Oxide Film Growth on Copper in Neutral Aqueous Solutions

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Abstract

The copper electrode potentials measured by the open circuit potential method in strongly aerated solutions of SO_4^{-2}, Cl^-, Br^-, I^-, CrO_4^{-2}, CO_3^{-2}, and NO_2^- with difference concentrations, till steady state values are attained. The copper electrode potentials of the all experiments increase from negative to more positive values indicating oxide film growth. The copper oxide film thickness attains maximum value at low and high concentrations of each aggressive and inhibitive anions respectively. The rate of oxide film thickening is determined by use the relation: E = a + b log t, where a and b are constants. The concentration of the inhibitive anions, CrO_4^{-2}, CO_3^{-2}, and NO_2^- that can withstand a certain concentration of the aggressive ions, , Cl^-, Br^-, and I^-, varies due to the relation: $\log C_{inh.} = A + n \log C_{agg.}$, where A and n are constants. The all experiments were investigated at 25°C in all electrolytes.

Keywords: Copper; oxide growth; passivity; open circuit potential.

Introduction

Corrosion of metals has been a persisting problem in society and, hence, it is an important area of research. Therefore, metallic plating such as zinc, nickel and their alloys have been widely used to protect metals like copper against corrosion, for many years(1). Thin top chromate conversion coatings and phosphate coatings on electrodeposited metal coatings enhance the corrosion resistance of copper, iron and mild steel(2-5). Copper has been widely used for many applications including automotive and electronic industries. However, it corrodes in aggressive media such as O_2, H^+ and Cl^-. There are studies aiming to develop better quality coatings for anticorrosive applications. Copper protection has been carried out using organic inhibitors(6,7), conducting polymer coatings(1,8-11), and formation of thick oxide film onto the surface of heavy metals(12). According to the theoretical potential-pH diagrams(13), the corrosion behavior of copper in aqueous media depends on the presence and/or the absence of oxidizing agents. Thus, in neutral solution, anodic oxidation of copper involves a passive region related to the formation of CuO layer. The aim of the present study is to investigate the role played by the type of anions and their concentration in the process of oxide film growth on copper. Thus, the open circuit potential of the copper electrode was followed with time in solutions of SO_4^{-2}, Cl^-, Br^-, I^-, CrO_4^{-2}, CO_3^{-2}, and NO_2^- till steady state values were reached. Useful conclusions regarding the rate of oxide film growth on the metal surface.

Experimental

Material and Sample Preparation:

The copper working electrode is a disk with surface area 0.1 cm^2 . The copper electrode was cut as a cylindrical rode of pure copper and mounted into glass tube of appropriate diameter with epoxy resin. The disk surface was polished prior to any experiment with 800 grit SiC paper, rinsed with distilled water and polished with an acetone-saturated paper towel to remove any grease and produce a relatively scratch free, smooth, shiny surface. It was then rinsed with triply distilled water(14).

The Electrolyte Media:

All chemicals were of analytical grade. Bi-distilled water was used to prepare all solutions of SO_4^{-2}, Cl^-, Br^-, I^-, CrO_4^{-2}, CO_3^{-2}, and NO_2^-. The anions were used in the form of their sodium salts, at concentrations ranging between 10^{-6} and 10^{-1}M.

The Electrolytic Cell and Potentials Measured :

A conventional two-electrode/one-compartment glass cell consisting of a copper disk, and Ag/AgCl electrode, were used as working and reference electrodes respectively. The cell has a double wall jacket through which water, at the adjusted temperature, was circulated. Measurements were carried out at a constant temperature 25±1 °C. The copper electrode potential (mV) of the all experiments measured by the open circuit potential method by use wenking potentiometer type PPT 70 relative to Ag/AgCl electrode.

The potential of the copper electrode was followed as a function of time in strongly aerated solutions of the tested anions till steady state values were attained. In another set of experiments, the copper electrode was first equilibrated in solutions of CrO_4^{-2}, CO_3^{-2}, and NO_2^- with varying concentrations until steady state potentials were reached. Increasing amounts of the aggressive salts, Cl^-, Br^-, I^-, were then added to each solution, allowing always sufficient time after each addition for the establishment of steady potentials. The steady state potentials were considered as those values, which did not change by more than ± 1mV in 10 minutes.

Vigorous agitation of the solution was performed by passing a stream of oxygen (two to three bubbles per second) for 10 minutes before the immersion of the electrode and during the whole duration of the experiment.

Results and discussion

Figures (1,2) and (3,4) display the variation of copper electrode potential, as a function of time and electrolyte anions concentrations, in strongly aerated solutions of SO_4^{-2}, Cl^- aggressive anions and CrO_4^{-2}, NO_2^- inhibitor ions respectively to reach steady state values of reversible potential. Similar curves are reported for other aggressive and inhibitor anions such as: Br^-, I^- and CO_3^{-2} respectively. This case was simply related to form thicker oxide film; associated with insulator properties, with time. Hence, the copper electrode potential, of each experiment, increases with increase the thickness of copper oxide film to reach steady state value of reversible potential; $E_{st.}$. It is essential to note also that the oxide film formation rate increases with decrease the concentration of electrolyte anion of aggressive media. In the word, the thickness of copper oxide film attains maximum value at low concentration of each aggressive anion. This case was simply related to the competition between oxide film formation by oxygen in solution and its destruction by the electrolyte aggressive anions(15). The results indicated that the copper oxide film formation depended on the nature of electrolyte anion.

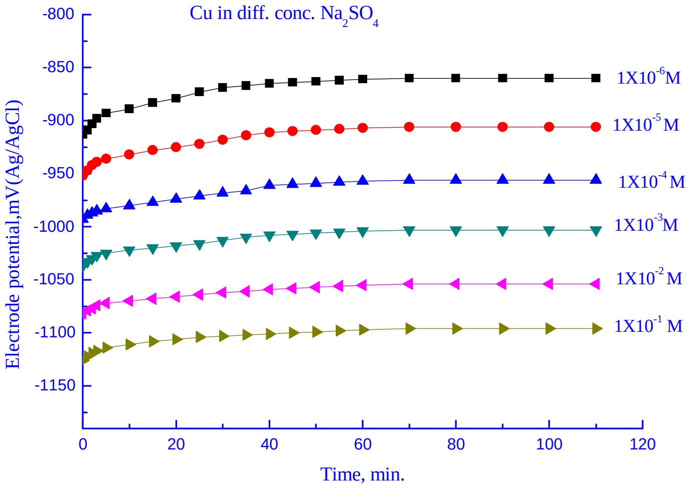

Fig.1. Variation of the open circuit potential of the Cu electrode with time in aerated Na_2SO_4 solution with different concentrations.

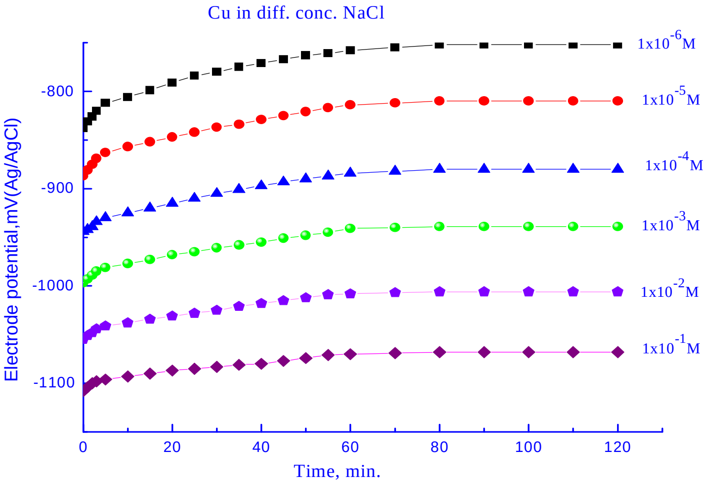

Fig.2. Variation of the open circuit potential of the Cu electrode with time in aerated NaCl solution with different concentrations.

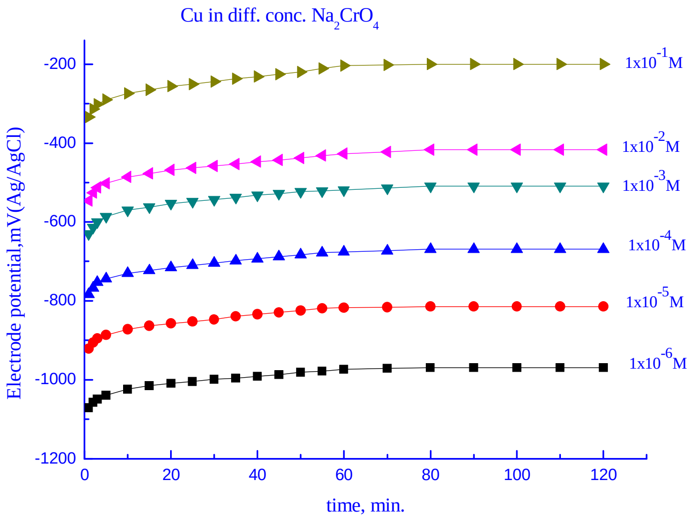

Fig. 3. Variation of the open circuit potential of the Cu electrode with time in aerated Na_2CrO_4 solution with different concentrations.

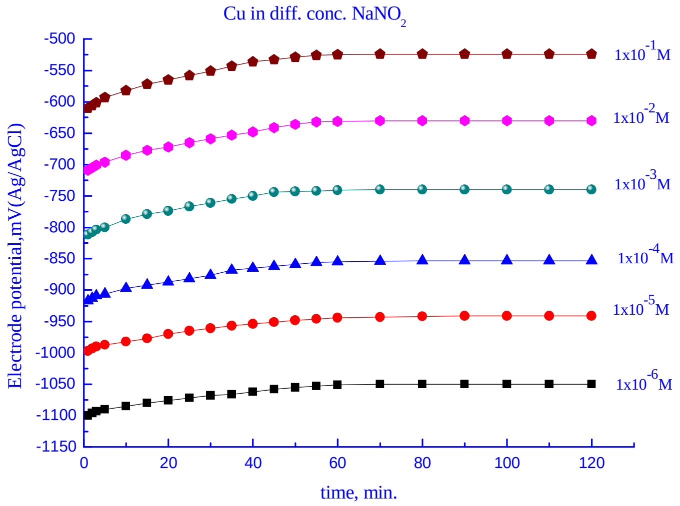

Fig. 4. Variation of the open circuit potential of the Cu electrode with time inaerated $NaNO_2$ solution with different concentrations.

Figure (5) displays a variation in steady state potential ($E_{st.}$) of copper electrode with logarithm of aggressive anions concentrations. The figure shows that the steady state potentials ($E_{st.}$) developed by the copper electrode decrease linearly with increase the aggressive anions concentrations. This case was simply related to the corrosion rate of copper increased than the rate of oxide film growth with increase the molar concentrations of aggressive anions according to the follow relation$^{(16)}$,

$$E_{st.} = a_1 - b_1 \log c \qquad \text{----------} \ (1)$$

Where a_1, b_1 are constants and $E_{st.}$ is the steady state potential. Also $E_{st.}$ related to the follow equation,

$$E_{st.} = \Phi_1 + \Phi_2 + E_f \qquad \text{----------} \ (2)^{(17)}$$

Where, E_f is the copper oxide film potential difference and changeable with oxide film growth during each experiment. Both Φ_1 and Φ_2 are the phase boundary potentials difference among copper oxide film and, copper metal and also electrolyte respectively. Φ_1 unchanged during the experiment because it depends on the types of electrode and its oxide$^{(17)}$. But, Φ_2 unchanged for each experiment; in one type of electrolyte, but changed with change the electrolyte anions. Figure (5) shows also that the values of $\partial E_{st.} / \partial \log c_{agg.}$(slope) increases in the order of $Na_2SO_4 <$ NaCl<NaBr< NaI. This means that the thickness of copper oxide film increased in the same order. In the other word, the corrosion rate of copper metal increased in the opposite order. This means that the corrosives degree of anions toward copper increases in the order, $I^- < Br^- < Cl^- < SO_4^{-2}$.

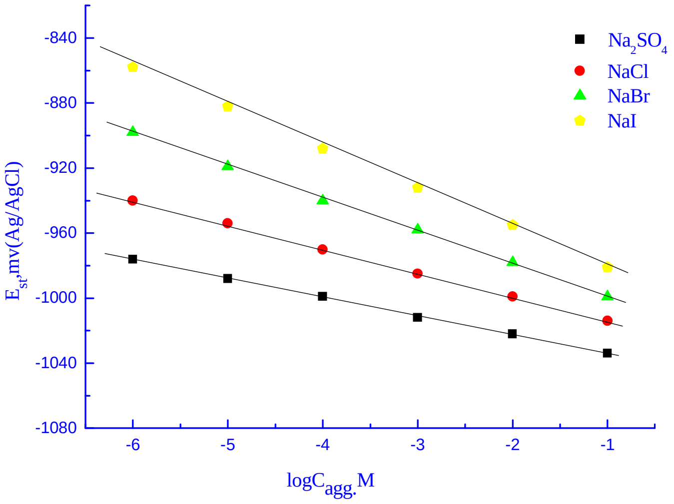

Fig.5. Variation in the steady-state potential, $E_{st.}$, of the Cu electrode with the logarithm of concentration of Na_2SO_4, NaCl , NaBr and NaI.

Figure (6) clears that the steady state potentials are reached from negative values indicating oxide film repair and growth.

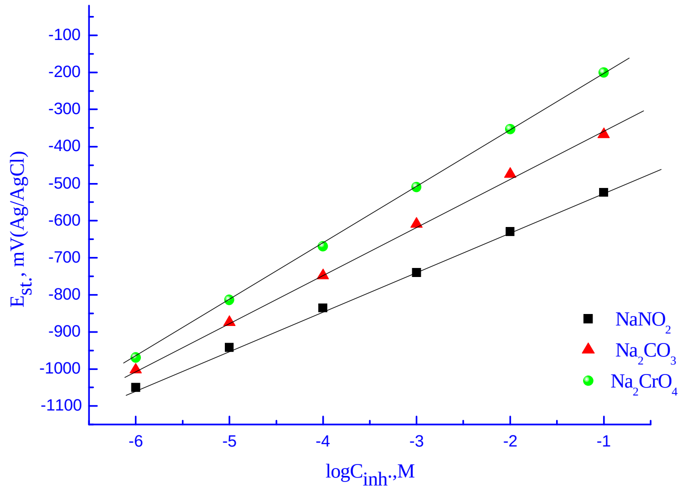

Fig.6. Variation in the steady-state potential, $E_{st.}$, of the Cu electrode with the logarithm of concentration of Na_2CrO_4 , Na_2CO_3 and $NaNO_2$.

This case was simply related to the rate of oxide film growth on copper increased than the rate of metal corrosion with increase the molar concentrations of inhibitor anions according to the follow relation,

$$E_{st.} = a_2 + b_2 \log c , \qquad \text{----------} (3)$$

where a_2 and b_2 are constants. The constant a_2 represent the steady state potential of Cu electrode in 1M anion solution. This means that the inhibition efficiency of the tested anions toward copper metal increase in the order, NO_2^-, CO_3^{-2} and CrO_4^{-2}.

Figures (7-10) Show the open circuit potential (E) varies linearly with the logarithm of the immersion time t (in minute) according to the follow relation,

$$E = a_3 + b_3 \log t \qquad \text{----------} (4),$$

where a_3 and b_3 are constants in the presence of the corrosive and inhibitive anions. The curves of figures (7,8) represent the behavior in solution of Na_2SO_4 and NaCl, and, as examples of the behavior of the aggressive anions. The curves of figures (9,10) represent the behavior in solutions of Na_2CrO_4 and $NaNO_2$ as examples of the inhibitive anions. Figures (7,8) reveal that the steady state potentials ($E_{st.}$) of copper metal, in solutions of the aggressive anions, SO_4^{-2}, Cl^-, Br^- and I^-, go to more noble potential with decrease the concentrations. This case was simply related to the oxide film healing and thickening. The b_3 values of equation 4 decrease with increase the aggressive anion concentration. The values of b_3, in solution of constant aggressive anion concentration, increase in the order $SO_4^{-2} < Cl^- < Br^- < I^-$.

Figures (9,10) show that, in solutions of the inhibitive anions: CrO_4^{-2}, CO_3^{-2} and NO_2^-, the values of $E_{st.}$ become more noble at higher concentration of these ions. The b_3 values increase with increase inhibitor anion concentration. In solutions of constant inhibitor anion concentration, b_3 values increase in the order $NO_2^- < CO_3^{-2} < CrO_4^{-2}$.

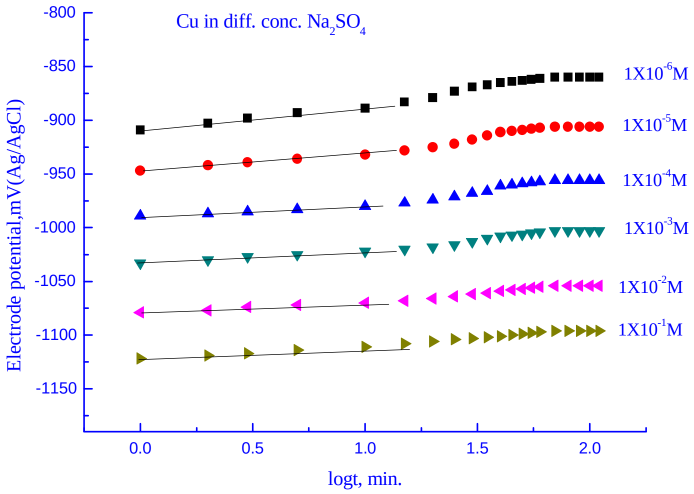

Fig. 7. Variation of the open circuit potential of the Cu electrode with log time, t, in aerated Na_2SO_4 solution with different concentrations.

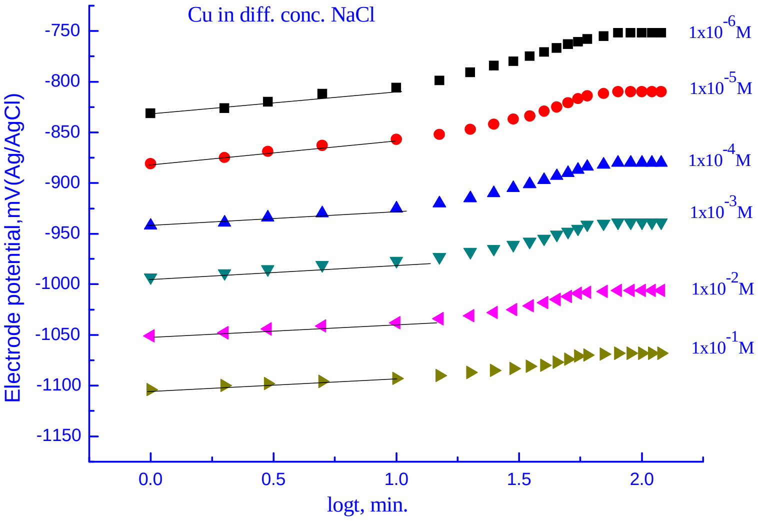

Fig. 8. Variation of the open circuit potential of the Cu electrode with log time, t, in aerated NaCl solution with different concentrations.

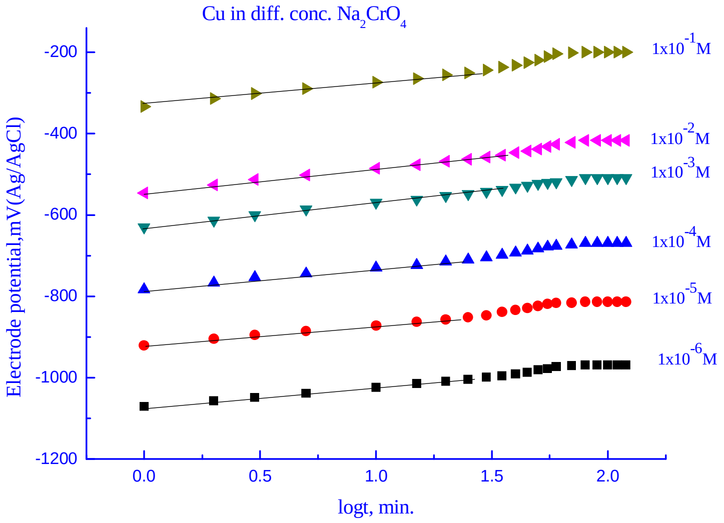

Fig. 9. Variation of the open circuit potential of the Cu electrode with log time, t, in aerated Na_2CrO_4 solution with different concentrations.

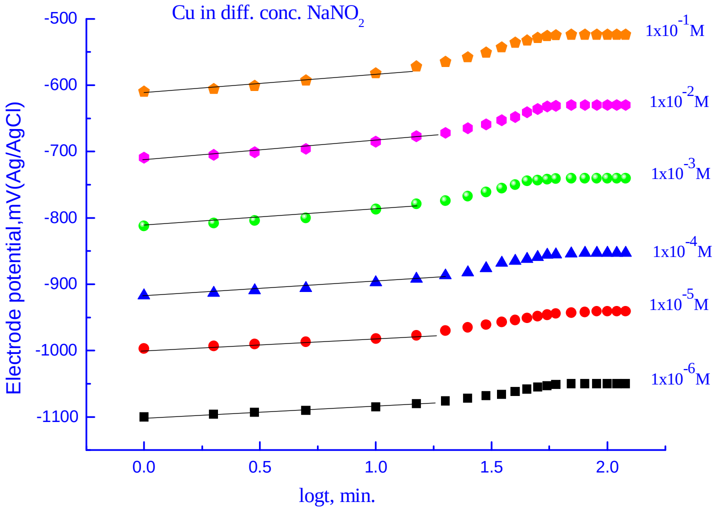

Fig. 10. Variation of the open circuit potential of the Cu electrode with log time, t, in aerated $NaNO_2$ solution with different concentrations.

The copper electrode potential go to more noble, when immersed in strongly oxygenated solutions of the studied ions. This denotes that the pre-immersion air formed tarnish oxide film on the metal surface is not sufficient to impart passivity in these media(18). Moreover thickening of the oxide film continues until steady state values are reached(16,19,20); anodic reaction. On the other side the reduction of oxygen represents the cathode reaction of the corrosion process in oxygenated media according to the follow reaction,

$$O_2 + 2H_2O + 4e^- \Longleftrightarrow 4OH^- \quad \text{----------- (5)}$$

The necessary electrons for reaction in equation 5 are acquired from the ionization of the Cu atoms entering the oxide phase to growth it as follow reaction,

$$2Cu \Longleftrightarrow 2Cu^{+2} + 4e \quad \text{------------ (6)}$$

$$2Cu^{+2} + 2H_2O \Longleftrightarrow 2Cu + 4H^+ \quad \text{------------- (7)}$$

The Cu^{+2} ions interflow the oxide film to oxide ⁄solution interface to form a new oxide(21). Abd El Kader and Shams El Din(16) assumed that, under the influence of strong electric fields, a detectable ionic current i_a can follow. Under such a high field strength, Ohm's law does not apply, and ion transfer is governed by the familiar Gűntherschulze and Betz relationship(22),

$i_a = K_a e^{BH}$ -------------- (8),

where K_a and B are constants for forward reaction and H is the effective field strength. Under the open circuit conditions, the electric fields are assumed to originate from the specific adsorption of anions on the oxide covered metal(16). An image charges of the same magnitude but of opposite sign will be created by induction at the oxide metal interface. These charges promote ions transfer through the oxide film on the metal surface. However the potential difference (E) equals $\Phi_1 + \Phi_2 + E_f$. But Φ_1 and Φ_2 are constants during the oxide growth. Hence, the value of E_f can replace by E. So equation 8 was replaced to be,

$i_a = K_a e^{BE/\delta}$ -------------- (9),

where the field strength H in equation 8 is substituted by the term E/δ, where E is the measured open circuit potential of the copper electrode relative to the reference Ag/AgCl electrode and δ is the thickness of the oxide film. The potential value (E) of copper electrode increases to more noble with increase the copper oxide film. So the field strength E/δ remains constant specially at the initial stages of oxide film growth(23). Abd El Kader and Shams El Din(16) derived a relation which describes the variation of the open circuit potential (E) with time,

$E = \text{constant} + (2.303\ \delta^{-}/B) \log t$ ------------- (10),

where δ^{-} is the rate of oxide film thickening per unit decade of time. The value of B equals $(nf/RT)\alpha^{=}$ (24), where α is the transfer coefficient ($0<\alpha<1$) and $\alpha^{=}$ is the width of the energy barrier. Assuming $\alpha = 0.5$ and $\delta^{=} = 1.0$nm, then B = 39nmV^{-1}. From the slopes of the (E versus logt) curves of figures (7-10) and the like, the values of the rate of oxide film thickening on copper surface, in solutions of difference concentrations of the various studied anions, have been calculated and listed in table 1.

Table 1: Rate of oxide film thickening, δ^{-}, in solutions of different concentrations of the anions, nm per unit decade of time.

Conc., M	Na_2SO_4	NaCl	NaBr	NaI	$NaNO_2$	Na_2CO_3	Na_2CrO_4
$1\text{x}10^{-6}$	0.499	0.745	0.801	0.831	0.483	0.724	0.903
$1\text{x}10^{-5}$	0.424	0.658	0.723	0.814	0.542	0.737	0.944
$1\text{x}10^{-4}$	0.351	0.597	0.663	0.766	0.629	0.784	0.987
$1\text{x}10^{-3}$	0.309	0.510	0.585	0.697	0.717	0.841	1.041
$1\text{x}10^{-2}$	0.273	0.427	0.530	0.621	0.786	0.923	1.099
$1\text{x}10^{-1}$	0.255	0.333	0.444	0.524	0.856	1.001	1.169

Table (1) clears that the values of the rate of oxide film thickening δ^{-}, in solutions of the aggressive anions, SO_4^{-2}, Cl^-, Br^- and I^-, is found to depend on the anion type and concentrations. Thus the rate of oxide film growth decreases with increase the aggressive anion concentration of each type. This behavior was simply related to increase the oxide film dissolution. However, the rate of oxide film thickening on copper electrode in constant aggressive anion concentration decreases in the order, $I^- > Br^- > Cl^- > SO_4^{-2}$. This sequence related to the aggressivity of each anion type toward the copper metal. It clears also that the rate of oxide film thickening δ^{-}, in solutions of the inhibitor anions, CrO_4^{-2}, CO_3^{-2} and NO_2^-, increases with increase the inhibitive anion concentration of each type. However, the rate of oxide film thickening on copper electrode in constant inhibitive anion concentration increases in the order, $NO_2^- < CO_3^{-2} < CrO_4^{-2}$. This sequence was simply related to the inhibition efficiency of each anion type toward the copper metal.

The steady state potentials of Cu electrode calculated in oxygen saturated solutions of inhibitive ions, CrO_4^{-2}, CO_3^{-2} and NO_2^-, of difference concentrations before and after addition different weights of aggressive ion (Cl^-) for each concentration of the same inhibitive ion. Similar experiments repeat with addition difference weights of another aggressive ions, Br^- and I^- in each inhibitive ion of difference concentrations.

Figures (11-13) represent a relation between the steady state potentials of Cu electrode in each inhibitive ion of difference concentrations with difference weight of sodium chloride, grams. Similar curves of NaBr and NaI were also obtained.

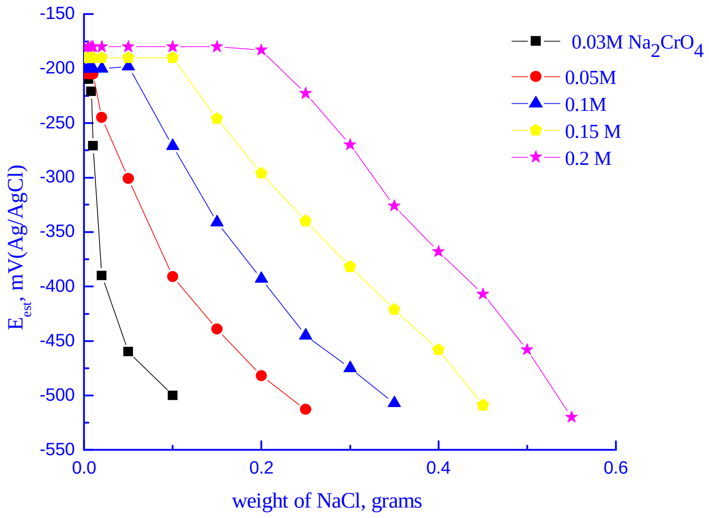

Fig. 11. Variation of steady state potential of the Cu electrode in aerated solution of different concentrations of Na_2CrO_4 before and after additive amounts of NaCl.

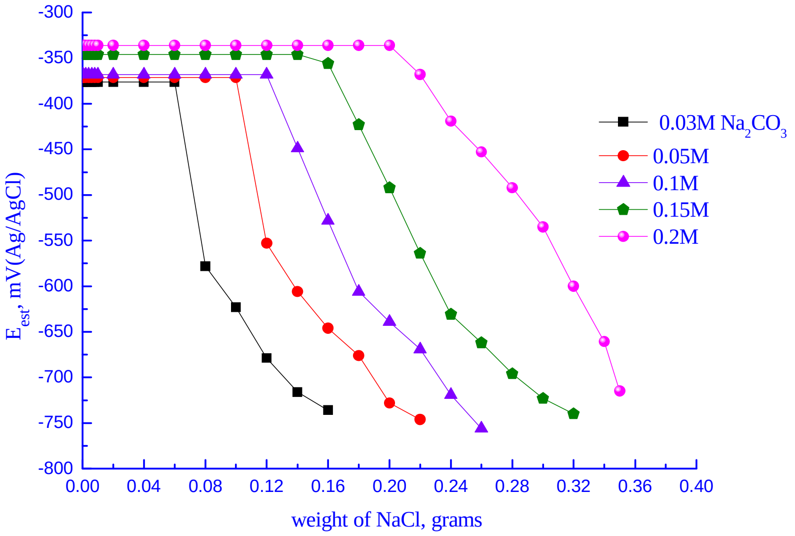

Fig. 12. Variation of steady state potential of the Cu electrode in aerated solution of different concentrations of Na_2CO_3 before and after additive amounts of NaCl.

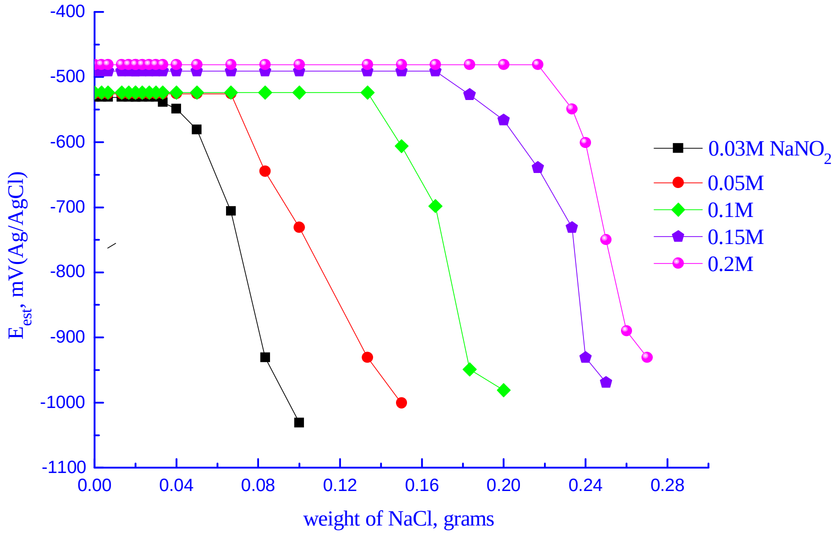

Fig. 13. Variation of steady state potential of the Cu electrode in aerated solution of different concentrations of $NaNO_2$ before and after additive amounts of NaCl.

These curves could be used to determine the concentration of the passivating anions that can withstand a certain concentration of the aggressive ions. These figures clear also that the steady state potentials, measured in the absence of the aggressive ions, increase slightly with increase the concentrations of the passivating (inhibiting) anions in solution. At the same time, the change of potential rate at the inflexion points of the curves is inversely proportional with the concentration of inhibiting anions. This phenomenon was simply related to initiate pitting corrosion onto Cu electrode easily in dilute inhibiting solutions than in concentrated ones. It is essential to note that the solution required more aggressive ions with increase the concentrations of inhibiting anions. Figures (11-12) and similar curves of other aggressive anions reveal also that the amount of aggressive salts NaCl, NaBr and NaI required to cause inflexions in the potential-time curves and initiation of pitting corrosion on Cu electrode in the presence constant concentration of one inhibitor increases in the order $Cl^- < Br^- < I^-$. This order is in accordance with the aggressiveness of these ions. On the other side, the amount of one type of aggressive salt required to cause inflexion in the potential-time curves on Cu electrode in the presence difference inhibitors of constant concentration increases in the order $NO_2^- < CO_3^{-2} < CrO_4^{-2}$. This means that the efficiency of passivating anions against corrosion increases in the order $NO_2^- < CO_3^{-2} < CrO_4^{-2}$. It is essential to note from the curves of figures (11-13) that there is no definite critical corrosion potential, above which the copper metal retards attack and below which it undergoes corrosion. Therefore, the choice of such potential to be taken as a basis for comparison is thus arbitrary. But the initial potential of copper electrode, in aggressive media, depends on the ambient concentration of the inhibitive anions. Therefore the choice of a constant potential for all solutions is not free from error. Shams El Din and Abd El Haleem(25,26) assumed that pitting corrosion is operative to the same extent in all solutions when enough of the aggressive anion is added to displace the initial potential to the active direction by a constant value. Therefore, the inflexion point of each curve is considered the starting potential (0mV displacement); critical corrosion potential.

Figures (14-16) display the variation of logarithm inhibitors anions concentration as a function of logarithm aggressive anions concentrations at the inflexion points (0mV displacement) and after them, more negative potentials than the starting potentials namely 100, 200 and 300mV.

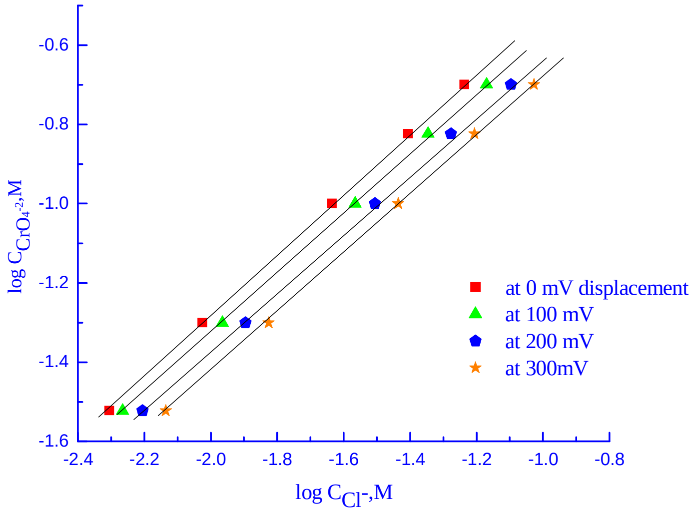

Fig. 14. Variation of log C_{CrO4}^{-2} with log C_{Cl}^{-} at different potentials.

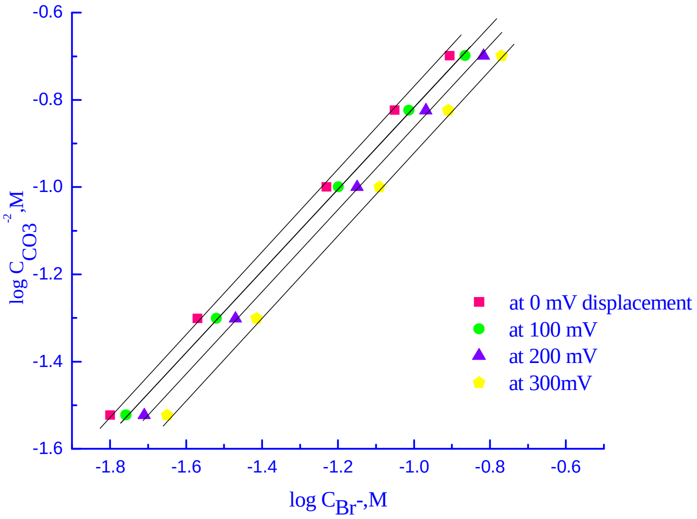

Fig. 15. Variation of log C_{CO3}^{-2} with log C_{Br}^{-} at different potentials.

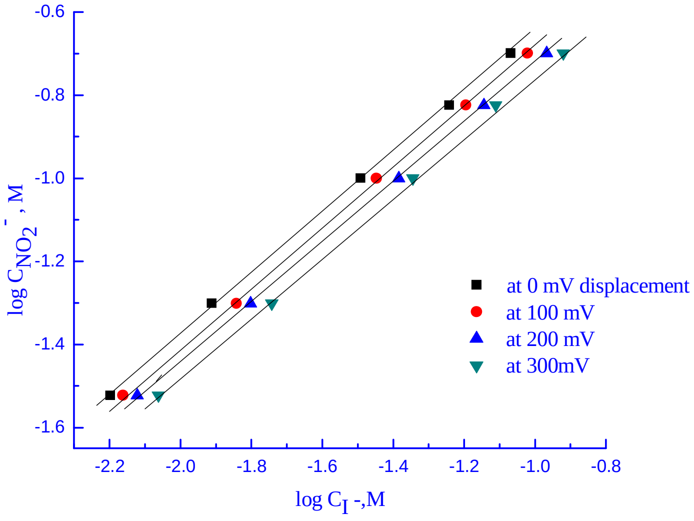

Fig. 16. Variation of log C_{NO2}^- with log C_I^- at different potentials.

Straight lines are obtained satisfying the follow relation,

$$\text{Log } c_{inh.} = A + n \log c_{agg.} \quad \text{------------ (11),}$$

where A and n are constants. The values of n for the solutions of CrO_4^{-2}, CO_3^{-2} and NO_2^-, in the presence of the aggressive halide anions Cl^-, Br^- and I^- are listed in table2.

Table 2: The values of the exponent " n" of equation (11)

aggressive	Inhibitors		
	CrO_4^{-2}	CO_3^{-2}	NO_2^-
Cl^-	1.30	1.036	1.132
Br^-	1.21	1.15	1.25
I^-	1.13	1.062	1.377

According to the theoretical derivation of equation (11) by Shams El Din and Abd El Haleem(25,26) as well as the prediction assumed by Brasher(27), n is found to be the ratio of electrical charges of the inhibitive to aggressive anions. Equation (11) holds not only the points of inflexion, but also the points at other more active potentials as long as they are referred to the starting potentials, measured in the aggressive free solutions. Table (2) clears that the values of n in the case of CrO_4^{-2} and CO_3^{-2} is more or less than in case of NO_2^- ions. However, in CrO_4^{-2} and CO_3^{-2}, the values of the expected n are lower than the expected value 2. Thus, n has values ranging from 1.036 to 1.30 in the case of these two inhibitive anions. This case was simply attributed to the partial existence of CrO_4^{-2} and CO_3^{-2} in monovalent forms, $HCrO_4^-$ and HCO_3^- (27).

Conclusions

The following conclusions can be drawn from this work:

1 - There is a competition between oxide film formation by oxygen in solution and its destruction by aggressive anions.

2 -The rate of oxide film thickening depends on the anion types and its concentration.

3 - Copper oxide film formation rate increases with increase the concentration of inhibitive anions

4 -The steady state potentials $E_{st.}$developed by the copper electrode decrease linearly with increase the aggressive anions concentrations.

5 -The steady state potentials are reached from negative values indicating oxide film repair and growth.

6 -The steady state potentials vary linearly with the logarithmic of anions concentration.

7 -The concentration of inhibitive anions that can sustain certain concentration of aggressive anions varies according to: Log $c_{inh.} = A + n \log c_{agg.}$, where A and n are constants.

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