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Influence of Purine on Brass Behavior in Neutral and Alkaline Sulphate Solutions

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The behavior of Cu37Zn brass in the presence of purine in the wide concentration range ($1\cdot10^{-6}$mol/dm^3-$1\cdot10^{-2}$mol/dm^3) in a neutral and weakly alkaline 0.5mol/dm^3 Na_2SO_4 solution is studied using potentiodynamic polarization and chronoamperometry. Potentiodynamic polarization shows that purine acts like mixed-type inhibitor with a stronger influence on the corrosion processes in the weakly alkaline sulphate solutions. Protective effect of purine is caused by the formation of the layer on the brass surface. Chronoamperometric measurements were confirmed results obtained potentiodynamic measurements, indicating that the stability of the protective layer increase with increasing concentration of the inhibitor. Adsorption of purine on the brass surface proceeds according to the Langmuir adsorption isotherm.

Keywords: brass, purine, corrosion inhibiton, polarization

1. INTRODUCTION

Copper and its alloys have a wide range of applications in many branches of industry owing to their superior properties. Brass as one of the most important copper alloy has a wide range of application owing to his good corrosion properties. However, brass has relatively high corrosion resistance in different aggressive media. It is the reason why brass has been used for shipboard condenser and heat exchanger [1]. However, despite the good corrosion resistance brass is susceptible to corrosion in chloride and sulfate mediums [2-4]. That is way brass behavior was investigated in chloride [5, 6] and sulfate solutions [7, 8]. Metal dissolution as undesirable phenomenon must be reduced to the smallest possible degree and for that purpose inhibitors can be used. The greatest applications as corrosion inhibitors have organic compounds from different groups especially azoles: triazole [9-11], tetrazole [12], thiadiazole [13], imidazole [14-16]. The inhibitory properties of organic compounds depend of their structure and composition and presence of hetero atoms (N, S, O) in their structure improve inhibitory characteristics. Inhibition effect of compounds are closely related with adsorption on metal surface in the interaction between π-orbitals of the inhibitors and d-orbitals of the surface atoms which is also related with greater adsorption of the inhibitor molecules on alloy surface [17, 18]. Organic compounds from azoles group generally show good inhibitory properties but theirs main disadvantage is toxicity. In the scientific and professional community interest for finding effective and relatively cheap inhibitors grow which are biodegradable and nontoxic [19, 20, 21, 22]. Just a purine as a nontoxic compound investigated like copper corrosion inhibitor [23]. Purine structure is presented in Fig. 1.

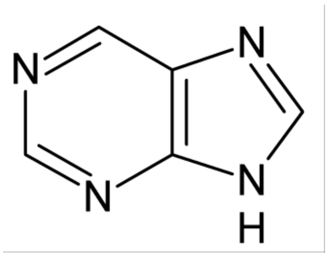

Figure 1. Purine structure

Purine and its derivatives were studied as aluminium [24], steel [25] and copper [23, 26, 27] corrosion inhibitors in acidic and neutral solutions. However, there are no studies on its effect on brass corrosion in neutral and alkaline medium and this is the reason why the main goal of this paper is examination of electrochemical behavior of brass in neutral and weakly alkaline sulphate solution in the presence of different concentration of purine.

2. EXPERIMENTAL

2.1. Materials

The following compounds were used in preparation of the solution: sodium sulphate (Na_2SO_4, Zorka Pharmacy Šabac), sodium hydroxide (NaOH, Zorka Pharmacy Šabac) of p.a. purity. During the experiments various concentrations of purine were used ($1\cdot10^{-6}$mol/dm^3, $1\cdot10^{-5}$mol/dm^3, $1\cdot10^{-4}$mol/dm^3, $1\cdot10^{-3}$mol/dm^3 and $1\cdot10^{-2}$mol/dm^3). A $2\cdot10^{-2}$mol/dm^3 sodium hydroxide solution was used for pH regulation of the working solution with and without the addition of purine. The pH value of all the solutions used during experimental work was measured with pH meter CyberScan pH 510 Euteh. The working electrode, whose surface was 0.49cm^2, was obtained by upcasting procedure. The sample used during the investigation was α+β brass containing 63% Cu and 37% Zn. Prior to each measurement, the brass electrode was polished with alumina paste (0.3μm Al_2O_3, Buehler USA) then rinsed with distilled water and dried afterwards.

2.2. Methods

Electrochemical measurements were performed using a potentiostat (Polarographic Analyzer PA2, Laboratorni Přistroje Prague, Czechoslovakia) that was directly connected to a computer via an AD card. The measurements were performed in a three-electrode system consisting of the brass working electrode, saturated calomel electrode (SCE), as the reference electrode and the platinum auxiliary electrode.

The open-circuit potential measurements (OCP), potentiodynamic measurements and chronoamperometry were the methods used for electrochemical investigation of brass in a Na_2SO_4 solution with the addition of purine as a corrosion inhibitor. All the measurements were read at least three times and the shown curves were obtained by averaging these values. The open circuit potential was recorded for 10 min, upon which cathode polarization was performed from the open circuit potential value to -0.5V vs. SCE.

Also, anodic polarization curves were recorded from the open circuit potential value to 0.5V vs. SCE. Chronoamperometric measurements were done for 5min at a potential of 0V vs. SCE. The surface of Cu37Zn electrode was observed through a metallographic microscope (Carl Zeis Jena 413609 Epytip 2) and with the help of digital photography (exposition time 1/160s). Metallographic recordings were performed with the aim of examining the structure of the electrode surface subsequent to treatment in a pure sulphate solution as well as in a sulphate solution containing the inhibitor.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization measurements in neutral 0.5mol/dm^3 Na_2SO_4 solution

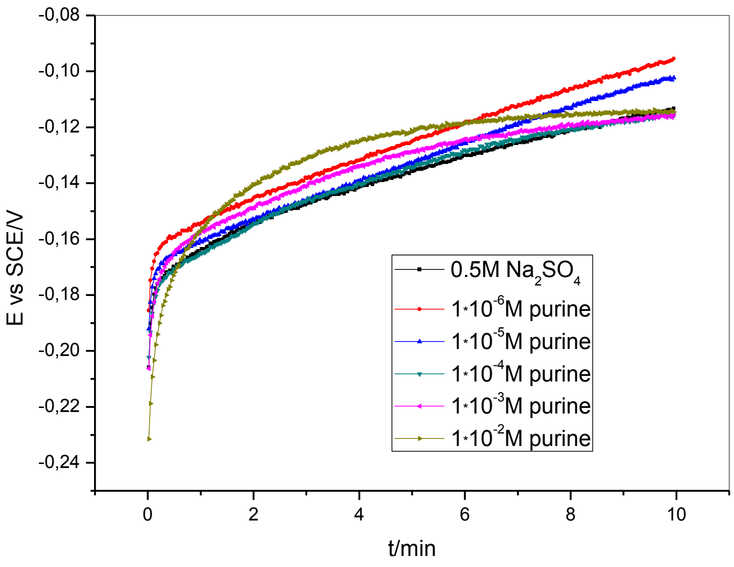

Figure 2. Open circuit potential of Cu37Zn brass in a neutral 0.5 mol/dm^3 Na_2SO_4 solution with and without the addition of various purine concentrations

Open circuit potential curves presented on Fig. 2 shows that with addition of $1\cdot10^{-5}$ and $1\cdot10^{-6}$mol/dm^3 purine OCP values go to the positive direction in the comparison with Na_2SO_4 solution without inhibitor and it is due to a more pronounced effect of the inhibitor on the anodic than on the cathodic reaction [28]. In other cases, in concentration interval from $1\cdot10^{-4}$ to $1\cdot10^{-2}$ mol/dm^3 OCP had values similar to the OCP recorded in the blank sulphate solution. Observed small shift in the OCP values indicated purine adsorption on brass surface which leads to blocking the active sites without influence on the mechanism of the corrosion processes [29].Fig. 3 shows potentiodynamic curves obtained by cathodic and anodic polarization of brass in a sodium sulphate solution with different purine concentrations ($1\cdot10^{-6}$-$1\cdot10^{-2}$mol/dm^3).

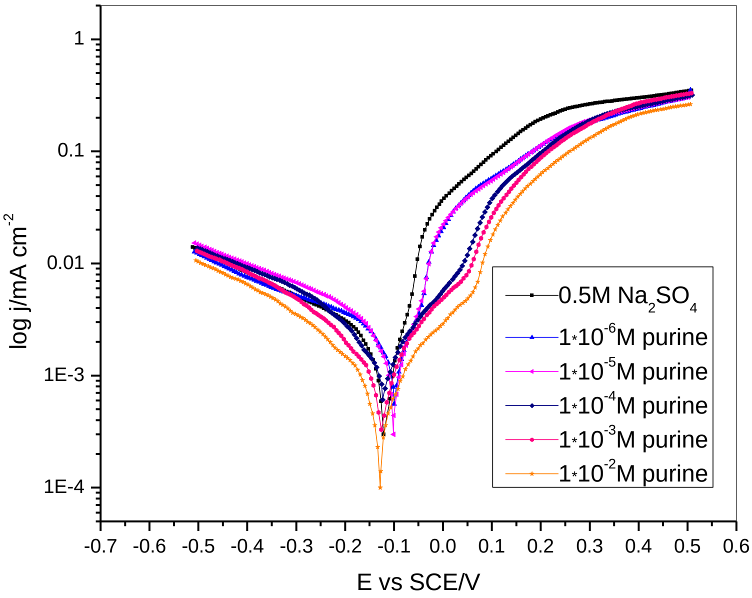

Figure 3. Polarization curves of brass in a neutral 0.5mol/dm^3 Na_2SO_4 solution with the addition of purine. Scan rate 1mV/s

Cathodic polarization curves indicate that purine no significant effect on the cathodic processes in sulphate medium. No effect of inhibition of purine in the concentration $1\cdot10^{-6}$ and $1\cdot10^{-5}$mol/dm on cathodic processes and in this cases higher cathodic current densities were observed than in blank sulpahe solution. The cathode reaction in a neutral Na_2SO_4 solution is [30]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

In the concentration range from $1\cdot10^{-4}$ to $1\cdot10^{-2}$mol/dm^3 purine shows inhibition effect which becomes most pronounced with increasing concentration. In the sulphate solution with purine concentration $1\cdot10^{-4}$mol/dm^3 at potentials more negative than -0.23V vs. SCE higher values of cathodic current densities were recorded than in the sulphate solution without purine. In the solutions with purine concentration $1\cdot10^{-3}$ i $1\cdot10^{-2}$mol/dm^3 cathodic current density was lower in the whole potential range in the comparasion with Na_2SO_4 solution.

The effect of purine on the anodic dissolution of brass in 0.5mol/dm^3 Na_2SO_4 can be seen in Fig. 3 and two anodic peaks were observed at anodic polarization curves in the blank sulphate solution. Potential of the first peak in the surroundings of the corrosion potential indicates to the Cu_2O formation while the second peak at 0.28V vs SCE is repercussion of CuO formation. Also, according to the literature data CuO formation by electrooxidation of the Cu_2O at potentials more positive than 0.25V vsSCE is confirmed [7]. In the presence of small amount of purine ($1\cdot10^{-6}$ and $1\cdot10^{-5}$mol/dm^3) only one anodic peak was observed which corresponding to the formation of Cu_2O while the second peak in these solutions was not observed which can be attributed to the inhibition action of purine. Despite the fact that purine influences the formation of copper oxide purine also affect on the anodic current density decrease. Influence of purine on the current density decrease becomes more pronounced with concentration increase in the whole observed potential range. This phenomenon may also indicate that purine acts like brass corrosion inhibition in neutral sulphate solution. Inhibition action of purine may be due to the formation of protective film on the electrode surface. In the sulphate solution during anodic polarization oxidation of copper to the Cu^+ was occurred [31]. These ions react with purine and form a protective complex according to reaction [26]:

$$Cu^{+} + PUH = \left[Cu - PU\right]_{ads} + H^{+}$$

$[Cu\text{-}PU]_{ads}$ layer compose strong barrier thus preventing mass transport and significantly slows electrode dissolution [23]. Purine adsorption mechanism on the electrode surface depends on pH solution due to purine can remain in the cation, anion or neutral molecule form in the dependence of the pH solution. In pH interval from 5 to 9 dominant purine form is neutral molecule which react with metal throw C_8 and N_1 atoms where negative charge is localized or throw N_9 atom where positive charge is localized [23]. During anodic polarization of brass influence of the inhibitor concentration on stability of formatted film was followed and accordingly it is obviously that with increase of purine concentration increase stability of formatted layer on brass surface. However, at higher potentials current density increase thereby protective layer crack which leads to the anodic dissolution of the alloy and formation of Cu(II)products.

Since zinc is a more electronegative metal than copper, the dissolution of zinc is expected to occur at lower potentials though copper dissolution occur later at higher potentials. In the sulphate solutions alloy dissolution is consequence of sulphate ions action hindering the formation of adsorb layers. The high aggressiveness of sulphate ions can be result of local pH increase near to metal surface [31]. Nevertheless, when the purine is present in the solution then probably purine molecules repress sulphate ions and take more spaces on electrode surface. However, in the neutral sulphate solutions without inhibitor, SO_4^{2-} ions can be adsorbed on the electrode surface and can cause further anodic dissolution of metal with form Cu_2SO_4 [2].

The electrochemical corrosion parameters of brass such as: corrosion potential (E_{corr}), corrosion current density (j_{corr}), the cathodic and anodic Tafel slopes (β_c and β_a) are shown in Table 1. The values of E_{corr}, j_{corr}, β_c and β_a were obtained on the basis of polarization curves shown in Fig. 3. Besides the kinetic parameters, the inhibition efficiency for different concentration is also given in Table 1 and is calculated according to the following equation:

$$IE = \frac{j_{corr} - j_{corr(inh)}}{j_{corr}} \cdot 100[\%]$$

where j_{corr} and $j_{corr(inh)}$ represent corrosion current density in the absence and presence of the inhibitor.

Table 1. Electrochemical parameters of brass oxidation in a neutral 0.5 mol/dm^3 Na_2SO_4 solution in the presence of various purine concentrations

C_{inh}/mol dm^{-3}	E_{corr}vs SCE/V	β_c	β_a	j_{corr}/μA cm^{-2}	IE/%
/	-0.121	-0.189	0.050	4.6	/
$1\cdot10^{-6}$	-0.100	-0.660	0.124	3.0	34.8
$1\cdot10^{-5}$	-0.101	-0.396	0.108	2.2	52.2
$1\cdot10^{-4}$	-0.123	-0.368	0.174	1.9	58.7
$1\cdot10^{-3}$	-0.126	-0.242	0.183	1.0	78.3
$1\cdot10^{-2}$	-0.128	-0.218	0.191	0.68	85.2

As it can be seen from Table 1, with the addition of the inhibitor E_{corr} values did not change significantly. However, with purine addition in small amount ($1\cdot10^{-6}$ mol/dm^3 and $1\cdot10^{-5}$ mol/dm^3) E_{corr} is shifted to more positive direction. Conversely purine in the higher concentrations ($1\cdot10^{-4}$-$1\cdot10^{-2}$ mol/dm^3) shift corrosion potential slightly to the negative values compared to E_{corr} obtain in a blank sulphate solution. However, corrosion potential shift in solutions with purine addition are not higher than 21mV compared to corrosion potential obtained in a sulphate solution without purine which indicate that purine acts like mixed-type inhibitor in neutrale sulphate medium [32]. Also, purine has influence on β_c and β_a values suggestion that inhibitor decrease aggressive accessible surface particles [33]. Near with corrosion potential, anodic and cathodic Tafel slopes in Tabele 1 values of the corrosion current density are present. Compared values for j_{corr} obtained in Na_2SO_4 solution with and without purine indicate that purine decrease current density and that effect is more pronounced with inhibitor concentration increase. Furthermore, as the inhibitor concentration increases, the degree of efficiency increase as well.

3.2. Potentiodynamic polarization measurements in a weakly alkaline 0.5mol/dm^3 Na_2SO_4 solution

Open circuit potential is followed in the weakly alkaline solution and obtained, as opposed to neutral sulphate solution that OCP become more negative with inhibitor addition compared to blank sulphate solution. However, OCP shift in the solution with purine is maximum 55mV compared to Na_2SO_4 solution without inhibitor. The slight open circuit potential shift indicates that even in a weakly alkaline medium purine behaves as a mixed- type inhibitor [28].

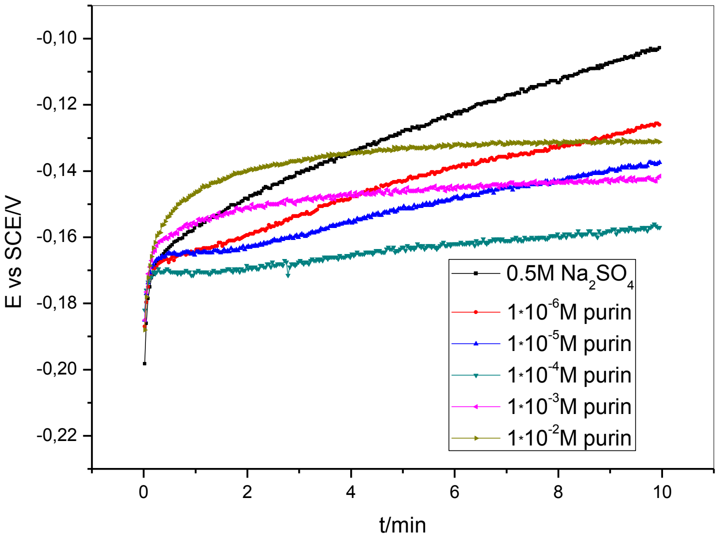

Figure 4. Open circuit potential of Cu37Zn brass in a 0.5 mol/dm^3 Na_2SO_4 alkaline solution without and with the addition of various purine concentrations

Potentiodynamic measurements were performed in a weakly alkaline Na_2SO_4 solution with and without purine and obtained curves were presented at Fig. 5. On the base of cathodic and anodic polarization curves it can be said that presence of purine decrease cathodic and anodic current density. Inhibitor concentration may largely affect on inhibition effect and importances of the concentrations of purine are present on Fig. 5. In the vicinity of the corrosion potential purine influence on cathodic processes is evident and with further shift of the potential to the more negative values purine action is not insignificant. During anodic polarization in the vicinity of the corrosion potential decrease of current density is distinct in the presence of different amount of purine compared with blank sulphate solution.

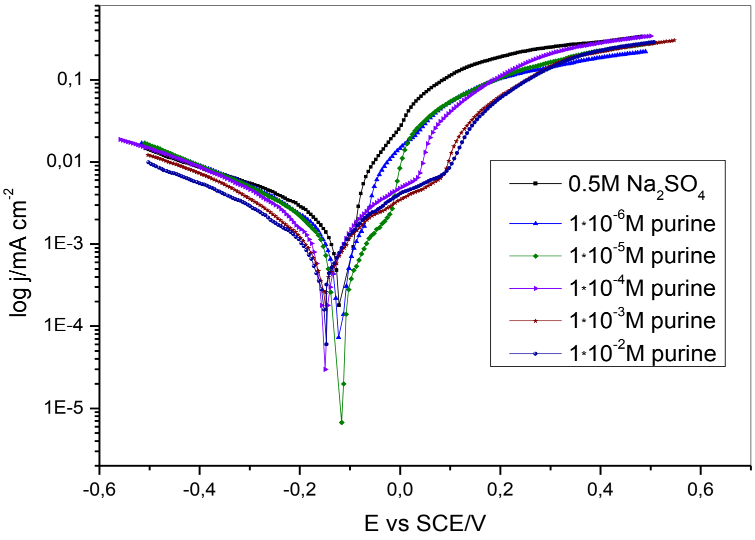

Figure 5. Polarization curves for brass in a weakly alkaline 0.5mol/dm^3 Na_2SO_4 solution with the addition of purine. Scan rate 1mV/s

Only at potentials more positive than 0.3V vs. SCE inhibition action become weak depending on the present concentration of purine. Nonetheless, according to potentiodynamic measurements purine in the weakly alkaline solution acts like mixed-type inhibitor with larger influence on anodic corrosion processes. Nevertheless, from anodic polarization curves in the concentration range from $1\cdot10^{-4}$ to $1\cdot10^{-2}$mol/dm^3 existence of potential area where the current density grow slowly with potential increase was observed. This potential area become more pronounced with purine concentration increase and likely indicates formation of protective layer on the electrode surface. In the solutions with lower purine concentration ($1\cdot10^{-6}$ mol/dm^3 and $1\cdot10^{-5}$mol/dm^3) this influence of the anodic current density of potential shift did not observed as a consequence of insufficient amount of the inhibitor required for the formation of a stable complex [34]. In this regard compared clean polished brass surface (Fig. 6A) with brass surface after OCP measurement in the solution with purine (Fig. 6B) color change was observed which indicates the formation of the film on the brass surface.

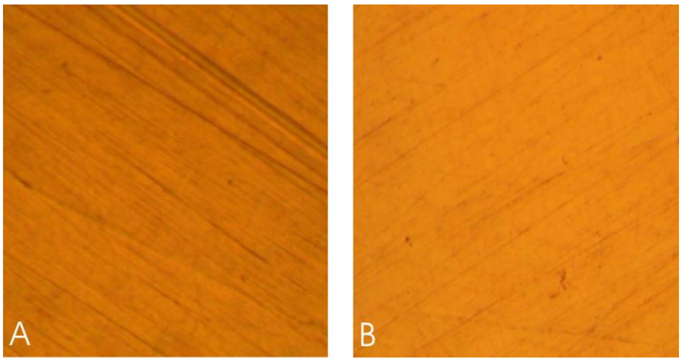

Figure 6. Brass Cu37Zn surface after polishing (A) and after OCP measurement in 0.5 mol/dm^3 Na_2SO_4 solution with $1\cdot10^{-4}$mol/dm^3 purine (B) (magnified 200x)

From Fig. 5, it can be seen that with further polarization leads to area when current density rises sharply which can be correlated with reducing protective effect of the film and its breakdown. Breakdown potential depends of the inhibitor concentration in such a way that the increase of the concentration shifts breakdown potential to the more positive values. Stability of the protective film as a function of the potential scan is shown in Fig. 7. As can be seen from Fig. 7A at 0V vs. SCE formatted film is stable, but with further potential increase film dissolves and comes to brass oxidation (Fig. 7B and 7C) which is in agreement with results obtained during potentiodynamic polarization. During the anodic oxidation with the increase potential on brass surface first comes to Cu_2O adsorption that is replaced, at higher potential, by thermodynamically stable CuO. Nevertheless, CuO layer is being destroyed rapidly in contact with SO_4^{2-} it comes to building soluble sulphate and formation of pits. In this process $CuSO_4\cdot3Cu(OH)_2$ is formed that in alkaline solution transforms in more stable $Cu(OH)_2$ making the pit structure more complex [35].

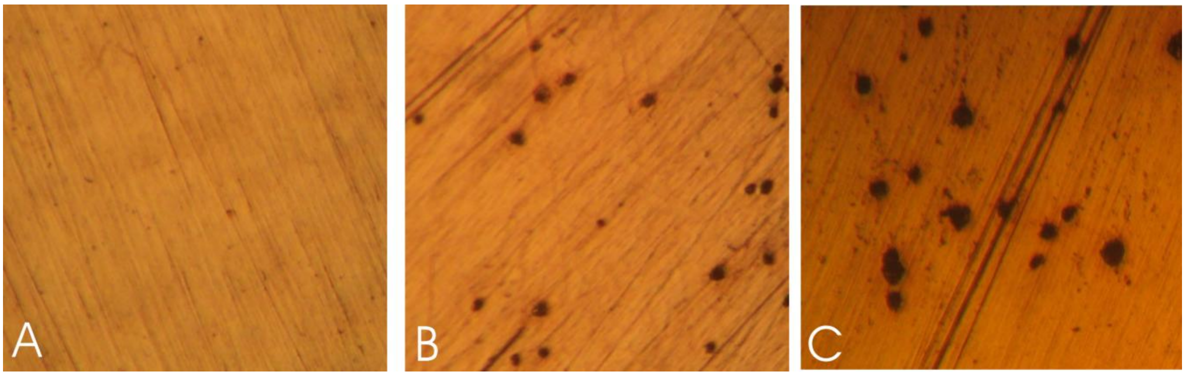

Figure 7. Brass surface after potentiodynamic measurements in alkaline 0.5mol/dm^3 Na_2SO_4 solution with $1\cdot10^{-2}$mol/dm^3 purine at 0V vs. SCE (A), 0.2V vs. SCE (B), 0.5V vs. SCE (C) (magnified 200x)

Corrosion parameters of brass oxidation in a weakly alkaline sulphate solution with different amount of purine (Table 2) were obtained according potentiodynamic curves presented in Fig. 3.

Table 2. Electrochemical parameters of brass oxidation in a weakly alkaline 0.5 mol/dm^3 Na_2SO_4 solution in the presence of various purine concentrations

C_{inh}/mol dm^{-3}	E_{corr}vs SCE/V	β_c	β_a	j_{corr}/µA cm^{-2}	IE/%
/	-0.122	-0.936	0.163	3.0	/
$1\cdot10^{-6}$	-0.123	-0.274	0.105	1.2	60.0
$1\cdot10^{-5}$	-0.117	-0.203	0.1	0.83	72.3
$1\cdot10^{-4}$	-0.149	-0.168	0.156	0.78	74.0
$1\cdot10^{-3}$	-0.148	-0.162	0.146	0.54	82.0
$1\cdot10^{-2}$	-0.147	-0.098	0.066	0.27	91.0

E_{corr} values as well as β_c and β_a for brass in alkaline medium indicate similar brass behavior as in neutral solutions. Compared j_{corr} values in neutral and weakly alkaline Na_2SO_4 solutions shows that in the presence of purine j_{corr} has lower values in alakline media indicating stronger effect on the inhibition.

3.3. Chronoamperometry

Chronoamperometric curves obtained in neutral and weakly alkaline solutions at a potential of 0V vs. SCE in the presence of the inhibitor are presented in Fig. 8 and Fig. 9 and indicate similar behavior.

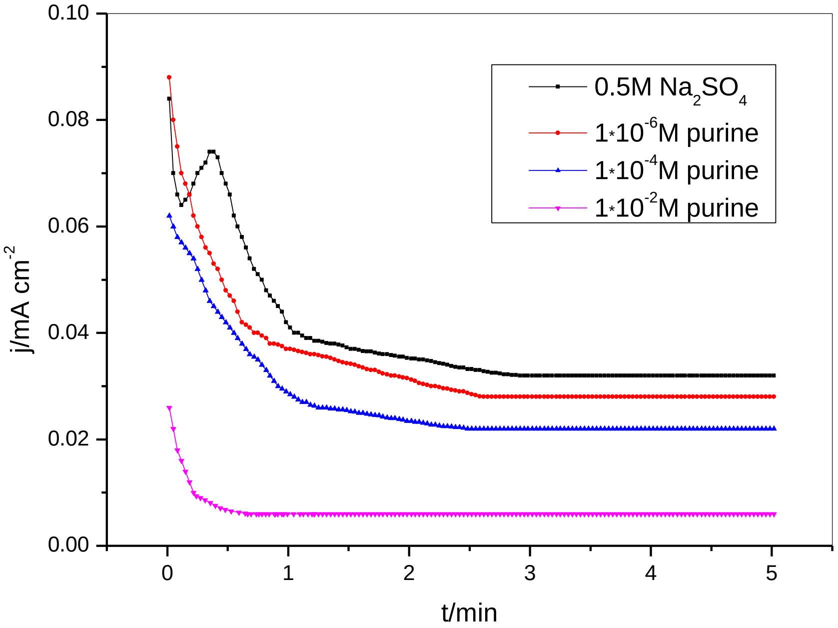

Figure 8. Chronoamperometric curves recorded at 0V vs. SCE in a neutral Na_2SO_4 solution with the addition of purine

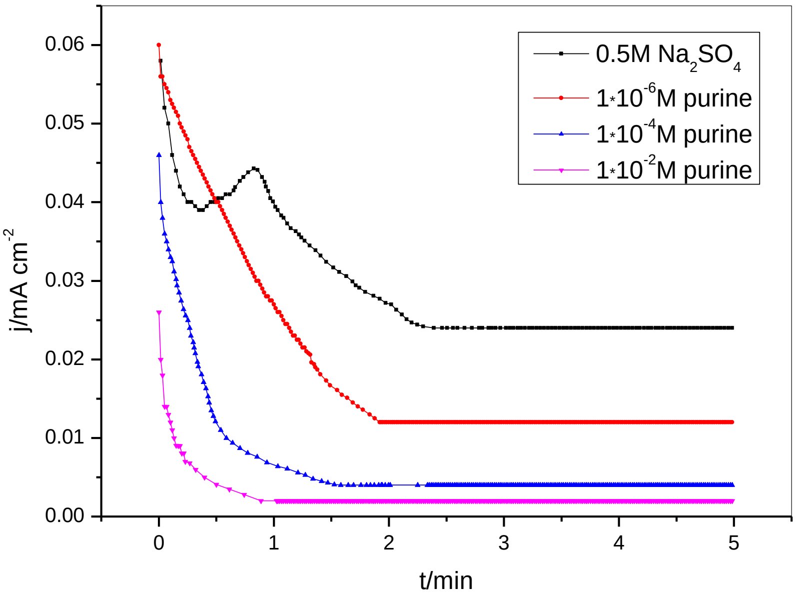

Figure 9. Chronoamprometric curves recorded at 0V vs. SCE in a weakly alkaline Na_2SO_4 solution with the addition of purine

Existence of current peaks in neutral and weakly alkaline Na_2SO_4 solutions without purine detected in Fig. 8 and Fig. 9 probably indicates the formation of brass oxidation products [36]. Also, in sulphate solution with different purine amount current density decrease which can presumably indicative of the formation of the protective layer on the brass surface [37, 38]. Nevertheless, compared current density obtained in neutral and weakly alkaline solutions lower values were noted in alkaline media ascribed to the stronger purine effect on corrosion processes and enhanced activities of purine can be correlated to its structure in alkaline solutions. Nonetheless, in the alkaline media besides molecular form of purine occurred negative ions which increased inhibition effect and facilitate adsorption [27, 39]. Brass oxidation and corrosion products formation in blank Na_2SO_4 solutions as well as stable protective layer formation in presence of purine confirmed after examination of brass surface after chronoamperometric measurements as shown in Fig. 10.

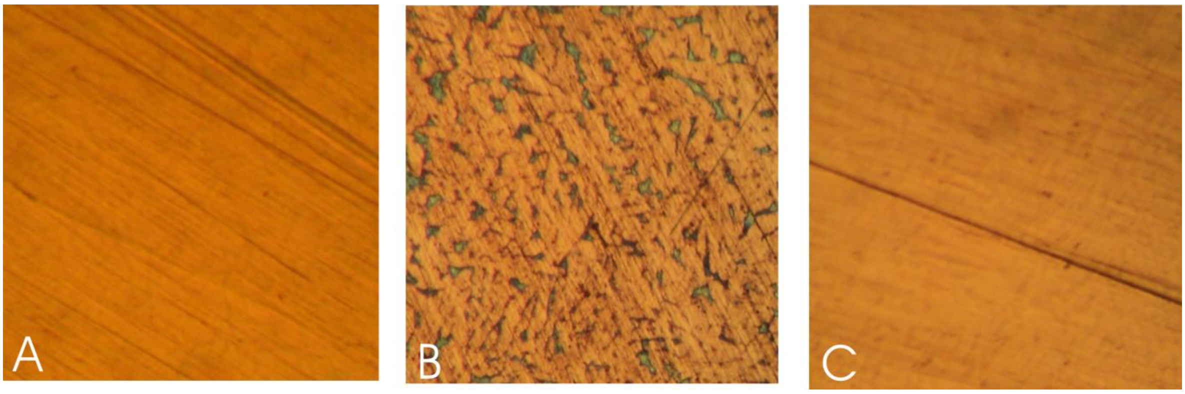

Figure 10. Brass surface after polishing (A), after chronoamperometric measurements at 0V vs. SCE in weakly alkaline 0.5mol/dm^3 Na_2SO_4 solution (B) and after chronoamperometric measurements at 0V vs. SCE in weakly alkaline 0.5mol/dm^3 Na_2SO_4 solution with $1\cdot10^{-2}$ mol/dm^3 purine (C) (magnified 200x)

3.4. Adsorption isotherms

Importances of adsorption isotherms are to provide the information about the interaction between the inhibitor and the electrode surface. Adsorption isotherms complements data obtained by electrochemical measurements and gives a more detailed picture of the effect of inhibitors and mechanisms of inhibition. The effects of inhibitors may be subject to physical adsorption or chemisorption of the inhibitor on the surface of the investigated metal [40]. Fig. 11 and Fig. 12 show plots of C/θ against purine concentration in neutral and weakly alkaline solutions. The results show that purine adsorption follows the Langmuir adsorption isotherm and adsorption equation reads:

$$\frac{\theta}{1-\theta} = AC\exp\left(\frac{-\Delta G}{RT}\right) = KC$$

where K- represents adsorption constant, ΔG-adsorption energy, C- purine concentration and θ-surface coverage degree:

$$\theta = \frac{\left(j_{corr} - j_{corr(inh)}\right)}{j_{corr}}$$

Adsorption equation can be also written in the following form:

$$\frac{C}{\theta} = \frac{1}{K} + C$$

Adsorption constant can be calculated from the following equation:

$$K = \frac{1}{55.55}\exp\left(-\frac{\Delta G}{RT}\right)$$

Adsorption energy is calculated using the following equation:

$$-\Delta G = \left(\ln K - \ln\frac{1}{55.55}\right)RT$$

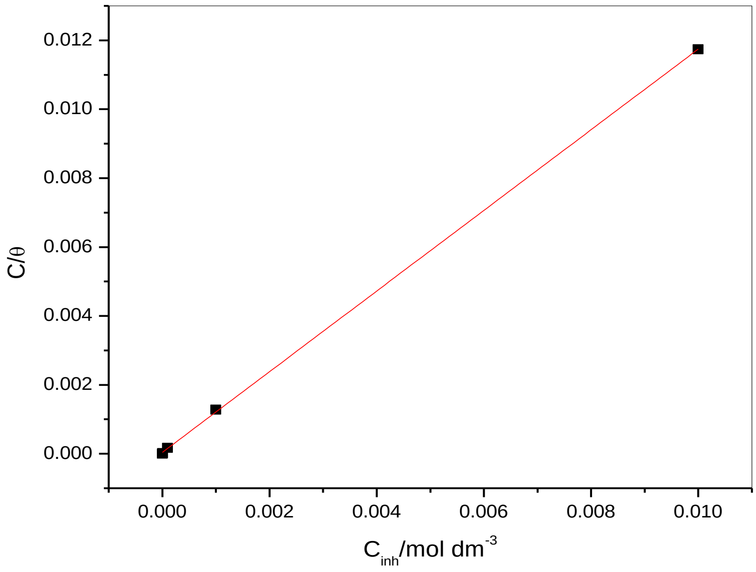

Figure 11. Langmuir adsorption isotherm of purine in a neutral 0.5mol/dm^3 Na_2SO_4 solution

The values of the Gibbs adsorption energy in neutral and weakly alkaline solutions as well as values of the slope are presented in Table 3. It can be seen that the value of the slope in neutral and in weak alkaline sulphate solutions diverge from the ideal case which shows the interaction between the adsorbed molecules on the surface of the brass [26, 41]. The negative values of ΔG indicate that a spontaneous adsorption occurs on the electrode surface. The values of the Gibbs adsorption energy suggest that both in neutral and weakly alkaline media cysteine chemisorption take place on the brass surface. Close values for ΔG indicates that there is no significant difference in the mechanism of adsorption of inhibitor in both media on the surface of the electrode.

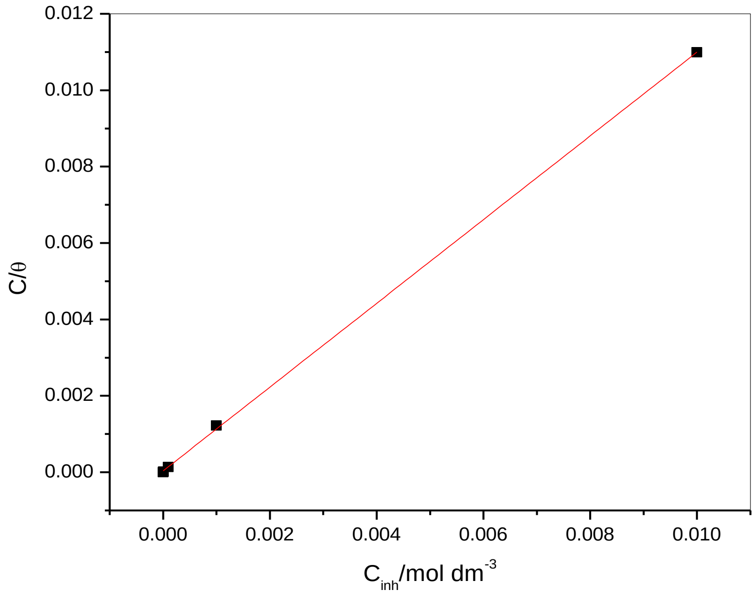

Figure 12. Langmuir adsorption isotherm of purine in a weakly alkaline 0.5mol/dm^3 Na_2SO_4 solution

Table 3. Adsorption energy values of purine in 0.5mol/dm^3 Na_2SO_4

	pH 7	pH 9.2
Slope	1.17	1.09
R^2	0.9999	0.9998
ΔG/ kJ mol	-34.4	-34.7

4. CONCLUSION

On the basis of potentiodynamic measurements can be said that purine acts like mixed-type inhibitor with a stronger influence on the corrosion processes in the weakly alkaline sulphate solutions. Protective effect of purine is caused by the formation of the layer on the brass surface with the increasing concentration of the inhibitor efficiency increases. Chronoamperometry measurements were confirmed results obtained potentiodynamic measurements, indicating that the stability of the protective layer increase with increasing concentration of the inhibitor. Purine adsorption on the brass surface proceeds in accordance with the Langmuir adsorption isotherm. The values of the Gibbs energy of adsorption point to a spontaneous chemisorption of the inhibitor on the electrode surface in neutral and weakly alkaline sodium sulphate solutions.

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