>.

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Generally, the corrosion effect produced by a mixture of two or more inhibitors rarely corresponds to the sum of individual effects. Instead, we observe a disproportionate increase or a decrease in individual effects. According to Horner and Röttger<sup>[18]</sup>, the inhibitors of cationic and anionic type act on different sites from a metal in a corrosive medium. Consequently, a mixture of these two types of inhibitors should show an additive or a phenomenon of synergy of the individual anticorrosive effects.

Gonzalez and coll.<sup>[19]</sup> showed a significant synergistic effect between the ethylxanthate of potassium and the benzotriazole against corrosion of the copper in 0,1M NaCl in the pH range 7-11. The ethylxanthate of potassium increases the compactness of the passive movie formed in the presence of the benzotriazole. On the other hand, Sockalingum et al.<sup>[20]</sup> have shown that benzotriazole and tolytriazole coadsorbent to the surface of copper when present simultaneously in the same solution. According to these authors, the tolytriazole film is formed preferentially at sites not covered by the film of benzotriazole.

The study of electrochemical behavior of copper in mixtures 3-amino 1, 2, 4-triazole (ATA) with 1-hydroxybenzotriazole (BTAOH), 3-amino 1, 2, 4-triazole (ATA) with Benzotriazole (BTAH) and Benzotriazole (BTAH) with 1-hydroxy-benzotriazole (BTAOH), in a solution of chlorinated borate (0.2 M NaCl) showed that, in the case of (ATA BTAH) and (BTAH, BTAOH), the medium has the same behavior as the only BTAH and BTAOH and ATA improves efficiency BTAH against the anodic dissolution of copper. To the mixture (ATA BTAOH), the measured current densities are low. The shape of the polarizations curves is comparable to that of the ATA to 10 mM. The BTAOH improves the efficiency of ATA<sup>[21]</sup>.

Thus, the presence of two or more inhibitors may lead to the development of a film more protective than that formed in the presence of each compound. It seemed then interesting to study the electrochemical behavior of the mixture (ATA + BiTA) against corrosion of the alloy Cu-30Ni in NaCl 3% in the presence of ammonia will be reported.

#### **EXPERIMENTAL CONDITIONS**

A classic electrochemical cell with three-electrode

configuration was used in this study: a platinum grid as counter electrode, a rotating disk of Cu–30Ni as working electrode, and Ag/AgCl in 3M KCl (SSE) as reference electrode. All potentials in this paper are referred to this electrode.

The working electrode was made of cylinder rod of Cu-30Ni (Good fellow) of 12.5mm in diameter. A cylinder rod of about 1 cm height was fixed to a stainless-steel shaft, and then the lateral part was covered with a cataphoretic epoxyamine base paint (PPG; WT724 + P962). First, the paint was deposited at a constant voltage of 180V during 4 min, and then cured at 180 æ%C for 30 min. After that, the electrode was embedded into an epoxy resin (Buhler; Epoxycure), and worked out to the cylinder shape, the outer diameter of which was 21 mm. Only the cross-section of the alloy rod embedded in the epoxy resin was used to form a rotating disk electrode. The cataphoretic coating allowed avoiding any infiltration of electrolyte between the metal and epoxy resin interface. Just before each experiment, the electrode surface was abraded by emery-paper up to 1000 grade.

The corrosion test solution was prepared with deionized water and reagent grade chemicals: 3 wt %NaCl + 0.05M NH4OH + 0.05M NH4Cl. The pH of this buffer solution was 9.25. ATA (Fluka; Purum) was used as received without any further purification, BiTA was synthesized.

The surface morphology of the electrode was examined with a scanning electronic microscope (SEM; Leica Stereoscan 440), and element analyses were performed with EDAX (Princeton Gamma-Tech).

#### **RESULTS AND DISCUSSION**

# Surface film formed upon Cu–30Ni surface by corrosion

Figure 1a presents the surface morphology after 24 h of immersion in ammoniac containing NaCl 3% solution in absence of ATA (reference solution). It can be seen that the alloy surface is covered by spongy corrosion products. In contrast, in presence of BiTA, ATA and mixture (Figure 1b, c and d), almost no corrosion is revealed, and the grooves due to the initial surface abrasion remain clearly visible after 24 h im-



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mersion. Some precipitates observed are NaCl crystals appeared because of insufficient surface rinsing. The comparison of these figures reveals a marked inhibiting efficiency of inhibitors.

Figure 2a presents the results of EDAX analysis. The copper, nickel, chloride, and oxygen were detected at the electrode surface for the alloy specimen immersed in the reference solution during 24 h, as can be seen in Figure 2b, c and d. If the electrode was dipped in the solution containing 1mM of inhibitors, the peak due to the oxygen decreased dramatically. In contrast, C and N peaks appeared in this solution, which suggest the adsorption of inhibitor on the electrode surface. The formation of a thin inhibitor film is in agreement with the SEM observations.

The corrosion rate will be evaluated quantitatively first by polarization curves then by electrochemical impedance spectra.

#### **Polarization curves**

Cathodic and anodic polarization curves of Cu-30Ni alloy corrosion in 3% NaCl polluted by ammoniac in the absence and presence of the examined inhibitors, were plotted after 30 min of immersion time at free corrosion potential. The effect of the tested inhibitors was studied. Values of associated electrochemical parameters such a corrosion potential ( $E_{corr}$ ), cathodic Tafel slop ( $b_c$ ), corrosion current density ( $I_{corr}$ ) and inhibition efficiencies (E%) for the tested inhibitors at the concentrations 1 mM and 10 mM are given in TABLE 1.

#### Anodic curves

The anodic polarization curves of the action of mixture (ATA + BiTA) are presented in Figure 3 and 4. On the same figures are represented the curves recorded in the presence of ATA and BiTA alone. The addition of mixture to the corrosion test solution decreases the rate of alloy dissolution. The current peak, observed at -200 mV in absence of mixture, disappears by increasing the inhibitor concentration while moving towards more positive potential values.

When the mixture of inhibitors is present in the solution at a concentration of 10 mM, the anodic curve is modified and presents a passive domain, which is clearly observed compared to blank essay. This effect can be explained by the fact that the product tested acts by adsorption on the surface of the material and contributes to an establishment of anodic film formation. This



Figure 1 : SEM picture of Cu-30Ni electrode surface after 24 h immersion in 3% NaCl pH 9.25 (corrosion test solution), (a) Blank, (b) BiTA, (c) ATA, (d) ATA+BiTA.





Figure 2 : EDAX spectra obtained of Cu-30Ni electrode surface after 24 h immersion in 3% NaCl pH 9.25 (corrosion test solution), (a) Blank, (b) BiTA, (c) ATA, (d) ATA+BiTA.

passivity is broken with anodic overtension higher than 100 mV for 1mM of mixture concentration. This effect can be allotted to the destruction or the desorption of film formed by the mixture on the surface of the electrode.

#### **Cathodic curves**

Cathodic curves of Cu-30Ni alloy in aerated 3% NaCl solution polluted by ammonia, without and with the tested inhibitors are shown in Figure 5 and 6. A small current peak, at "0.36 V versus Ag/AgCl, can be noticed when immersed in the reference solution. This peak may correspond to the reduction of corrosion products formed at the open-circuit conditions before potential sweep<sup>[22]</sup>.

In presence of inhibitors, the action of the mixture (ATA, BITA) also results in a decrease of current densities from 1 mM of the mixture, with disappearance of the peak cathodic recorded in the absence of inhibitor. The disappearance of this peak can be explained by the formation of a complex mixed-alloy - (ATA, BITA). We also note the appearance of a wide range of linearity, assigned to the Tafelien field. This shows that there's a change in the kinetics of interfacial processes, more pronounced with the combination of both inhibitors.

At high concentrations (ATA, BITA), the cathode current density is much lower.

The extrapolation of cathodic polarization curve to the open-circuit corrosion potential  $E_{\rm corr}$  allowed evaluating the corrosion current density. The results are summarized in TABLE 1. The inhibiting efficiency E in percent was calculated according to the following expression:

$$E = 100 \times \frac{i_{corr}^{\theta} - i_{corr}}{i_{corr}^{\theta}}$$
(1)

where  $i_{corr}^{\theta}$  and  $i_{corr}$  stand, respectively, to the corrosion current density without and with inhibitor.

These results show that the addition of mixture in the solution is accompanied by a decrease of the current density values in the vicinity of the corrosion po-

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TABLE 1 : Effect of BiTA, ATA and mixture on the electrochemical kinetics of Cu-30Ni in aerated 3% NaCl pH 9.25

Medium	1mM				10 mM			
Wieulum	b <sub>c</sub> (mV/dec)	E <sub>corr</sub> (mV <sub>Ag/AgCl</sub> )	I <sub>corr</sub> (µA cm <sup>-2</sup> )	E (%)	b <sub>c</sub> (mV/dec)	E <sub>corr</sub> (mV <sub>Ag/AgCl</sub> )	I <sub>corr</sub> (µA cm <sup>-2</sup> )	E (%)
Blank	- 267	- 298	91,3	-	-267	-298	91,3	-
BiTA	- 213	- 214	4.5	95	-195	-197	1,96	97,8
ATA	- 198	- 217	1,7	98,1	-219	-215	1,33	98,5
ATA+BiTA	- 220	- 153	1,81	98	-201	-151	1,4	98,4

tential. The inhibition efficiencies reached 98% at 1 mM of mixture.

#### **Electrochemical impedance spectroscopy (EIS)**

We will firstly determine the effect of the inhibitor concentration for a given immersion time, here 0.5 h, and then the influence of immersion period will be estimated.

#### Influence of concentration

The impedance diagrams in Nyquist plot for different inhibitor concentrations are presented in Figure 5 and 6. The high frequency part of impedance is displayed with an enlarged scale in the insert. It can be noticed that the impedance modulus increased dramatically in presence of inhibitor.

Though not clearly separated, these diagrams may be split into two capacitance loops. However, in contrast to the case of copper electrode<sup>[23]</sup>, with the alloy

 TABLE 2 : The results of non-linear regression for the impedance spectra presented in Figure 7 and 8

Medium	$\frac{R_e}{(\Omega cm^2)}$	$\frac{R_f}{(k\Omega cm^2)}$	$C_f$ ) ( $\mu F.cm^{-2}$	$\frac{R_t}{(k\Omega cm^2)}$	C <sub>dl</sub> (µF.cm <sup>-2</sup>	E ) (%)
Blank	9.31	-	-	0.450	145	-
			1mM			
BiTA	15.62	2.054	58	4.591	138	90.20
ATA	32,88	0.169	17.3	11.164	17	95.96
ATA+BiTA	27.7	0.150	29.9	17.427	22.8	97.42
		1	10 Mm			
BiTA	10.118	2.299	26.4	7.058	29.09	93.62
ATA	9.43	170	11.71	20.695	1.6	97.82
ATA+BiTA	28	72.7	11.4	17.924	12.1	97.50

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Electrochemistry An Indian Journal electrode, the addition of inhibitor does not induce a new time constant, they remained always two. The impedance spectra are then analyzed with a non-linear regression calculation with a Simplex algorithm with two R-C ladder circuits. The calculation results are presented in TABLE 2. The equivalent circuit and the  $\chi^2$ function used are given elsewhere<sup>[24,25]</sup>. Whereas the low frequency elements are related to the oxidation– reduction contribution of the corrosion products ( $R_{\rm F}$ –  $C_{\rm F}$ ). There is no contribution of the latter couple in the absence of inhibitor. Moreover, the values determined for this couple from the numerical simulations of the diagrams are not discussed in the text since it appears that they are scattered probably due to the fact that they are likely ascribed to corrosion products.

In the context of a detailed study published elsewhere<sup>[22,26]</sup>, the spectra obtained in the presence of the mixture present also three capacities loops. Even if we do not distinguish clearly three loops, the adjustment of



Figure 3 : Anodic polarization curves of Cu-30Ni in 3% NaCl in presence of ammonia (pH 9.25) without and with the tested inhibitors at the concentration 1 mM,  $\Omega = 1000$  rpm; |dE/dt| = 30 m/Vs.

parameters can be made correctly only with three constants of time.

In this table,  $R_{\rm e}$  indicates the electrolyte resistance. At high frequencies, the first loop characterized by  $R_{\rm f}$  and  $C_{\rm f}$  is associated with the dielectric film surface; the second loop is attributed to the charge transfer resistance  $R_{\rm t}$  and the double layer capacitance  $C_{\rm dl}$ . In presence of inhibitor,  $C_{\rm dl}$  decreases, corresponding to the surface coverage by inhibitor observed by EDAX analysis.



Figure 4 : Anodic polarization curves of Cu-30Ni in 3% NaCl in presence of ammonia (pH 9.25) without and with the tested inhibitors at the concentration 10 mM,  $\Omega = 1000$  rpm; |dE/dt| = 30 m/Vs.



Figure 5 : Cathodic polarization curves of Cu-30Ni in 3% NaCl in presence of ammonia (pH 9.25) without and with the tested inhibitors at the concentration 1 mM,  $\Omega = 1000$  rpm; |dE/dt| = 30 m/Vs

If we interpret the action of the mixture by the variation of  $R_t$ , the examination of the diagrams can be noted that the  $R_t$  increased from 0.450 k $\Omega$ cm<sup>2</sup> to 17.427 and



Figure 6 : Cathodic polarization curves of Cu-30Ni in 3% NaCl in presence of ammonia (pH 9.25) without and with the tested inhibitors at the concentration 10 mM,  $\Omega = 1000$  rpm; |dE/dt| = 30 m/Vs.



Figure 7 : Impedance diagrams of Cu–30Ni in the corrosion test solution in absence or in presence of 1 mM of ATA, BiTA and mixture after 30 min of stabilization period.  $\Omega = 1000$  rpm

17.924 k $\Omega$ cm<sup>2</sup> in presence of 1 mM and 10 mM of mixture respectively. This significant increase can be interpreted by effective protection of the alloy by the mixture.

#### Influence of the immersion time

Figure 9 and 10 presents the evolution of impedance spectra with respect to the immersion period.

As can be seen in this figure, the impedance diagram in the Nyquist plot becomes larger with time. The increase of the polarization resistance with the immersion period is often reported for the inhibiting action of heterocyclic on copper corrosion<sup>[27–31]</sup>.





Figure 8 : Impedance diagrams of Cu–30Ni in the corrosion test solution in absence or in presence of 10 mM of ATA, BiTA and mixture after 30 min of stabilization period.  $\Omega = 1000$  rpm



Figure 9 : Evolution of impedance spectra with immersion period. Cu–30Ni in the corrosion test solution in presence of 1 mM of mixture.  $\Omega = 1000$  rpm

These diagrams show a capacitive behavior of the interface in the frequency range examined. The module of the impedance at a given frequency increases with time and with the concentration of the mixture.

The spectra obtained in the presence of the mixture also present three capacitive loops. Even if you do not clearly distinguish between the three loops, the adjustment of parameters can not be done properly with three time constants. Figures 9 and 10 shows, for different immersion times and for both concentrations studied, the fitted curves are superimposed to the experimental curves well. The evolution of the characteristic parameters associated with the capacitive loop with time is summarized in TABLE 3. This table also presents the

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**Electrochemistry** An Indian Journal values of characteristic parameters obtained of measured impedances, by operating in simplex.

The first loop at high frequencies, characterized by  $R_f$  and  $C_f$  is associated with the dielectric film surface. TABLE 3 shows that the evolution of the parameters is similar for both concentrations in combination with different values. For a concentration of 1 mM in a mixture, there is an increase in resistance of the film changes from 150.86  $\Omega$ cm<sup>2</sup> for 30 minutes immersion 452.1



Figure 10 : Evolution of impedance spectra with immersion period. Cu–30Ni in the corrosion test solution in presence of 10 mM of mixture.  $\Omega = 1000$  rpm

TABLE 3 : Variables representing experimental EIS data in presence of mixture for  $\Omega = 1000$  rpm

Medium	Time (h)	$R_{\rm f}$ ( $\Omega.cm^2$ )	$C_{f}$ ( $\mu$ F.cm <sup>-2</sup> )	$\begin{array}{c} R_t \\ (k\Omega.cm^2) \end{array}$	$C_{dl}$ ( $\mu$ F.cm <sup>-2</sup> )	E' (%)
	0,5	-	-	0.450	145	-
Blank	2	-	-	0.372	171	-
Diank	4	-	-	0.196	123	-
	24	-	-	0.177	90.1	-
	0,5	150,8	29.9	17.427	2,28	97.42
Mixture	2	174,5	20	17.872	10.7	97.92
1mM	4	165	11.7	28.792	10.6	99.32
	24	452	6	22.511	14.1	99.21
	0,5	72,7	11.4	17.904	12.1	97.49
Mixture	2	108,5	9.3	21.745	6.9	98.29
10mM	4	114	7.9	31.589	6.01	99.38
	24	201.9	7.6	252 640	1.37	99.93

 $\Omega$ cm<sup>2</sup> after a day of immersion. In the presence of 10 mM, this resistance is 72.665  $\Omega$ cm<sup>2</sup> après 30 minutes of immersion. For an immersion time of 24 hours it was 201.9  $\Omega$ cm<sup>2</sup>. In parallel, the ability of the film C<sub>f</sub> decreases with time, indicating a thickening of the film formed with the immersion time. These values are smaller for a concentration of 10 mM. This indicates that the film formed with 10 mM inhibitor in the mixture is thicker than the other concentration.

The second loop obtained in medium frequencies, indicates the presence of the protective film on the surface of the alloy. This loop is characterized by  $(R_t, C_d)$  for the double layer capacity  $(C_d)$  in parallel with the charge transfer resistance  $(R_t)$ . The evolution of these two parameters is shown in the TABLE 3.

As can be seen in this figure, the impedance diagram in the Nyquist plot becomes larger with time

For both concentrations tested, there was a significant increase of the charge transfer resistance from the immersion of the electrode. It goes from  $0.450 \text{ k}\Omega.\text{cm}^2$ without mixture to  $17.427 \text{ k}\Omega.\text{cm}^2$  and  $17.904 \text{ k}\Omega.\text{cm}^2$ in the presence of 1 mM and 10 mM of mixture respectively. As can be seen in this table, this resistance becomes larger with time, indicating an empowerment of mixture the inhibitors (ATA + BITA). Any time the values of R<sub>t</sub> recorded in the presence of 10 mM are more important. This value reaches a maximum 252.640 k $\Omega.\text{cm}^2$  after 24 hours of immersion time.

The values of the double layer capacity  $(C_{dl})$  decrease with the concentration and with the time. These values correspond to the capacity of double layer in the presence of the mixture film.

The values of inhibition efficiency (E') for different immersion time in the presence of 1 mM and 10 mM of mixture (ATA+BITA) are grouped in TABLE 3 is calculated by:

$$E = 100 \times \frac{R_t^i - R_t^0}{R_t^0} \tag{2}$$

where  $\mathbf{R}_{t}^{i}$  and  $\mathbf{R}_{t}^{o}$  are respectively charge transfer resistance with and without inhibitor, corroborate those obtained with the stationary curves of polarization.

In the whole cases, the protective effectiveness is higher than 99%. Furthermore, the inhibiting efficiency tends to increase with immersion period.

#### Synergism consideration

Synergistic inhibition effect of inhibitors takes place when the total action of compounds is higher than the sum of each one individually.

The synergism parameter (*S*) was calculated using the following equation:

$$S = \frac{1 - (\eta_1 + \eta_2)}{1 - \eta'_{1+2}}$$
(3)

where  $\eta_1$  is inhibition efficiency of BiTA,  $\eta_2$  is the inhibition efficiency of ATA and  $\eta'_{1+2}$  is inhibition efficiency of BiTA+ ATA. The value of *S* is calculated as 1.98 which is greater than unity indicates that the enhanced inhibition efficiency is due to synergistic effect of BiTA and ATA<sup>[33,34]</sup>.

The values of faradic capacity (TABLE 4) recorded at different immersion times are lower than those calculated in the absence of the inhibitor. These values are lower in the presence of 10mM. This shows that the complex formed with the mixture is more protective and adhering to this concentration ( $R_{t}$  large).

#### DISCUSSIONS

Electrochemical study showed that the mixture (ATA+BiTA) product tested is a good corrosion inhibitors, against Cu-30Ni corrosion in 3% NaCl polluted by ammonia at pH 9.25. The mixture acts at the same time on the anodic and cathodic electrochemical processes. Polarization curves showed that the inhibiting effect of this compound results in a clear reduction of the cathodic and anodic current density values especially in the vicinity of corrosion potential. At 10 mM, the alloy presents a domain of passivity wider than that obtained in the presence of 1 mM. This shows that the complex formed in this concentration is more protective. On the cathodic branches and for both studied concentrations, the action of the mixture (ATA, BiTA) also results a decrease of the current densities values in the vicinity of the corrosion potential from 1mM. This decrease is accompanied by the disappearance of the peak raised in the absence of mixture and which is due to the reduction of CuCl, on other hand can be explained by the formation of a complex alloy - (ATA, BiTA)<sup>[21,32]</sup>. These results were confirmed by imped-

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ance tests where it was observed that the effect of inhibitor addition is distinguished by an increase of the resistance and a strong reduction of the electrochemical interface capacity value. The specters of impedances were also adjusted by a circuit 3R-C. For both concentrations tested, there was a significant increase of the charge transfer resistance from the immersion of the electrode. It goes from  $0.450 \text{ k}\Omega.\text{cm}^2$  without mixture to 17.427 k $\Omega$ .cm<sup>2</sup> and 17.904 k $\Omega$ .cm<sup>2</sup> in the presence of 1 mM and 10 mM of mixture respectively. As can be seen in this table, this resistance becomes larger with time, indicating an empowerment of mixture the inhibitors (ATA+BITA). These observations prove that (ATA, BiTA) acts by formation of a protective complex film on the surface of the alloy that improves with time. The analysis of elements by EDAX confirms the presence of this complex on the surface of the alloy.

#### CONCLUSION

The comparative analysis of the results obtained in this work with the examined inhibitors, namely ATA, BiTA and their mixture shows that:

The ATA, BiTA and mixture act at the same time on the reactions anodic and cathodic of the process of corrosion. Indeed the cathodic domain is characterized for the examined inhibitors, by decrease of the current density values in the vicinity of the corrosion potential and disappearance of the cathodic peak, recorded in the absence of inhibitors. The anodic polarization curves show a decrease of the current density values with disappearance the current peak recorded in the absence of the examined inhibitors. For both concentrations, the action of ATA is limited to low anodic overvoltage. While the BiTA and the mixture show a good protection, even in the strongest anodic overvoltage. The shape of the curve recorded in the presence of the mixture is comparable to that in the presence of BITA alone. This suggests an improvement the efficiency of BITA by the ATA, in other words there is preferential adsorption of the BiTA on the surface of the alloy and the ATA improves the resistance of the film formed.

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