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Investigation of Anodic Behavior of Nickel in H_2SO_4 Solutions Using Galvanostatic Polarization Technique. II. Initiation and Inhibition of Pitting Corrosion by Some Inorganic Passivators

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The anodic polarization of nickel in dilute sulfuric acid media was investigated in the absence and presence of ClO_4^- ions, at a constant current density. The anodic polarized curve is characterized by a sudden jump in potential owing to the decay of H-over voltage, followed by two oxidation arrests, passive and O_2 evolution regions. The presence of ClO_4^- ions distorts the polarized curve owing to the damage in the passive film with the initiation of localized pitting corrosion, at pitting potential, E_{pit}. E_{pit} displaces into active direction with rising amounts of the ClO_4^- ions. The presence of various concentrations of Na_2HPO_4, Na_2MoO_4 and Na_2CrO_4 shift the E_{pit} into more positive values, confirming the suppression of pitting corrosion. The anions of these salts displace the E_{pit} into the more noble direction due to a competition with the ClO_4^- ions. The inhibition effect towards the pitting corrosion of Ni follows the sequence Na_2HPO_4 > Na_2MoO_4 > Na_2CrO_4. Thermodynamics activation energies required for the destruction of the passive film, E_a, are estimated and explained in the absence and presence of the different anions.

Keywords: Nickel; Galvanostatic; Pitting Corrosion; Inhibition; Oxide film; Passivity.

1. INTRODUCTION

Ni and its alloys indicate high corrosion immovability in various electrolytic media due to the presence of a stationary passive oxide layer on its external surface [1-7]. The quality of consistence of

such film relies on considerable factors within which the strength of the solution, *p*H, existence of corrosive or inhibitive ions, and the solution temperature [8-10].

The resistance of Ni to the corrosion process is attributed to the presence of a preventative oxide, a hydrated oxide film[11], and/or to a chemical adsorbed O-layer on its surface[12]. The passivity of nickel in aqueous acidic solutions could be attributed to the rising in the conductivity of the formed oxide film[13]. Previous investigations about the potentio-kinetic polarization for Ni indicated considerable conflicts [14-16]. These were ascribed to nature and the impurities in each of the investigated metals [14] and electrolytes, as well as the variations in the experimental procedures [15].

Localized pitting corrosion initiates when the passive film is emaciated at a definite weak point on the metal surface, performing quick corrosion for the protected metal [17-21]. Many investigators indicated that a localized type of attack takes place when the passive metal is exposed to electrolytic solutions containing halide anions [10,17-22]. Also, such a type of attack may also occur in the presence of ClO_3^- and ClO_4^- ions[23-27]. Breakdown of passivity in the presence of ClO_4^- ions is usually restricted to certain potential ranges [25].

The current paper is to highlight the effect of ClO_4^- ions in the initiation and propagation of localized pitting corrosion on nickel in 0.01 M H_2SO_4 solutions using the anodic galvanostatic polarization method. Trails are done to inhibit such a type of attack employing Na_2HPO_4, Na_2MoO_4 and Na_2CrO_4. The influence of temperature on the initiation and inhibition of pitting corrosion are investigated. The activation energies required for oxide film destruction and initiation of pitting corrosion are calculated and explained in the absence and presence of such passivators. Surface examination for some corroded Ni samples is investigated in the absence and presence of corrosive and inhibitive anions.

2. MATERIALS AND METHODS

2.1. Materials

The working electrode employed in this investigation was a pure nickel metal was described in the recent literature of this study [4]. The electrical connection of the Ni electrode was carried by using a pure thick copper wire with 2 mm diameter. The rod was fixed into a borosilicate glass pipe using an epoxy resin leaving 0.97 cm^2 of a naked free cross-sectional surface area. Prior to running the experiment, the surface area of the Ni electrode was cleaned mechanically by abrading with various grades of fine polished papers. Then, the electrode was cleaned by rinsing with acetone followed by bi-distilled water and the test solution before inundation in the investigated solution.

The required solutions were prepared from A.R. H_2SO_4 and $NaClO_4$ (Fluka) and a bi-distilled water. Various amounts of Na_2HPO_4, Na_2MoO_4 and Na_2CrO_4 are added to 0.01 M H_2SO_4 containing 0.01 M $NaClO_4$. Experiments were done at 25°C, except otherwise carried at various temperatures. The scanning electron microscope, JEOL TM, JSM- T100 (Japan), is used to examine the surface of some

corroded Ni surfaces in 0.01 M H_2SO_4 + 0.01 M $NaClO_4$ in the absence and presence of 0.01 M Na_2MoO_4.

2.2. The Electrolytic cell

The used electrolytic cell was described early [28-31]. Three kinds of electrodes are employed (platinum wire as a counter electrode, nickel as a working electrode, and a saturated calomel electrode, SCE, as a reference electrode). An ultra-thermostat Polyscience-type (USA) was used for adjusting the reaction temperature. Each test was done with a newly prepared electrode and a neoteric solution. The potential-time curves at a constant applied current were plotted on a recorder unit, Cole Parmer Instruments (USA).

3. RESULTS AND DISCUSSION

3.1. The effect of ClO_4^- ions concentration

Figs 1 depicts the anodic polarized curves of nickel in 0.01M H_2SO_4 solutions without and with the additions of various amounts of ClO_4^- ions, at 1.0 mA/cm^2 and 25°C.

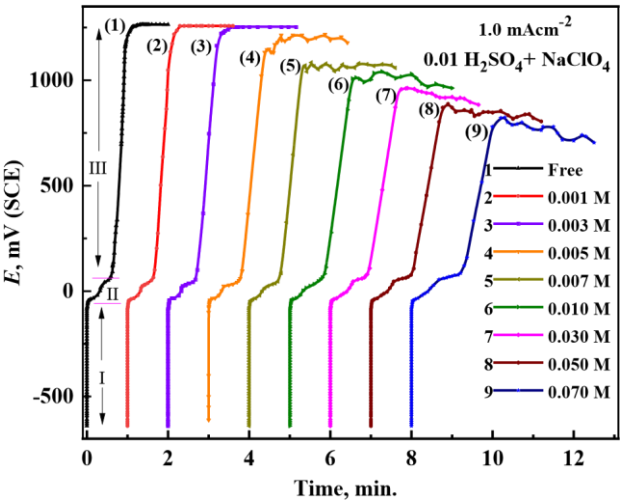

Figure 1. Galvanostatic anodic polarization curves of Ni, at 1.0 mA/cm^2, in 0.01 M H_2SO_4 containing different concentrations of $NaClO_4$, at 1.0 mA/cm^2 and 25°C.

The curves are distinguished by a swift jump of the potential (region I) confirming the decay of hydrogen over-potential on the nickel surface accompanied by charging of the electrical double layer at the metal/solution interface [4, 32,33]. Prior to the decay step (region I), the potential of the nickel electrode modifies slowly with reaction time to give two distinct dissolution arrests, **a** and **b** (zone II) followed by an oblique rise in the potential-time curve (zone III). However, the ClO_4^- ions free

polarized curve indicated different characteristic regions assuring different oxidation stages followed by passive film formation and O_2 evolution regions. The oxidation processes indicated by the arrests **a** and **b** generate monovalent and divalent nickel cations which are easily turned to NiO by the effect of water[4, 34-36]:

$$Ni^{2+} + H_2O \rightarrow NiO + 2H^+ + e \quad (1)$$

The hop in the *E* towards the noble values, after the active oxidation process, could be imputed to the precipitation of the nickel oxides on the anode surface, producing the passive oxide film [4]. However, It is clear from the curves of Fig 1 that the presence of different amounts of ClO_4^- ions could impact the shape of the anodic polarized curves. Few additions of ClO_4^- ions (< 0.003 M) do not influence the general shape of the polarized curve gained in ClO_4^- ions-free electrolyte. Relatively higher additions of ClO_4^- ions (> 0.003 M) distort the anodic polarized curves owing to the damage of the passive oxide film with the initiation of localized pitting corrosion at localized active cells[10, 32]. The initiation of localized pitting attack on the passive nickel oxide film can take place at a specific additions of the ClO_4^- ions and above a critical value [32, 37].

Furthermore, Fig 1 depicts that the presence of 0.003M ClO_4^- ions produces little potential fluctuations during the O_2 evolution-region. Such attitude elucidates that the ClO_4^- ions interpose with the O_2 evolution [37]. The presence of fluctuations in this region may be referred to the truth that the passivation process happens jointly with the process of oxide film destruction. A state at which the rate of oxide film destruction is slightly exceeded that of oxide film formation, metastable pits are created [10]. The formed metastable pits are characterized by a very finite existence, that they passivated again and the potential, *E*, returned to the O-evolution region [37].

Is noteworthy to see that the fluctuations in potential are increased and shift to more negative directions as the amount of the added ClO_4^- ions raises above the critical concentration[37]. These fluctuations in the potential may be referred to the destruction of passivity in the existence of ClO_4^- ions and the passivation of the oxide film by the effect of the anodic current [37].

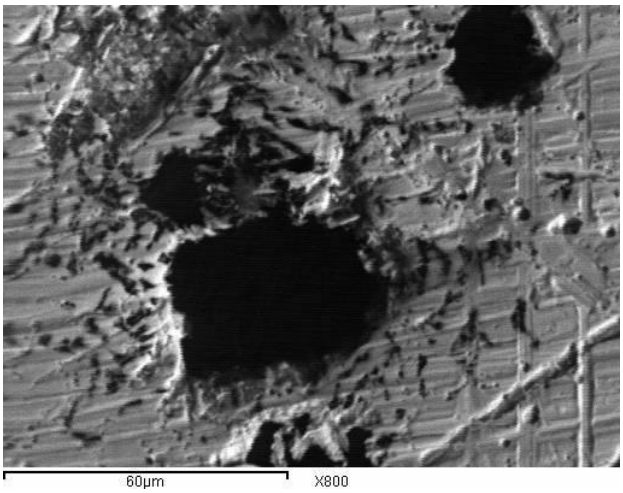

Figure 2. Scanning electron micrograph (SEM) of the anodically polarized Ni sample in 0.01 M H_2SO_4 + 0.01M ClO_4^- ions.

Higher concentrations of ClO_4^- ions $\geq$ 0.007 M cause variable changes in the general shape of the anodic polarized curve. The duration of the oxidation process, region II (arrests **a** and **b**), τ, increases whereas the rate of oxide film formation, $\partial E/\partial t$, reduces. Moreover, the breakdown of the passive film is attained at a definite potential, E_{pit}. At this potential, E_{pit}, fluctuations in the potential with time are noted without attaining the oxygen evolution, i.e., the damage of the passive oxide-film with the initiation of the localized pitting corrosion is observed [37, 38]. The pitting corrosion potential, E_{pit}, relocates into more active values, less positive, as the amounts of ClO_4^- ions are raised. Fig. 2 shows the scanning electron micrograph (SEM) of the anodic polarized Ni sample in 0.01 M H_2SO_4 containing 0.01M ClO_4^- ions. The photograph indicates a number of irregularly distributed pits on the surface of the passive film. This confirms that the existence of ClO_4^- ions destruct the passive film with a generation of well-defined pits, distributed on the surface of the passive oxide film.

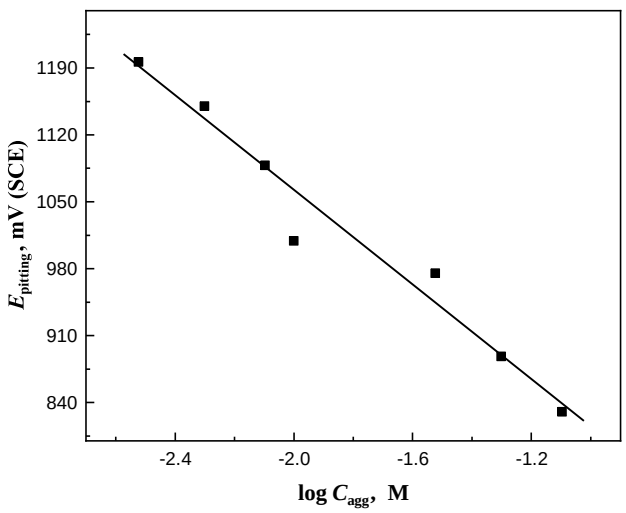

Figure 3. Variation of $E_{pitting}$ with log C_{agg} for Ni in 0.01 M H_2SO_4, at 25°C.

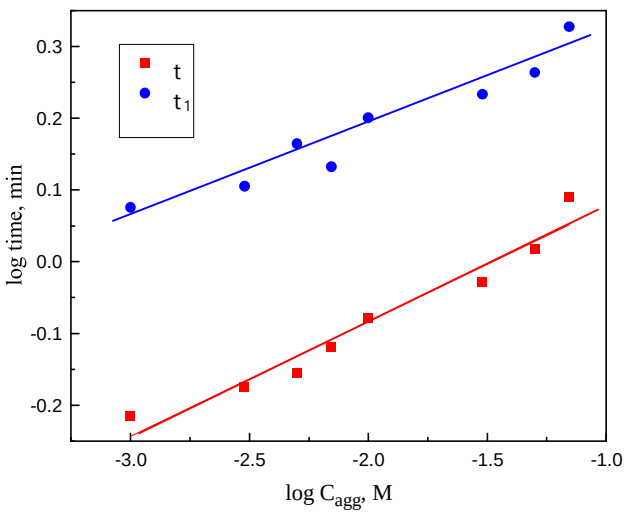

Figure 4. Variation of log τ and logτ_1 against log C_{ClO4^-} for Ni in 0.01 M H_2SO_4, at 25°C.

The variation of the galvanostatic pitting corrosion potential, E_{pit}, with the logarithm of the added amount of ClO_4^- ions can be depicted in Fig 3. This figure illustrate the lowering of E_{pit} with the aggressive ions concentration according to the relation:

$$E_{pit} = \xi - \gamma \log C_{ClO_4^-} \quad (2)$$

where ξ and γ are constants that rely on the solution composition and the type of the aggressive anion. It is seen that the pitting potential, E_{pit}, decreases gradually with increasing the ClO_4^- ions concentration, due to the enhancement in the initiation of localized pits producing localized-type of attack, extremely pitting corrosion.

However, it noted from Fig 1 that the period of the active anodic oxidation indicated by the arrests **a** and **b** of region II, τ, was also dependent on the concentration of ClO_4^- ions. Also, the exposure time of Ni electrode required for pit formation and the initiation of pitting corrosion is considered as the induction time, τ_1 [39]. The period of the arrests **a** and **b**, τ, as well as, the induction time required for pitting corrosion, τ_I, are elongated as the concentration of ClO_4^- ions is increased. A straight line relation is obtained when log $\tau(\tau_1)$ values are plotted against log $C_{ClO_4^-}$ (Fig 4) satisfying the following relation:

$$\log \tau = \alpha' + \beta' \log C_{ClO_4^-} \quad (3)$$

where α' and β' are constants that rely on the solution composition and its type.

Fig 5 depicts the divergence in the rate of oxide-film formation, ($\partial E/\partial t$), with the log C of the added ClO_4^- ions.

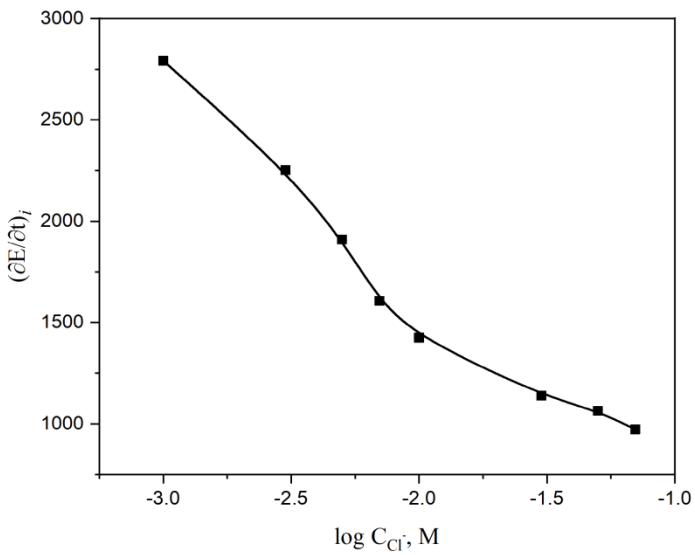

Figure 5. Variation of the rate of oxide-film formation, ($\partial E/\partial t$), with the log $C_{ClO_4^-}$ ions for Ni in 0.01 M H_2SO_4, at 25°C.

This figure depicts the reduction in the $\partial E/\partial t$ values with the added ClO_4^- amounts, according to the segmented S-shaped curve. This attitude could confirm the existence of an adsorption process for ClO_4^- anions on the passive oxide-film before the permeation of this film and initiation of the localized pitting corrosion[40].

From another point of opinion, Pagitsas et al. have confirmed that the provenance of localized pitting corrosion generated by ClO_4^- ions is due to the penetration of this film by the formed Cl^- ions[23,24]. The chloride ions are formed via the reduction of perchlorate ions by Ni^{2+} following the overall equation [23, 24]:

$$ClO_4^- + 8\,Ni^{2+} + 8\,H^+ \rightarrow 8\,Ni^{3+} + Cl^- + 4H_2O \qquad (4)$$

Thus, increasing the addition of ClO^-_4 ions boosts the oxide destruction since more chlorides are produced and adsorbed on the passive metal surface. The initiation of pits is owing to the ability of ClO^-_4 and/or Cl^- ions to impede oxide film formation causing further metal dissolution [41] and more Cl^- ions migrated into the breakdown metal area.

3.2. The influence of additions of inorganic passivators as inhibitors.

The effect of the addition of Na_2HPO_4, Na_2MoO_4 and Na_2CrO_4 on the anodic polarization curve of nickel in 0.01 M H_2SO_4 containing 0.01 M ClO_4^- ions was studied. Fig 6 depicts the galvanostatic anodic polarized curves for nickel in 0.01 M H_2SO_4 containing 0.01 M ClO_4^- ions in the existence of various additions of Na_2MoO_4, at 1 mA/cm^2 and 25°C. Comparable data are gained with the additions of Na_2HPO_4 and Na_2CrO_4 (curves not shown). Fig 6 and the likes indicate that the addition of the different inhibitors reduces the period of the oxidation process, increase the rate of oxide film formation, $(\partial E/\partial t)_i$, and shift the pitting potential, E_{pit}, into the noble direction to an extent that depends on the amount and the kind of the used salt, C_{inh}.

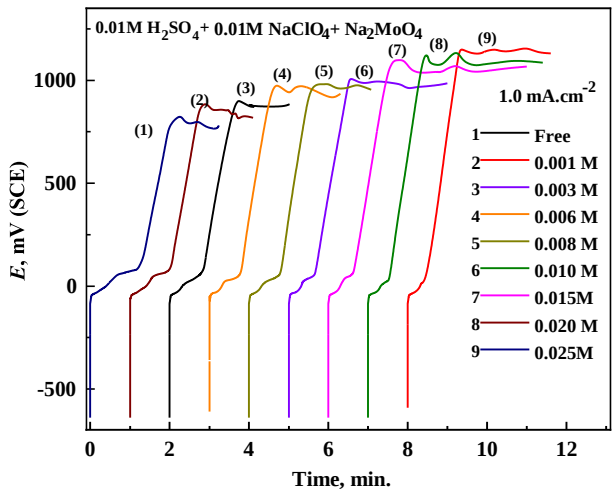

Figure 6. Galvanostatic anodic polarization curves of Ni in 0.01 M H_2SO_4 containing 0.01 M $NaClO_4$ and different additions of Na_2MoO_4, at 1.0 mA/cm^2 and 25°C.

Fig 7 explores the reliance of the $(\partial E/\partial t)_i$ on the amount of the added salt, C_{inh}. S-shaped curves are gained when $(\partial E/\partial t)_i$ values are plotted against the log C_{inh}, confirming the existence of an adsorption process competing with the ClO_4^- ions [42].

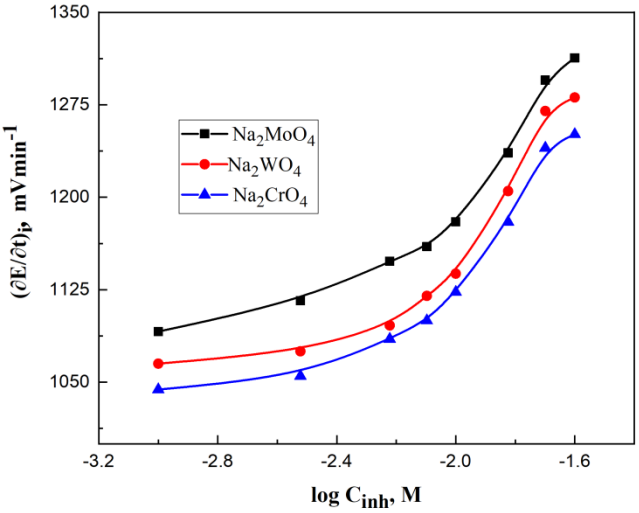

Figure 7. Variation of $(\partial E/\partial t)_i$ with the concentration of the inhibitor, C_{inh} for Ni in 0.01M H_2SO_4 containing 0.01 M $NaClO_4$, at 25°C.

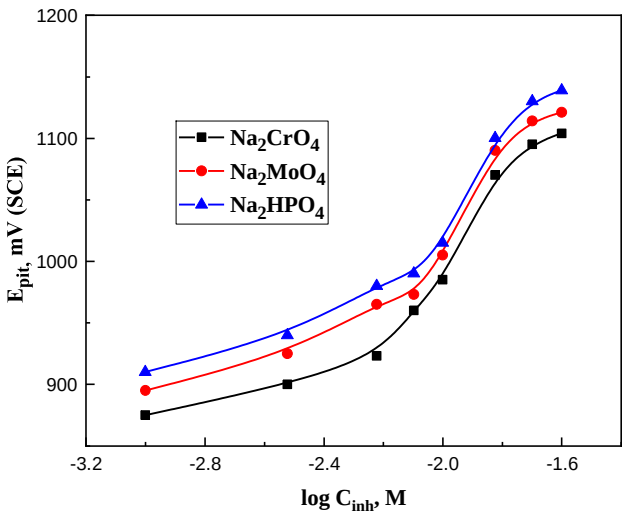

Figure 8. Variation of $E_{pitting}$ with log C_{inh} for Ni in 0.01 M H_2SO_4 containing 0.01 M Na_2ClO_4, at 25°C.

The reliance of the pitting corrosion potential, E_{pit} of the Ni electrode on the amount of the added inhibitor is depicted in Fig 8. S-shaped curve is obtained with a displacement in the E_{pit} values into the more positive values (noble direction) with raising the concentration of the inhibitor. Such behavior confirms that the added salt act as an effective inhibitor competing with ClO_4^- ions to prevent the attack of ClO_4^- ions by the way of an adsorption mechanism [42].

The existence of the various used anions tolerates the pitting corrosion of Ni in 0.01 M H_2SO_4 and 0.01 M ClO_4^- ions following the sequence: phosphate > molybdate > chromate. This trend confirms the increased tendency of the used salts towards pitting corrosion. Molybdate is minimal while HPO_4^{2-} is strongly efficacious as pitting corrosion passivators. The inhibition influence of the using salts could be related to the competitive adsorption between the corresponding anion and the ClO_4^- ions on the passive Ni surface which retards the destructive effect of ClO_4^- ions by shifting E_{pit} into the positive direction preventing pitting corrosion[43]. The adsorbed anions may be combined into the passive film improving the passivity against the destructive effect of ClO_4^- ions[43].

The inhibition influence of the HPO_4^{2-} anions may be owing to the specific passivation of nickel by the precipitation of the nickel-phosphate from the investigated solution, the coagulation on the nickel-phosphate salts on the Ni surface sustains the conditions appropriate for common oxide film [44].

The inhibition effect of MoO_4^{2-} ions discussed before by Rafaey et al. [44-46] on the basis of reduction of the Mo^{6+} to Mo^{4+} that is incorporated in the passive film as a MoO_2 sustaining the healing resistance of oxide film, (reaction 5):

$$MoO_4^{2-} + 4\,H^+ + 2e^- \leftrightarrow MoO_2 + 2H_2O \qquad (5)$$

The reduction of the MoO_4^{2-} ions into MoO_2 could furnish supplemental oxygen that imped the capability of ClO_4^- and/or Cl^- ions to adsorb on the Ni electrode surface, preventing the formation of local active cell [42]. Fig 9 depicts the scanning electron micrograph (SEM) of the anodic polarized Ni sample in 0.01 M H_2SO_4 containing 0.01M ClO_4^- and 0.01M MoO_4^- anions. The photograph indicates a less corroded surface with corrosion products spread on the passive metal surface, which confirms the protective effect of the added MoO_4^- anions.

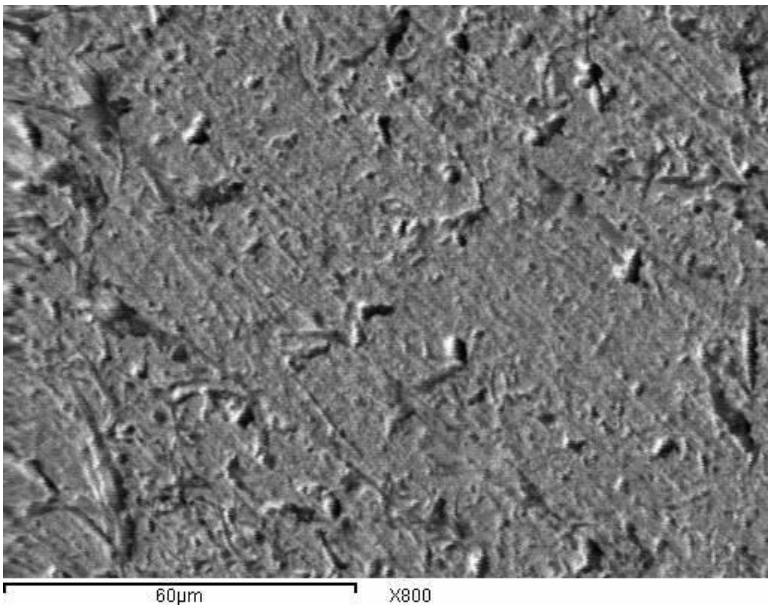

Figure 9. Scanning electron micrograph (SEM) of the anodically polarized Ni sample in 0.01 M H_2SO_4 containing 0.01M ClO_4^- and 0.01M MoO_4^- ions.

The inhibition effect of Na_2CrO_4 could be interpreted on the basis of the reduction of the hexavalent chromium Cr^{6+} to trivalent chromium Cr^{3+} to form Cr_2O_3 which is easily incorporated into the passive Ni-oxide film in similar to the Fe-passive film [42, 46, 47]. From another point of view, Rafaey et al. [44] attributed the inhibition influence of chromate anions on the pitting of steel is due to the ability of these anions to block the pores spread on the surface of the passive oxide film rising the resistance towards the pitting corrosion.

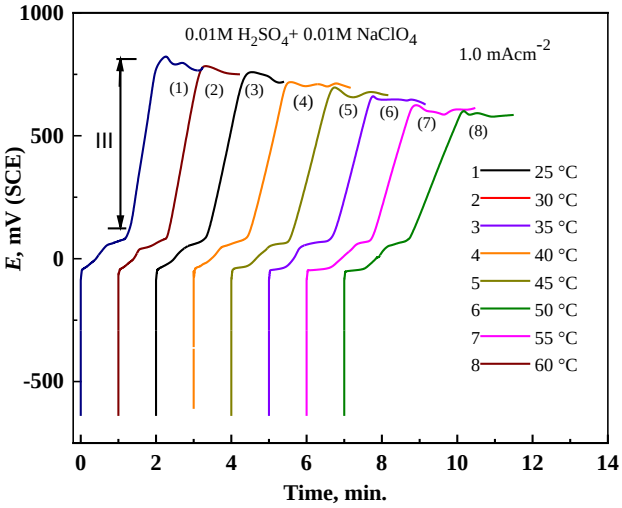

Figure 10. The effect of temperature on the anodic polariziation curves of Ni in 0.01 M H_2SO_4 containing 0.01 M $NaClO_4$ solution.

3.3. The influence of temperature

The influence of temperature on the anodic polarized curves of Ni in 0.01M H_2SO_4 containing 0.01 M ClO_4^- ions without and with the additions of 0.01 M of different passivators was investigated. Fig 10 explores the influence of temperature (15-60°C) on the anodic polarized curves of nickel in 0.01 M H_2SO_4 containing 0.01 M $NaClO_4$ solution. Similar curves are done in presence of 0.10 M H_2SO_4 + 0.01 M ClO_4^- containing 0.01 M of different inhibitors (curves not shown). It is noted that the raise in the solution temperature increases the induction time needed for the active corrosion and the pitting corrosion. On the another hand, the rate of oxide film formation is decreased with shifting the pitting corrosion potential, E_{pit}, (in the absence and presence of the inhibitive anions) into more active values with rising the temperature. The increase in the induction time required for Ni oxidation with the reduction in the rate of building of the Ni oxide film by increasing in the temperature can be explained to the probability of increasing the mobility of ions [48].

The induction period required for the passivation and pitting corrosion processes, τ_1, are raised with temperature, while the rate of oxide film formation is reduced through lowering in the slope of the potential-time curve (zone III) of Fig 10. This attitude can be confirmed by Fig 11 which depicts a straight-line relation between the log τ and the temperature, T.

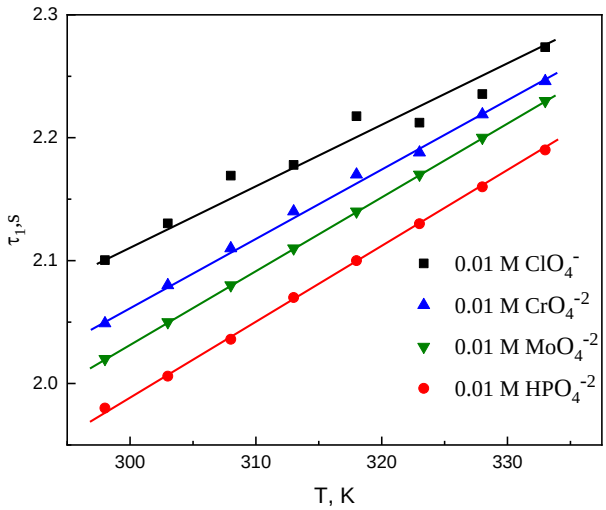

Figure 11. Variation of the induction period τ_1 on the temperature, T, for Ni in 0.01 M H_2SO_4 containing 0.01 M $NaClO_4$ solution in the absence and presence of 0.01 M of different anions.

However, the Arrhenius equation [4, 49-58] can be used to calculate the activation energy, E_a, for damage of the passive oxide film on Ni and initiate the pitting corrosion without and with the used anions.

$$\log r = \frac{-\Delta E_a}{2.303RT} + \log A \qquad (11)$$

where r depicts the rate of corrosion reaction represented by the quantity of electricity (Q_a) required to reach E_{pit}, E_a is the apparent activation energy, T is the absolute temperature, A is the Arrhenius constant and R is the gas constant.

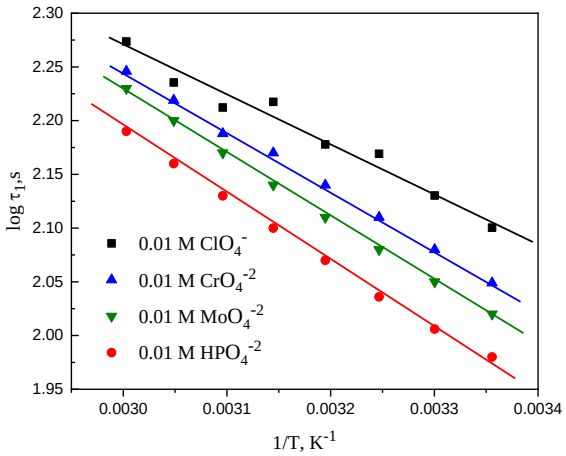

Figure 12. Arrhenius plots for Ni in 0.01M H_2SO_4 containing 0.01 M NaCl and 0.01 M of different inhibitors.

The values of log r (in units of mC/cm^2), calculated at various temperatures are plotted against 1/T, Fig 12, in the case of 0.01 M H_2SO_4 + 0.01 M $NaClO_4$ without and with 0.01 M of various inhibitors. The activation energies, E_a were determined from the slope values, Table 1. The activation energy, E_a, for the pitting corrosion of Ni in 0.01 M H_2SO_4 containing 0.01 M $NaClO_4$ was 9.39 kJ/mol. The existence of the different passivators rise the value of E_a to be 11.28, 12.63 and 14.36 kJ/mol with CrO_4^{2-}, MoO_4^{2-} and HPO_4^{2-}, successively. The increase in the E_a values with the used passivators explain the increase in the energy barrier, which is accompanied by the reduction in charge and mass transfer [50].

4. CONCLUSION

The anodic polarization of Ni in dilute H_2SO_4 containing 0.01 M $NaClO_4$ was examined without and with various additions of CrO_4^{2-}, MoO_4^{2-} and HPO_4^{2-}. The data indicated that:

- The existence of activation region due to the oxidation accompanied by a linear increase in the potential owing to the oxide film formation followed by O_2 production.

- Presence of ClO_4^- ions destructs the oxide film passivity at E_{pit} with initiation of localized pitting corrosion.

- The rate of oxide film formation was reduced with the more additions of ClO_4^- ions

- E_{pit} shits into less positive values with increasing rising the amount of ClO_4^- ions.

- The increase in the induction time with the amount of ClO_4^- ions was attributed to the adsorption of the added ions.

- The activation energies required for oxide film destruction and initiation of pitting, E_a, are increased in the presence of the passivators.

Table 1. The activation energy for pitting corrosion, E_a, of Ni in 0.01 M H_2SO_4 containing 0.01 M ClO_4^- ions in the absence and presence of different passivators.

Type of anions	r^2	E_a, kJ mol^{-1}
0.01 M ClO_4^-	0.988	9.39
0.01 M ClO_4^- + 0.01 M CrO_4^{2-}	0.999	11.28
0.01 M ClO_4^- + 0.01 M MoO_4^-	0.998	12.63
0.01 M ClO_4^- + 0.01 M HPO_4^{2-}	0.998	14.34

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