

POTENTIODYNAMIC POLARIZATION AND GRAVIMETRIC EVALUATION OF CORROSION OF COPPER IN 2M H₂SO₄ IN ABSENCE AND PRESENCE OF AMMONIUM DICHROMATE AS AN INHIBITOR

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ABSTRACT

Corrosion resistance behaviour of copper was evaluated in 2M H₂SO₄ in absence and presence of ammonium dichromate as an inhibitor. The experiments were performed at ambient temperature of 25°C using gravimetric and potentiodynamic polarization measurements. The values of the corrosion rate, the polarisation resistance and the inhibitor efficiency were estimated. The results obtained verified copper susceptibility in H₂SO₄ in absence of an ammonium dichromate inhibitor and in its presence a good corrosion inhibition of the metal was achieved.

Keywords: copper, corrosion, sulphuric acid, ammonium dichromate, polarization, inhibition.

INTRODUCTION

Copper and its alloys have excellent corrosion resistance. This quality is coupled with combinations of other desirable properties that include superior electrical and thermal conductivity, ease of fabricating and joining, a wide range of attainable mechanical properties, and resistance to biofouling [1 - 3]. The metal and its alloys provide very good, and in most cases, superior service in many of the applications which include roofing and other architectural uses, hardware, building fronts, grille work, hand rails, lock bodies, doorknobs, and kick plates. They are also used for freshwater supply lines and plumbing fittings, which require very good corrosion resistance in aqueous and soils environments, for heat exchangers and condensers, electrical wiring, hardware and connectors, printed circuit boards, electronic applications, lead frames and connectors, industrial and chemical plant process equipment, marine applications, etc.

The significant importance of copper in general and its protection in adverse corrosive environments determined the great research interest [1 - 11]. Weeks et al. [1] investigated the mechanism of copper initial corrosion in hydrochloric acid solutions using a radioactive tracer technique. The authors obtained kinetic data

showing the effect of pH, that of dissolved oxygen and chloride ions present, as well as that of temperature on the corrosion rate. They determined the specific rate constants, the enthalpies and entropies of activation of the rate determining step. The data obtained provided the elaboration of the mechanism of the corrosion process studied.

Sherif [12] reported the corrosion behaviour of unalloyed copper (99.999 % Cu) in hydrochloric acid pickling and its inhibition by different concentrations of 3-amino-1,2,4-triazole (ATA) and 3-amino-5-mercapto-1,2,4-triazole (AMTA). He performed the experiments using potentiodynamic polarization, chronoamperometry, electrochemical impedance spectroscopy (EIS), and Raman spectroscopy. He confirmed that the inhibition of copper corrosion in an acid solution was achieved through the strong adsorption of these organic molecules on the copper surface preventing thus the formation of cuprous chloride and oxy-chloride complex compounds.

The rate of corrosion of copper in presence of methyl amine, dimethyl amine, diethyl amine, triethyl amine, diethanol amine, and triethanol amine was determined [13] by measuring the anodic limiting current. The effect of the type of the organic amine compounds, their concentration, H₃PO₄ concentration, the solution viscosity,

density, diffusion coefficient, and rate of rotation was also studied. The inhibition rate increased in the order: methyl amine, dimethyl amine, diethyl amine, triethyl amine, diethanol amine, and triethanol amine. The rate of corrosion in presence of each inhibitor studied depended on the concentration of H_3PO_4 and on the electrode height.

Shahrabi et al. [14] studied the inhibition effect of some nitrogen heterocyclic compounds like 2-mercaptobenzimidazole (2-MBI), 2-mercaptobenzoxazole (2-MBO) and 2-mercaptobenzo-thiazole (2-MBT) on copper corrosion in 0.5M sulphuric acid. It was found that the inhibition efficiency of all compounds investigated increased with their concentration increase. Furthermore, their adsorption on the copper surface was found to obey the Langmuir adsorption isotherm and besides they all acted as mixed inhibitors. The latter conclusion was drawn on the ground of Tafel polarization studies. A number of studies [15 - 20] were performed on copper corrosion in different media using different organic compounds as inhibitors.

2M H_2SO_4 is used in the present investigation as a test medium. Sulphuric acid is a very versatile inorganic acid with wide industrial applications. It is known that copper does not displace hydrogen from non-oxidizing acids like HCl or dilute H_2SO_4 . However, concentrated sulphuric acid is an oxidizing agent and when copper is heated in it a redox reaction occurs and the acid is reduced to sulphur dioxide. Ammonium dichromate ($(NH_4)_2Cr_2O_7$) used as an inhibitor in this work is an inorganic compound. Chromium is in a +6 oxidation state in this compound, as in all chromates and dichromates. It is commonly known as hexavalent chromium. It is a salt consisting of ammonium ions and dichromate ions.

This work aims at evaluating the corrosion resistance of copper in dilute sulphuric acid and its corrosion protection in presence of ammonium dichromate as an inhibitor. Results of economic/technological benefit are expected.

EXPERIMENTAL

Specimens' preparation

Copper of 99.9 % purity was used in this investigation. The copper metal sample was cut into 20 mm x 20 mm coupons for weight loss and potentiodynamic polarization measurements. The test samples used for the weight loss experiment were ground with various grades

of emery paper and then polished to 6 μm . They were further rinsed in distilled water to remove any corrosion products and then degreased with acetone. The prepared samples were stored in a desiccator for subsequent use. The samples for the corrosion polarization experiments were cleaned following the procedure described above. Then they were mounted in resin to ensure that only the tested surface of the sample was exposed to the corrosive medium. Prior to the mounting, copper wire was spot welded to each of the samples.

Weight loss experiment

The weighed test specimens were immersed for 20 days in the test medium placed in a 200 ml beaker. Two test coupons were used for each test and the average weight was further used. The experiments were performed in 2M H_2SO_4 in absence and presence of ammonium dichromate of a various concentration. The ammonium dichromate was used as received, without dilution and was taken as 100 % inhibitor concentration. Its subsequent appropriate dilution at a given proportion gave the rest % concentrations used.

The specimens were taken out of the test medium every 2 days during the experimental period, washed with distilled water, rinsed in methanol, air-dried, re-weighed and then re-immersed in the test solution for continued study. The plots of accumulated weight loss and of corresponding calculated corrosion rate versus the exposure time are respectively presented in Figs. 1 and 2. The corrosion rate was calculated using Eq. (1):

$$C. R. (mmpy) = 87.6 \times (W / DAT) \quad (1)$$

where C.R. was the corrosion rate, mmpy stood for millimetres per year, W was the weight loss in milligrams, D was the metal density (g/cm^3), A was the exposed area of sample (cm^2), while T was the time of exposure (h).

The inhibitor efficiency (%), P, was evaluated on the ground of:

$$P = 100[1 - W_2/W_1] \quad (2)$$

where W_1 and W_2 were the corrosion rates in absence and presence of ammonium dichromate, respectively. The results obtained are used to plot the curve and the chart of the inhibition efficiency vs. the exposure time (Figs. 3 and 4).

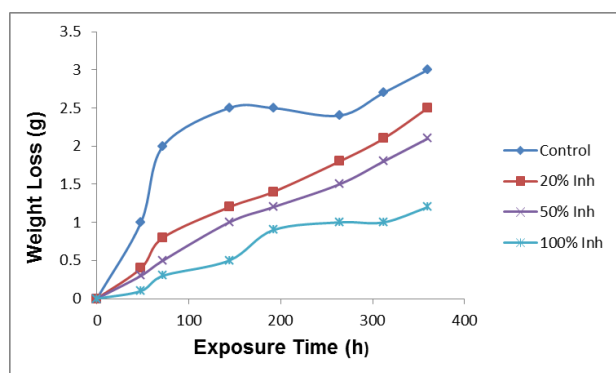


Fig. 1. Copper weight loss versus exposure time in 2M sulphuric acid solution with and without ammonium dichromate addition.

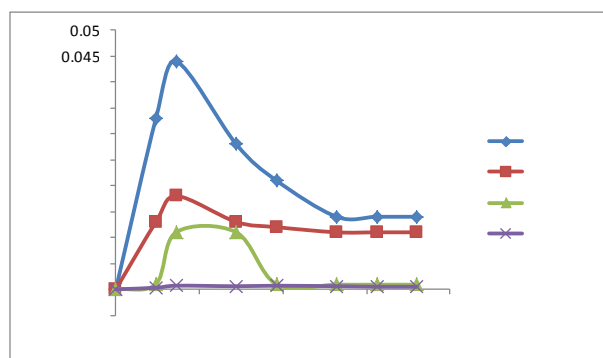


Fig. 2. Copper corrosion rate versus exposure time in 2M sulphuric acid solution with and without ammonium dichromate.

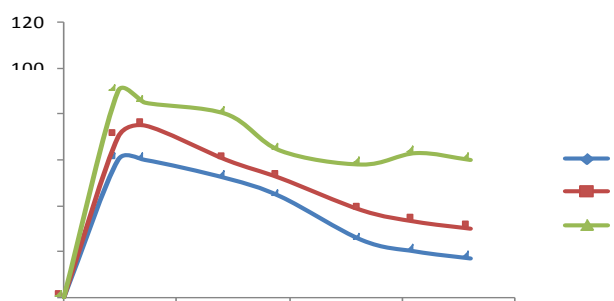


Fig. 3. Ammonium dichromate inhibition efficiency versus exposure time in 2M H₂SO₄.

Potentiodynamic polarization experiments

Potentiodynamic polarization experiments were performed using the mounted specimens. The latter were immersed in an acid test medium in absence and presence of ammonium dichromate.

1 cm² surface area of the specimen was exposed to the test solution at room temperature. The experiments were performed using a polarization cell with a three

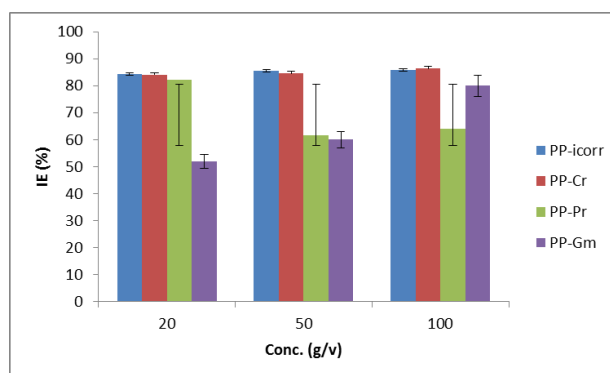


Fig. 4. Inhibition efficiency (IE) in 2M sulphuric acid obtained in the course of PP-CR, PP-Icorr, PP-LPR and PP-GM (PP-CR-potentiodynamic polarisation corrosion rate; PP-I_{corr} = potentiodynamic polarisation corrosion current density; PP-LPR = potentiodynamic polarisation

electrode system consisting of a reference electrode (silver chloride electrode, SCE), a working electrode (WE) and two carbon rod counter electrodes (CE). The potentiodynamic studies were made at a scan rate of 0.00166 V/s from -1.5 V to +1.5 V. The polarization cell was connected to a potentiostat (Autolab PGSTAT 30 ECO CHIMIE) and interfaced with a computer for data acquisition and analysis. The corrosion currents were recorded. All chemicals used were of an analytic reagent grade (AR).

SEM/EDS Characterisation

Uninhibited and inhibited copper samples were examined to determine their surface morphology using a scanning electron microscope (SEM studies). Representative micrographs are presented in Figs. 7 and 8. Energy dispersive spectroscopy and optical microscopy were also applied. Some of the photomicrographs obtained are presented in Fig. 9.

RESULTS AND DISCUSSION

Weight loss experiments

The results referring to the weight loss of copper immersed in H₂SO₄ in absence and presence of ammonium dichromate of a different concentration are presented in Fig. 1. The weight loss (g) increases with the exposure time increase. Weight loss of 3.1 g, 2.5 g, 2.05 g and 1.2 g was recorded in the course of the control experiment (in inhibitor absence) and in presence of 20 %, 50 %

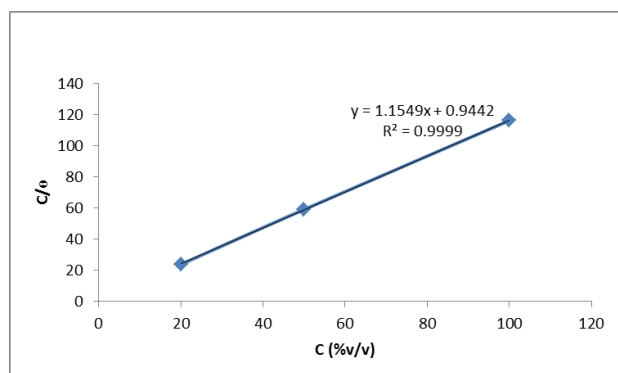


Fig. 5. Langmuir isotherm trend referring to the adsorption of ammonium dichromate inhibitor on copper surface in 2M sulphuric acid solution.

and 100 % (an inhibitor concentration) during the test duration of 360 h. Apparently the higher the inhibitor concentration added, the less the weight loss is. Thus it can be concluded that the ammonium dichromate provides significant corrosion inhibition, particularly at high concentrations. The corresponding corrosion profile is presented in Fig. 2. The corrosion rate values decrease with the inhibitor concentration increase. This trend achieves a near zero value of 0.001 mmpy for 100 % $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ concentration and also for 50% concentration after 200 h (8th day) of the experiment.

The inhibition efficiency obtained on the ground of the corrosion rate data (Fig. 3) and the polarization data (Fig. 4) confirm the effectiveness of ammonium dichromate as an inhibitor of copper corrosion in 2M H_2SO_4 . Fig.3 shows that the inhibition efficiency increases initially but then starts to decrease with the exposure time increase. This can be explained with the test environment change attributed to the stifling effect of the corrosion deposits emanating from the corrosion reaction.

Table 1. Polarisation results referring to copper corrosion in 2M H_2SO_4 and its inhibition by $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

Inhibitor concentration	ba (V/dec)	bc (V/dec)	E _{corr} , Obs (V)	j _{corr} (A/cm ²)	Corr. rate (mm/y)	Polarization resistance (Ω)	E Begin (V)	Inhibitor efficiency (%)
Uninhibited.	0.93448	0.33299	-0.21064	.005622	3.1154	18.964	-1.1269	0
2 ml (20 %)	0.008568	0.036325	.052609	0.00089	0.49602	8.3834	0.03265	84.08
5 ml (50 %)	0.029333	0.025737	0.1197	.000816	0.47916	7.2933	0.08850	84.62
10 ml (100 %)	0.019844	0.03466	0.23278	0.0008	0.42509	6.8474	0.2063	86

The IE obtained in case of 100 % inhibitor concentration ranges from 85 % to 62 % for 50 h and 360 h duration, correspondingly. These are the best inhibition values. They are followed by those obtained in 50 % inhibitor presence. Table 1 shows that the inhibitor efficiency increases with inhibitor concentration increase reaching values of 84.08 %, 84.62 % and 86 % for 20 %, 50 % and 100 % inhibitor concentrations, respectively.

Adsorption isotherm

Molecular adsorption is suggested to explain the corrosion inhibition observed. The factors which influence the adsorption process [22] include the charge distribution in the inhibitor molecule, the nature and the surface charge of metal, the chemical structure of the organic compound studied as an inhibitor, and the type of aggressive medium.

Studying the adsorption behaviour is very important in determining the mechanism of organo-electrochemical reactions [22]. The experimental data obtained are best fitted by the Langmuir adsorption isotherm:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (3)$$

where $\frac{C}{\theta}$ is the ratio of the inhibitor concentration, C , and the surface coverage, θ , while K_{ads} is the adsorption equilibrium constant. Fig. 5 shows that the adsorption isotherm describes well the experimental data (the correlation coefficient is 0.9999). The latter value indicates a strong adherence of the adsorption characteristics of the inhibitor to the model of Langmuir.

Potentiodynamic polarisation method

Table 1 shows the summary of the results obtained in the analysis of copper corrosion and the respective

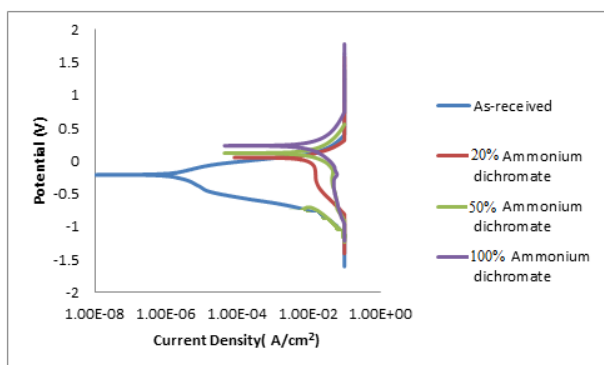


Fig. 6. Polarization curves of copper in 2M sulphuric acid solution in absence and presence of ammonium dichromate.

inhibition in H_2SO_4 . The potentiodynamic polarisation results referring to various concentrations of ammonium dichromate are illustrated in Fig. 6. The data in Table 1 shows that the corrosion current density, i_{corr} (A/cm^2), values decrease with inhibitor concentration increase.

The uninhibited sample has the highest corrosion current density value. As expected, the corrosion rate (mm/y) and the polarisation resistance (Ω) values decrease with inhibitor concentration increase. These results indicate that the inhibitor effectiveness increases with the inhibitor concentration increase. They also show progressive increase of the inhibition passivity engendered by the inhibitor's passive film that adheres to the electrode's surface. The open corrosion potential designated by E_{corr} (V) increases, that is, the potential values shift anodically with increase of the inhibitor concentration – the highest shift is observed at the greatest inhibitor concentration studied (Fig. 6).

Surface morphology

The surface morphology of the samples of the uninhibited and inhibited copper is studied by SEM and Energy dispersive spectroscopy (EDS). The results obtained are illustrated in Figs. 7 and 8. The photomicro-

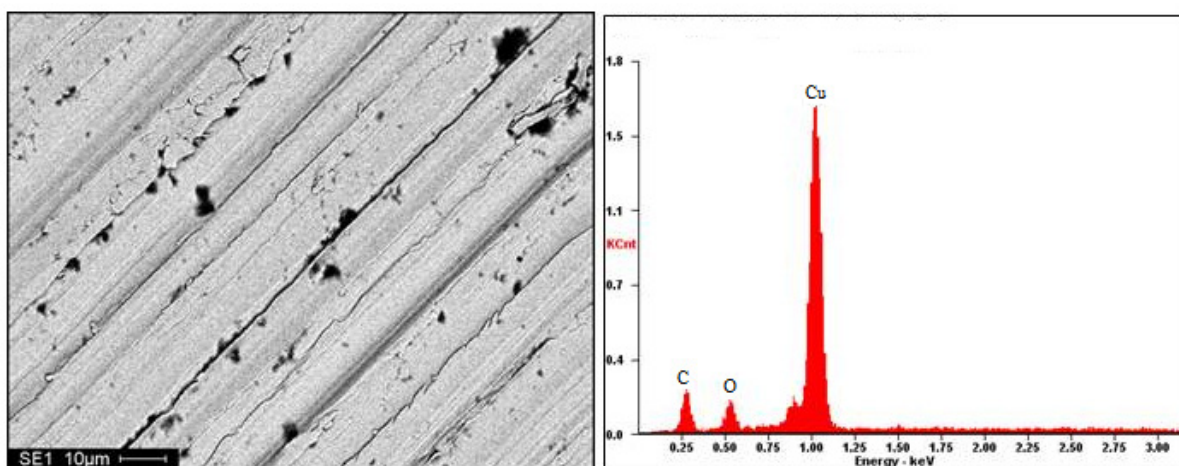


Fig. 7. SEM/EDS micrograph of copper (as received) in 2M sulphuric acid solution.

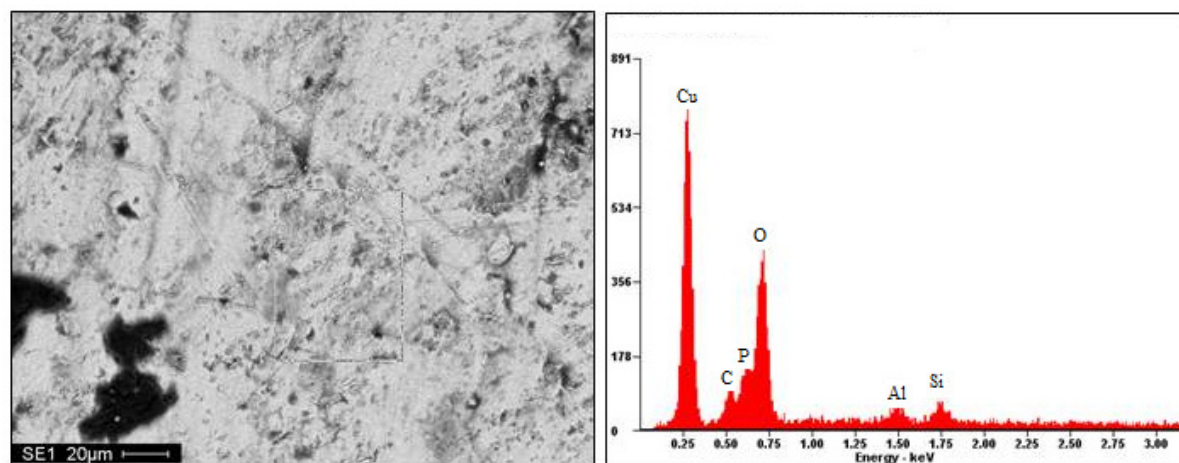


Fig. 8. SEM/EDS micrograph of copper in 2M sulphuric acid solution in presence of 100 % ammonium dichromate.

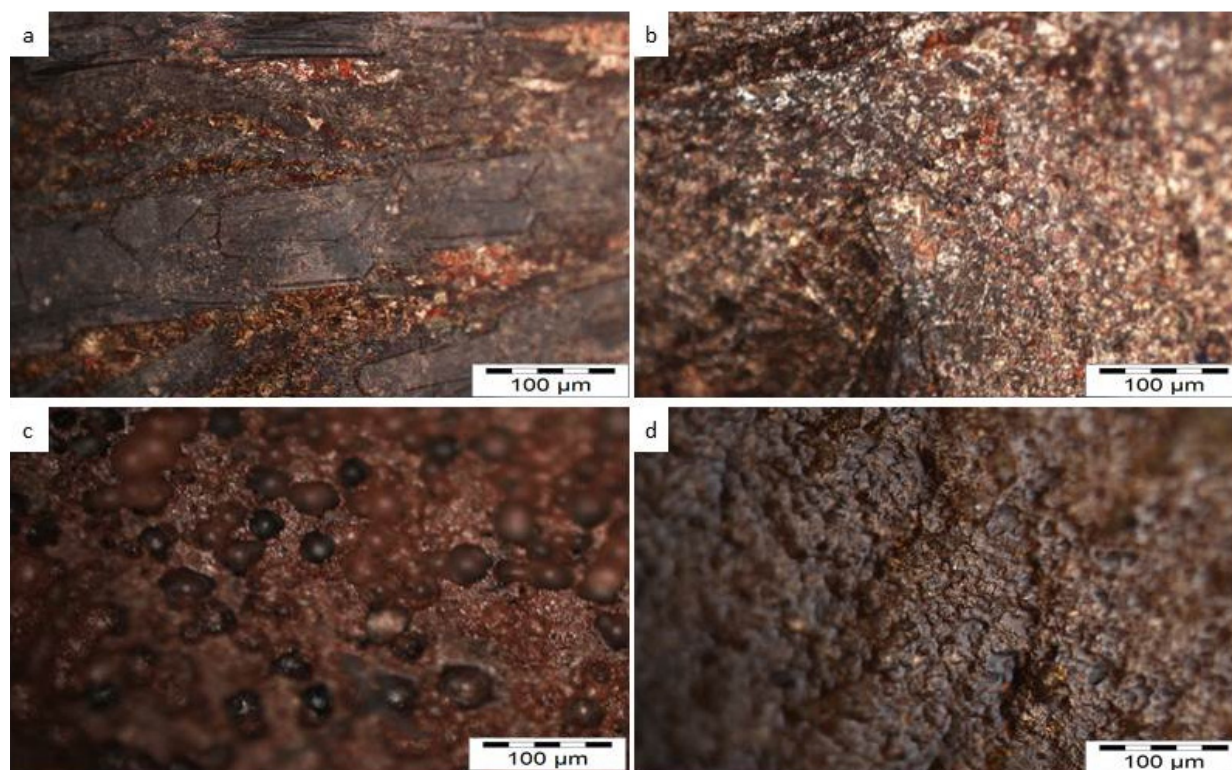


Fig. 9. Optical micrographs of corroded Cu in 2M H₂SO₄: (a) in presence of 100 % inhibitor, (b) in presence of 50 % inhibitor, (c) in presence of 20 % inhibitor, (d) in inhibitor absence.

graphs of the surface corrosive degradation as observed with an optical microscope are presented in Fig. 9. Fig. 7 shows that there is no apparent surface defect attributed to corrosion as the sample is directly cut from the metal received. The EDS shows mainly the copper peak. The oxygen and carbon peaks outlined are most probably due to the exposure to the atmosphere or the rinsing medium.

Fig. 8 shows the SEM and EDS micrograph of a test sample after the experiment. The surface is slightly degraded due to the protective action of the inhibitor through the corresponding surface film formation. The EDS shows mainly the copper peak. However, traces of C, P, Si, O, and Al are also seen. It must be noted that (NH₄)₂Cr₂O₇ consists of hetero atoms – N and O. The presence of these electron donating atoms in the organic compound is crucial for efficient corrosion inhibition as they facilitate [24] the inhibitor adsorption on the metal surface. Besides, the sequence O < N is valid.

Fig. 9 shows the photomicrographs of the corroded surface of copper in sulphuric acid. Apparently, the inhibitor concentration of 100 % provides a near perfect surface protection as observed in Fig. 9(a), while the uninhibited test specimen's surface is severely corroded,

Fig. 9(d). The effectiveness of the ammonium dichromate (NH₄)₂Cr₂O₇ inhibitor is thus also confirmed.

In summary, the test medium used is strongly acidic and thus corrosive to copper. Ammonium dichromate is found effective as an inhibitor by providing a protective film barrier on the metal surface thus preventing the metal surface-test solution interactive corrosion reactions.

CONCLUSIONS

This work concludes that:

- Copper is susceptible to corrosion in 2M H₂SO₄.
- At all concentrations used the inhibitor, (NH₄)₂Cr₂O₇, provides an effective corrosion protection of the test electrode in the environment used. This is confirmed by both the gravimetric and electrochemical results obtained. However, the inhibitor concentration of 100 % gives the best corrosion inhibition performance.
- The results referring to the anodic and cathodic Tafel slope (ba and bc) values presented in Table 1 confirm the fact that ammonium dichromate is a mixed type inhibitor.

• The adsorption of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ on the substrate's surface is well described by the Langmuir adsorption isotherm.

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