

## Electrochemical behaviour of copper corrosion and its inhibition in acidic media. A review

*The literature dealing with the electrochemical behavior and corrosion characteristics of copper in acidic media was studied. Factors affect the inhibition efficiency of the organic compounds in acidic media were discussed. The dissolution of copper in different acids and the adsorption mechanisms of the compounds were discussed. The effect of temperature and synergistic inhibition were identified.*

**Key words:** copper, corrosion, inhibition, behaviour, acid.

### INTRODUCTION

Copper is a material with excellent electrical and thermal conductivity and is often used in heating and cooling systems. Scale and corrosion products have a negative effect on heat transfer, and cause a decrease in the heating efficiency of the equipment, which accounts for the necessity of periodic descaling and cleaning of acidic pickling solutions. Corrosion inhibitors effectively eliminate the undesirable destructive effect of acids on equipment. Copper corrosion inhibitors have been widely investigated because of their practical applications. The investigations of various compounds have shown that the inhibitory action is connected with such factors as: (i) the structure of molecules, (ii) the type of adsorption, (iii) the distribution of charge in the molecule and (iv) the type of interaction between organic molecules and the metallic surface. Typical corrosion inhibitors are heterocyclic compounds containing nitrogen, oxygen or sulphur.

Many studies [1–4] have been done to obtain optimum corrosion protection for copper in various aqueous solutions by either finding new inhibitors or improving the inhibition efficiency.

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### CORROSION INHIBITION OF COPPER IN HNO<sub>3</sub>

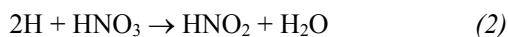
The kinetics of copper dissolution in nitric acid solutions has been studied by a number of authors [5-8]. Various corrosion inhibitors were suggested for copper inhibition in nitric acid solutions, but not all of them can be used for a long time [9-14]. However, it remains an important objective that one can either find a new inhibitor or to improve the efficiency of a known inhibitor by applying a synergistic technique [15 -18].

The effect of substituted benzoyl benzaldehyde hydrazone derivatives on the inhibition of copper corrosion in 1 M nitric acid solution at 303 K was investigated [19] by potentiodynamic and weight loss measurements. A significant decrease in the corrosion rate of copper was observed in the presence of the investigated compounds. The corrosion rate was found to depend on the nature and the concentrations of the inhibitor. Tafel slope was approximately constant independent on the concentration of the inhibitor. The corrosion data indicate that the inhibition of copper corrosion is due to the surface adsorption of the inhibitor molecules which follow the Langmuir adsorption isotherm. The results of potentiodynamic measurements indicate that all the investigated compounds act mainly cathodically.

The inhibition effect of some phthalimide derivatives on the corrosion of copper in acidic media was [20] investigated by weight loss and polarization techniques. Results obtained revealed that these organic compounds are good inhibitors. Galvanostatic polarization studies showed that these compounds are mixed-type inhibitors. The adsor-

ption of these inhibitors on the copper surface obeys Temkin's adsorption isotherm. The effect of temperature on the corrosion behavior of copper in nitric acid in presence of definite concentration of the inhibitors was studied in the temperature range 30–45°C. The associated activation corrosion and free adsorption energies have been determined.

The efficiency of two newly developed organic compounds of the triazoles type namely: bis [4-amino-5-hydroxy-1, 2, 4-triazol-3-yl] methane and bis [4-amino-5-hydroxy-1, 2, 4-triazol-3-yl] butane as corrosion inhibitors for copper in 4.0 M HNO<sub>3</sub> solutions at 25°C was investigated [21] using both weight loss and galvanostatic polarization techniques. The results showed that the predominant action of the inhibitors was cathodic. The two inhibitors proved to be effective (>99%) with long term effectiveness. Galvanostatic polarization measurements confirm weight loss measurements. Weight loss was also determined at various time intervals in the absence and in the presence of some selected concentration of the inhibitors. All curves are characterized by an initial induction period followed by a straight line could be interpreted as the time needed to build up the HNO<sub>2</sub> concentration which is needed for the initiation of autocatalytic reaction according to the following mechanism:



The influence of (2E)-3-amino-2-phenylazobut-2-enitrile and its derivative as corrosion inhibitors for copper in 0.5 M HNO<sub>3</sub>. Electrochemical techniques (potentiodynamic polarization, polarization resistance and impedance spectroscopy) as well as weight loss measurements were employed [22] to study the corrosion inhibition. The investigated compounds have shown inhibition efficiency in 0.5 M HNO<sub>3</sub>. Inhibition efficiency of these compounds has been found to vary with the concentrations of the compounds. The adsorption of these compounds on the copper surface from the acid solution has been found to obey Langmuir adsorption isotherm. The results revealed that the compounds are mixed type inhibitors. The effect of temperature on the inhibition efficiency was studied.

The inhibition efficiency of some nonionic, amphoteric, cationic and anionic surface active

agents (surfactants) on the dissolution of copper in 4.5M HNO<sub>3</sub> was studied [23] at 25°C by the weight loss method. The percentage inhibition increases as the concentration of the cationic, non-anionic and amphoteric substances increases and reaches a limiting value. It is suggested that this is due to the formation of a monolayer on the surface of the metal: the Langmuir adsorption isotherm was confirmed. In the case of anionic surface agents, the percentage inhibition values were at highest at low surfactant concentrations and decreased as the concentration of the surfactant increased.

Effects of imidazole on the pure copper (Cu) corrosion in 1M HNO<sub>3</sub> were studied [24]. Solution analyzing potentiodynamic polarisation curves, potentiostatic anodic current transient, AC impedance spectra and X-ray photoelectron spectra (XPS) were employed. By adding imidazole to HNO<sub>3</sub> solution, the polarization curves showed decrease in the corrosion current and the cathodic current, suggesting that imidazole acts as an effective cathodic inhibitor to Cu corrosion. From the measured anodic current transients, it is inferred that the protective Cu-/imidazole complex film is simultaneously formed with the Cu oxide in the presence of imidazole during the early stage of the anodic polarization. Analysis of the AC impedance spectra revealed that the values of the charge transfer resistance  $R_{ct}$  obtained in imidazole-containing HNO<sub>3</sub> solution were greater than that value in imidazole-free one and at the same time steadily increased with immersion time to the constant value.

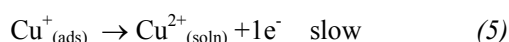
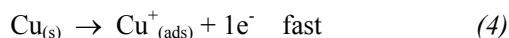
The effect of the addition of some tetrazolic type organic compounds: 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT), 1,2,3,4-tetrazole (TTZ), 5-amino-1,2,3,4-tetrazole (AT) and 1-phenyl-1,2,3,4-tetrazole (PT) on the corrosion of brass in nitric acid was studied [25] by weight loss, polarization and electrochemical impedance spectroscopy (EIS) measurements. The explored methods gave almost similar results. Results obtained reveal that PMT is the best inhibitor and the inhibition efficiency (E %) follows the sequence: PMT > PT > AT > TTZ. Polarization measurements also indicated that tetrazoles acted as mixed-type inhibitors without changing the mechanism of the hydrogen evolution reaction. Partial p-charge on atoms has been calculated. Correlation between the highest occupied molecular orbital energy EHOMO and inhibition efficiencies was sought. The adsorption of PMT on the brass surface followed the Langmuir isotherm. Effect of temperature was also studied.

The kinetics of copper dissolution in nitric acid especially, the phase of dissolution at the beginning of incubation period was investigated [26]. Two techniques, the anodic stripping voltammetry and the conductance measurements, were used for the first time in this concern. Galvanostatic polarization measurements using very simple circuit used to study the corrosion process of copper in nitric acid. The effect of several factors was studied, namely nitric acid concentration, the copper surface area and stirring. The effect of inorganic substances and their role as inhibitors or promoters was also investigated. By applying the anodic stripping voltammetric technique it was found that the rate of copper dissolution during the incubation period is constant and time independent. Also, stirring prevents the corrosion of copper almost completely.

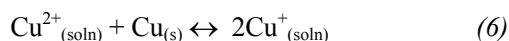
The inhibitive efficiency of some nonionic, amphoteric, cationic, and anionic surface active agents (surfactants) on the dissolution of copper in 4.5 M HNO<sub>3</sub> was studied [27] at 25°C by the weight loss method. The percentage inhibition I increases as the concentration of the cationic, non-ionic, and amphoteric substances increases and reaches a limiting value. It is suggested that this is due to the formation of a monolayer on the surface of the metal; the Langmuir adsorption isotherm was confirmed. In the case of anionic surface agents, the percentage inhibition values were at their highest at low surfactant concentrations and decreased as the concentration of the surfactant increased.

#### CORROSION INHIBITION OF COPPER IN H<sub>2</sub>SO<sub>4</sub>

According to the Mattson and Bockris mechanism [28], the dissolution of copper in sulphuric acid takes place through two steps (Eqs. (4) and (5)):



Eq. (5) is the rate-determining step. Cuprous ions are in equilibrium through the first reaction, but apparently they remain on the copper surface and do not diffuse into solution. Nevertheless, low concentrations of cuprous ion can be found in solution according to the equilibrium:



The equilibrium constant is:

$$K = \frac{(\text{Cu}^+)^2}{(\text{Cu}^{2+})}$$

and K has a value of about  $1 \times 10^{-6}$  at 25 °C [29].

The corrosion inhibition of commercial copper by means of isatin was studied [30] in aerated 0.5M H<sub>2</sub>SO<sub>4</sub> in the temperature range 25–55°C using weight-loss, potentiodynamic and spectrophotometric tests, and determination of double layer capacitance. Inhibition efficiencies up to 94% in the concentration range of  $1 \times 10^{-4}$ – $7.5 \times 10^{-3}$  M of isatin were obtained. The corrosion rates estimated with weight-loss measurements were higher than those correspondingly determined with the potentiodynamic test, especially at higher concentrations of inhibitor. This is in accord with other researches that have pointed out the limitation of the Tafel line extrapolation method in the determination of corrosion rates. The kinetics of cuprous and cupric ion formation and UV–visible spectra support the formation hypothesis of a complex between copper and isatin. The adsorptive behaviour of isatin on copper 0.5 M H<sub>2</sub>SO<sub>4</sub> was also investigated.

Triphenylmethane derivatives, namely fuchsin basic (FB) and fuchsin acid (FA), were studied [31] for their possible use as copper corrosion inhibitors in 0.001 to 1.0 M sulphuric acid solutions. Benzotriazole (BTA) was also tested for comparative purposes. These inhibitors were studied in concentrations from  $1 \times 10^{-5}$  to  $1 \times 10^{-1}$  M at temperatures from 298 to 328 K. The gravimetric method was employed to study the protective effect of FB, FA and BTA. The order of inhibition efficiency was BTA > FB > FA. Up to nine adsorption isotherms were tested to fit the experimental data. The best fit was obtained using the Frumkin isotherm model. A thermodynamic/kinetic model of adsorption was also fitted. The projected molecular area of the inhibitors was calculated to elucidate inhibitor orientation in the adsorption process.

Benzotriazole (BTA) has been known to be an excellent inhibitor for copper since the pioneering work of Dugdale and Cotton [32]. Basically two mechanisms have been proposed: namely the adsorption of single BTA molecules on the copper surface [33] or the formation of a polymeric coating with a ‘‘bidentate structure’’, where the BTA molecules are arranged in flat zigzag chains and connected by a N–Cu–N bond [34, 35].

Cuprous oxide has been claimed to be essential for the formation of the Cu–BTA film, though the formation of a Cu–BTA film on an oxide-free copper surface has also been reported. Another controversial point is the information that chemisorbed BTA is nearly identical on both clean and oxide-covered copper surfaces [36]. The Cu–BTA film provides better protection on oxidized copper than on an oxide free surface [37]. On the other hand, there is also a lack of agreement regarding the orientation of BTA on the copper surface. Some authors propose a flat orientation on the surface and bonding through the lone-pair nitrogen orbitals, with lone nitrogen atoms bonded to two copper atoms [38–40]. The loss of the imino hydrogen converts each BTA molecule into a BTA<sup>-</sup> ion, with a conjugated p structure delocalized over the three nitrogen atoms [41, 42]. It has also been claimed that BTA does not lie flat on the surface, but that the nitrogen lone-pair orbitals bond to the copper surface atoms [36]. The temperature and pH value of the media are two important parameters of the inhibition efficiency (IE) of BTA. IE drops dramatically in acid solutions. Thus, to achieve good corrosion protection for copper in acid solutions requires improving IE or finding new inhibitors. On the other hand, from a health point of view there is a need for alternatives to the use of BTA. In an attempt to find alternatives to the BTA inhibitor, two nitrogen-containing organic compounds which are derivatives of triphenylmethane, fuchsin basic (FB) (rosaniline chloride) and fuchsin acid sodium salt (FA), were tested as new copper corrosion inhibitors. These compounds were thought to be good candidates for corrosion inhibition due to the presence of chloride ion in the FB and the polar or charged nature of the more complex FA surfactant molecule. The aim of this paper is to study the corrosion inhibition mechanism of two new compounds which are derivatives of triphenylmethane, FB and FA, for copper corrosion in sulphuric acid solutions. The results are compared with those obtained using the conventional BTA inhibitor. Finally, the study is completed by calculating the surface areas of FB, FA and BTA based on the projected molecular area.

The influence of the molecular structure on the inhibiting properties of organic compounds in corrosion processes in acid media was studied [43]. The inhibiting efficiency of non-toxic imidazole derivatives on copper corrosion in sulphuric acid is investigated. The investigation is performed using

electrochemical methods of potentiodynamic polarisation as well as gravimetric measurements. The results of the investigation show that the inhibiting properties of substituted imidazoles depend on molecular structure. The best protection (93%) is obtained by adding a phenyl ring to the imidazole structure. The values of standard free energies of adsorption, as calculated from the Freundlich isotherm, indicate that in the presence of sulphuric acid imidazole derivatives adsorb on copper by a physisorption-based mechanism.

The effect of cysteine (cys) on the anodic dissolution of copper in sulfuric acid media was studied [44] at room temperature using electrochemical methods. The anodic polarization curves showed two different regions: in the low overpotential range, the inhibitory effect of cys on the anodic dissolution was verified and in the high overpotential range this amino acid does not influence the copper anodic dissolution. Moreover, a limiting current was observed for cys concentrations higher than  $10^{-3}$  mol l<sup>-1</sup> which was attributed to the formation of a film on the copper surface. The electrochemical impedance diagrams obtained at the current plateau showed a typical diffusion process. These results suggest that the mass transport through this film is the rate determining step for copper oxidation in this medium. According to the copper electrodisolution mechanism proposed for sulfate media, in the absence of cys, the main species present on the copper surface at low anodic polarization is the intermediate Cu(I)ads. This statement shows that the cys inhibitory effect is over this intermediate and suggests that the film formed at higher cys concentrations ( $10^{-3}$  and  $10^{-2}$  mol l<sup>-1</sup>) is a Cu(I)–cys complex. The cys effect is not significant at high overpotentials, where the Cu(II)ads is the main species present at the copper surface.

Inhibition of the corrosion of copper in aerated 0.5M sulphuric acid solutions containing various concentrations of indole-5-carboxylic acid was studied [45] in the temperature range 25–55°C using potentiodynamic curves (Tafel lines), weight loss, analytical methods, and determination of double layer capacitance. The corrosion rates reveal good corrosion inhibition, up to 95% in the concentration range of  $1 \times 10^{-4}$  –  $4 \times 10^{-3}$  M. Tafel anodic slopes in inhibited acid solutions are considerably higher than those in uninhibited acid solutions. These points to a change in the corrosion mechanism of copper in the presence of indole-5-carboxylic acid. Under these conditions, copper

could electro-oxidize primarily to  $\text{Cu}^+$  rather than to  $\text{Cu}^{2+}$ , forming slightly soluble  $[\text{Cu}-(\text{indole-5-carboxylic})_n]^+(\text{ads})$  complexes. Corrosion rates determined by the weight loss method in both the absence and presence of inhibitor are much higher (on average by a factor of about 6) than those obtained with the potentiodynamic method. This points to a limitation of the Tafel line extrapolation method in corrosion rate determination. The double layer capacitance-potential curves indicate considerable adsorption of the inhibitor over a wide potential range ( $-600$  to  $+200$  mV with regard to  $E_{\text{corr}}$ ).

The influence of the molecular structure on the inhibiting properties of organic compounds in corrosion processes in acid media. The inhibiting efficiency of non-toxic imidazole derivatives on copper corrosion in sulphuric acid was investigated [46]. The investigation is performed using electrochemical methods of potentiodynamic polarization as well as gravimetric measurements. The results of the investigation show that the inhibiting properties of substituted imidazoles depend on molecular structure. The best protection (93%) is obtained by adding a phenyl ring to the imidazole structure. The values of standard free energies of adsorption, as calculated from the Freundlich isotherm, indicate that in the presence of sulphuric acid imidazole derivatives adsorb on copper by a physisorption-based mechanism.

The effect of sodium dodecylsulfate (SDS) on copper corrosion in sulfuric acid media was studied [47] in the absence and presence of benzotriazole (BTAH), at room temperature using electrochemical impedance and surface tension ( $\gamma$ ) measurements. SDS provides a slight inhibition of copper corrosion, however, it promotes synergistic effect on the inhibitive action of BTAH, when stationary copper electrode is used. SDS does not change the copper dissolution mechanism in sulfuric acid media at the corrosion potential but it reduces significantly the inhibitive effect of BTAH on the copper corrosion in  $\text{H}_2\text{SO}_4$  media under hydrodynamical conditions. The interaction of BTAH-SDS was also observed at  $\text{H}_2\text{SO}_4$  solution/air interface where the BTAH presence increases the SDS effect on the decreasing of surface tension values.

Azadirachta indica leaves extract (AI) was investigated [48] as a copper corrosion inhibitor in 0.5 M sulphuric acid. Inhibition efficiency of AI was compared to that of the already proven good inhibitors 2-acetamino-5-mercapto-1,3,4-thiadiazole (AAMTDA) and 1,2,3-benzotriazole (BTAH).

The inhibition properties were studied using electrochemical polarization and weight loss techniques. In the region of active copper dissolution, the highest inhibition efficiency was exhibited by AAMTDA (92.7%). AI exhibited somewhat higher efficiency (86.4%) than the widely used BTAH (85.5%), showing that the extract could serve as an effective substitute for currently preferred copper corrosion inhibitors in sulphuric acid. The weight loss results were interpreted by means of the Frumkin isotherm of adsorption on the metal surface. The values of  $\Delta G_{\text{ads}}$  equal to  $-41.96$  kJ mol $^{-1}$  for AAMTDA and  $-35.22$  kJ mol $^{-1}$  for BTAH indicate strong spontaneous adsorption while the surface coverage dependence on the  $\log c$  following the Frumkin isotherm is suggestive of chemisorption in case of all three tested inhibitors.

The inhibition effects of sodium dodecylbenzenesulphonate (SDBS) and 2-mercaptobenzoxazole (2-MBO) on corrosion of copper in sulphuric acid solution were studied [49] using electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements. For 2-MBO, a monotonous increase in inhibition efficiency was observed as a function of concentration. For SDBS, however, an optimum in the inhibition efficiency was observed for a certain concentration, which is ascribed to the formation of hemi-micellar aggregates that provoke inhibitor desorption from the metal/solution interface at higher concentrations. Upon mixing 2-MBO and SDBS inhibitors, concentrations range showing synergistic inhibition behaviour were identified, and it is concluded that electrostatic interactions between the adsorbed ions. Different adsorption isotherms were tested for describing the adsorption behaviour of both 2-MBO and SDBS.

Self-assembled monolayers (SAMs) of benzenethiols chemisorbed on copper show [50] good inhibiting properties against Cu corrosion in 0.5  $\text{MH}_2\text{SO}_4$ . The structure of the inhibitors influences their inhibition efficiency and is strongly affected by the type and the position of the substituent functional group on BT. The results indicate that the inhibition efficiencies of the para substituted BT molecules increase in the following order:  $-\text{CH}(\text{CH}_3)_2 > -\text{CH}_3 > -\text{F} > -\text{NHCOCH}_3 > -\text{NH}_2$ . The nature and the degree of the electronic perturbations (electron donating or withdrawing) by the substituents affect the bonding reaction of the benzenethiol and the copper surface. More importantly, the hydrophobicity and the size of the substituent influence the barrier properties of the film,

as it serves as an additional protective layer in blocking out corrosive ionic species from reaching the Cu substrate. The effect of the ring position of the substituent on the inhibition efficiency, as demonstrated using NH<sub>2</sub> substitution on the ring, increases from: ortho > meta > para, relative to the -SH position. The position of the substituent on the benzene ring influences the resonance effect of the ring. As a result, the transmission mechanism of the electrons within the ring is affected. These results are important in providing the rationale for the selection and the molecular design of inhibitors against Cu corrosion in aqueous media.

#### CORROSION INHIBITION OF COPPER IN HCl

Extensive research on the mechanism of the anodic dissolution of copper in HCl solutions has been performed [51-63] and a number of different dissolution mechanisms have been proposed. It is generally accepted that Cu anodic dissolution is influenced by chloride concentration independently of pH [64, 65].

The effect of hexadecyl pyridinium bromide (HPB) and hexadecyl trimethyl ammonium bromide (HTAB) on the corrosion behaviour of copper in hydrochloric and sulphuric acid solutions has been investigated [66] by potentiodynamic polarization and Tafel extrapolation methods. The polarization curves indicate that the two compounds behave as mixed inhibitors, but the cathode is more inhibited. HPB is more effective than HTAB in both acids; this is explained on the basis of the charge located on the nitrogen atom on the two compounds. The inhibition efficiency of the compounds investigated is more effective for in HCl than in H<sub>2</sub>SO<sub>4</sub>, which is explained on the basis of the potential of zero charge of the metal surface and the adsorption ability of both Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> on the metal surface. Potentiodynamic polarization curves for copper in 1 M HCl were studied at different sweep rates, ranging from 20 to 400 mVs<sup>-1</sup>. As the scan rate increases, the current density increases. Fig. 1 shows the potentiodynamic polarization curves for copper in 1 M HCl at different sweep rates, ranging from 20 to 400 mVs<sup>-1</sup>. As the scan rate increases, the current density increases and the peak current (I<sub>p</sub>) increases, and its corresponding peak potential E<sub>p</sub> shifts to a more positive potential. The addition of different concentrations of HPB and HTAB to 1 M HCl affects the characteristic shape of the voltammogram. It is found that the peak current I<sub>p</sub> increases and its corresponding peak potential E<sub>p</sub> shifts to more positive potentials. Fig. 2 shows the effect of addition of

10<sup>-5</sup> M from HPB. It is clear that the current density decreases markedly. With an increase of the concentration of HPB to more than 1x10<sup>-4</sup> M, the current drops very close to zero. This means that this compound has a marked inhibition effect on the corrosion of copper in HCl.

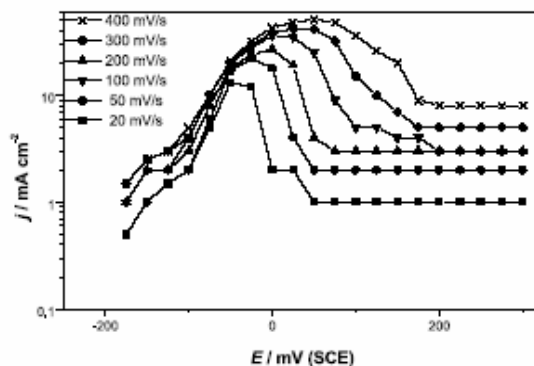


Fig. 1. Potentiodynamic polarization curves of copper in 1 M HCl at different scan rates

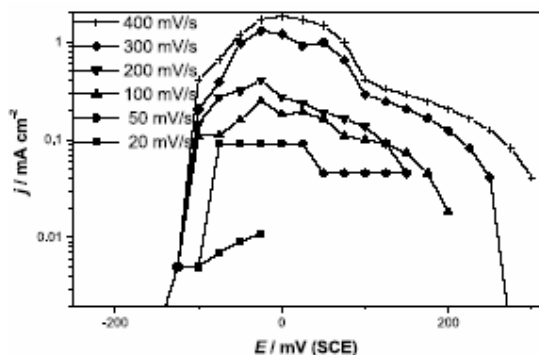


Fig. 2. Potentiodynamic polarization curves of copper in 1 M HCl in the presence of 10<sup>-5</sup> M of HPB at different scan rates

Fig. 3. shows the effect of addition of 10<sup>-5</sup> M from HTAB; it is clear that the current density decreases in comparison to the values without inhibitors.

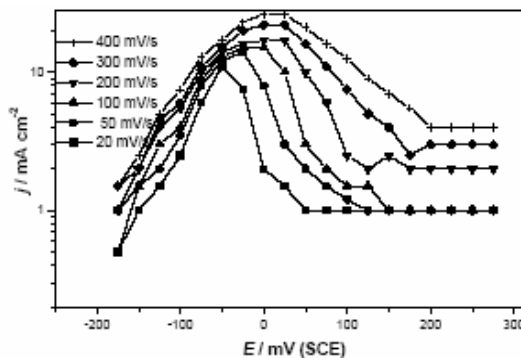


Fig. 3. Potentiodynamic polarization curves of copper in 1 M HCl in the presence of 10<sup>-5</sup> M of HTAB at different scan rates

Fig. 4 shows that a linear relation is obtained by plotting the peak current density ( $I_p$ ) of copper in 1 M HCl in the absence and in the presence of both  $10^{-5}$  M.

HPB and HTAB vs. the square root of the potential scan rate ( $v^{1/2}$ ) [67]. The height of the current peak increases according to a linear relationship of  $I_p$  vs.  $v^{1/2}$ , and this suggests the participation of a diffusion process in the positive direction. For HPB, the plot is in the form of a straight line with the ordinate at its origin equal to zero, indicating that the process depends on diffusion through the film formed on the copper surface. The other two plots do not cross the origin, which may indicate that the reaction is under mixed kinetic and diffusion control. The results obtained in the presence of HPB yield smaller current peaks, according to a lesser dissolution compared to free inhibitor solution and HTAB. The corresponding slopes increase with respect to the following order HCl > HTAB > HPB; this is because the metallic surface attack depends on the amount of aggressive species dissolved in the electrolyte. Thus, the formation of soluble anodic products is enhanced in the absence of additives and consequently an increase in the current peaks occurs. Fig. 5 shows the relation between the peak potential ( $E_p$ ) of copper in 1 M HCl and the square root of the potential scan rate ( $v^{1/2}$ ).  $E_p$  shifts to more positive potential with increasing scan rate.

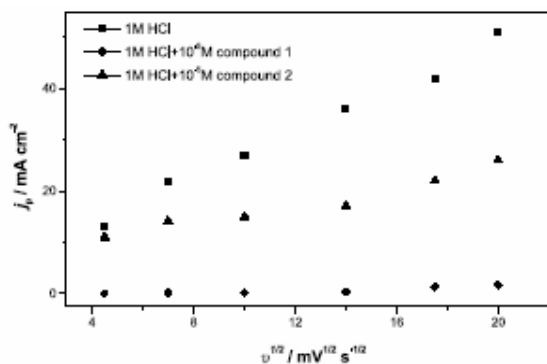


Fig. 4. Dependence of the peak current density for copper in 1M HCl on the square root of the potential scan rate  $v^{1/2}$

Effects of 3-amino-1,2,4-triazole (ATA) on the inhibition of copper corrosion in 0.5 M HCl solutions was studied [68] using gravimetric, electrochemical, and Raman spectroscopy investigations. Weight-loss measurements after varied immersion periods revealed that the dissolution rate of copper decreased to a minimum, while the inhibition efficiency and consequently the degree of surface co-

verage ( $\theta$ ) increased with the presence of ATA and the increase of its concentration. Potentiodynamic polarization, chronoamperometric, and electrochemical impedance spectroscopy (EIS) measurements after 0, 24, and 48 h immersion of the copper electrode in the test solutions showed that the presence of ATA molecules significantly decreased cathodic, anodic, and corrosion ( $j_{\text{corr}}$ ) currents and corrosion rates ( $R_{\text{corr}}$ ) and greatly increased polarization resistance ( $R_p$ ),  $\zeta\%$ , and  $\theta$ ; this effect was increased on increasing the ATA content in the solution. Raman spectroscopy confirmed that ATA molecules strongly adsorbed onto the copper surface, blocking its active sites and preventing it from being corroded easily.

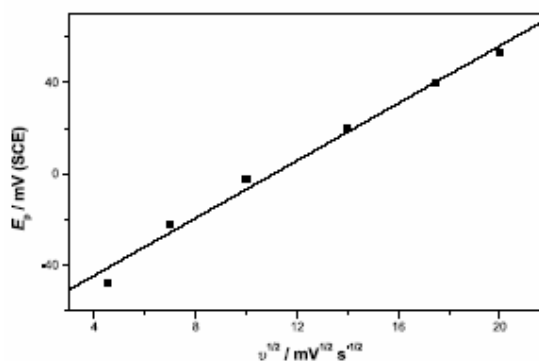


Fig. 5. Dependence of the peak potential for copper in 1 M HCl on the square root of the potential scan rate  $v^{1/2}$ .

Aniline derivatives, namely 2-chloroaniline, 2-fluoroaniline, 2-amino-phenetole, 2-ethylaniline, *o*-aminoanisole and *o*-toluidine were studied [69] for their possible use as copper corrosion inhibitors in 0.5 M HCl. These compounds were studied in concentrations from  $10^{-3}$  to  $10^{-4}$  M at temperature 298 K. Effectiveness of these compounds was assessed through potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. These compounds inhibit the corrosion of copper in HCl solution to some extent. In each case, inhibition efficiencies increase with increasing concentration. A suggested model for the interface as well as some kinetic data is presented. These inhibitors obey the Temkin adsorption isotherm. A correlation between structure and inhibition efficiencies is suggested.

The effect of *N*-propyl amino lauryl amide (I) and three of its ethoxylated derivatives (II, III and IV) as corrosion inhibitors of carbon steel in 1M hydrochloric acid solution was studied by weight loss and galvanostatic polarization techniques [70].

A significant decrease in the corrosion rate of carbon steel was observed in the presence of the investigated inhibitors. The study revealed that, the inhibition efficiency ( $I$ , %) increases with increasing the inhibitors concentration. All the tackled inhibitors seem to have obeyed the Langmuir adsorption isotherm. The galvanostatic polarization data indicated that, the inhibitors were of mixed type, but the cathodic effect is more pronounced. The slopes of the cathodic and anodic Tafel lines are approximately constant and independent on the inhibitor concentration. The relation between the surface tension of the inhibitor ( $\gamma$ ) and the logarithm of their concentrations ( $\log C$ ) was investigated to obtain the adsorption ability of the inhibitors on the carbon steel surface. Scanning electron microscopy was used to examine the surface morphology of the carbon steel specimens after immersion in 1M HCl for 6 days in absence and presence of 500 ppm of the inhibitor **IV**. The mechanism of inhibition was discussed in the light of the chemical structure of the undertaken inhibitors.

The inhibiting action of two new Schiff bases namely SB1: 2-( $\beta$ -1-methyl-3-[(2-sulfanylphenyl)imino]butylidene)amino)-1-benzenethiol and SB2: 2-( $\beta$ -1,2-diphenyl-2-[(2-sulfanylphenyl)imino]ethylidene)amino)-1-benzenethiol on the corrosion of copper in hydrochloric acid was studied [71]. The impedance measurements were carried out at the open circuit potential ( $E_{ocp}$ ) in the frequency range from 200 kHz to 0.02 Hz with a signal amplitude perturbation of 5mV by using a computer-controlled potentiostat (same model of AUTOLAB which is mentioned). Impedance data were analyzed using a Pentium IV computer and FRA software. All the impedance spectra are analyzed in terms of the equivalent circuits shown in Fig. 6.

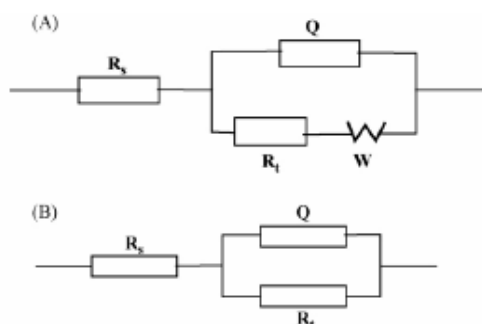


Fig. 6. The equivalent circuit of the impedance spectra

Generally these circuits fall into the classic parallel capacitor and resistor combination with the

series resistance being that of the bulk solution. The impedance spectra,

Involving Warburg impedance are analyzed using the equivalent circuit shown in Fig. 6(A) the other spectra are fitted in terms of the equivalent circuit shown in Fig. 6(B). The FRA software is used for impedance data and the fit parameters are listed in

Table 1. In the circuits,  $W$  stands for the Warburg impedance,  $R$  represents a resistor ( $R_s$  represents solution resistance;  $R_t$ , charge-transfer resistance),  $Q$  a constant phase element (CPE) whose admittance is described as:

$$Q = Y_0(j\omega)^n \quad (7)$$

where  $j$  is the imaginary root,  $\omega$  the angular frequency,  $Y_0$  the magnitude and  $n$  is the exponential term [72]. The impedance loops measured are often depressed semicircles with their centre below the real axis. This kind of phenomenon is known as dispersing effect [73,74]. Similar results have been reported in literature for the corrosion of copper in 5% HCl in the presence of Schiff bases [75]. The impedance of a double-layer does not behave as an ideal capacitor in the presence of the dispersing effect this is why a CPE is used as a substitute for capacitor in equivalent circuit to fit more accurately the impedance behavior of the electric double-layer. Constant phase elements have been widely used to account for deviations brought about by surface roughness of electrode [72]. In the case of the electrochemical impedance spectroscopy, the inhibition efficiency ( $\eta_z$ ,%) is calculated using charge transfer resistance as follows [76]:

$$\eta_z (\%) = \frac{R_{t0} - R_t}{R_{t0}} \times 100 \quad (8)$$

$R_t$  and  $R_{t0}$  are the electron transfer resistance in uninhibited and inhibited solution, respectively. The corrosion of copper is obviously inhibited in the presence of the inhibitors. As the inhibitor concentration increased, the  $R_t$  value and subsequently inhibition efficiency increase. This fact suggests that inhibitor molecules are absorbed on the copper surface, to protect its surface from corrosion. Figs. 7 and 8 show the complex plane display for copper in a 15% HCl solution with and without various concentrations of SB1 and SB2 at room temperature (25 °C) with an immersion time of 0.5 h. Characteristic features of these figures were the presence of a diffusive contribution at low frequencies in the absence and low concentration of



the inhibitors, which are called Warburg impedance. This result indicated that the dissolution mechanism of copper was being controlled by the mass transport rate in the absence and low concentration of the inhibitors [77–80].

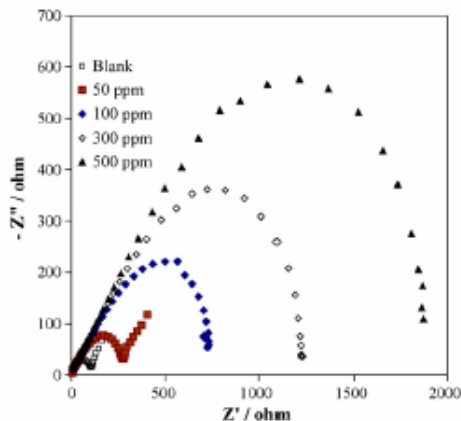


Fig. 7. Impedance plots for the copper in 15% HCl in the absence and presence of different concentrations of SBI.

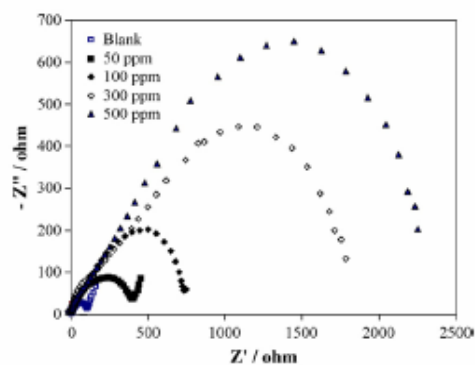


Fig. 8. Impedance plots for the copper in 15% HCl in the absence and presence of different concentrations of SB2.

Results of electrochemical impedance and Tafel polarization measurements consistently identify both compounds as good inhibitors. Differences in inhibition efficiency between SB1 and SB2 are correlated with their chemical structures. Langmuir isotherm is found to provide an adsorption description of Schiff bases.

The corrosion inhibition of copper in 0.1 M HCl in the presence of pyrazole was studied [81] using potentiodynamic techniques with rotating disc and rotating ring disc electrode (RRDE). It was observed that the presence of pyrazole changes the mechanism of Cu dissolution in 0.1 M HCl. RRDE measurements showed that  $\text{Cu}^+$  was detected

in the whole potential range studied, while  $\text{Cu}^{+2}$  was formed only at high anodic overpotentials. The addition of pyrazole decreases the rate of cuprous species formed and increases that of cupric species. Pyrazole behaves like a cathodic inhibitor and the inhibition efficiency is influenced by mass transport.

#### SYNERGISTIC EFFECT

The effect of 2-MBI and the synergistic effect of 2-MBI and surfactant SDBS on corrosion of copper in acidic solutions was studied [82,83]. The inhibition efficiency of 2-MBO and its synergistic effect with cyanide ions for the corrosion inhibition of copper in aqueous chloride media is investigated using electrochemical and surface-enhanced Raman spectroscopic techniques [84]. The study of surfactants adsorption on metal surfaces is extremely important in a variety of fields such as corrosion inhibition and metallic electrodeposition. The latter approach offers further advantages to inhibition enhancement such as detergency, dispersibility and improved wetting power of the solutions, and has already been found in several industrial applications [85,86]. Previously [87] the inhibition effects of sodium dodecyl benzenesulphonate (SDBS) and hexamethylenetetramine (HA) on corrosion of mild steel in sulphuric acid solution has been studied. It has been shown that SDBS acts as a corrosion inhibitor and presents a synergistic effect on inhibitive action of HA. Recently, Villamil et al. [88] have observed a synergistic effect of sodium dodecylsulphonate (SDS) and Benzotriazole (BTAH) on corrosion inhibition of 304 stainless steel in  $2.0 \text{ mol dm}^{-3}$  sulphuric acid solution at several BTAH–SDS concentration ratios.

The inhibitive action of the four surfactants, cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate, sodium oleate and polyoxyethylene sorbitan monooleate (TWEEN-80), on the corrosion behavior of copper was investigated [89] in aerated  $0.5 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  solutions, by means of electrochemical impedance spectroscopy. These surfactants acted as the mixed-type inhibitors and lowered the corrosion reactions by blocking the copper surface through electrostatic adsorption or chemisorption. The inhibitor effectiveness increased with the exposure time to aggressive solutions, reached a maximum and then decreased, which implies the orientation change of adsorbed surfac-

tant molecules on the surface. CTAB inhibited most effectively the copper corrosion among the four surfactants. The copper surface was determined to be positively charged in sulfuric acid solutions at the corrosion potential, which is unfavourable for electrostatic adsorption of cationic surfactant, CTAB. The reason why CTAB gave the highest inhibition efficiency was attributed to the synergistic effect between bromide anions and positive quaternary ammonium ions.  $C_{16}H_{33}N(CH_3)_4^+$  ions may electrostatically adsorb on the copper surface covered with primarily adsorbed bromide ions. On the basis of the variation of impedance behaviors of copper in the surfactant-containing solutions with the immersion time, the adsorption model of the surfactants on the copper surface was proposed.

The effect of sodium dodecylsulfate (SDS) on copper corrosion in sulfuric acid media was studied [90] in the absence and presence of benzotriazole (BTAH), at room temperature using electrochemical impedance and surface tension ( $\gamma$ ) measurements. SDS provides a slight inhibition of copper corrosion, however, it promotes synergistic effect on the inhibitive action of BTAH, when stationary copper electrode is used. SDS does not change the copper dissolution mechanism in sulfuric acid media at the corrosion potential but it reduces significantly the inhibitive effect of BTAH on the copper corrosion in  $H_2SO_4$  media under hydrodynamical conditions. The interaction of BTAH-SDS was also observed at  $H_2SO_4$  solution/air interface where the BTAH presence increases the SDS effect on the decreasing of surface tension values.

Copper corrosion inhibitors were tested [91] including benzotriazole (BTA), thiourea, potassium ethyl xanthate (KEtX), octadecyl mercaptan. The corrosion breakdown potentials were evaluated using the electrochemical quartz crystal nanobalance (EQCN) technique, by recording linear potential scan voltammetric ( $i-E$ ) and piezogravimetric ( $m-E$ ) characteristics. Effects of single inhibitors and their mixtures on the value of the breakdown potential were investigated. Previously found synergistic effects for a mixture of BTA+KEtX and a mixture of TU+KEtX inhibitors were confirmed. The most effective among the copper corrosion inhibitors tested appeared to be Bricorr-288. The representative inhibitor films were subsequently tested using the quartz crystal admittance (QCI) technique. New equations based

on experimental admittance data were derived to characterize the film acoustic resistance and the resonator parallel capacitance. On the basis of these equations, a new procedure to evaluate passive elements of the equivalent BVD electrical circuit, has been proposed. A decrease in the admittance maximum, appearing near the resonance frequency, was observed for octadecyl mercaptan and Bricorr-288 films on copper.

The corrosion inhibition behavior of mercaptobenzothiazole (MBT) on copper in 0.1 M  $H_2SO_4$  solutions was investigated [92] by bulk acoustic wave (BAW) sensor under open-circuit condition in this paper. The growth process of Cu-MBT complex film was monitored by the BAW sensor and the frequency shift curves were acquired. The frequency shift curves were fitted with a proposed model and the maximum frequency shift and the apparent rate constant of film formation were obtained. The relations between them and the concentration of MBT indicated the inhibition ability of the Cu-MBT complex film. The synergistic effects of  $Br^-$  and  $I^-$  on the Cu-MBT complex film formation were also compared. It was found that the effect of  $I^-$  was more obvious than that of  $Br^-$  at the same concentration of MBT and the growth kinetics of Cu-MBT film changed with the concentration of KI.

## CONCLUSION

The primary step in the action of organic corrosion inhibitors in acid solutions is usually adsorption at the metal-solution interface. The adsorption process depends on the electronic characteristic of the molecules (adsorbate), the chemical composition of the solution, nature of the metal surface, temperature of the reaction and on the electrochemical potential at the metal-solution interface [93]. The adsorption requires the existence of attractive forces between the adsorbate and the metal. According to the type of forces, adsorption can be physisorption or chemisorption or a combination of both [94]. Physisorption is due to electrostatic attractive forces between inhibiting organic ions or dipoles and the electrically charged surface of the metal. Chemisorption is due to interaction between unshared electron pairs or p electrons with the metal in order to form a coordinate type of bond. It may take place in presence of heteroatoms (P, Se, S, N, O), with lone-pair electrons and/or aromatic rings in the adsorbed molecules [95-98].

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