

ELECTROCHEMICAL STUDY OF FeS DISSOLUTION IN ACID SOLUTIONS IN THE PRESENCE OF BENZOTHAZOLIC COMPOUNDS

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The corrosion and inhibition behaviour of iron monosulfide (FeS) in 0.1M HCl solution in the absence and the presence of 2-(cyclohexylaminomercapto)-benzothiazole (CMB) and 2-mercaptobenzothiazole (MBT) was investigated using electrochemical measurements such as: Tafel polarization (TP) and electrochemical impedance spectroscopy (EIS). The morphology of FeS surface was examined using scanning electron microscopy (SEM) analysis. The inhibition efficiency (IE %) increased with benzothiazolic compounds concentration and the experimental results suggest that the presence of CMB and MBT in the solution increases the surface coverage (θ) and therefore, indicate the adsorption of organic compounds. The adsorption of CMB compound on the metal surface obeys Temkin's adsorption isotherm. SEM images showed the evidence modification of FeS surfaces morphology corroded in presence of the inhibitors.

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1. Introduction

The Fe-chalcogenide superconductors are the simplest Fe-based superconductors. Fe chalcogenides form several types of crystal structures, according to the elemental composition, synthesis process and synthesis conditions of temperature or pressure. Oxidation reactions and mechanisms of this compounds type were analysed in different ways and different experimental conditions [1-3].

Oxidation of sulphide surface produced oxygen-sulphur species, which exchanged further with the anion present in the solution to form a complex. Oxidation products of sulphide mineral are affected by pH as well as time. At relative low potentials, the surface of sulphide were oxidized to produce elemental sulphur. At higher potentials, the surface of sulphide were oxidized to produce sulphate, thiosulphate, metal hydroxide and metal sulphate. It was generally agreed that the oxidation rate of sulphide minerals were faster at high potential than at low potential. Also, the oxidation rate are higher in the presence of a ionic corrosive species and lower in the presence of a metal-ligand complex former anion.

One of the most important methods in corrosion protection of different substrates is the use of organic inhibitors to protect the material surface from the corrosive media [4-13]. Sulfur compounds have a strong affinity to transition metal surfaces. Organic sulfur compounds coordinate very strongly to the surface of the different materials. The number of reported surface-active organic sulfur compounds that form layers on metal surfaces has increased in recent years. The available results show that most inhibitors act by adsorption on the substrate surface [14-21]. The inhibition efficiency of organic compounds is strongly dependent on the structure and chemical properties of the layer formed on the surface under particular experimental conditions. CMB and MBT were tested as inhibitors for corrosion of carbon steel in alkaline media [18, 20]

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and in acidic solution [19]. In order to study the inhibition of organic sulfur compounds in the selected medium, a number of methods can be used. Among the rapid methods of detection are electrochemical measurements [22].

This study discusses the results of characterization techniques like potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and SEM images, for behavior of unmodified and modified surfaces of FeS with benzothiazolic compounds namely: 2-(cyclohexylaminomercapto) benzothiazole (CMB) and 2-mercaptobenzothiazole (MBT) in acidic media.

2. Experimental

Electrochemical measurements

For electrochemical measurements a standard cell has been used with a plate working electrode (surface 1.5 cm²) made of FeS, a platinum auxiliary electrode (surface 1 cm²) and a Ag/AgCl, KCl_{sat} reference electrode. The electrode made of FeS was polished with metallographic paper, washed in distilled water, degreased in acetone and dried in warm air. For each determination the samples were introduced for 15 minutes, at room temperature in following media: 0.1 M HCl blank solution and 0.1 M HCl solutions containing different concentrations of MBT and CMB: 0.2mM; 0.3mM; 0.4mM; 0.5mM. All reagents were obtained from Merk. A potentiostat VoltaLab 40 connected to a Computer with VoltaMaster 4 software was used in the measurements.

Surface characterization

The morphology of FeS surface, before and after treatment was examined using a Vega Tescan electronic microscope.

3. Results and discussion

Potentiodynamic polarization

Potentiodynamic polarizations were recorded for a FeS electrode (surface area was 1.5 cm²) immersed in 0.1 M HCl and 0.1 M HCl solutions containing different concentrations of MBT and CMB: 0.2mM; 0.3mM; 0.4mM; 0.5mM, at room temperature, with a scan rate of 1 mV/s. The extrapolation of anodic and cathodic Tafel lines of charge transfer controlled corrosion reaction gives the corrosion current density, i_{corr} , (e.g. Figure 1).

The cathodic and anodic curves obtained exhibit Tafel - type behavior. Addition of MBT and CMB increased both the cathodic and anodic overvoltages and caused mainly parallel displacement to the more negative and positive values, respectively. The corrosion current density (i_{corr}) decreased with increasing the concentration of MBT and CMB, which indicates that these compounds act as inhibitors, and the inhibition degree depends on the concentration and type of inhibitors. For example, in 0.1 M HCl i_{corr} decreases from 342 $\mu\text{A}\cdot\text{cm}^{-2}$ (in the absence of inhibitors) to 65 $\mu\text{A}\cdot\text{cm}^{-2}$ ([CMB] = 0.5mM) and 95.8 $\mu\text{A}\cdot\text{cm}^{-2}$ ([MBT] = 0.5mM). The coverage degree (θ) of the FeS surface were calculated using the following relation:

$$\theta = \frac{i'_{corr} - i_{corr}}{i'_{corr}} \quad (1)$$

where i'_{corr} and i_{corr} are the corrosion current density for the FeS surface in absence and presence of inhibitors, respectively, obtained by extrapolation of the anodic and cathodic Tafel lines to the corrosion potential. The coverage degree increases with inhibitors concentration and decreases

with corrosion current density increase (Figure 2). The presence of a benzothiazolic ring and S-atoms in CMB and MBT molecules can enhance the binding between FeS surface and organic compounds, which consequently results in the formation of impermeable assembled layer. This layer restrains faradaic processes such as electrode oxidation and the exchange of electrons between the electrode and solution. The property of this blocking is attributed to the compactly packed structure of the layer, which obstructs the approach of solution Cl^- ions to the electrode surface. The inhibition efficiency (IE %) was calculated using the relation 2.

$$\text{IE} = \theta \cdot 100 \quad (2)$$

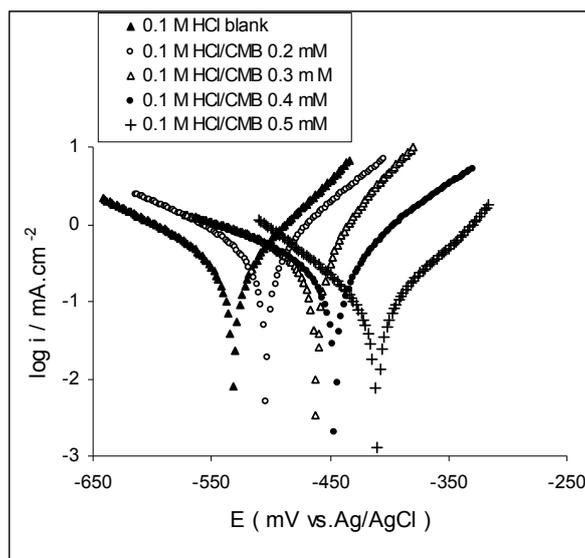


Fig. 1. Tafel diagram of FeS corroded in 0.1 M HCl solutions in absence and presence of CMB inhibitor.

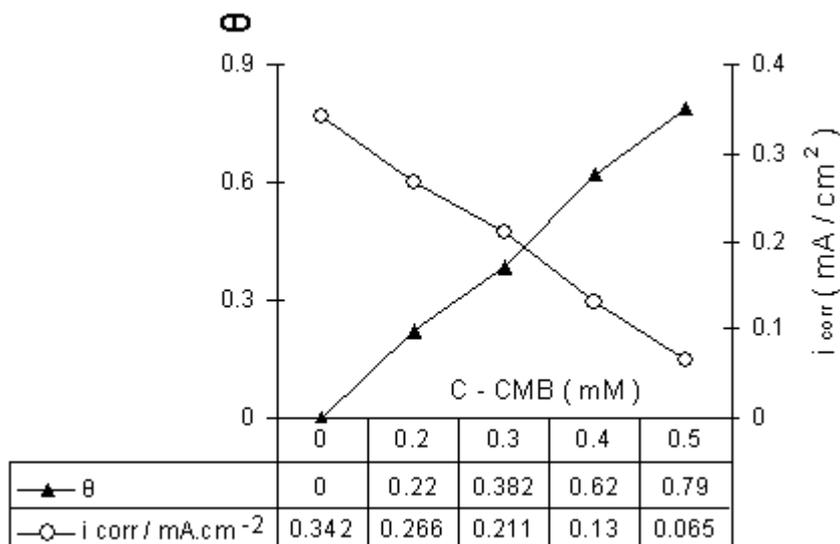


Fig. 2. Variation of corrosion current density (i_{corr}) and the coverage degree (θ) with the concentration of CMB for the FeS electrode in 0.1 M HCl.

Similar curves were also obtained for MBT inhibitor. The inhibition efficiency (IE %) at 0.5mM inhibitors concentration in 0.1 M HCl solution reaching a maximum value of 81 % for CMB and 72 % for MBT respectively, indicating that CMB is more efficient as inhibitor than

MBT. The comparative polarization curves between MBT and CMB inhibitors are presented in Figure 3.

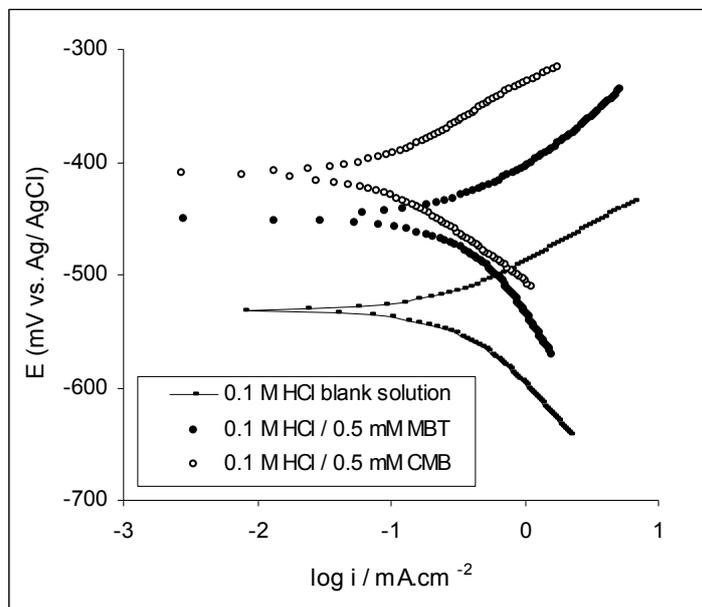
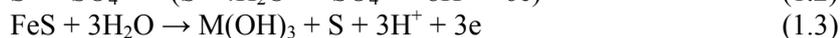
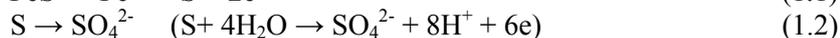


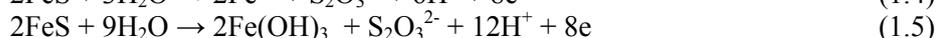
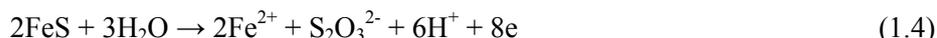
Fig. 3. Polarization curves of FeS corroded in 0.1 M HCl solution in absence and presence of benzothiazolic compounds.

According to the experimental data we proposed the following dissolution mechanism of iron monosulphide (FeS):

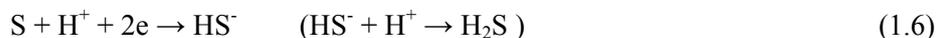
The initial oxidation (anodic reactions) of iron sulphides in acid solution corresponds to a reaction of the type:



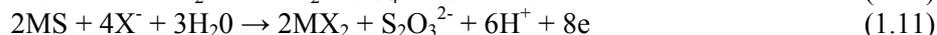
Alternative oxidation reactions may lead to the production of oxy-sulphur species



Cathodic reactions:



The reaction mechanism of inhibitors chemisorption



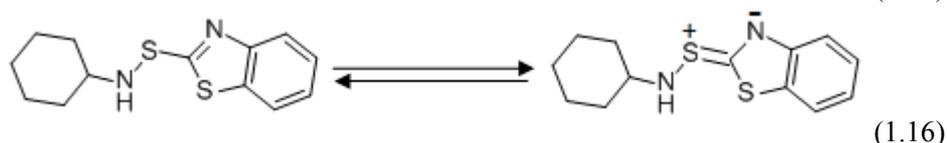
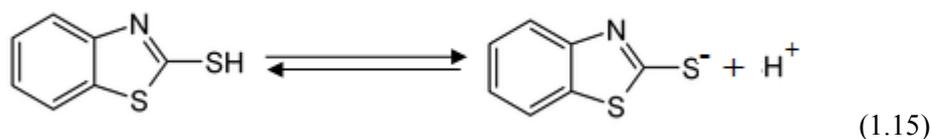
where X^- represents a (thio) ion and MS represents the sulphide mineral.

The overall reactions were





The molecular structures for the anion X^- are presented in the following reactions:



Electrochemical impedance spectroscopy

The electrochemical impedance measurement (EIS) is a technique that has been used for a long time to study electrochemical processes at the electrode surface. It is a valuable and convenient method to give information on impedance changes of the electrode surface in the modified process. In electrochemical impedance experiments, a small ac voltage is applied to an electrode/solution interface and corresponding electrochemical impedance is obtained. Impedance measurements were carried out at the open circuit potential (E_{ocp}), which was determined from open circuit (Figure 4).

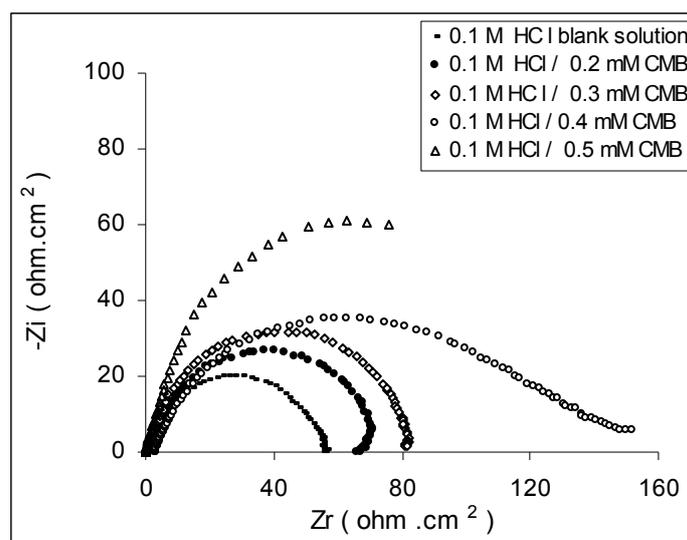


Fig. 4. The measured impedance of FeS corroded in 0.1 M HCl solution in absence and in the presence of CMB.

Fig. 4 shows the impedance measurements of a FeS electrode in 0.1 M HCl solution and in 0.1 M HCl containing CMB in different concentrations vs. Ag/AgCl, KCl_{sat} reference electrode, in the frequency range from 10^5 to 10^{-1} Hz with a value of 10 mV for the amplitude. In the case of the inhibitor adsorption, the impedance spectrum is represented like a Nyquist diagram with a capacitive arc of circle more or less leveled, which presents a phase shift comparative with the real axis. This phase shift is due to the density variations or to the composition of the film or of the electrode surface coating.

The size of the capacitive arcs of circles phase differed comparative with the axes is increasing in the case of solution containing the inhibitor. The formed film is not tridimensional; the impedance diagram would be more complex. For an enough thick film (some μm), the impedance spectrum from the Nyquist plot is formed from two capacitive arcs of circles more or less

uncoupled at certain frequencies. As show the Figure 4 a typical Nyquist diagram is obtained; when CMB is adsorbed from 0.1 M HCl solution on the FeS electrode a semicircle with a different diameter is obtained, in higher frequency region related to charge transfer process. This region is electrically described by a resistance in parallel with a capacitor related to the double-layer (figure 4). In this region the reaction is purely kinetically controlled. According to the data obtained from Nyquist plots it can observed that R_p increases with increasing CMB concentration (see table 1). It is clear that the presence of CMB film produced a higher R_p value, which is an indication of the formation of an effective protective layer that hindered corrosion, which indicates that these compounds act by adsorption on the substrate and the degree of inhibition depends on the concentration and type of inhibitors present. The electrode coverage (θ) is a key factor, which can be used to estimate the surface state of the electrode and it is related to the charge transfer resistance. According to this assumption, the following equation for the apparent fractional coverage of the electrode can be used:

$$\theta = 1 - \frac{R_p^0}{R_p} \quad (3)$$

where R_p^0 is the polarization resistance of FeS corroded in acidic medium in absence of the inhibitors and R_p is the polarization resistance of FeS corroded in acidic medium in presence of the inhibitors.

The similar diagram was also obtained for MBT inhibitor. It can be concluded that R_p increases from $33.4 \Omega \cdot \text{cm}^2$ in the absence of inhibitors to $175.4 \Omega \cdot \text{cm}^2$ and $119.3 \Omega \cdot \text{cm}^2$ in the presence of CMB and MBT, respectively, in 0.1 M HCl solution containing 0.5 mM inhibitors. The data obtained for the inhibition efficiency (IE %) at 0.5 mM inhibitors concentration in 0.1 M HCl solution namely 79 % for CMB and 71 % for MBT respectively, confirm that CMB is more efficient as inhibitor than MBT. The comparative Nyquist diagram obtained for MBT and CMB is presented in Figure 5.

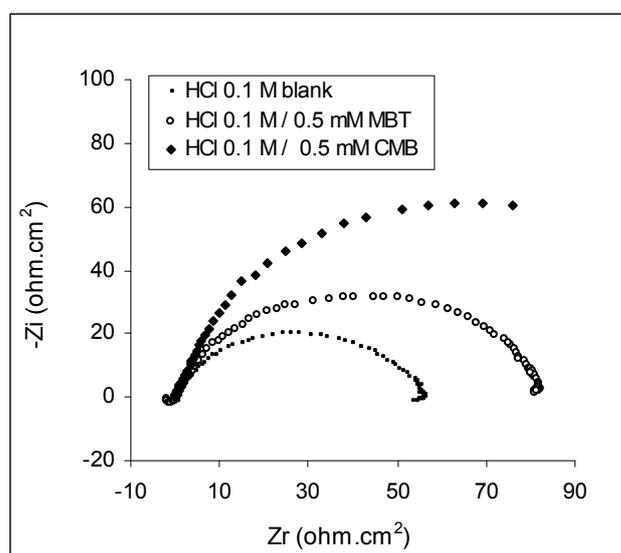


Fig. 5. The measured impedance of FeS corroded in 0.1 M HCl solution in absence and in the presence of inhibitors.

The variation of R_p and the coverage degree (θ) with the concentration of CMB for the FeS electrode in 0.1 M HCl is presented in Figure 6.

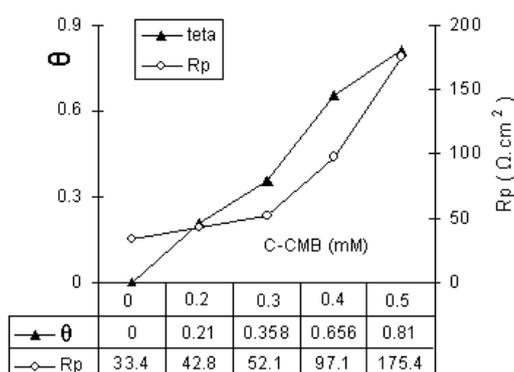


Fig. 6. Variation of R_p and the coverage degree (θ) with the concentration of CMB for the FeS electrode in 0.1 M HCl.

These results are consistent with those obtained by Tafel polarization.

Adsorption isotherm study

By studying the CMB inhibitor we have reached the conclusion that the experimental data characterize an adsorption isotherm of Temkin type expressed by linearization form (equation 4); an example is shown in Figure 7.

$$\theta = \frac{2.303}{f} \log K + \frac{2.303}{f} \log C \quad (4)$$

where f is a Temkin factor; θ is degree of coverage; K is the equilibrium constant of the adsorption-desorption process, C is CMB concentration.

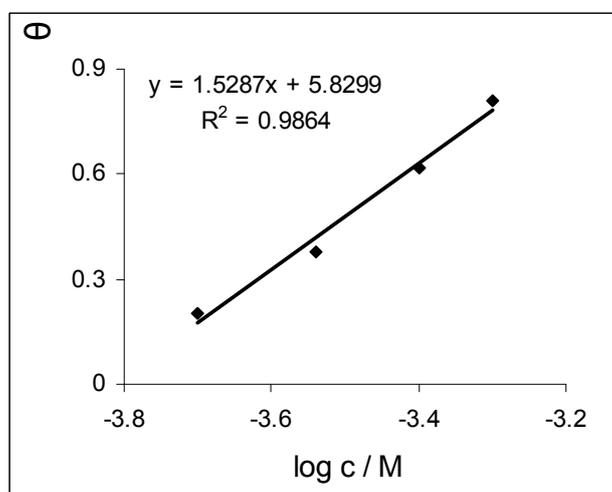


Fig. 7. The results of a Temkin diagram in the case of corrosion inhibition of FeS electrode in 0.1 M HCl solution with CMB, at room temperature.

The data plotting gave a straight line; the slope of this line represents $2.303/f$ and the intercept with the ordinate representing $(2.303/f) \log K$. It can be observed that K has a high value of $7700 \text{ L}\cdot\text{mole}^{-1}$. The equilibrium constant K varies towards the same direction, in the sense that higher values of K imply a better adsorption. The standard free energy of adsorption ΔG_{ads}^0 was calculated using equation (5):

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^0}{R \cdot T}\right) \quad (5)$$

where R is the ideal gas constant, T is temperature and 55.5 is the molar concentration of water in the solution. The value of ΔG_{ads}^0 is negative ($-32 \text{ KJ}\cdot\text{mol}^{-1}$), which shows that the process of adsorption is spontaneous.

The observed corrosion data in presence of CMB and MBT, namely:

- the decrease of corrosion current with increase in concentration of benzothiazolic compounds;
- the shift in Tafel lines to higher potential regions;
- the degree of coverage increases with inhibitors concentration and decreases with increasing in the corrosion current density;
- R_p increases for the surfaces which were corroded in 0.1 M HCl solution in the presence of various concentrations of CMB and MBT;
- the inhibition efficiency was shown to depend on the number of adsorption active centers in the molecule and their charge density.

The corrosion inhibition is due to adsorption of CMB and MBT, respectively, at the electrode/solution interface, the extent of adsorption of an inhibitor depends on the nature of the substrate, the mode of adsorption of the inhibitors and the surface conditions. The adsorption of CMB and MBT molecules also produces important modifications in the structure of the double electric layer. The effect of surface blockage becomes dominant, which leads to a decrease in the number of active centres. CMB and MBT are organic compound that contain both N- and S- atoms in the molecules. These inhibitors can be easily adsorbed on the surface of the FeS. Up to date, most of the investigations suggest that inhibitors are bound to the surface mainly through S-atom bond and formation of a substrate-S bond occurs. However, it has been suggested that CMB and MBT might bind to the FeS surface through their N-atom. The inhibitors form stable layer on the substrate surface, which increases the corrosion resistance of FeS in 0.1 M HCl solution.

Surface characterization

SEM images examination of FeS surface corroded in 0.1 M HCl solution in absence and presence of CMB was carried out (Figure 8).

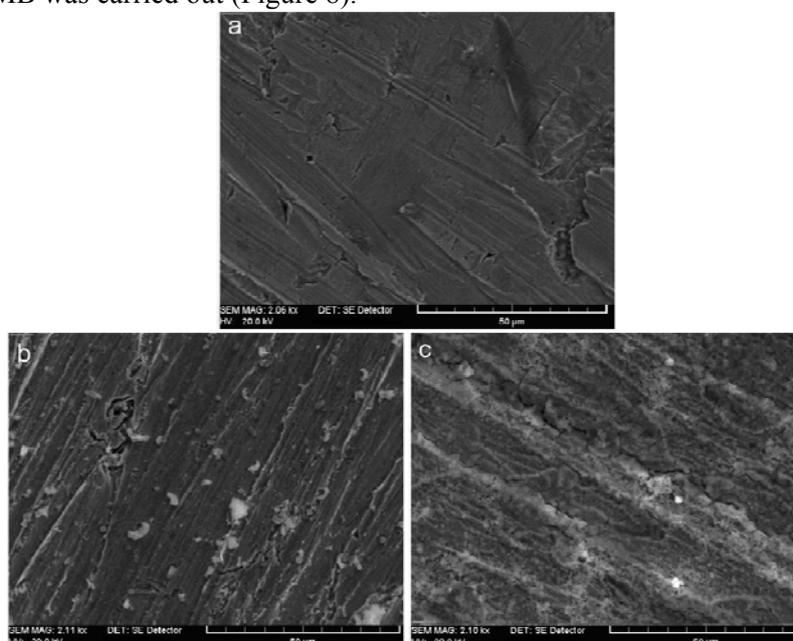


Fig. 8. SEM images of the FeS surfaces: (a) before corrosion; (b) immersed in 0.1 M HCl blank solution; (c) immersed in 0.1 M HCl/0.5 mM CMB.

In case “8b” random spread corrosion spots can be noticed. In „8c” case the texture is modified and the corrosion spots have a low intensity; the layer uniformity is more apparent and

the feature of a coating, forming a matrix in which are embedded certain inhibitor molecules is relatively nuanced.

4. Conclusions

CMB and MBT are inhibitors for FeS corrosion in a solution of 0.1 M HCl. The data obtained from Tafel polarization, for the inhibition efficiency (IE %) at 0.5mM inhibitors concentration in 0.1 M HCl solution indicated 81 % for CMB and 72 % for MBT respectively, confirming that CMB is more efficient as inhibitor than MBT.

According to the data obtained from Nyquist plots it can be observed that R_p increases with increasing CMB and MBT concentration; the inhibition efficiency (IE %) at 0.5 mM inhibitors concentration in 0.1 M HCl solution namely 79 % for CMB and 71 % for MBT respectively, confirm that CMB is more efficient as inhibitor than MBT.

These results are consistent with those obtained by Tafel polarization. CMB and MBT act through adsorption on the FeS surface. The adsorption of CMB compound on the metallic surface obeys Temkin's adsorption isotherm; the standard free energy (ΔG_{ads}^0) is negative, showing that the adsorption process of CMB on the FeS surface is spontaneous.

SEM images shown the evidence modification of FeS surfaces morphology corroded in presence of the inhibitors.

Acknowledgments

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