

Breakdown of passivity of nickel electrode in sulfuric acid and its inhibition by pyridinone derivatives using the galvanostatic polarization technique

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Abstract

The effect of Cl^- and Br^- anions as aggressive species to breakdown the passivity of Ni electrode in H_2SO_4 solution was studied using galvanostatic polarization technique. Low concentrations of these anions lower than 1×10^{-4} M have no effect on the passivity of nickel, while high concentrations of these anions destroy the passivity and initiate the pitting potential before the oxygen evolution region. Raising the solution temperature shifts the breakdown potential towards the more negative direction. This could be attributed to the more destruction of the passivity by halides anions with increasing temperature. The addition of some synthetic pyridinone derivatives to the aggressive chloride solutions shifts the pitting potential to more positive values indicating the resistance to pitting attack in chloride containing solution.

Keywords: nickel, galvanstatic polarization, H_2SO_4 , aggressive anion, pitting corrosion, inhibitors.

1. Introduction

Nickel and nickel alloys exhibit excellent corrosion resistance in aqueous environments due to the formation of a stable passive film on the metal surface [1]. The nature and the mechanism of formation of the passive film depend, among other factors, on the composition and pH of the electrolyte [2] as well as, on the metal structure modification [3]. NiO was proved to be the main constituent of the passive film on Ni surface [4, 5]. Whatever the nature of the passive film, the presence of certain anions, particularly chloride, destroys passivity and leads to localized corrosion. Mac-Dougall and Graham [6] are of the opinion that the breakdown of passivity of nickel occurs on a surface covered with an oxide having a small number of local breaks or defects in the film.

The use of organic compounds containing nitrogen, oxygen or sulfur in their chemical structure to inhibit the acidic and pitting corrosion of nickel has been studied [7–18]. These

compounds inhibit the corrosion by adsorption on the nickel surface and block the active sites on the surface thereby reducing the corrosion rate.

The aim of the present investigation is to study the role of chloride and bromide ions in the breakdown of passivity of Ni in 1×10^{-2} M H_2SO_4 solution. The effect of the addition of some pyridinone derivatives to inhibit the pitting corrosion in chloride containing solution was also studied.

2. Experimental

2.1. Working electrode

The nickel electrode used in the present work was cut from pure rod provided by Johnson and Matthey (England). It has a surface area of 0.97 cm^2 . It was fixed to Pyrex glass tubing using a suitable resin (Araldite). Electrical contact was made through thick copper wire soldered to the end of electrode not exposed to the solution. Before being used, the electrode surface was mechanically polished using different grades of emery papers, then degreased with acetone and washed with running distilled water. The surface pretreatment was carried out immediately before each experiment and with a fresh portion of the solutions. Measurements were carried out at room temperature $25 \pm 1^\circ\text{C}$.

2.2. Electrolytic cell

The electrolytic cell used for galvanostatic polarization was composed of two components separated by a fitted glass disc to prevent mixing of anolyte and catholyte. The cell has a double jacket through which water at the adjusted temperature was circulated. A conventional three-electrode system was used. A platinum sheet was used as an auxiliary electrode, the working electrode was Ni electrode, and the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary positioned close to the working electrode surface in order to minimize the ohmic potential drop. The Ni electrode was subjected to a cathodic pretreatment process for 10 min in the test solution at the same polarizing current density. This process was done to reduce any oxide film that formed spontaneously on the metal surface before the experiment. After that, the polarizing current was then reversed to anodic direction, and the potential was recorded as a function of time (anodic polarization). All chemicals used were of the analytical grade quality and were used without further purification.

2.3. Organic inhibitors

There are four synthetic organic compounds used as corrosion inhibitors. They are listed in Table 1.

i. Synthesis of compound I

In a necked flask 0.01 mole cyanoacetamide was added to 0.01 moles of acetylacetone in the presence of acetone as a solvent and drop of triethylamine. The mixture was refluxed

for a period of one hour; the precipitate was filtered off, dried and recrystallized from ethanol, after cooling.

ii-Synthesis of compound II

0.01 mole of compound I was dissolved in 2 mole NaOH followed by adding 0.01 mole H_2O_2 in a necked flask. The mixture was stirred for a period of 2 hours, acidified by using HCl, filtered off, dried and recrystallized.

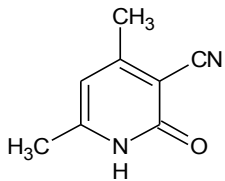
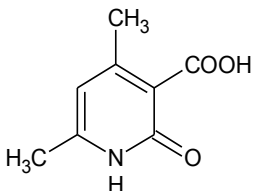
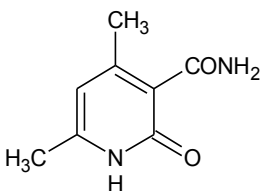
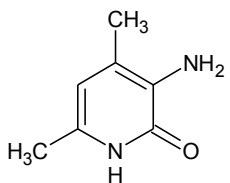
iii. Synthesis of compound III

0.01 mole of compound II was dissolved in a mixture of 10 ml acetic acid and 0.01 mole of HCl, followed by adding 0.01 mole of sodium nitrite. The mixture is cooled using ice bath and the product was filtered off, dried and recrystallized.

iv. Synthesis of compound IV

0.01 mole of compound II was dissolved in 2 mole NaOH and 0.01 mole bromine solution was added. The mixture left over night and the product was acidified by acetic acid, filtered off, dried and recrystallized.

Table 1: The chemical structure of the pyridinone derivatives.

No.	Name	Structure	Molecular weight	Melting point
I	4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile		148	287
II	4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carboxylic acid		167	297
III	4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carboxamide		166	324
IV	3-amino-4,6-dimethylpyridin-2(1H)-one		138	341

3. Results and Discussion

3.1. Effect of NaCl and NaBr

The curves of Figures 1 and 2 show the galvanstatic anodic polarization curves of Ni electrode in 1×10^{-2} M H_2SO_4 solution in the absence and presence of NaCl and NaBr as pitting corrosion agents, at a current density of 2.6 mA/cm^2 . These figures indicate that, at low concentrations of aggressive anions, $\leq 1 \times 10^{-4}$ M, there is no change in the general shape of polarization curves. The data of the curves in case of free and in presence of 1×10^{-4} M aggressive ions show a rapid and almost linear change of potential (region I) due to the decay of hydrogen over potential on metal surface and the subsequent charging of the electrical double layer at the metal/solution interface [19]. Subsequent to this rapid process, the potential of Ni electrode changes more slowly with time giving rise to a arrest, **a**, followed by a another small one, **b**. These arrests, **a** and **b** are related to Ni oxidation as Ni^+ ions and Ni^{2+} ions species. The rising in potential after arrest **b** can be related to the formation of NiO on the anode surface giving rise to a passivation film. The similarity in the polarization curves in absence and presence of these lower concentrations of the aggressive anions indicates that these ions do not interfere the formation of passivity on Ni electrode surface expect that they cause a slight reduction of the over potential associated with the oxygen evolution reaction. Similar findings were reported during the pitting corrosion of metals in different electrolytes [19] The initiation of pits on the passive metal cannot occur unless the concentration of the aggressive anions in the solution is above a certain value.

Further inspection of the curves of Figures 1 & 2 show that, the high concentrations of aggressive ions, $\geq 1 \times 10^{-4}$ M, cause a change in the anodic polarization curve of nickel at a fixed potential. This potential is found to depend on the type and concentration of the aggressive ion. Moreover, the appearance of a breakdown in the passive region, before reaching oxygen evolution and the shift in the potential towards active direction is due to the initiation of pitting corrosion on the passive Ni metal. This potential is called the breakdown potential, E_b . At this potential, the potential is observed to decrease with time to reach a new steady-state value, without attaining oxygen evolution. The breakdown potential, E_b , of Ni electrode shift towards more negative values as the concentration of aggressive anion increases in the solution. The dependence of the breakdown potential on the concentration of the halide anions can be seen in Figure 3. This figure represents the plot of the breakdown potential, E_b , vs. the logarithm of the halide anions, C_{agg} . This fulfills the following equation [19]:

$$E_b = \alpha_1 - \beta_1 \log C_{\text{agg}} \quad (1)$$

where α_1 and β_1 are constants. The slope β_1 of the nearly parallel lines is 878 mV/decade. The values of the constant α_1 are equal to -1650 and -1700 mV/decade for Cl^- and Br^- , respectively, which reflects its tendency aggressiveness towards the pitting action.

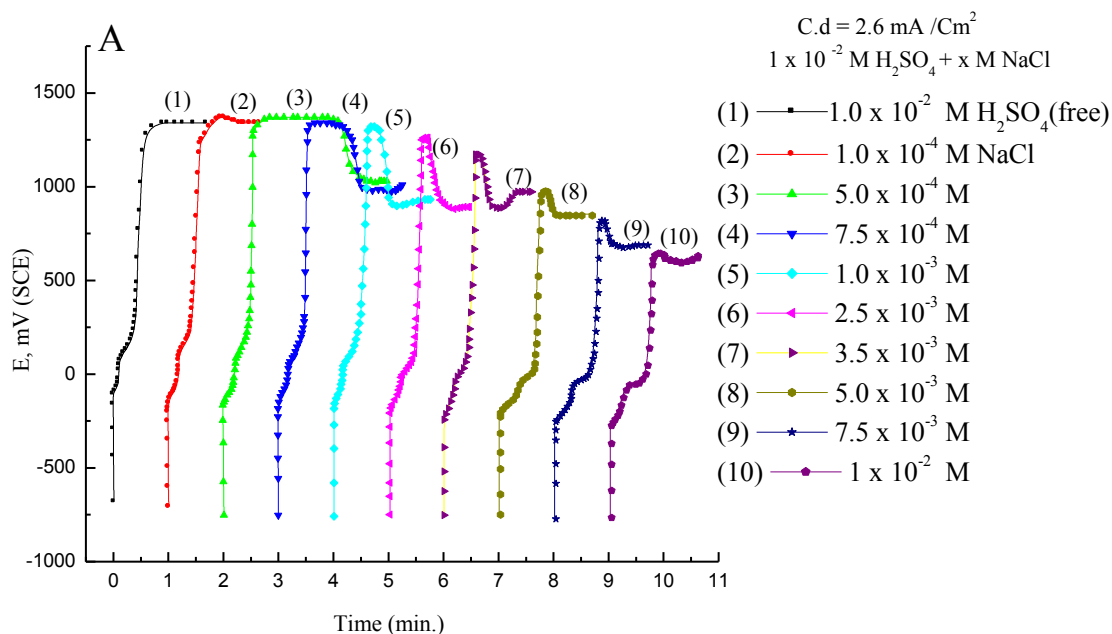


Figure 1. Anodic polarization curves for Ni in $1 \times 10^{-2} \text{ M H}_2\text{SO}_4$, at 2.6 mA/cm^2 in absence and presence of different concentration of NaCl.

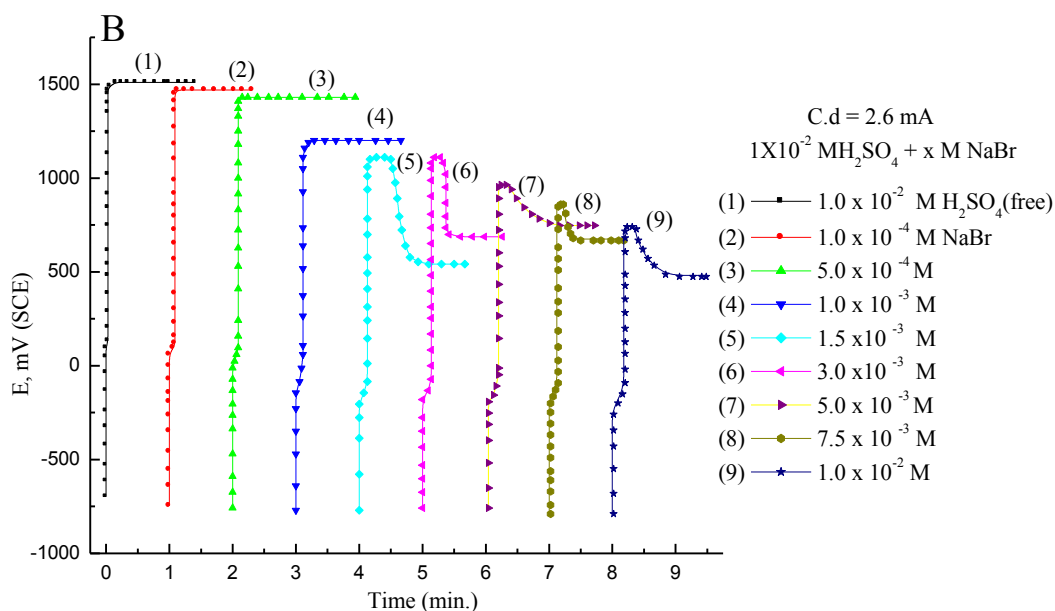


Figure 2. Anodic polarization curves for Ni in $1 \times 10^{-2} \text{ M H}_2\text{SO}_4$, at 2.6 mA/cm^2 in absence and presence of different concentrations of NaBr.

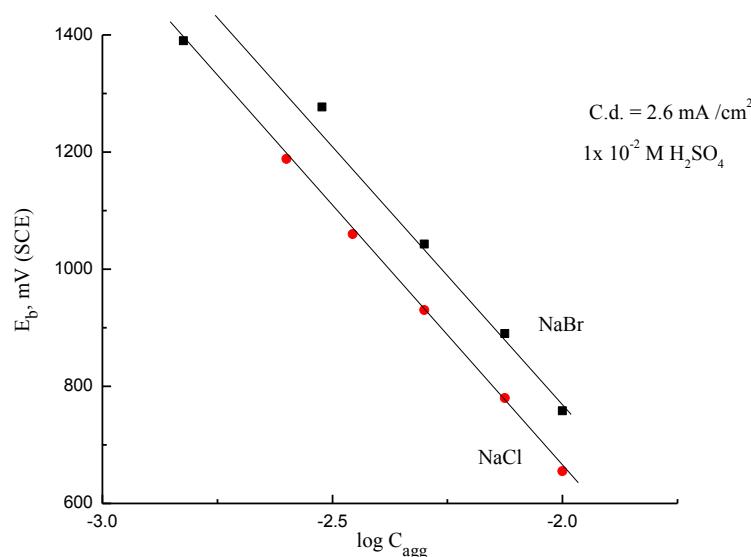


Figure 3. Variation of the breakdown potential, E_b , with logarithm concentration of NaCl and NaBr.

Examination of the electrode surface after polarization experiments showed visible pits whose number per unit increased with increasing the aggressive ion content in the test solution. Scanning electron micrographs (SEM) of the polarized nickel electrode sample in solutions of 1×10^{-2} M H_2SO_4 solution in the presence of 5×10^{-3} M NaCl [as an example of pitting corrosion agent] at a current density of 2.6 mA/cm^2 for 15 min is shown in Figure 4. A number well-defined pits and few fine pits are spreader on the sample surface are shown. This demonstrates that the presence of Cl^- anions causes the formation of these pits, which is randomly distributed in the passive film.

3.2. Effect of temperature on aggressive anion

Figure 5 (A&B) shows the anodic polarization curves of the nickel electrode in 1×10^{-2} M H_2SO_4 in the presence and absence of 1.5×10^{-3} M NaCl and NaBr solutions were investigated at different temperatures ranging from 15 to 45°C , at a constant current density, 2.6 mA/cm^2 , respectively. It is shown that as the temperature increased, the breakdown potential, E_b , and the time required for passivation processes, were influenced. It is observed that, as the temperature increases, the rate of breakdown potentials of passivity, are decreased by 11 and 20 mV/degree for Br^- and Cl^- ions, respectively. This behavior could be attributed to the increase of the solubility of nickel oxide with increasing temperature.

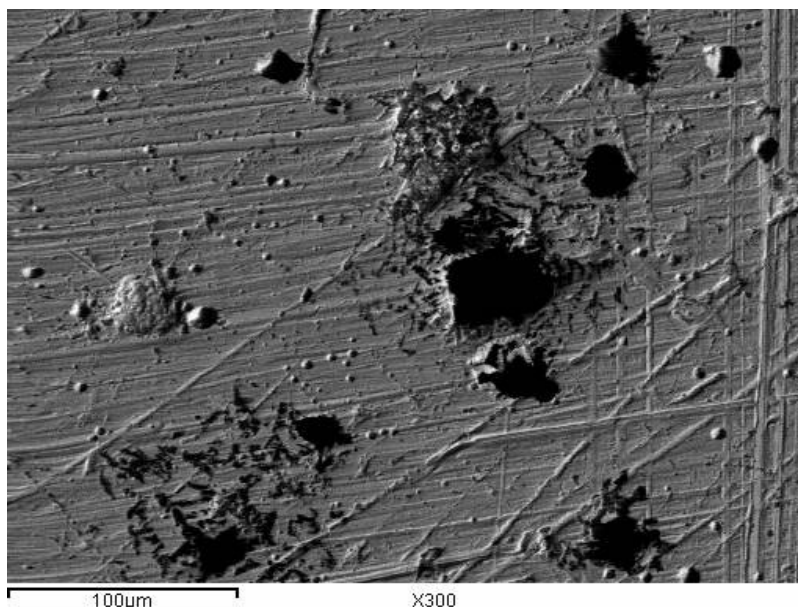


Figure 4. Scanning electron microscopy of nickel in 1×10^{-2} M H_2SO_4 solution in the presence of 5×10^{-3} M NaCl.

Figure 6 shows a linear relation between the breakdown potential, E_b , and temperature. As the temperature increases, the breakdown potential, E_b , is shifted towards more negative values. This indicates that the protective properties of the passive film towards the breakdown potential are altered [20]. Wang *et al.* [21] illustrated the variation of E_b with temperature in terms of film porosity or its chemical and/or physical modification with increasing temperature.

3.3 Inhibition of the pitting corrosion of Ni using some pyridinone derivatives

The curves of Figures 7–10 represent the effect of addition of increasing concentrations of the pyridinone derivatives compounds as pitting inhibitors on the galvanstatic polarization curves of Ni electrode in 1×10^{-2} M H_2SO_4 + 1.5×10^{-3} M NaCl at current density of 2.6 mA/cm^2 at 25°C .

Small concentrations of the used additives shift the pitting potential towards more positive values. Apparently, the additives compete with the aggressive Cl^- ions for adsorption sites on the metal surface reducing, thus, their surface concentration. As the concentration of the compounds are further increased, the extent of pitting potential is markedly decreased and finally reaches a stable potential whose value depends on the type of the added inhibitor. The attainment of a steady potential in the presence of compounds is attributed to complete protection of the Ni surface against pitting corrosion. It is assumed that the added inhibitors adsorb well on the metal surface and prevents the aggressive ions to cause film destruction.

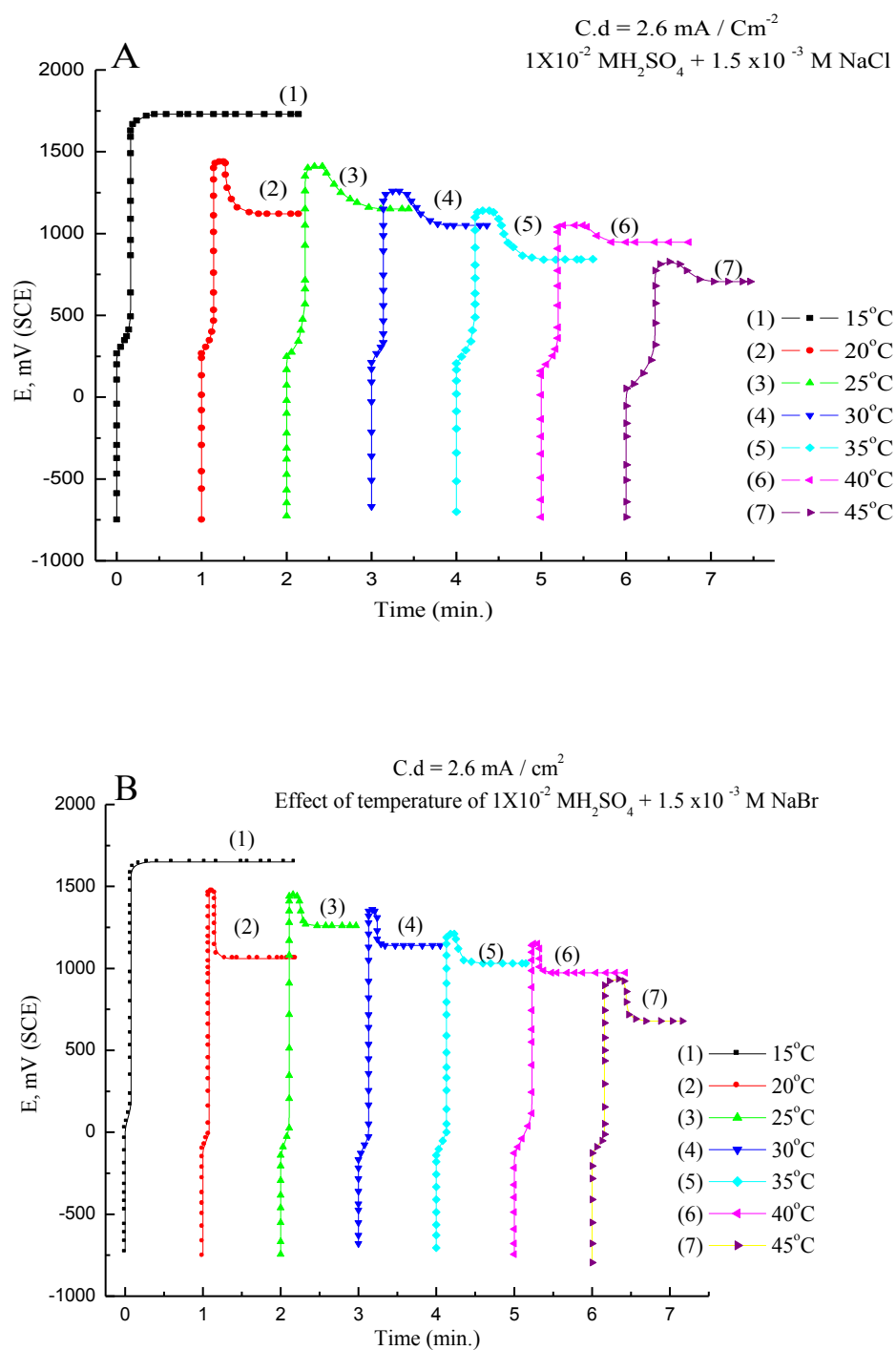


Figure 5. Effect of temperature on the anodic polarization curves for Ni in 1×10⁻² M H₂SO₄ + (A) 1.5×10⁻³ M NaCl, (B) 1.5×10⁻³ M NaBr solutions at 2.6 mA/cm².

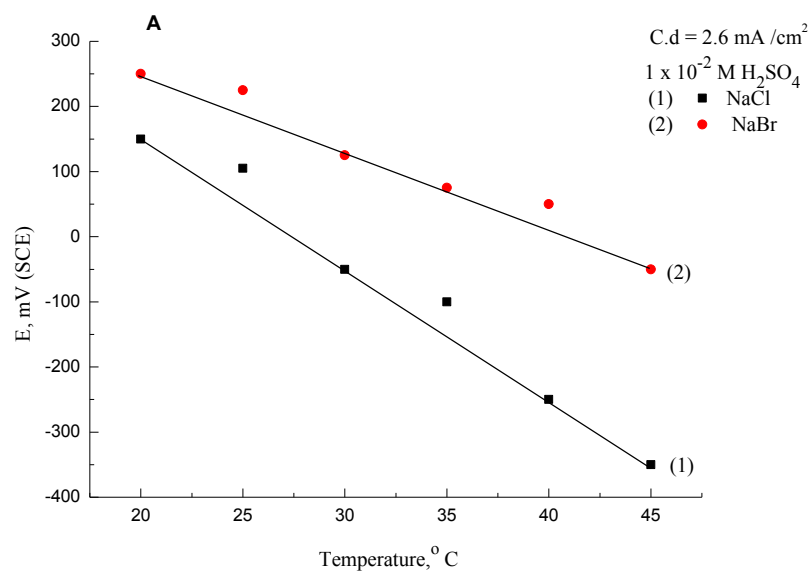


Figure 6. Variation of the breakdown potential E_b with temperature.

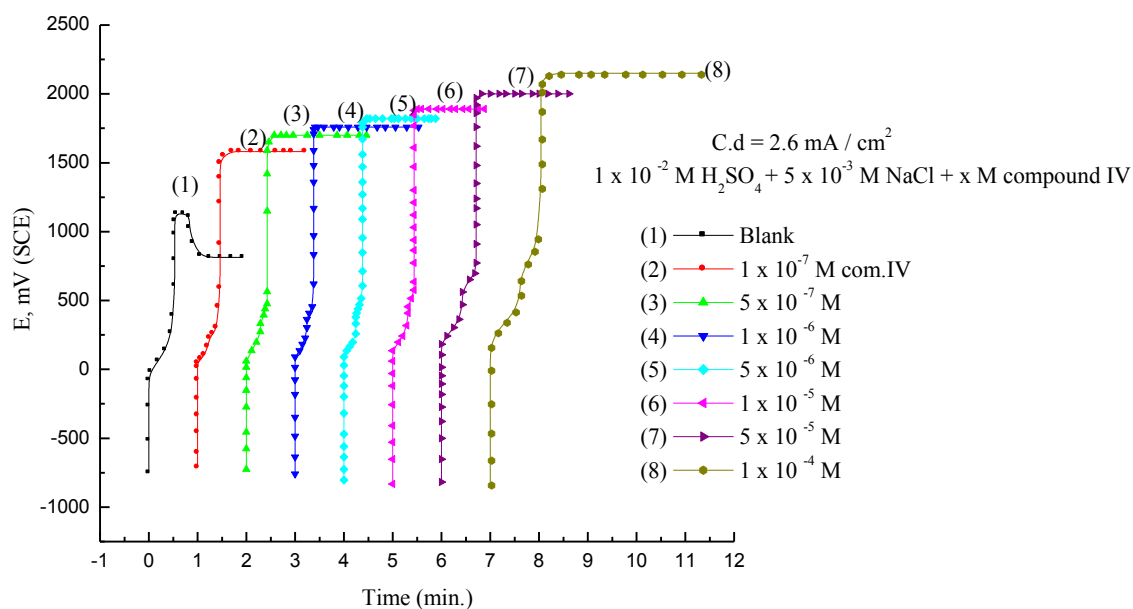


Figure 7. Anodic polarization curves of Ni in 1×10^{-2} M $H_2SO_4 + 1.5 \times 10^{-3}$ M NaCl + x M of compound I at a current density of 2.6 mA/cm^2 at 25°C .

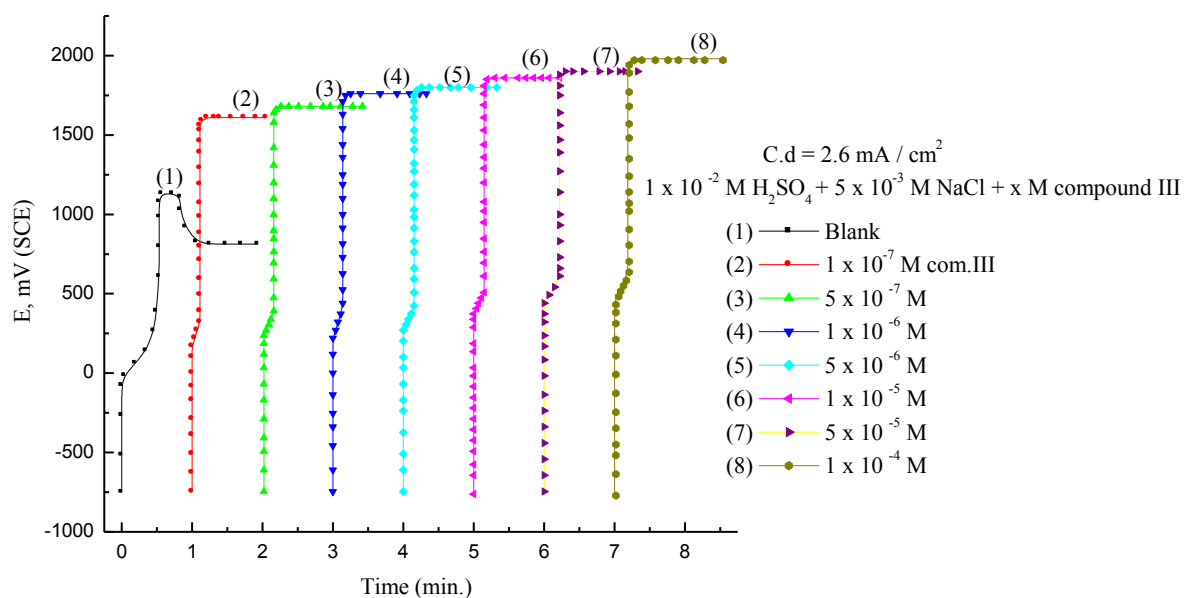


Figure 8. Anodic polarization curves of Ni in 1×10^{-2} M $\text{H}_2\text{SO}_4 + 1.5 \times 10^{-3}$ M NaCl + x M of compound II at a current density of 2.6 mA/cm^2 at 25°C .

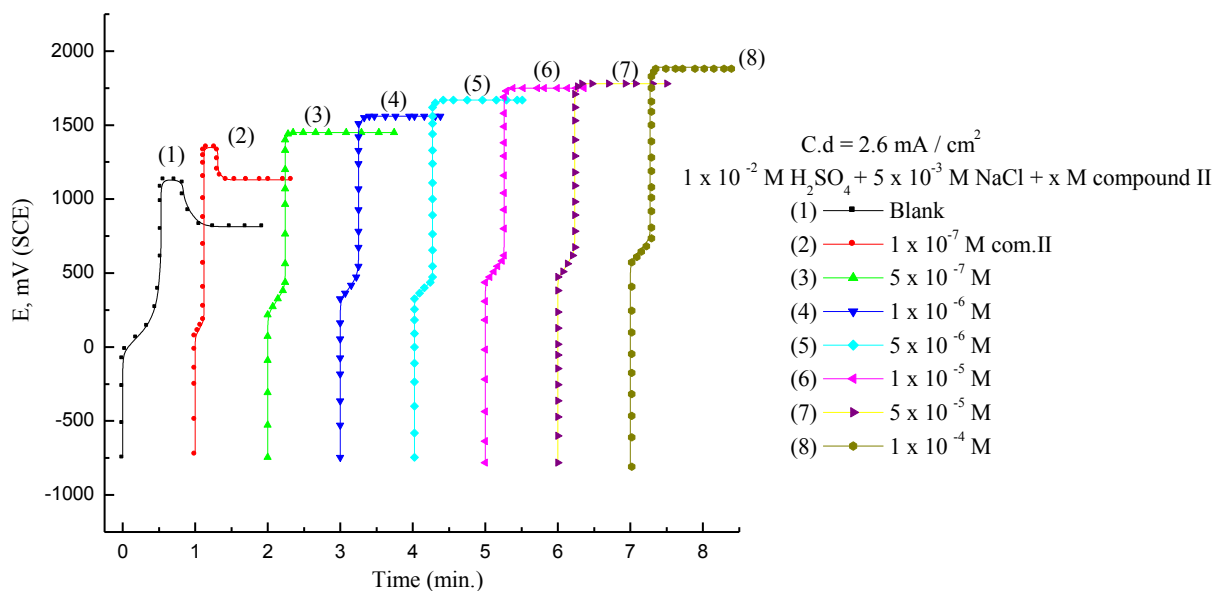


Figure 9. Anodic polarization curves of Ni in 1×10^{-2} M $\text{H}_2\text{SO}_4 + 1.5 \times 10^{-3}$ M NaCl + x M of compound III at a current density of 2.6 mA/cm^2 at 25°C .

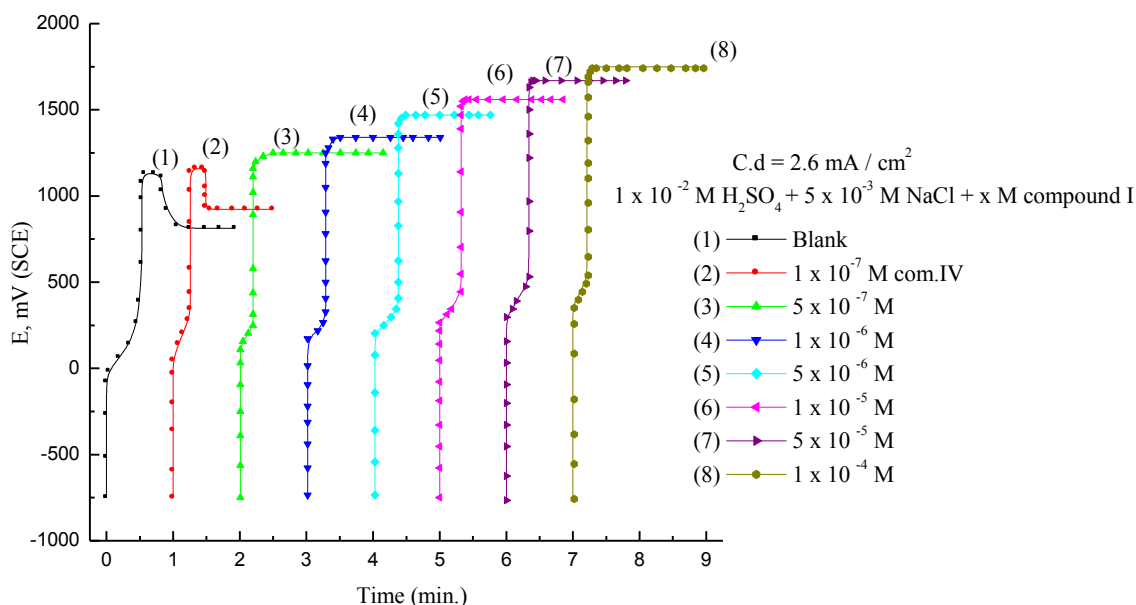


Figure 10. Anodic polarization curves of Ni in 1×10^{-2} M H_2SO_4 + 1.5×10^{-3} M NaCl + x M of compound IV, at a current density of 2.6 mA/cm^2 at 25°C .

The dependence of the pitting potential of Ni electrode, $E_{\text{pitt.}}$, on the concentration of the added pyridinone derivatives can be seen by the curves of Figure 11. This figure represents the variation between $E_{\text{pitt.}}$ and $\log C_{\text{inh.}}$ according to the following relation:

$$E_{\text{pitt.}} = \alpha_2 + \beta_2 \log C_{\text{inh.}}, \quad (2)$$

where α_2 and β_2 are constants.

The concentration of the added compounds required to cause a marked shift in potential in the noble direction increases in the order:

compound IV > compound III > compound II > compound I

It is clear from these sequences that, compound IV is more inhibiting action than compound III which is more inhibiting action than compound II and compound I. The variation in the sequence will be discussed later.

Scanning electron micrographs (SEM) of the polarized nickel electrode sample in solutions of 1×10^{-2} M H_2SO_4 + 5×10^{-3} M NaCl solution in the presence of 1×10^{-3} M compound IV (as an example of inhibitor agent) at a current density of 2.6 mA/cm^2 for 15 min is shown in Figure 12. From this figure, the presence of inhibitor cause inhibition of Ni metal from Cl^- ions attack.

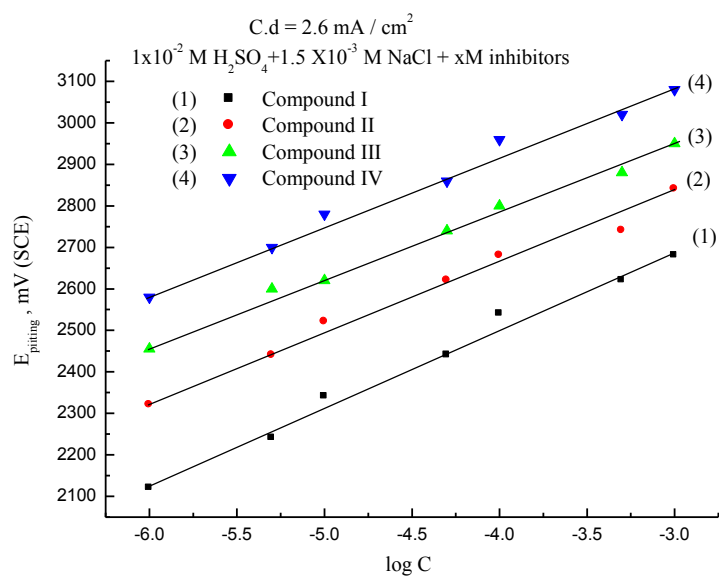


Figure 11. Variation of E_{pitting} with $\log C_{\text{inh}}$ of inhibitor concentrations.

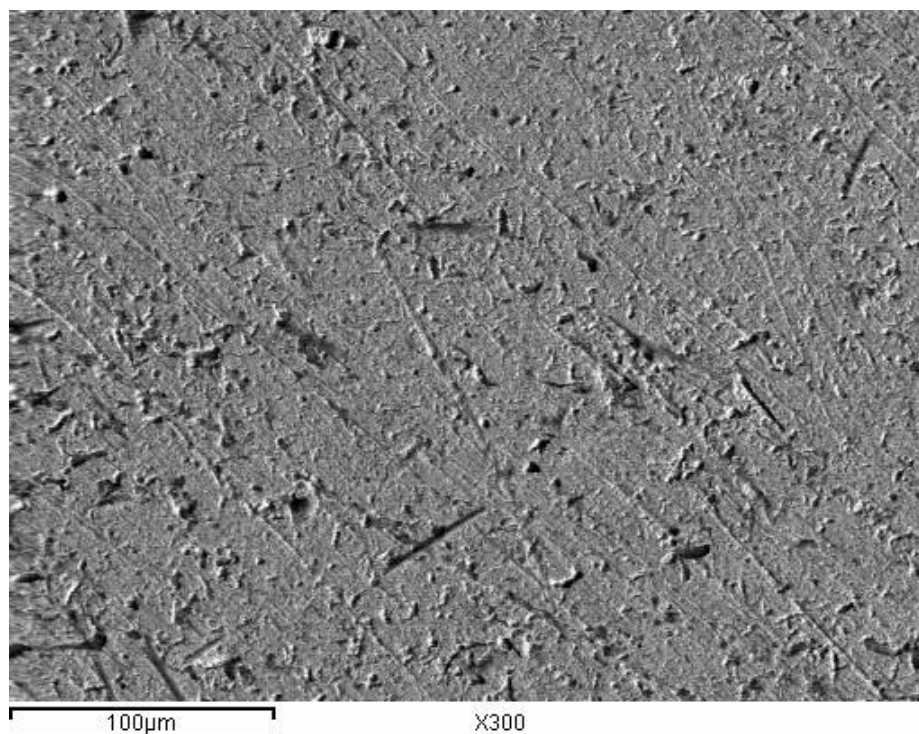


Figure 12. Scanning electron microscopy of nickel in $1 \times 10^{-2} \text{ M H}_2\text{SO}_4 + 5 \times 10^{-3} \text{ M NaCl}$ solution in presence of compound IV.

3.4. The chemical structure of the inhibitors and corrosion inhibition

The inhibition of pitting corrosion of nickel electrode by some pyridinone derivatives was found to depend on the concentration and the type of inhibitor. The corrosion inhibition occurs by adsorption of the inhibitor at the electrode/solution interface [22]. The nature of inhibitor interaction on metal surface during corrosion inhibition has been known from its adsorption characteristics [23].

However, the inhibition efficiency (%IE) of the organic additives depends [24] on many factors which include the number of adsorption sites in the molecules and their charge density, molecular size, stability of these derivatives in acidic solutions, the mode of adsorption and formation of metallic complexes.

It was found that, the order of increasing inhibition efficiency (%IE) of the tested compounds in H₂SO₄ for nickel decreases in the following order:

compound IV > compound III > compound II > compound I

The corrosion inhibition of these compounds towards the pitting corrosion of nickel in H₂SO₄ may be attributed to the presence of the lone pair of electrons on a hetero atom and the bi- bond which are responsible for adsorption of inhibitors on the metal surface. The adsorption of these compounds at the metal/solution interface, where the adsorbed molecules mechanically screen the coated part of the metal surface from the action of the corroding. The extent of the adsorption of an inhibitor depends on the nature of the metal, the mode of adsorption of the inhibitors, and the surface conditions. The results indicate that the (%IE) of the organic compounds is more or less dependent on the nature of the constituents. Skeletal representation of the structure of the pyridinone derivatives as inhibitors for nickel in H₂SO₄ is shown in Table 1. The orders of (%IE) and the positive shift of pitting corrosion potential decreased in the following order:

compound IV > compound III > compound II > compound I

This sequence may be attributed to: compound IV has the most inhibition efficiency due to the presence of amino group (NH₂) which contains a lone pair of free electrons on N atom. So it acts as an electron donating group which increase on the compound, where compound III has less inhibition than compound IV due to the presence of the carbonyl group (C=O) with (NH₂) which has ability to decrease the electron density of NH₂ group by inductive effect, where the carbonyl group act as electron accepting group so there is a resonance between the carbonyl groups lead to a decrease in the basicity on compound III. Compound II follows III and IV in inhibition efficiency due to it the presence of carboxylic group which act as electron acceptor and the absence of NH₂ group. However, the presence carbonyl group accepts electron from benzene ring and there is a resonance to the lone pair of electron in O atom between 2 oxygen atoms. The lower inhibition effect is observed with compound I. This is due to the presence of cyano group (CN) which is highly electron accepting group, accept electron from benzene ring.

4. Conclusion

1. The chloride and bromide anions breakdown the passivity of Ni electrode in H₂SO₄ solution.
2. The pitting corrosion of Ni in H₂SO₄ solution is initiated at concentrations of these anions higher than 1×10^{-4} M.
3. The destruction of passive film increases with rising temperature
4. The addition of some pyridinone derivatives to chloride containing solution increased the resistance to pitting attack

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