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# Chloride induced pitting corrosion of nickel in alkaline solutions and its inhibition by organic amines

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ABSTRACT

Cyclic voltammetry, potentiodynamic and potentiostatic anodic polarization techniques complemented by SEM investigation are used to study the initiation and inhibition of pitting corrosion of nickel in NaOH solutions. The presence of $Cl^-$ ions locally destroys the passive film formed on the nickel electrode at the pitting potentials, $E_p$, which are more active the higher the concentration of the $Cl^-$ ions. $E_p$ varies with the logarithm of $Cl^-$ ions concentration according to sigmoidal S-shaped curves.

The change in the integrated anodic charge amount, $\Delta q_a$, in the presence and absence of $Cl^-$ ions, is taken as a measure of pitting corrosion likelihood to take place. The logarithm of $\Delta q_a$ changes linearly with the $C_{Cl^-}$ according to:

$$\log \Delta q_a = a_1 + b_1 \log C_{Cl^-}, \quad \text{where} \quad a_1 \quad \text{and} \quad b_1 \quad \text{are constants.}$$

Addition of monomethylamine, monoethylamine, and dimethylamine up to a certain threshold concentration, which depends on amine type, causes complete depression of the dissolution current peak and a marked shift of the critical pitting potential into the noble direction. Following this threshold concentration, the critical pitting potential, $E_p$, changes with the inhibiting agent concentration according to the following equation:

$$E_p = \alpha_1 + \beta_1 \log C_{\text{inh}}, \quad \text{where} \quad \alpha_1 \quad \text{and} \quad \beta_1 \quad \text{are constants.}$$

Hydrazine enhances the active dissolution and pitting corrosion. The pitting potential is shifted into the active direction at all its concentrations. This behavior is attributed to the formation of hydrazine Ni-complexes. Urea behaves bifunctionally, inhibiting pitting corrosion of nickel when present in low concentrations, and enhancing the attack at higher concentrations.

## 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 [2,3], as well as, on the metal structure modification [4,5]. In alkaline environments, NiO was proved to be the main constituent of the passive film on Ni surface [6]. Okuyama and Haruyama [7], on the other hand, showed the passive film on Ni to have a duplex structure of NiO and $Ni_3O_4$ which transformed to $NiO_2$ at high potentials. Other investigators [8,9] found that the first anodic film is a thin layer of $NiO \cdot nH_2O$ which transforms to $Ni(OH)_2$ or β-NiOOH [10]. Whatever the nature of the passive film is, the presence of certain anions, particularly chloride, destroys passivity and leads to localized corrosion [3,11]. MacDougall et al. [12] are of the opinion that 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 main role of the aggressive anions in initiating pitting corrosion is to hinder oxide repassivation at the local sites in the passive oxide film rather than to the direct breakdown or thinning of the passive film [1].

The aim of the present investigation is highlighting the role of chloride ions in the processes of pit initiation and pit propagation of Ni in alkaline solutions. The techniques of potentiodynamic, potentiostatic anodic polarization and cyclic voltammetry complemented with scanning electron microscope investigation are used. Attempts are made to inhibit the pitting corrosion of nickel using some organic amines.

## 2. Experimental

Spectroscopically pure nickel electrode was made from spec-pure nickel rod (Johnson-Matthey, U.K.). The electrode was fixed to a borosilicate glass tube with epoxy resin so that the total exposed surface area was 0.16 cm$^2$. Electrical contact

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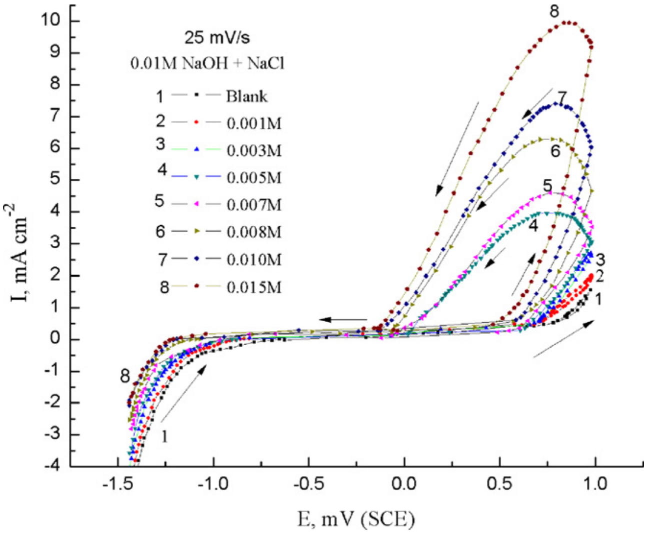

**Fig. 1.** Cyclic voltammograms of Ni electrode in 0.01 M NaOH in absence and presence of different concentrations of NaCl.

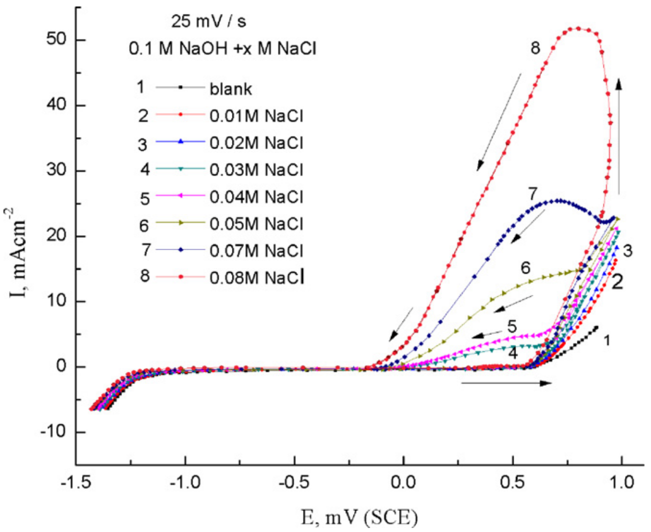

**Fig. 2.** Cyclic voltammograms of Ni electrode in 0.1 M NaOH in absence and presence of different concentrations of NaCl.

was achieved through a copper wire soldered to the end of the rod not exposed to the solution. Before being used the electrode was abraded with the finer grades emery papers to mirror finish. It was then rinsed with acetone and finally washed with triply distilled water.

The electrolytic cell used for electrochemical experiments was composed of two compartments separated by a fritted glass disc to prevent mixing of anolyte and catholyte. The cell has a double-walled 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 ohmic potential drop. Before carrying polarization, the nickel electrode was subjected to cathodic pretreatment for 20 min in the test solution at −1.5 V (SCE) to reduce any overlying oxides film that would be formed on the metal surface before running the experiment.

Electrolytic solutions were prepared from analytical grade reagents and triply distilled water. Experiments were carried out in carbonate-free NaOH solutions in the presence of NaCl as an aggressive anion. Furthermore, the effect of some primary aliphatic amines on the pitting corrosion of Ni electrode was investigated. The surface of some electrode samples after immersion in the aggressive solutions for a period of 10 min at the respective pitting potential was investigated using a Jeol scanning electron microscope, JSM-T 100 (Japan).

Measurements were carried out at a constant temperature, 25 ± 1 °C, using an ultra-thermostat. Electrochemical polarization was made using a Wenking Potentioscan Type POS 73. The data of current density–potential curves were recorded on an *X*–*Y* recorder, Type Advance HR 2000. Each experiment was carried out in a fresh portion of solution and with a newly polished electrode.

## 3. Results and discussion

### *3.1. Cyclic voltammetry measurements*

The effect of increasing concentrations of Cl$^-$ ions on the stability of the passive film formed on the nickel electrode in solutions of naturally aerated NaOH of different concentrations is examined using the cyclic voltammetry and the potentiodynamic anodic single sweep techniques.

The curves in Figs. 1 and 2 show the cyclic voltammograms of the nickel electrode in 0.01 M and 0.1 M NaOH solutions, respectively, in absence and presence of increasing concentrations of NaCl, as pitting corrosion agent, at a sweep rate of 25 mV s$^{-1}$. Similar curves are obtained in 0.05 M NaOH (curves not shown here).

Inspection of the cyclic voltammograms of the nickel electrode in Figs. 1 and 2 reveals the following conclusions to be drawn:

(i) In Cl$^-$ ions-free solutions, the cyclic voltammograms are characterized with an elongated passive region before the marked increase in current density due to the evolution of oxygen gas on the metal surface. No active-dissolution region is detected due to the lower sensitivity of the current density scale. The latter will be clarified on discussing the potentiodynamic anodic behavior of the nickel electrode (shown later).

(ii) The presence of increasing concentrations of Cl$^-$ ions causes slight weak fluctuations in the passivating current before the initiation of stable pitting corrosion. These fluctuations are observed only when the potential span of the passivating region is zoomed, and appear clearly in Fig. 5B which will be discussed later. The concentration of Cl$^-$ ions that causes current fluctuations depends on the OH$^-$ concentration, being higher the higher the concentration of the electrolyte. These current fluctuations may be ascribed to the formation of metastable pits [13–16]. During this process nucleation, growth and repassivation of metastable pits on the metal surface take place [13–16]. Some of these pits grow to form stable pits at the pitting potential, while the others undergo repassivation [17]. Many interesting models on the growth of metastable pits have been proposed. Williams et al. [18,19] proposed a statistical model which depends on the rates of nucleation of unstable and stable pits and the probability of repassivation of unstable ones. Frankel et al. [20], on the other hand, reported that the performance of the film causes a main influence on pit growth. However, Burstein and Pistorius [13,21,22] suggested a diffusion control model for growth of metastable pits. A metastable pit will develop into stable stage if a critical product of current density and pit depth is reached. Zuo et al. [17] were of the opinion that metastable pits may grow at two stages. At the early stage of growth, a metastable pit should be open and the growth current density may be controlled by concentration diffusion. The second stage begins when the passive film is undermined at maximum diffusion rate through pit mouth.

(iii) The effect of Cl$^-$ ions on the passive film on nickel electrode can be recognized by the marked increase of the flowing currents at the pitting potentials, $E_p$, lying in the passive region. $E_p$ becomes more active the higher the concentration of the Cl$^-$ ions, Figs. 1 and 2. The increase in current could be attributed to the destruction of the passive film with the initiation of pitting corrosion. The minimum concentration which causes breakdown of passivity and the initiation of pitting corrosion depends on the OH$^-$ ion concentration, being higher the higher the OH$^-$ ion concentration as shown in Table 1.

**Table 1**
The minimum concentrators of $Cl^-$ ions which cause break down of passivity.

| NaOH concentration (M) | Minimum $Cl^-$ ion concentration (M) |
|---|---|
| 0.01 | 0.001 |
| 0.05 | 0.005 |
| 0.10 | 0.010 |

(iv) The more interesting feature of these curves is the fact that when the potential of the working electrode is reversed into the cathodic direction, currents start to decrease gradually with decreasing electrode potential. The flowing currents always remain in the positive branch of the cyclic voltammograms and finally reach the zero value at the protection potential, $E_{pp}$, which depends also on the $Cl^-$ ions content of the solution, being more active the higher the $Cl^-$ ions concentration. One may attribute the existence of these currents with positive values while the potential of the working electrode is decreasing to the continuous propagation of the formed pits. When the potential of the nickel electrode becomes sufficiently active, the formed pits cease to propagate and the flowing currents decrease to minimum at the protection potential, $E_{pp}$. This phenomenon causes the formation of large dissolution current areas which are highly enlarged in value with increasing the $Cl^-$ ions content of the solution. These anodic areas are integrated between the value of the critical pitting potential, $E_p$, in the anodic direction and the value of protection potential, $E_{pp}$, in the cathode direction, at each $Cl^-$ ions concentration. Under these conditions, one may consider the change in the anodic charge amount, $\Delta q_a$, in the presence and absence of $Cl^-$ ion, as a measure of the extent of pitting corrosion likelihood. The latter increases markedly with increasing the concentration of the pitting corrosion agent.

Fig. 3 represents the variation of log $\Delta q_a$, in coulomb cm$^{-2}$, with the logarithm of the molar concentration of $Cl^-$ ions. The value of log $\Delta q_a$ changes only slightly with the $Cl^-$ ions concentration and at a threshold concentration which depends on the $OH^-$ ions concentration, it changes markedly and linearly with log $C_{Cl^-}$ according to:

$$\log \Delta q_a = a_1 + b_1 \log C_{Cl^-}. \tag{1}$$

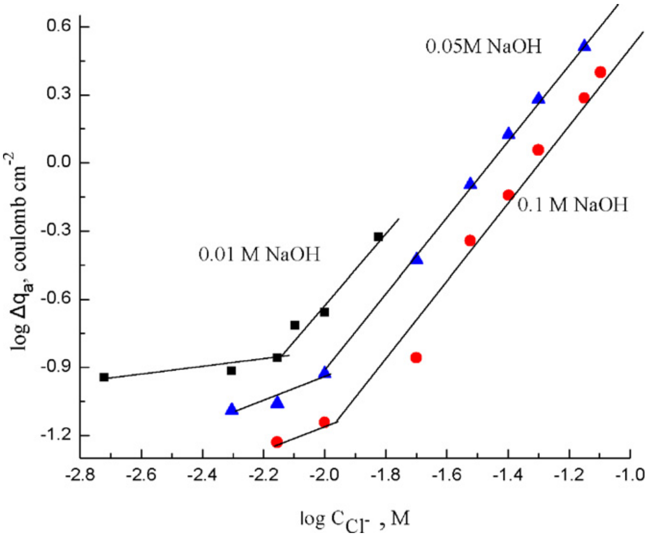

**Fig. 3.** Variation of log $\Delta q_a$, coulomb cm$^{-2}$, with the logarithm of the molar concentration of $Cl^-$ ions.

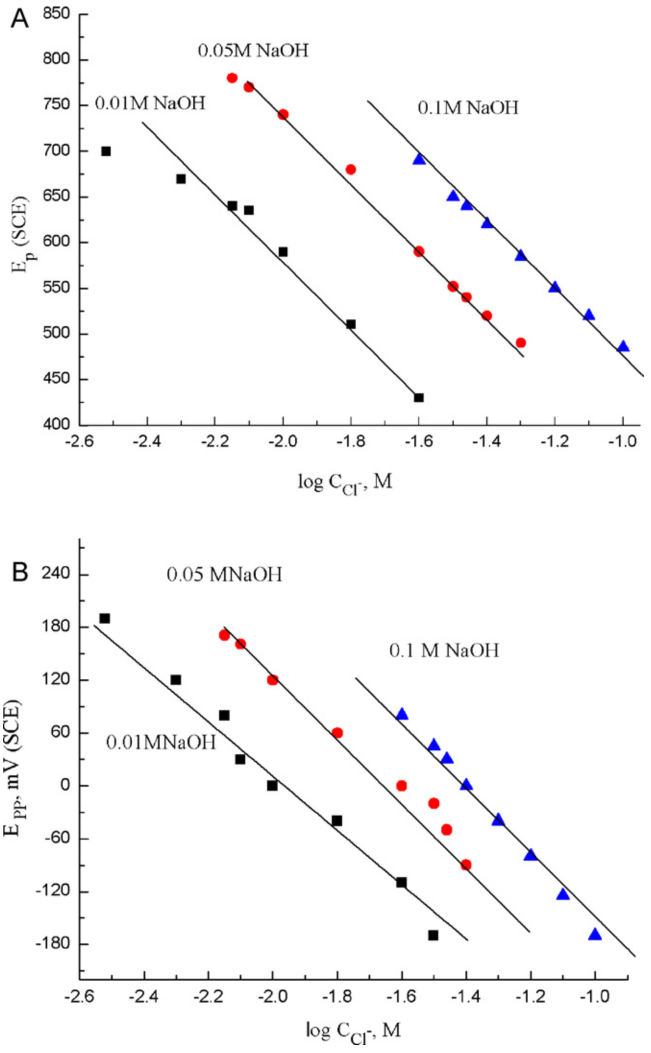

**Fig. 4.** Variation of the pitting potential, $E_p$ (A) and the protection potential, $E_{pp}$ (B), respectively, as function of the logarithm of the molar $Cl^-$ ions concentration, in 0.01, 0.05 and 0.1 M NaOH solutions.

where $a_1$ and $b_1$ are constants which depend on the solution composition and scanning rate [23,24]. The constant $a_1$ has the values 2.54, 2.50 and 2.35 coulomb cm$^{-2}$ for 0.01 M, 0.05 M and 0.1 M NaOH, successively, while $b_1$ takes the value 1.7 coulomb cm$^{-2}$ decade$^{-1}$ which is independent of $OH^-$ ions concentration. In the presence of low $Cl^-$ ions concentrations, the formed pits are not completely active, while at higher concentrations the formed pits become continuously propagated [25–27].

The pitting tendency of the metal can also be estimated from the determination of the critical pitting potential, $E_p$, for the test material in a given environment or by the determination of the minimum aggressive ions concentration required to initiate pitting corrosion [28]. The critical pitting potential is always defined as the potential below which the metal surface remains passive and above which pits can be nucleated and developed.

It should also be further noted that pitting performance of a given metal or alloy does not only depend on the critical pitting potential, $E_p$, but also on the protection or repassivation potential, $E_{pp}$. This potential corresponds to the potential below which already initiated pits undergo repassivation and depends on the extent to which previous pits are grown [29]. In Fig. 4(A and B) both the critical pitting potential, $E_p$, and the protection potential, $E_{pp}$, as estimated from the cyclic voltammograms of Figs. 1 and 2, are plotted, as function of the logarithm of the molar concentration of

**Table 2**
The values of the constants $a_2(a_3)$ and $b_2(b_3)$ of Eqs. (2) and (3).

| NaOH concentration (M) | $a_2$ ($mV_{SCE}$) | $b_2$ ($mV_{SCE}$ decade$^{-1}$) | $a_3$ ($mV_{SCE}$) | $b_3$ ($mV_{SCE}$ decade$^{-1}$) |
|---|---|---|---|---|
| 0.01 | −198 | −393 | −637 | −327 |
| 0.05 | −13 | −379 | −526 | −325 |
| 0.10 | 145 | −336 | −584 | −419 |

the $Cl^-$ ions in solutions of 0.01, 0.05 and 0.1 M NaOH, respectively. Inspection of curves of Fig. 4(A and B) reveals that both potentials vary linearly with the logarithm of $C_{Cl^-}$ according to:

$$E_p = a_2 - b_2 \log C_{Cl^-}. \qquad (2)$$

$$E_{pp} = a_3 - b_3 \log C_{Cl^-}. \qquad (3)$$

where $a_2(a_3)$ and $b_2(b_3)$ are constants which have the values listed in Table 2.

The value of the difference $(E_p - E_{pp})$ was taken as a relative measure of the pit repassivation ability [30–33]. Some others [34] attributed it to the possible occurrence of crevice corrosion which is not recognized in the present investigation. The smaller the difference between $E_{pp}$ and $E_p$, the greater the tendency for pitting repassivation would be. In Table 3, the values of $(E_p - E_{pp})$ for the Ni electrode, in 0.01, 0.05 and 0.1 M NaOH solutions in the presence of increasing concentrations of $Cl^-$ ions, are shown. As is evident from Table 3, the values of the difference $(E_p - E_{pp})$ depend on the concentration of both NaOH and $Cl^-$ ions in the solution. Thus, in one and the same NaOH concentration, the difference $(E_p - E_{pp})$ increases with increasing the $Cl^-$ ion concentration, while in the presence of constant $Cl^-$ ion concentration, e.g. 0.02 M $Cl^-$ ion, for example, $(E_p - E_{pp})$ decreases with increasing the NaOH concentration. This implies that pit repassivation tendency increases with increasing the $OH^-$ ion concentration and decreases with increasing the aggressive ions concentration.

### 3.2. Potentiodynamic anodic polarization measurements

One of the most important parameter in potentiokinetic analysis is the sweep rate at which the potential range is traversed. If a high sweep rate is used, as shown by cyclic voltammetry, *E*/*I* data for both transient (e.g. oxide formation) and continuous reactions (e.g. gas evolution or metal dissolution) are obtained. Further, the data for the continuous reactions do not correspond to those for steady-state conditions. Thus, it was decided first of all to determine the sweep rate which when applied to nickel in NaOH solution free from chloride gave *E*/*I* curves that, as far as possible, eliminated the transient and approached steady-state conditions. A sweep rate of 1 mV $s^{-1}$ was found suitable for this purpose.

**Table 3**
Variation of the $(E_p - E_{pp})$ with the concentration of NaOH and $Cl^-$ ions.

| Concentration (M), NaCl | $E_p - E_{pp}$ ($mV_{SCE}$) | | |
|---|---|---|---|
| | 0.01 M NaOH | 0.05 M NaOH | 0.1 M NaOH |
| $3.0 \times 10^{-3}$ | 480 | – | – |
| $5.0 \times 10^{-3}$ | 590 | – | – |
| $7.0 \times 10^{-3}$ | 610 | – | – |
| $8.0 \times 10^{-3}$ | 635 | 605 | – |
| $1.0 \times 10^{-2}$ | 640 | 610 | – |
| $1.5 \times 10^{-2}$ | 640 | 615 | – |
| $2.0 \times 10^{-2}$ | 640 | 618 | 595 |
| $3.0 \times 10^{-2}$ | – | 623 | 605 |
| $4.0 \times 10^{-2}$ | – | 625 | 610 |
| $5.0 \times 10^{-2}$ | – | | 620 |
| $7.0 \times 10^{-2}$ | – | – | 625 |
| $8.0 \times 10^{-2}$ | – | – | 630 |

Figs. 5(A and B) and 6 represent the potentiodynamic anodic polarization curves of nickel in 0.01 and 0.1 M NaOH solutions, respectively, at a sweep rate of 1 mV $s^{-1}$, upon the addition of increasing concentrations of $Cl^-$ ions. Similar curves are obtained in $5 \times 10^{-2}$ M NaOH solution (curves not shown here). Inspection of the curves of these figures and similar ones reveals the following conclusions to be drawn:

(i) In chloride ion-free NaOH solution, the anodic polarization *E*–*I* curves are characterized by an ill defined active dissolution peak which corresponds to the dissolution of Ni metal to $Ni^{2+}$ ions

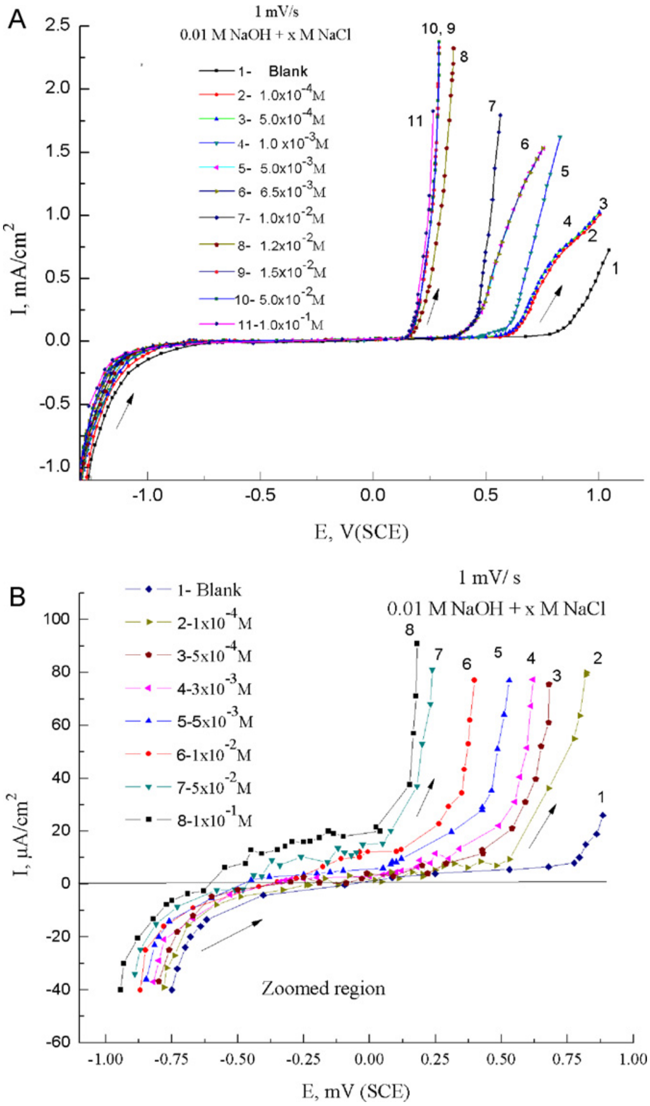

**Fig. 5.** (A) Potentiodynamic anodic polarization curves of Ni in 0.01 M NaOH solutions upon the addition of increasing concentrations of $Cl^-$ ions. (B is the passive current zoomed region). (B) Passive current zoomed region in potentiodynamic anodic polarization curves of Ni in 0.01 M NaOH solutions upon the addition of increasing concentrations of $Cl^-$ ions.

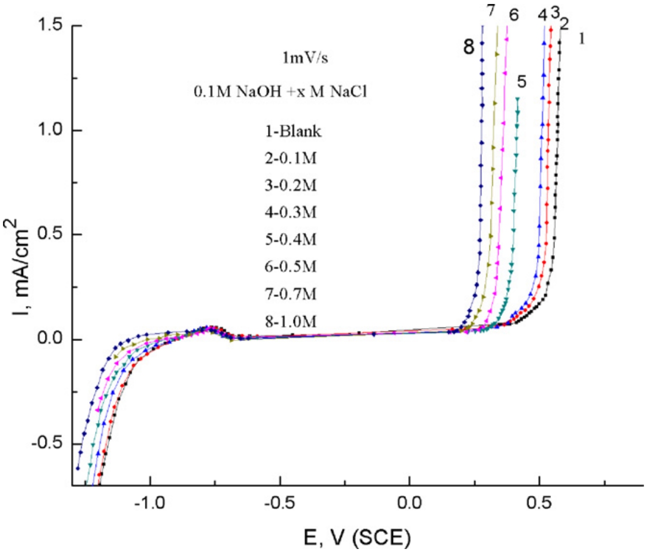

**Fig. 6.** Potentiodynamic anodic polarization curves of Ni in 0.1 M NaOH solutions upon the addition of increasing concentrations of $Cl^-$ ions.

and an extended passive region upon which the current density remains more/or less unchanged before the increase in current due to oxygen evolution. The active dissolution peak becomes noticeable on increased the alkali concentration.

(ii) Presence of $Cl^-$ ions in increasing concentration causes the shift of the corrosion potential into the active direction and an exaltation of the dissolution current peak. Both effects could be attributed to the adsorption of $Cl^-$ ions on the bare metal surface [35].

(iii) Addition of $Cl^-$ ions up to a certain concentration, which depends on the alkali concentration, has little effect on the current densities flowing along the passive range. The passive current density increases only slightly with increasing the $Cl^-$ ion concentration (Fig. 5B) due to adsorption of $Cl^-$ ions on the metal surface [35].

(iv) When the $Cl^-$ ion concentration reaches a threshold value which depends on the alkali concentration, the current flowing along the passive range increases suddenly and markedly at some definite potential denoting the destruction of the passivating oxide film and the initiation of visible pits. These potentials are referred to as the pitting potentials; $E_p$. The minimum concentrations of $Cl^-$ ions which cause breakdown of passivity and initiation of pitting corrosion of Ni electrode in different NaOH concentrations are shown in Table 4. It is of interest to note that similar findings were reported by Engell and Stolica [36] during the pitting of iron in sulphuric acid and by Abd El Haleem for zinc and zinc alloys [25–27], and for steel [37,38]. Pourbaix et al. [39], on the other hand, are of the opinion that this critical halide concentration depends on the nature of the metal or alloy, its thermal treatment and the state of its surface.

**Table 4**
The minimum concentrations of $Cl^-$ ions required to initiate pitting corrosion in different NaOH concentrations.

| NaOH concentration (M) | Threshold $Cl^-$ ion concentration (M) |
|---|---|
| 0.01 | 0.0001 |
| 0.05 | 0.0009 |
| 0.10 | 0.1000 |

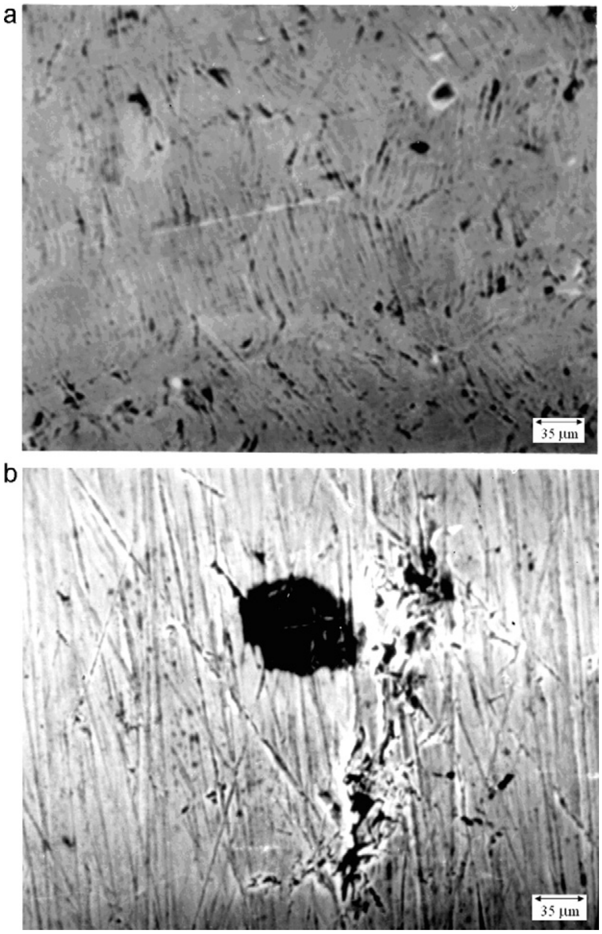

**Fig. 7.** (A) SEM micrograph of nickel electrode specimen after potentiostatic anodic polarization in 0.01 M NaOH + 0.01 M NaCl, at the corresponding $E_p$ for a period of 10 min. (B) SEM micrograph of nickel electrode after potentiostatic anodic polarization in 0.05 M NaOH + 0.6 M NaCl, at the corresponding $E_p$, for a period of 10 min.

(v) The effect of increasing the $Cl^-$ ion concentration of the solution is to shift the critical pitting potential of the working electrode into the active (negative) direction. Fig. 7(A and B) shows the SEM micrographs of the Ni electrode surface after carrying potentiostatic polarization in: (A) 0.01 M NaOH + 0.01 M NaCl and (B) 0.05 M NaOH + 0.6 M NaCl at the corresponding $E_p$ for a period of 10 min. Inspection of the SEM micrographs of Fig. 7(A and B) reveals that the pits formed in the dilute NaOH solutions are numerous and intense fine, Fig. 7A, while in 0.05 M NaOH in the presence of high $Cl^-$ content, the number of intense fine pits decreases and some of which expanded equally laterally as well as inwardly so that they appear as large attacked areas.

The dependence of the pitting corrosion potential of the nickel electrode on the concentration of $Cl^-$ ion can be seen in Fig. 8 which represents the plots of $E_p$ versus $\log C_{agg}$, in 0.01, 0.05 and 0.1 M NaOH solutions, respectively. Usually most of the investigations carried out on the pitting corrosion potentials revealed a straight line relationship between $E_p$ and $\log C_{agg}$, in a form like [40–42]:

$$E_p = \alpha + \beta \log C_{agg}. \quad (4)$$

where $\alpha$ and $\beta$ are constants. However, in the case under consideration, such a relationship cannot be directly obtained. A plot of the two variables gives rise to curves of sigmoidal nature, Fig. 8, in which Eq. (4) is obeyed only within a certain range of $Cl^-$ ion concentrations [26,27,43]. At lower $Cl^-$ ion concentrations, the critical pitting potential shifts slightly in the negative direction as the con-

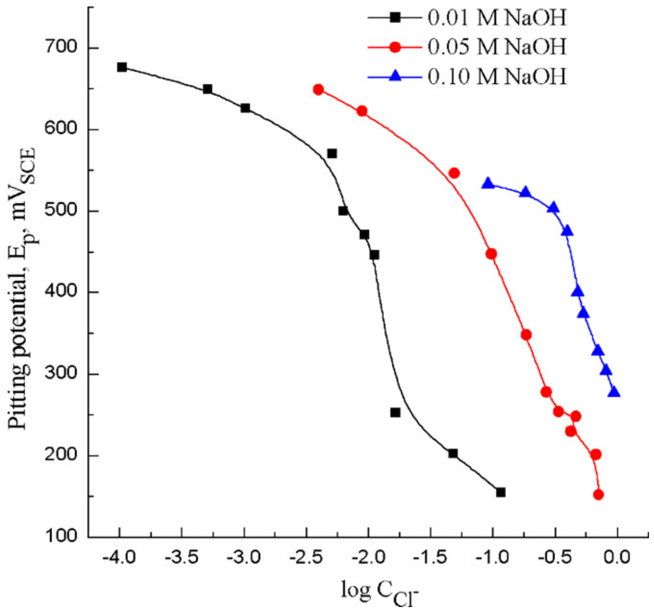

**Fig. 8.** Dependence of the pitting corrosion potential, $E_p$, of nickel electrode on the logarithmic concentration of $Cl^-$ ion.

centration of the halide ion is increased. One can conclude here that these $Cl^-$ ions are not sufficient to destroy completely the passivating film on the metal surface, or that the pits formed are not completely active and may undergo repassivation [3,26,27]. This conclusion is arrived from the potentiostatic current-time curves of Fig. 9 reported for the Ni electrode in 0.01 M NaOH solution containing different concentrations of $Cl^-$ ions, which cover the three regions of the S-shaped curve of Fig. 8, when the potentials remain constant at the corresponding pitting corrosion potentials. In the presence of low concentrations of $Cl^-$ ions, the current starts to flow after the elapses of an induction period, which depends on the $Cl^-$ ion concentration, due to the initiation of pitting corrosion. Following then, the current starts to decrease continuously with time to reach a minimum value, curve 1 of Fig. 9. This behavior is attributed to the repassivation of the pits that have been already formed [3,26,27].

At higher $Cl^-$ ions concentrations, which lie in the straight line portion of the sigmoidal curve of Fig. 8, the current following the induction period, starts to increase with time to reach a limiting value which increases with increasing the $Cl^-$ ion concentration, curve 2 of Fig. 9. The pits formed within this concentration range of $Cl^-$ ion, where Eq. (4) is obeyed, are assumed to be of the limiting active type [3,26,27]. However, at still higher concentrations of $Cl^-$ ions, which represent the latter part of the curves of Fig. 8, the pits formed are assumed to be non passivatable active pits. These concentrations of $Cl^-$ ions are sufficient to cause continuous propagation of the pits already formed and/or the increase in the number of newly generated pits [25–27,33]. This can be easily seen from the potentiostatic current–time, curve 3 of Fig. 9, recorded in the presence of 0.1 M $Cl^-$ ions, at the corresponding pitting potential. In this case, the current increases continuously with time without reaching a limiting value.

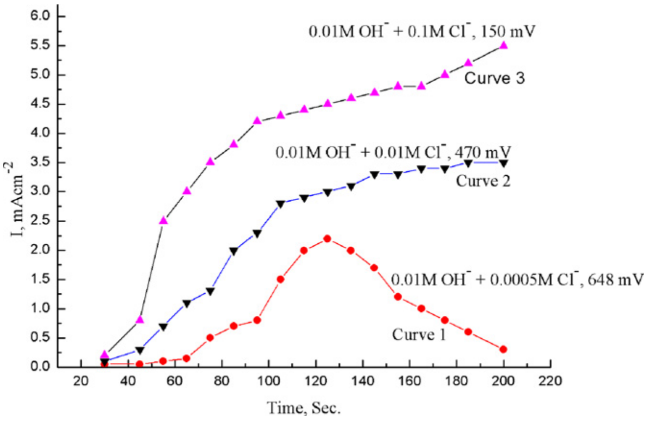

**Fig. 9.** Potentiostatic anodic polarization curves of Ni electrode in 0.01 M NaOH in the presence of different $Cl^-$ ions concentrations, at their corresponding pitting potentials, $E_p$.

The differentiation between pit initiation and pit propagation is well explained by Aziz and Gadard [44]. A pit can be started by artificial stimulation at an otherwise normal site on the metal surface, yet continues to propagate if given the right environmental conditions. Several theories and mechanisms have been advanced to characterize the breakdown of passivity and the initiation of pitting corrosion. According to the adsorption-induced thinning theory, the aggressive $Cl^-$ ions breakdown passivity by competitive adsorption with hydroxyl groups at the passive film surface [41,45,46]. However, the penetration-induced mechanism involves the sub-surface insertion and transport of $Cl^-$ ions to the metal/oxide interface under the influence of an electrostatic field across the film/solution interface [38,47–49]. The inhibiting healing mechanism, on the other hand, attributes the initiation of pitting corrosion to the alternate breakdown and repair of the passive film and alternate poisoning by the aggressive $Cl^-$ ions [50,51].

Marcus et al. [52,53], on the other hand, proposed a model of breakdown of passivity by $Cl^-$ ions, on Ni surface, based on the effect of the nanostructure of the passive film on the interfacial potential drop and its role on local occur of passivity breakdown. They are also of the opinion that the adsorption of $Cl^-$ ions by exchange with surface hydroxyl groups is energetically favorable but it does not promote metal dissolution [53–56].

According to the point defect model [57], $Cl^-$ ions incorporate to the passive film by occupying anion vacancies. This results in a decrease of anion vacancies and increase of cation vacancies [57]. When the latter start to pile up at the metal interface, a breakdown of the passive film occurs with the initiation of pitting corrosion.

### 3.3. Inhibition of pitting corrosion by some organic amines

While literature contains many investigations which deal with the use of organic additives as restrainers of general corrosion, only minor information is available on their application to inhibit pitting corrosion. Herbsleb and Schwenk [58] reported the occurrence of pitting in $H_2SO_4$–$FeSO_4$ pickling bath containing some organic additives upon anodic polarization. Pitting is assumed to occur as a result of local desorption of inhibitors from the metal surface. Anilines, pyrillium perchlorates, benzaldehyde, azomethines and furylacrolines were reported to reduce the rate of pitting attack of 18-8 stainless steel in acid media without affecting the pitting potential [59]. Quinoline inhibited the pitting corrosion of 18-8 stainless steel through the interaction of quinoline cations and $Cl^-$ ions [60]. Shams El Din [61], on the other hand, found that pitting corrosion of iron in acid and alkaline media could be inhibited in the presence of small additions of gelatin, while higher concentrations enhance corrosion. Abd El Haleem et al. [62,63] used some organic amines to inhibit the pitting corrosion of mild and plain carbon steels in neutral and alkaline media. In the present work, attempts were made to use some organic amines to inhibit the pitting corrosion of nickel in NaOH solutions, in the presence of $Cl^-$ ions as a pitting corrosion agent. Monomethylamine, dimethylamine, monoethylamine, hydrazine and urea are used as pitting corrosion inhibitors.

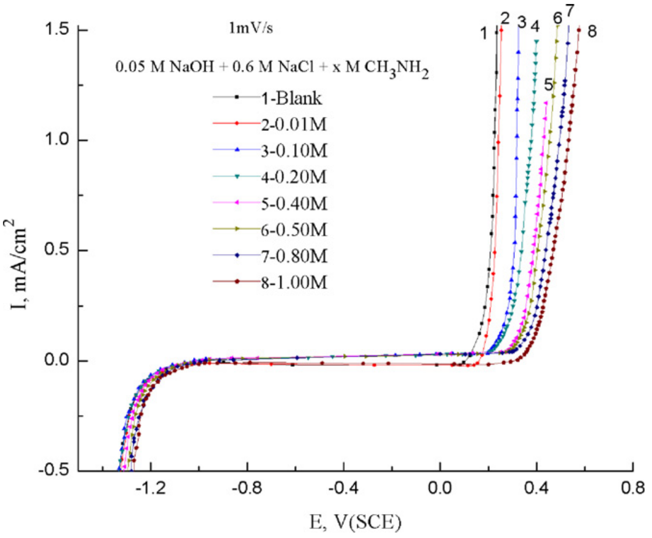

**Fig. 10.** Potentiodynamic anodic polarization of Ni electrode in 0.05 M NaOH + 0.6 M NaCl in absence and presence of monomethylamine, at a sweep rate of 1 mV $s^{-1}$.

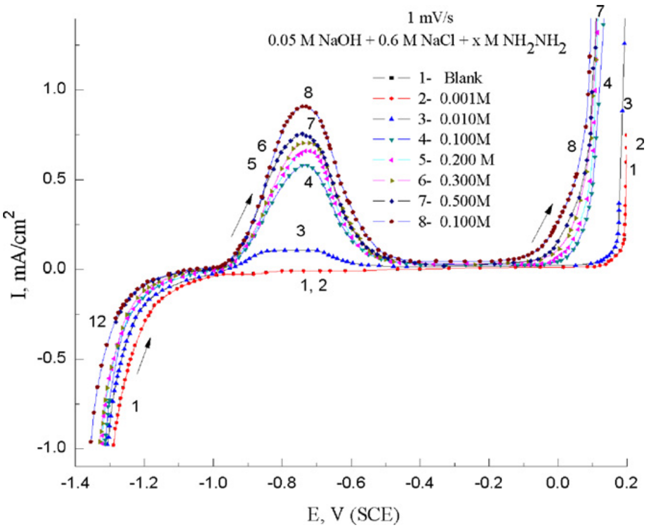

**Fig. 12.** Potentiodynamic anodic polarization of Ni electrode in 0.05 M NaOH + 0.6 M NaCl in absence and presence of hydrazine, at a sweep rate of 1 mV $s^{-1}$.

The curves of Figs. 10–12 represent the effect of addition of increasing concentrations of monomethylamine, dimethylamine and hydrazine, successively, as examples of the other compounds, on the potentiodynamic anodic polarization curves of the nickel electrode in 0.05 M NaOH + 0.6 M NaCl at a sweep rate of 1 mV $s^{-1}$. Similar curves are obtained in the presence of diethylamine as a pitting corrosion inhibitor.

Inspection of curves of Figs. 10 and 11 and the like reveals that the presence of increasing additives of monomethylamine and dimethylamine causes complete depression of the dissolution current peak and a marked shift of the critical pitting potential into the noble direction. Both effects denote increased resistance to both active corrosion and pitting attack in the presence of these simple aliphatic amines. However, hydrazine and urea have a different effect. These compounds enhance the active dissolution reaction to an extent which depends on the type and concentration of additives. Similar findings were reported by Shams El Din et al. in the presence of gelatin [61]. The effect of urea and hydrazine on the initiation of pitting corrosion of the nickel electrode and consequently on its pitting potential is of interest. Low concentrations of urea cause slight shift of $E_p$ into the positive direction indicating increased resistance towards pitting corrosion, while higher concentrations enhance the localized attack and $E_p$ starts to decrease with increasing its concentration. Hydrazine on the other hand, enhances the determined effect of $Cl^-$ ions and consequently accelerated the tendency of initiation of pitting corrosion of nickel. $E_p$ starts to shift markedly into the active direction. As the concentration of hydrazine is further increased the shift in the pitting corrosion potential to the negative direction is increased.

The dependence of the critical pitting potential of the nickel electrode, $E_p$, on the concentration of the organic additives can be seen by the curves of Fig. 13 which represent the plots of $E_p$ versus log $C_{inh}$. From these curves, the following conclusions could be drawn:

(i) Addition of aliphatic amines up to a certain concentration which depends on the type of additive causes the shift of the critical pitting potential, $E_p$, into the noble direction in accor-

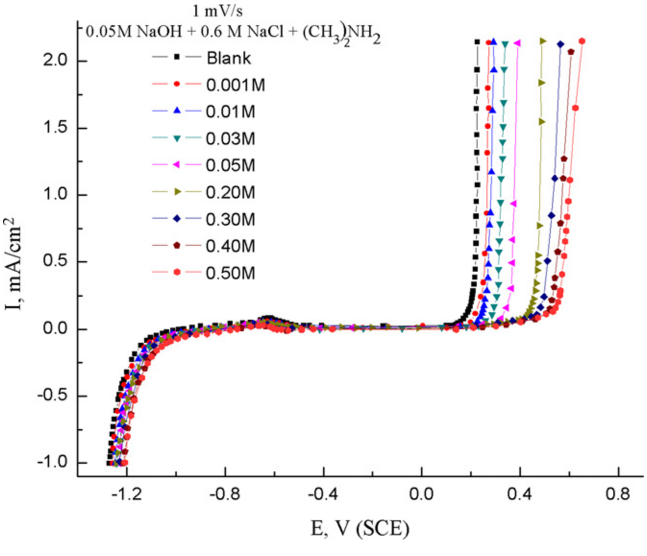

**Fig. 11.** Potentiodynamic anodic polarization of the Ni electrode in 0.05 M NaOH + 0.6 M NaCl in absence and presence of dimethylamine at a sweep rate of 1 mV $s^{-1}$.

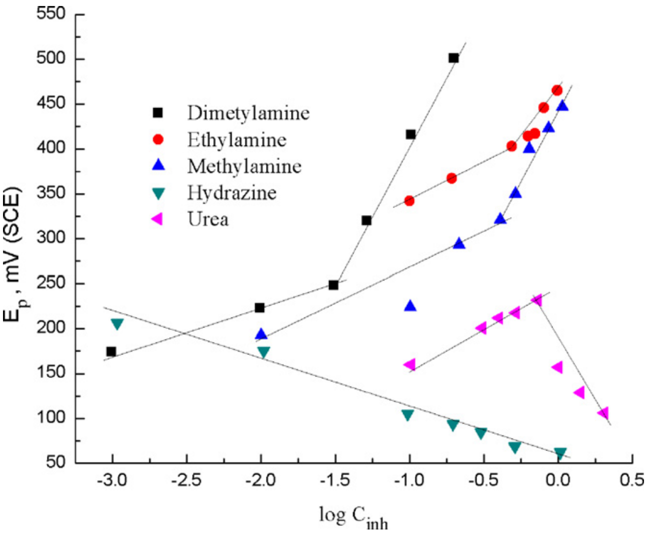

**Fig. 13.** Dependence of the pitting corrosion potential, $E_p$, of Ni on the logarithmic concentration of inhibitors, log $C_{inh}$.

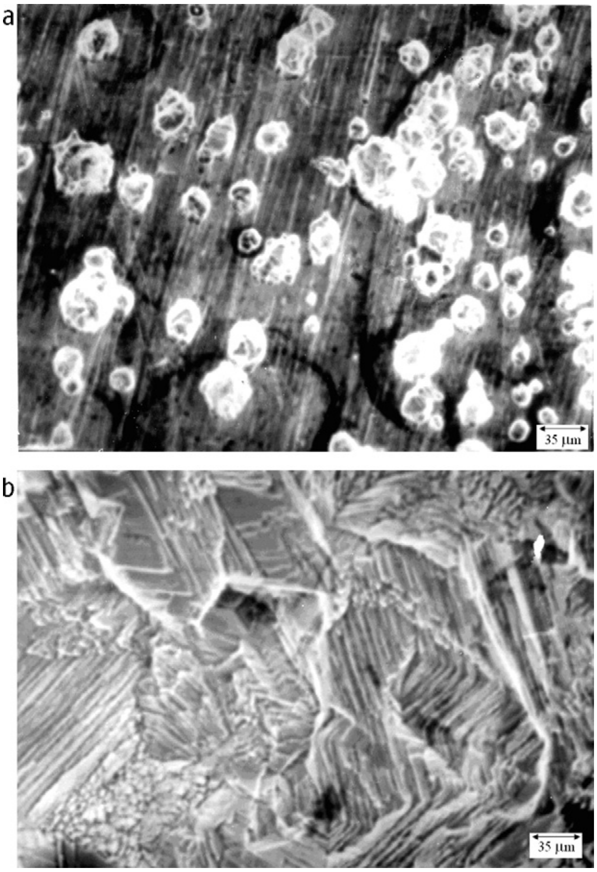

**Fig. 14.** (A) SEM micrograph of Ni surface after potentiostatic anodic polarization in 0.05 M NaOH + 0.6 M NaCl in the presence of 0.5 M monomethylamine, at the corresponding $E_p$, for a period of 10 min. (B) SEM micrograph of Ni surface after potentiostatic anodic polarization in 0.05 M NaOH + 0.6 M NaCl in the presence of 0.5 M dimethylamine, at the corresponding $E_p$, for a period of 10 min.

dance with the following equation:

$$E_p = \alpha_1 + \beta_1 \log C_{\text{inh}}. \quad (5)$$

where $\alpha_1$ and $\beta_1$ are constants.

(ii) At a certain definite concentration which depends also on the type of the amine used, a marked shift of the pitting potential into the noble direction is noticed indicating the onset of marked inhibition of pitting corrosion and no visible pits could be detected on the surface of the metal. Fig. 14(A and B) shows the SEM micrographs of the Ni electrode surface after potentiostatic anodic polarization for a period of 10 min in 0.05 M NaOH + 0.6 M NaCl in the presence of 0.5 M monomethylamine and dimethylamine, respectively. It is quite clear that in the presence of monomethylamine, the intense pits formed are covered by the reaction products while in the presence of dimethylamine the pits are completely disappeared.

The increased resistance for pitting corrosion of Ni by $Cl^-$ ions to take place in the presence of these aliphatic amines can be explained on the basis of the following mechanism.

Organic amines are usually obtained by the substitution of the respective organic radical for one or more hydrogen of the $NH_3$ molecule. The amine nitrogen with its two free electrons is assumed to combine with $H^+$ ions, formed from the partial ionization of $H_2O$ molecules, to give the corresponding organic cations with the libration of free $OH^-$ ions according to:

$$H_2O \leftrightarrow H^+ + OH^- \quad (6)$$

$$RNH_2 + H^+ \leftrightarrow RNH_3{}^+ \quad (7)$$

Inhibition of pitting corrosion is assumed to occur as a result of the following processes:

(a) Competitive adsorption between $OH^-$ and $Cl^-$ ions for adsorption sites on the metal surface. Therefore, a shift of the potential into the noble direction is required so as to enable the $Cl^-$ ion to reach a concentration in the double layer sufficient to overcome the inhibiting action of $OH^-$ ions, thereby destroying passivity and initiating pitting corrosion. The probable formation of basic nickel chloride, which might be precipitated on the metal surface, cannot be excluded.

(b) Organic cations with their positive charges are assumed to adsorb well on the cathodic sites on the metal surface, therefore, enhance the protection of nickel against pitting corrosion. The increased tendency of the amine studied to inhibit pitting corrosion of nickel in the order: monomethylamine < monoethylamine < di-methylamine is associated with the change in the electron density on the nitrogen of the amine, on one hand, and to the capacity to adsorb on the metallic surface, on the other.

(iii) Hydrazine cannot be used as pitting corrosion inhibitor for nickel in alkaline media since it enhances attack and causes the pitting potential to shift into the active direction at all concentrations. This behavior could be attributed to the formation of hydrazine Ni-complexes of the general formula $[Ni(N_2H_4)_n]Cl_2$, where $n$ ranged between 2 and 4, depending on hydrazine concentration [64]. In alkaline solutions, stabilization of $Ni^{2+}$ ions by hydrazine molecules could retard and prevent formation of $Ni(OH)_2/NiO$ which would act as the passivating film on Ni surface [65]. Therefore, passivity is destroyed with the continuous initiation of pitting corrosion and the consequent shift of $E_p$ into the negative direction.

(iv) Urea behaves bifunctionally, inhibiting pitting corrosion of nickel when present in low concentrations, and enhances attack at higher concentrations. This behavior could be attributed to the formation of a nickel–urea complex of the form $[Ni(H_2N–CO–NH_2)_4]Cl_2$ [66]. This compound is assumed to precipitate first on the metal surface causing the protection of Ni against corrosion with the consequent shift of $E_p$ into the positive direction. However, on further increasing of urea concentration, the formed complex behaves similar to that previously reported in the case of hydrazine. Thus, the urea molecules stabilize the $Ni^{2+}$ ions and prevent the formation of the protective $Ni(OH)_2/NiO$ with the subsequent shift of $E_p$ into the active direction.

## 4. Conclusions

From the cyclic voltammograms and the potentiodynamic anodic polarization curves of nickel in NaOH solutions in the presence of $Cl^-$ ions and organic amines the following conclusions could be drawn:

(1) The change in the integrated anodic charge amount, $\Delta q_a$, reported in the presence of $Cl^-$ ions is taken as a measure of pitting corrosion likelihood. The logarithm of $\Delta q_a$ varies linearly with the logarithm of $Cl^-$ ions concentration.

(2) The pitting corrosion potential, $E_p$, varies with the logarithm of $Cl^-$ ions concentration according to sigmoidal curves, depending on the type of pits initiated.

(3) Organic amines cause the inhibition of pitting corrosion as revealed from the shift of $E_p$ into the positive direction.

(4) Hydrazine enhances the pitting corrosion of nickel and $E_p$ shifts markedly into the active direction due to the formation of hydrazine Ni-complexes of the general formula $[Ni(N_2H_4)_n]Cl_2$.

(5) Urea behaves bifunctionally, it inhibits pitting corrosion when present in low concentrations and enhances it at higher concentrations.

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