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Pitting corrosion of copper in sulphate solutions: inhibitive effect of different triazole derivative inhibitors

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Abstract

The inhibitive effect of 3-amino 1,2,4-triazole (ATA) on the pitting corrosion of copper induced by sulphate ions was compared to that obtained with benzotriazole (BTAH) and 1-hydroxybenzotriazole (BTAOH) and to previous results obtained in chloride media. It was concluded that the inhibitive action of these compounds towards pitting corrosion was dependent on the aggressive species. For BTAH and BTAOH, the inhibitive efficiency was greater towards pitting induced by sulphate than towards pitting induced by chloride which was explained by referring to the surface area covered by the organic molecules and to the size of the aggressive species. For ATA, an opposite behaviour was observed and was explained by quantum chemical calculations. First, the binding energy between clusters of Cu^+ ions and Cl^- was much weaker than that between clusters of Cu^+ ions and SO_4^{2-}. Secondly, the adsorption of Cl^- on ATA linked to copper ions was more favourable than its adsorption on copper oxide. Moreover, the sulphate ion had a larger adsorption energy on copper ions than on ATA linked to copper ions.

1. Introduction

By virtue of its valuable physical and mechanical properties, long life and good resistance to corrosion in neutral water, copper is one of the most important nonferrous metals used in industry. However, it reacts easily in oxygen containing environments [1] leading to the formation of an oxide layer. This layer presents a duplex structure made up of an inner cuprous oxide layer and an outer cupric oxide layer, depending on the electrode potential [2, 3]. On account of the limited protection offered by the copper oxides, the metal is susceptible to pitting corrosion induced by different corrosive species such as chloride, sulphate and nitrate ions [4, 5]. Oxide film breakdown occurs after the pit nucleation time at localised sites when the potential is higher than a critical value. Often, nucleation times measured in the same experimental conditions are widely scattered and must be statistically analysed [6]. The pitting susceptibility is quantified by the pit nucleation rate (λ_0) deduced from the pit nucleation time distribution.

Since copper is not stable in oxygen-containing electrolytes, substantial improvement in its passivity could be achieved by using inhibitive species. The inhibition of localized corrosion processes is a very important field of research, not completely investigated until now. Concerning the inhibition of pitting corrosion, several studies on the action of inorganic substances have been carried out [7–10]. However, there are only a few papers dealing with inhibition of pitting corrosion using organic species [11, 12]. In contrast, the inhibition of generalized corrosion of copper in different media by organic inhibitors has been widely investigated [13–18]. The action of benzotriazole (BTAH) as a corrosion inhibitor of copper and its alloys in aqueous chloride media has long been of great interest to corrosion scientists and numerous studies [19–31] have been performed. The effectiveness of BTAH has been related to the formation of a $[Cu^+–BTA^-]_n$ film at low pH and positive electrode potential. This film is considered as being insoluble and polymeric [24–26]. Other triazole derivatives such as bitriazole and aminotriazole have been studied as cupronickel alloy corrosion inhibitors [32]. It was shown that aminotriazole (ATA) is the most efficient inhibitor. In the case of pure copper [33], it has been shown that the efficiency of ATA is related to the formation of a protective layer resulting from a link between Cu^+ ions and ATA molecules. The mechanisms of copper corrosion inhibition by benzotriazole and its derivatives were also studied in aqueous solutions containing sulphate ions [14, 34]. The authors showed that 4-hydroxybenzotriazole (4-OH–BTAH) is a more effective inhibitor than BTAH in neutral solutions, because of the formation of a

3D protective film due to hydrogen bonds involving hydroxyl groups or water molecules, whereas BTAH only led to a linear complex polymer. They also showed that 1-hydroxybenzotriazole (1-OH–BTA called BTAOH in our work) leads to the formation of a complex which is less protective than those involving BTAH and 4-OH–BTAH. The authors concluded that the triazole ring without substituent groups may be important in the inhibition of copper corrosion.

In previous work [35], we studied the possibility of inhibiting pitting corrosion of pure copper in borate-buffered solutions containing 0.2 M NaCl using ATA. Before adding chloride ions, the passive film was formed in the presence of ATA. The influence of BTAH and BTAOH on the pit nucleation susceptibility of pure copper in chloride-containing borate-buffered solutions was also investigated for comparison. It was shown that ATA was the most efficient inhibitor of pit nucleation. Electrochemical impedance and X-ray photoelectron spectroscopy (XPS) measurements showed, however, that the film formed before the addition of chloride ions was not very protective. Moreover, the resistance of the film decreased when the ATA concentration increased. BTAH and BTAOH showed impedance diagrams independent of the concentration but acted as inhibitors towards pitting corrosion only at high concentrations. However, BTAH presented a very protective film even at low concentration. Thus, when inhibitive species are present in solution, the properties of the passive film are not sufficient to explain the mechanism of inhibition. Interactions between aggressive ions and inhibitor molecules have to be considered. In order to check this assumption, we performed a similar study by using another aggressive species (i.e., sulphate ions) and compared the effectiveness of the inhibitors towards pitting corrosion in these two different aggressive media.

2. Experimental methods

2.1. *Materials*

The material used was pure copper (99.99%) in the form of a drawn copper rod. Ten specimens of the material were machined into 8 mm diameter and 10 mm length cylinders and embedded in epoxy resin on the same holder. They were tested simultaneously using a data acquisition system which allowed the current versus time to be recorded for each specimen. BTAH ($C_6H_5N_3$) was supplied by Prolabo and BTAOH ($C_6H_5N_3O$) and ATA ($C_2H_4N_4$) by Sigma. The purity of these compounds was 98%, 88% and 95%, respectively. Figure 1 shows the molecular structure of these organic compounds.

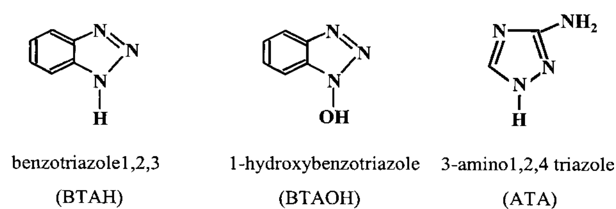

Fig. 1. Molecular structure of the inhibitors.

2.2. *Statistical analysis of pitting*

Before testing, the specimens were mechanically polished with 1000 grit SiC paper and rinsed with distilled water. Then, they were potentiostatically polarized for a time t_p in a borate-buffered solution (0.01 M H_3BO_3 + 0.01 M $Na_2B_4O_7$) (pH 9) with or without BTAH, BTAOH or ATA. This time (t_p) of prepolarization allowed an oxide film to grow on the specimen surface. Then, a sulphate-containing buffered solution was injected into the medium. All the experiments were performed at room temperature (22 °C). The first pit appeared on each specimen after randomly dispersed nucleation times which corresponded to the sudden increase of the anodic current. The distributions of nucleation times were determined from 100 measurements. The distribution curve was obtained by plotting $-\ln[1 - P(t)]$ against t, where $P(t)$ is the pitting probability calculated from experimental value of $n(t)/N$ ($n(t)$ being the number of specimens in which pitting occurred at time t and N the total number of specimens). The slope λ_0 of the distribution curve at its origin gives the pit nucleation rate and is representative of the resistance of the film developed at the end of the prepolarization period. So, the value of λ_0 was used to assess and compare the susceptibility to pit nucleation of copper in different experimental conditions [36].

The pit propagation rate was evaluated in the first stages of pit growth. The study of pit propagation also requires a statistical approach [37]. For a given sample, the current rises at time t_1 when a stable pit forms after the nucleation time (the time at which sulphates are added is taken as time zero). A data acquisition system allowed the current to be recorded during the whole experiment and until it reached a threshold value at time t_d. The threshold value was chosen as 20 μA because unstable pits usually become repassivated before reaching this current and are not considered. The rate of current variation with time, for a sample on which one pit formed, was considered as a significant measurement of the pit propagation rate. For different pits, the range $(t_1 - t_d)$ varied since their propagation rates were different. So, if N was equal to the total number of samples tested, that is, to the total number of pits studied, at time t there were only $n'(t)$ pits still active where $n'(t) < N$. The currents corresponding to the $n'(t)$ pits were totalled and a mean pit current $i_m(t)$ was calculated as being equal to the sum divided by $n'(t)$. When i_m was plotted versus time, the first stages of propagation were represented by a straight line. Its slope was equal to the mean pit propagation rate.

2.3. *Potentiokinetic curves*

The experiments were completed by plotting potentiokinetic curves in borate-buffered solutions containing

0.01 M sulphates and 10^{-4} or 10^{-2} M of BTAH, BTAOH or ATA. The scanning potential rate was 1200 mV h^{-1}. Before testing, the samples were immersed for 90 min in the solution at open circuit potential.

2.4. *Theoretical method*

The stationary Schrödinger equation of modelled systems was resolved by the well known Hartree–Fock approach. This consists in treating the electrons as moving independently at an effective potential representing all the other electrons and interacting with all the nucleons supposed fixed (Born–Oppenheimer approximation). The method was applied in the linear combination of atomic Orbitals (LCAO) method (*ab initio* calculation).

3. Experimental results

3.1. *Pitting corrosion of copper in sulphate containing borate-buffered solutions*

Experiments were first performed to evaluate the pitting corrosion resistance of the copper samples in borate-buffered solutions containing different concentrations of sulphate ions. Figure 2 shows that the logarithm of the pit nucleation rate λ_0 varies linearly with the logarithm of sulphate concentration, as follows:

$$\lambda_0 = k[SO_4^{2-}]^n \quad (1)$$

Other authors have also observed this type of law with other materials [38, 39]. For Foley [40], a complex forms between aluminium and the aggressive ions; the value of the constant n is related to the stoichiometry of the complex. In our work, n was found to be close to 2. Mankowski et al. [41] have studied the pit morphology on copper in sulphate-containing solutions. They showed that the passive film was initially composed of an outer layer of CuO and an under layer of Cu_2O. Sulphate ions were adsorbed on the cupric oxide and the outer layer was rapidly destroyed by the formation of soluble cupric sulphate. Corrosion products were identified, brochantite $CuSO_4 \cdot 3\,Cu(OH)_2$ which showed a Cu/SO_4 ratio of 4, but the intermediate complex was not. The same authors [42] also showed that the pit nucleation rate varied linearly with sulphate concentration, which was quite different from our results, since this gave a value of n equal to 1 for an applied potential of 300 mV vs SCE. This difference might be explained by the origin of the copper samples which could lead to differences of composition or grain size. However, it is worth noting that their study was performed for sulphate concentrations in the range 5×10^{-3} to 10^{-1} M. In the same way, Qafsaoui [43] showed that the logarithm of the pit nucleation rate for low alloyed copper samples varied linearly with the logarithm of the sulphate concentration with a value of n close to 4 in the 4×10^{-2} to 10^{-1} M concentration range and for an applied potential of 150 mV vs SCE. In the present work, the sulphate concentration range was 2×10^{-3} to 2×10^{-2} M. Szklarska–Smialowska reported that, for aluminium alloys, the n value varied from 0.1 to 11 depending on the chloride concentration range [44]. From these observations, it can be assumed that the law governing the pit nucleation rate versus sulphate concentration is complex and can be approximated to simpler laws depending on the concentration range of the aggressive species but also on the applied potential, on the passive film thickness and on the copper purity.

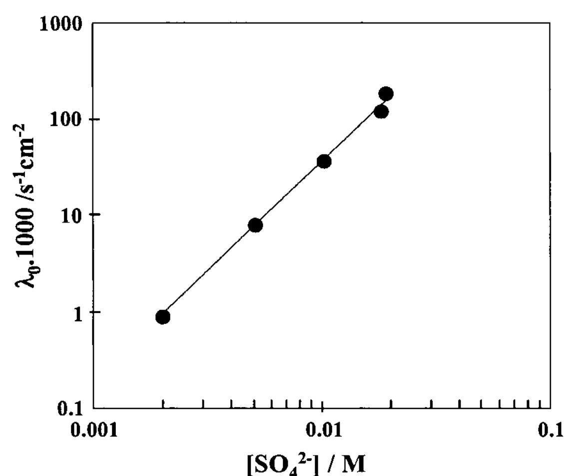

Fig. 2. Pit nucleation rate against sulphate concentration. Copper polarized for 1 h in a borate-buffered solution. After 1 h, sulphates are added.

Comparison of these results with those obtained in chloride-containing media [35] showed that sulphate ions are more aggressive than chloride ions. For copper samples polarized in borate-buffered solutions, the pit nucleation rate was 45 s^{-1} cm^{-2} when 0.2 M chloride was added. From Figure 2, the same value of λ_0 was obtained with a lower sulphate concentration of about 10^{-2} M. These results agree with those of Francis et al. [5] who estimated that sulphate ions were an order of magnitude more aggressive towards copper than chloride ions. In order to prove this conclusion, we performed some quantum chemical calculations. They were performed with *ab initio* methods in the Hartree–Fock approximation [45, 46]. Since the copper surface is covered with a Cu_2O layer, we modelled this surface by small Cu^+ clusters. Equilibrium geometry between the Cu^+ cluster and the chloride or sulphate ions was optimized by using a conjugate gradient method of minimization. The binding energy between Cl^- and clusters of Cu^+ was found to be about 85 kJ mol^{-1}, whereas the interaction of SO_4^{2-} with clusters of Cu^+ is about 240 kJ mol^{-1}. In both cases, the bound is strongly ionic. Thus, theoretical calculations agree very well with our experimental results and those of Francis et al. More details of these theoretical calculations will be given elsewhere.

A statistical analysis was also performed to evaluate the pit propagation rate. Figure 3 shows that the pit propagation rate increases as the sulphate concentration increases. The pit propagation rate values were measured with a significant imprecision and it was difficult to establish an accurate law to describe the variation of the pit propagation rate with sulphate concentration. A linear variation might be assumed but the actual position of the straight line could not be determined accurately. Physically, a critical concentration higher than zero might be determined corresponding to the sulphate concentration for which pits can nucleate but repassivate and thus not propagate. In the present work, it was difficult to determine this critical concentration because of the imprecision in the measurements. However, the results showed that sulphate ions were aggressive pitting species on copper and also influenced pit propagation.

3.2. *Evaluation of inhibitor efficiency on the pit nucleation rate and on the pit propagation rate*

Experiments were performed to compare the efficiency of ATA on copper pitting protection with those of BTAH and BTAOH. The inhibitive effect of these organic compounds on the pit nucleation and propagation rates was measured in the presence of each inhibitor and compared with the results obtained in the absence of these products. The influence of inhibitor concentration was studied over the range 10^{-6} to 10^{-2} M. Sulphate ions were added to a final concentration of 10^{-2} M. The sulphate concentration was chosen, by considering the pit nucleation rates obtained without inhibitor, so that the pit nucleation times were sufficiently long to allow the pit nucleation rate to be the more accurately evaluated. In addition, the concentration had to be kept sufficiently high because it was assumed that, in the presence of inhibitors, the pit nucleation times would be longer and the length of time necessary for the experiments was an important parameter. Figure 4(a) shows the pit nucleation rate λ_0 against inhibitor concentration for the three inhibitors. The dotted line represents the pit nucleation rate measured in inhibitor-free solution.

BTAH and BTAOH showed similar behaviour since a significant inhibitory effect was observed for both compounds as soon as they were present in solution with a concentration of 10^{-6} M. Over the whole concentration range, the pit nucleation rate decreased as the inhibitor concentration increased. Figure 4(b) shows the variation of the efficiency for the three inhibitors at different concentrations. The percentage efficiency, E, of an inhibitor was defined as the difference between the values of pit nucleation rate measured with (λ_0') and without (λ_0) the inhibitor divided by the value measured without inhibitor:

$$E = \left(\frac{\lambda_0 - \lambda_0'}{\lambda_0}\right) \times 100 \qquad (2)$$

When BTAH and BTAOH were present in solution at a concentration of 10^{-2} M, their efficiency was close to 100%. At this concentration pits may occur, but rarely

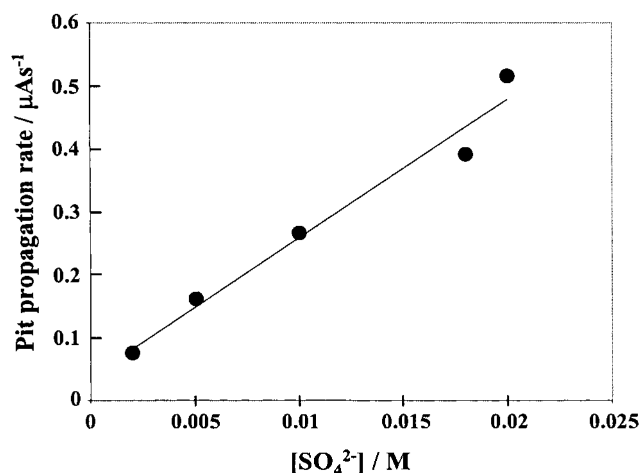

Fig. 3. Pit propagation rate against sulphate concentration. Copper polarized for 1 h in a borate-buffered solution. After 1 h, sulphates are added.

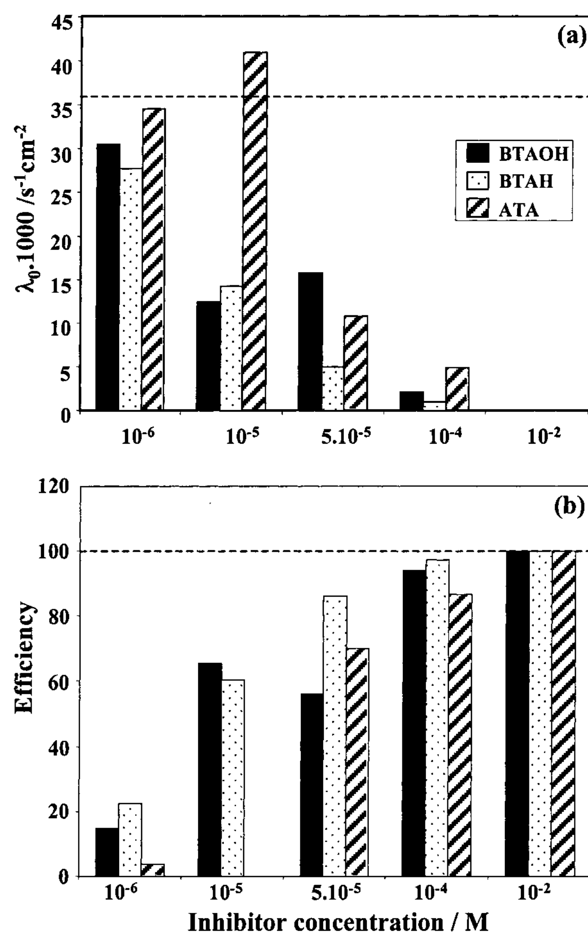

Fig. 4. Pit nucleation rate (a) and inhibitive efficiency (b) against BTAH, BTAOH and ATA concentrations. Copper polarized for one hour at +400 mV vs SCE in a borate-buffered solution containing one inhibitor. After 1 h, 0.01 M sulphates are added. Dotted line indicates pit nucleation rate measured without inhibitor.

do. When no pit appeared up to 24 h of experiment, samples were considered as nonpitted. BTAH and BTAOH showed similar efficiencies towards pit nucleation on copper over the whole concentration range with a critical efficiency of about 10^{-6} M. However, it can be concluded from the experimental results that BTAH was slightly more efficient. This was in agreement with the results obtained by Youda et al. [14] who showed that the inhibition of copper corrosion in aqueous solutions containing sulphate ions became stronger in the order BTAOH < BTAH in neutral solutions.

The behaviour of ATA was quite different since the critical concentration was higher (between 10^{-5} and 5×10^{-5} M). For concentrations in the 10^{-6}–10^{-5} M range, the inhibitory effect of ATA was nonexistent whereas BTAH and BTAOH were efficient. For ATA concentrations over 10^{-5} M, the pit nucleation rate decreased as the ATA concentration increased. For a concentration of 10^{-2} M, the ATA inhibitory efficiency was about 100%.

The results showed that, in sulphate-containing solutions, BTAH and BTAOH were found to be the best inhibitors towards pit nucleation on copper at low concentrations. For higher concentrations, the behaviour observed with the three organic compounds was similar. However, if we consider the whole concentration range, BTAH was as the best inhibitor for copper pitting in this aggressive medium. These results are to be compared with those obtained in chloride-containing solutions: statistical analysis showed that ATA was the most efficient inhibitor of copper pitting when the inhibitors were present in the media up to 10^{-2} M [35]. Moreover, in the 10^{-6}–10^{-2} M inhibitor concentration range, ATA was more efficient towards chloride attack than towards sulphate attack; by contrast, BTAH and BTAOH were more efficient towards sulphate attack. The results obtained in the two media (chloride and sulphate solutions) were thus quite different. This shows that the resistance of a material towards pit nucleation does not depend only on the protectiveness of the passive film, since the passive films formed on the samples exposed to sulphate or chloride ions were the same. It is necessary to take into account the interactions between the aggressive ions, the passive film and the inhibitor molecule.

For a more detailed study of the inhibitive effect of the three organic products, we also measured the pit propagation rate. Figure 5 shows the pit propagation rate versus inhibitor concentration for the three inhibitors tested. The dotted line represents the pit propagation rate measured in inhibitor-free solution. Two types of behaviour occurred. For BTAH and BTAOH, the pit propagation rate remains close to the value measured without inhibitor in the 10^{-6}–5×10^{-5} M concentration range. For higher concentrations, the pit propagation rate significantly decreases. For BTAH, at 10^{-2} M, it was not possible to calculate a value for the pit propagation rate since no pits were detected (Figure 4(a) showed that λ_0 was equal to zero). In contrast, for ATA, the pit propagation rates remained close to those measured without inhibitor over the whole concentration range tested. At 10^{-2} M, the pit propagation rate was calculated with only two pits detected since, for this concentration, λ_0 was very low and pitting very rare. Therefore, an inhibitor can give a protective effect towards pit nucleation without being efficient towards pit propagation. Indeed, for BTAH and BTAOH, the inhibitive effect towards pit nucleation increased with inhibitor concentration. This was also true for the inhibitive effect towards pit propagation. However, when ATA was present at high concentrations, it inhibited pit nucleation efficiently but did not influence pit propagation. This is an interesting result for engineering applications. For example, when we have to consider problems of mechanical depassivation, the breakdown of the passive film can be due to its abrasion so any inhibitors present in the solution that protect the material from pit nucleation are not effective. Moreover, if these compounds do not effectively protect against pit propagation, damage can be severe.

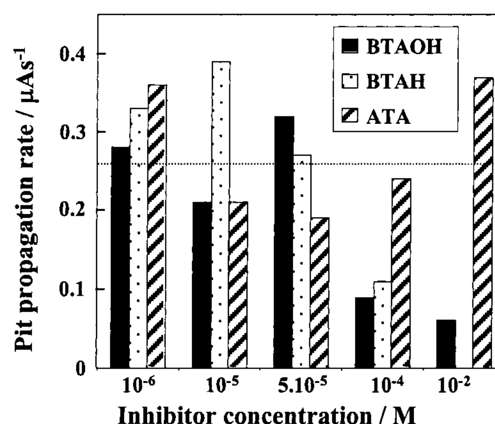

Fig. 5. Pit propagation rate against BTAH, BTAOH and ATA concentrations. Copper polarized for 1 h at +400 mV vs SCE in a borate-buffered solution containing one inhibitor. After 1 h, 0.01 M sulphates are added. Dotted line indicates pit propagation rate measured without inhibitor.

The results thus show that BTAH can be considered as the best inhibitor towards pit nucleation in sulphate-containing solutions, even though this molecule does not effectively protect against pit propagation. The effectiveness of BTAH is in agreement with results obtained by various authors who have shown that BTAH is an effective inhibitor towards the generalized corrosion of copper. But, the problem is that the other authors only studied the inhibition of generalized corrosion of copper. Nobody studied the inhibition of pitting corrosion and, in a previous study [35], we showed that the effectiveness of an inhibitor towards pitting corrosion and towards generalized corrosion were not necessarily correlated. In chloride-containing solutions, BTAH was found to be the best inhibitor of generalized copper corrosion but, on pitting corrosion, its effectiveness was not so significant, whereas that of ATA was significant.

Therefore, additional experiments were performed to compare the inhibitive efficiency of the different organic compounds on pitting corrosion and generalized corrosion in sulphate-containing solutions.

3.3. *Study of the efficiency of BTAH, BTAOH and ATA as inhibitive species towards generalized corrosion in copper*

Potentiokinetic polarisation curves were plotted for copper in borate-buffered solutions containing 0.01 M sulphate and the different inhibitors (Figure 6). The potentiokinetic curves were plotted in the presence of 10^{-4} and 10^{-2} M of each inhibitor. The concentrations were chosen to compare the efficiency of the three inhibitors towards generalized corrosion of copper when present in solution at a concentration for which their inhibitive effect towards pitting corrosion was similar. Moreover, we wanted to compare the results with those obtained in chloride-containing solutions with 10^{-2} and 10^{-4} M inhibitors [35].

Comparison of the curves plotted for copper in borate-buffered solution without inhibitive species and in the presence of 10^{-4} M inhibitors showed that BTAOH and ATA did not shift the pitting potential. For BTAH, the pitting potential was slightly shifted towards a higher value. For a concentration of 10^{-2} M, BTAOH allowed the pitting potential to be shifted from 200 to 600 mV. For ATA, this analysis was very difficult since there was no well-defined passivity plateau. In contrast, for BTAH, a passivity plateau was observed over the whole range of potential studied, showing that the pitting potential was shifted towards a very anodic value in BTAH-containing solutions. Thus, the analysis of the shift in pitting potential corroborated the notion that BTAH was the best inhibitor of pitting corrosion of copper in sulphate-containing solutions.

Furthermore, the potentiokinetic curves showed that, whatever the inhibitor concentration, BTAOH showed a behaviour similar to that observed without inhibitor, with two cathodic plateaus. By contrast with ATA, the first cathodic plateau (near the corrosion potential)

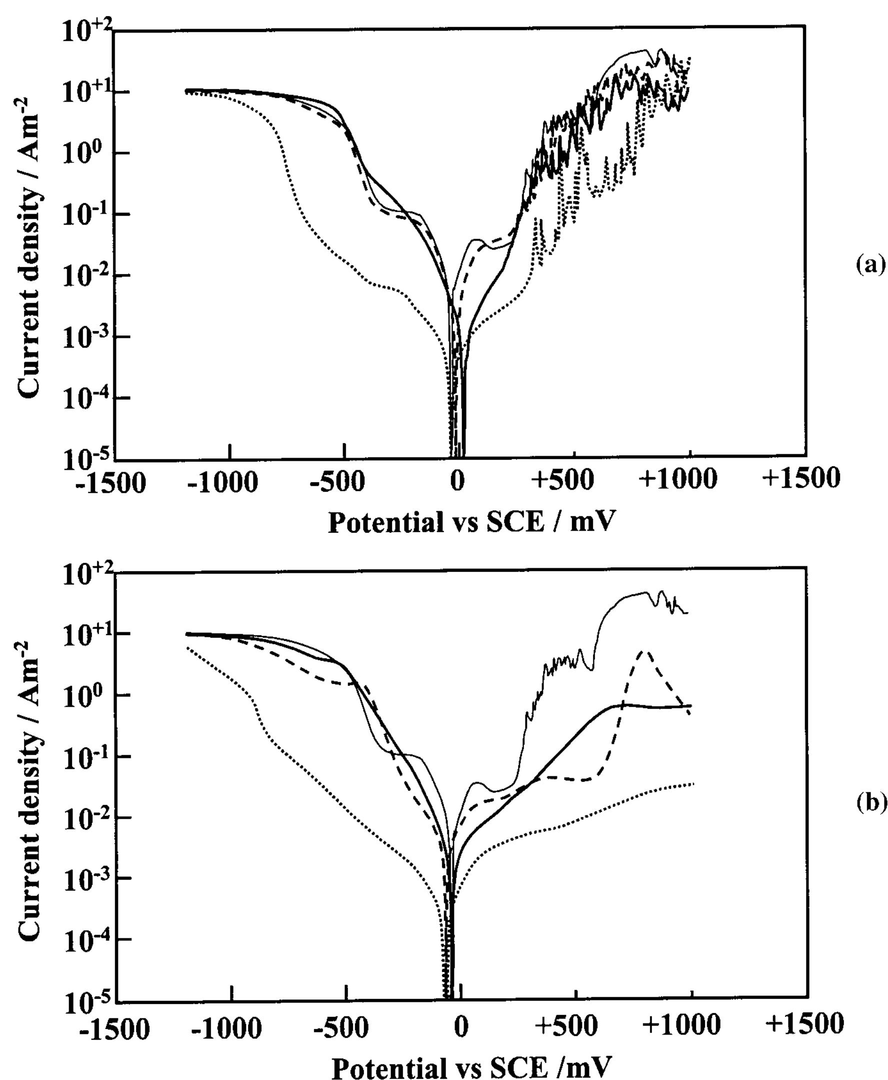

Fig. 6. Potentiokinetic polarization curves for copper in 0.01 M sulphate-containing borate-buffered solutions with (a) 10^{-4} M and (b) 10^{-2} M inhibitor. Potential scanning rate 1200 mV h^{-1}. Key: (——) without inhibitor; (······) BTAH (— — —) BTAOH (——) ATA.

disappeared. However, no significant difference was observed for the cathodic current densities. In the anodic range, no difference was observed between BTAOH and the reference for a concentration of 10^{-4} M. For ATA, a decrease in the anodic current density was first observed over a narrow potential range (0–200 mV) then, the potentiokinetic curve obtained was superimposable with those of BTAOH and the reference. At 10^{-2} M, the current densities measured for ATA and BTAOH were lower than those for the reference and, over the same potential range as before, the current densities measured for ATA were slightly lower than those for BTAOH. But, the main result was the significant influence of BTAH on the current densities. Indeed, this inhibitor led to a significant decrease of the anodic and cathodic current densities. Therefore, BTAH was found to be a very effective cathodic and anodic inhibitor of generalized corrosion in sulphate solutions. This is in agreement with the results obtained in chloride-containing solutions [35].

4. Discussion

In previous work [35], electrochemical impedance measurements, XPS analysis and passive current measurements helped us to evaluate the properties of the passive films formed in the presence of an inhibitor and thus the protection given by this compound against generalized corrosion of the material. The results showed that BTAH and BTAOH contributed to the formation of a very resistant passive film with a mixed structure of CuO, Cu_2O with the incorporation of the organic molecules. This film led to a high impedance and to a low passive current density. In contrast, the film formed in the presence of ATA was quite different. When ATA was present in solution, the oxide film was mainly composed of Cu_2O. For a high ATA concentration, the low oxygen content measured by XPS showed that it was essentially an organic film. Thus the film was of low impedance and had high current densities in the potentiokinetic curves. It can be assumed that copper was susceptible to generalized corrosion in ATA-containing solutions and, in fact, it seemed that there was a transition from a pitting corrosion mechanism to a generalized corrosion mechanism because there was replacement of the passive film by an organic film. This may explain the pitting corrosion results obtained in chloride media, where ATA was found to be the best inhibitor of pit nucleation on copper. However, results obtained in the present work with sulphate ions showed that ATA leads to an inhibitive effect on copper pitting when present in solution for concentrations higher than 10^{-5} M whereas in chloride solutions inhibition is efficient even for concentrations as low as 2×10^{-6} M. It can be concluded that the resistance to localised corrosion cannot be explained just by taking into account the properties of the passive film. The susceptibility of a metal to pitting corrosion also depends on the nature of the aggressive species and understanding the inhibitive effect of an organic compound requires understanding of the interactions which may occur between the inhibitor, the passive film and the aggressive species. The results obtained with BTAH and BTAOH support this since, in chloride media, the inhibitive effect of these two products was significant for concentrations higher than 5×10^{-4} M whereas in sulphate solutions a concentration of 10^{-6} M was sufficient. Therefore, comparison of the results of the present work and of those of a previous study [35] showed that the differences in behaviour towards generalized and localised corrosion of the two groups of inhibitors, that is, BTAH and BTAOH on the one hand and ATA on the other hand, can be explained by considering the modifications of the metal–oxide–electrolyte interfaces in the presence of the organic molecules. However, BTAH/BTAOH and ATA did not show the same inhibitive effect towards corrosion in chloride and sulphate solutions whereas the passive film was the same in the two aggressive media. Thus, the result obtained in the presence of the organic molecules showed that the aggressiveness of the medium was also a significant parameter in the study of the efficiency of the inhibitors.

To explain the results, the two parameters previously discussed (properties of the passive films and interactions with aggressive ions) were studied further. Statistical analysis of pit nucleation times allowed the pit nucleation rate to be calculated. The pit nucleation rates were proportional to the sample surface area. It was assumed that the inhibition of pitting corrosion just took place by the formation of a protective film on the copper which acted as a physical barrier against aggressive species. The fraction of surface covered by this film, θ, was then expressed by the ratio $E(\%)/100$. For BTAH, many authors [30, 47] have already shown that the inhibitive action of BTAH could be explained by surface absorption of the molecules followed by the formation of an insoluble polymer-type compound. Metikos-Hukovic et al. [48] showed that their results confirmed the structural model for the complex Cu(I)B-TA originally proposed by Cotton and Scholes [24] and modified by Rubim et al. [49] in which the overlap of Cu sp-hybrid atomic orbitals with the N hybridised lone-pair atomic orbitals occurs. Thierry et al. [50] claimed that their surface-enhanced Raman scattering (SERS) results suggested that adsorption of benzotriazole occurred solely via the triazole part, most likely through interaction of all three nitrogen atoms with the Cu substrate. They added that the difference in inhibiting ability of different molecules can be explained by the number and type of functional groups or atoms in the triazole ring that interact with Cu. As previously stated, the authors [14, 34] also showed that the triazole ring without substituent groups may be important in the inhibition of copper corrosion which explained the behaviour of BTAOH. Kertit et al. [51] showed that, in acidic media, ATA could adsorb on an iron surface with the establishment of ‘donor-acceptor’ links between the

Table 1. Fraction of copper surface covered by the protective film formed between the organic molecules and copper (values deduced from pitting experiments carried out in chloride or sulphate solutions)

Inhibitor concentration /M	BTAH		BTAOH		ATA	
	θ (Cl^-)	θ (SO_4^{2-})	θ (Cl^-)	θ (SO_4^{2-})	θ (Cl^-)	θ (SO_4^{2-})
10^{-5}	0.19	0.60	0	0.68	0.84	0
10^{-4}	0.49	0.97	0.11	0.94	0.95	0.86

empty d orbitals of iron and the pairs of free electrons on the nitrogen atoms. Thus, we considered that inhibitive effect of the three organic compounds was related to the formation of a physical barrier on the copper surface due to molecular absorption and film formation. Table 1 shows the θ values obtained for two concentrations of inhibitor (10^{-5} and 10^{-4} M) with chlorides or sulphates as aggressive species. It can be seen that, for BTAH and BTAOH, the θ values for sulphates are always higher than those for chlorides, whereas for ATA the opposite is observed. The parameter θ was assumed to measure the fraction of surface area covered by the protective film but, more precisely, it is related to the possibility that aggressive ions reach the copper surface via preferential paths such as pores in the protective film. By considering that sulphate ions are much bigger than chloride ions, θ values are higher in sulphate media than in chloride. Therefore, the model of absorption followed by the formation of a protective film on copper constitutes an interesting explanation for copper corrosion inhibition by BTAH and BTAOH. The differences in the inhibitive effect observed with the two aggressive species are only related to the size of the ions. This model is not sufficient for ATA and interactions between the inhibitor molecules and the aggressive ions must be considered.

Quantum chemical calculations were performed to estimate interaction energies between aggressive ions and ATA supported by Cu^+ ions. The geometrical conformation of ATA interacting with copper atoms in the presence or not of chloride and sulphate ions was optimised by a conjugate gradient method. The binding energy of Cl^- on the system (ATA–Cu_n^+) was found to be 13 kJ mol^{-1} higher than the binding energy of Cl^- on clusters of Cu^+ ions. In contrast, the binding energy of SO_4^{2-} on the system (ATA–Cu_n^+) was found to be 19 kJ mol^{-1} lower than the interaction energy between SO_4^{2-} ions and the clusters of Cu^+ ions. Thus, chloride ions will be preferentially adsorbed on the system (ATA–Cu_n^+) unlike sulphate ions, for which the adsorption on clusters of Cu^+ ions is more stable. These calculations explain the significant inhibitive effect of ATA in the presence of chloride ions. Indeed, chloride ions are strongly linked with the system (ATA–Cu_n^+) and do not attack the cuprous oxide. Therefore, they do not initiate pitting corrosion. However, sulphate ions preferentially attack the uncovered copper oxide which explains the low efficiency of ATA towards pitting corrosion in sulphate medium.

5. Conclusions

Various organic compounds (ATA, BTAH, BTAOH) can be used as inhibitors for copper pitting corrosion but their effects depend on their concentration and also on the nature of the aggressive ions (chlorides or sulphates). The effectiveness of an organic molecule is related to the properties of the protective film formed, but the interactions between the metal, the protective film, the aggressive ions and the inhibitor molecules were found to be non-negligible and had sometimes to be taken into account. For BTAH and BTAOH, a simple model based on absorption of the molecule followed by the formation of a complex is useful. The atypical behaviour of the ATA observed experimentally was validated by theoretical calculations using the Hartree–Fock approximation. These calculations showed that in contrast to the two other inhibitors, ATA is less efficient in sulphate medium than in chloride because of the strong interaction with chloride ions.

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