Anodic Dissolution of Nickel in Acidic Chloride Solutions

E.E. Abd El Aal, W. Zakria, A. Diab, and S.M. Abd El Haleem

The anodic dissolution of nickel was studied galvanostatically in hydrochloric acid solutions of various concentrations. The reaction orders of chloride ion and hydrogen ion concentrations were found to be 0.5 and 1.0, respectively. An anodic Tafel slope equal to 120 ± 10 mV $\cdot$ decade^{-1} was obtained. The dissolution rate of nickel at constant acid concentration was increased with stirring of the solution and increasing temperature. The activation energy, ΔH, for the anodic dissolution process was found to be 12 kcal $\cdot$ mol^{-1}. The presence of oxygen in solutions assisted the passivation process. The effect of addition of aniline and some of its derivatives (o-, m-, and p-anisidine) as inhibitors on the dissolution kinetics of Ni in 1 M HCl was also investigated. These compounds inhibited the anodic dissolution of nickel without affecting the Tafel slope, indicating that the adsorption of such inhibitors could not interfere with the mechanism of metal dissolution.

1. Introduction

According to thermodynamic considerations, Ni would be stable in neutral and moderately alkaline solutions, although not in acidic and strongly alkaline media.[1] In acid solutions the metal would be expected to dissolve as Ni^{2+} ions, with evolution of H_2. In practice, the corrosion resistance of Ni in acid solutions is better than that indicated from the potential-pH equilibrium diagrams.[1] Furthermore, the position of Ni in the electrochemical series, which is only moderately active with respect to the H^+/H_2 equilibrium, renders its corrosion rate in nonoxidizing acids slow in the absence of oxidants. On the other hand, passivity of Ni is attributed to the formation of a protective film of oxide or hydrated oxide[2] or to a chemisorbed layer of O_2.[3] Bockris et al.[4] considered the passivity of Ni in acid media to be due to the increased conductivity of the oxide film induced by a change in its stoichiometry. The potentiostatic and potentiokinetic polarization curves given for Ni by many authors showed numerous discrepancies.[5-7] These were attributed to the nature and the amount of impurities in both the metal[5] and solutions[6] and to the variations in the experimental procedures.[6]

The electrochemical behavior of nickel anodes in acid media depends, among other variables, on the composition and pH of the solution.[7-11] The influence of solution composition on the electrochemical behavior of nickel is considerable. This turns out to be very important in dealing with various technical processes such as the use of nickel anodes in the nickel-electroplating bath where the presence of Cl^- ions in the solutions keeps a sufficiently high anodic faradic efficiency to maintain the Ni^{2+} ion concentration constant through a prolonged operation.[7] On the other hand, pitting corrosion of Ni

can occur in solutions containing Cl^- under conditions of high Cl^- ion concentration and applied potential.[12] For these reasons the anodic dissolution of nickel in Cl^- ions has been extensively investigated.[13-18]

At present a number of publications report the direct participation of anions, particularly Cl^- ions, in the electrodissolution of nickel.[17,19] In contrast, the electrochemical behavior of Ni in solutions containing Cl^- shows the opposite result.[12,16] Therefore, it appears that the various interpretations of the influence of the Cl^- anion on the dissolution of nickel electrodes in aqueous solutions are not entirely consistent.[11]

In the work under consideration, the effect of solution composition, pH, temperature, stirring, and aeration on the anodic behavior of Ni in HCl solutions are examined. The effects of additions of aniline and some of its derivatives (o-, m-, and p-anisidine) on the anodic behavior are also investigated.

2. Experimental

The nickel electrode was made from specpure nickel sheet (John-Matthey, UK), with a dimension of $1.5 \times 1.5 \times 0.1$ cm. The electrode was fixed to borosilicate glass tubing with Araldite (Vantico Inc., Brewster, NY). Electrical contact was achieved through copper wire soldered to the end of the Ni sheet not exposed to the solution. Current densities were calculated on the basis of the apparent surface area. The electrode surface was polished with 0-, 00-, and 000-grade emery papers, until it appeared free of scratches and other defects. The surface was then rinsed with triple-distilled water before it was used.

The cell used for polarization measurements was composed of two compartments separated by a fritted glass disc to prevent mixing of anolyte and catholyte. The cell has a double wall jacket through which water at the adjusted temperature was circulated. A conventional three-electrode system was used. A platinum sheet was used as the auxiliary electrode, the working electrode was a nickel sheet, and the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary positioned close to the working electrode surface to minimize ohmic potential drop.

The electrolytic solutions were prepared from analytical

E.E. Abd El Aal, W. Zakria, A. Diab, and **S.M. Abd El Haleem,** Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt. Contact e-mail: emad_abdelaal@hotmail.com.
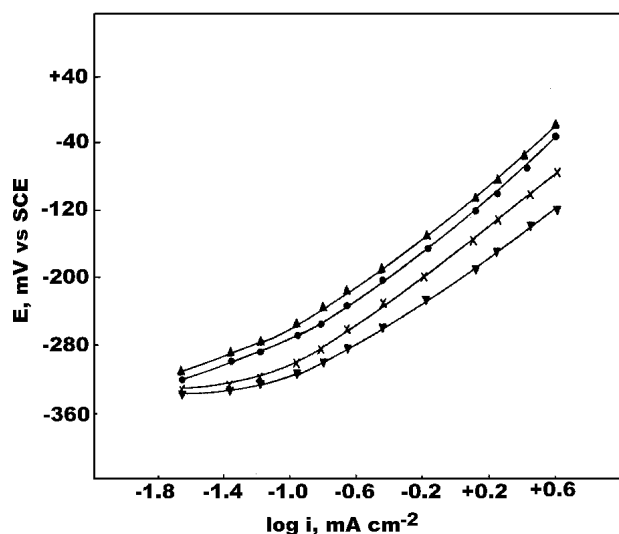
Fig. 1 Anodic polarization curves of nickel in various concentrations of HCl: (▲) 5×10^{-2}, (•) 1×10^{-1}, (x) 5×10^{-1}, and (▼) 1 M

Fig. 2 Reaction order plot with respect to chloride ion concentrations for nickel dissolution at potentials (x) −160 and (•) −120 mV

grade reagents and triple-distilled water. The pH was measured using the Expandable Ion Analyzer EA 920 (Orion Research, Beverly, MA) and pH was adjusted by appropriate addition of concentrated NaOH solution. All test solutions were deaerated with pure nitrogen gas for 2 h before the start of the polarization measurement to avoid the interference of oxygen with the polarization. Experiments were carried out in stagnant solutions and at a constant temperature, 25 ± 0.1 °C, except those related to the effect of stirring and temperature, respectively. The cell temperature was controlled using ultra thermostat type polyscience (USA). In some experiments, purified oxygen gas was allowed to pass through the solution for about 1 h before measurements were carried out.

The polarization measurements were conducted using the galvanostatic technique. Before starting the polarization, the electrode was immersed in the electrolyte until a steady corrosion potential was reached. Then polarization of the electrode was started from a low current density and followed to higher ones. The potential was recorded using a digital multimeter. For each current value, the steady-state potential of the metal was considered when its value did not change by more than 1 mV in 5 min. Each run was carried out in a fresh deaerated solution and with a newly polished electrode. The results were duplicated and the mean value was computed.

3. Results and Discussion

3.1 Effect of Acid Concentration

Figure 1 shows the anodic galvanostatic polarization of the nickel electrode in deaerated HCl solutions of concentration between 5×10^{-2} and 1 M at 25 °C. It is noted that increasing the HCl concentration shifted the polarization curves in the more active direction with a Tafel slope equal to 120 ± 10 mV decade^{-1}. The value of the slope is in a good agreement with that obtained by Vilche and Arvia[8] during the anodic polarization of nickel in acid solutions with a high chloride ion
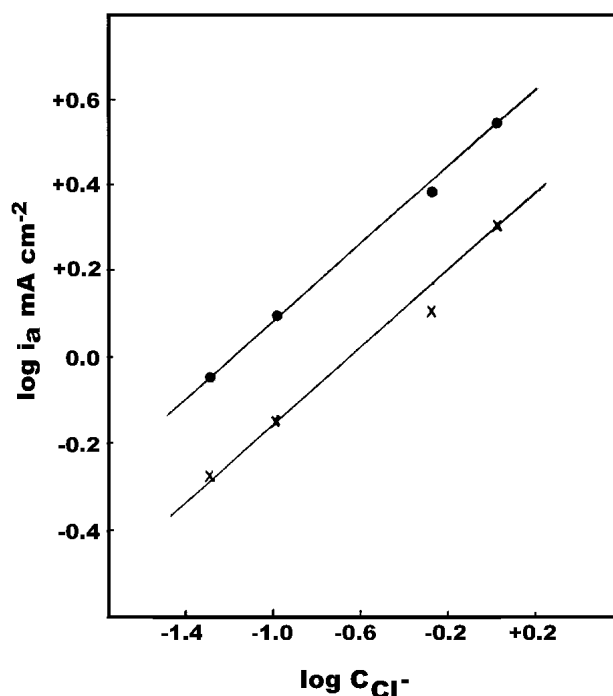
concentration in the range of 25-75 °C. The shift in the polarization curves into more active direction reveals that increasing acid concentration increases the rate of anodic dissolution.[20]

The reaction order at constant H$^+$ ion concentration with respect to chloride ion concentration for nickel dissolution can be determined from plots of current density versus concentration of chloride ion on a double logarithmic scale, at constant potentials (E = −160 and −120 mV) lying in the Tafel region. These plots are shown in Fig. 2 giving straight lines having a slope of:

$$\left(\frac{d \log i_a}{d \log [Cl^-]} \right)_{E[H^+]} = 0.5 \qquad \text{(Eq 1)}$$

3.2 Effect of pH

The anodic polarization was also carried out at a constant Cl$^-$ ion concentration of 1 M solutions and 25 °C at different pH values (not shown). From the results obtained, a decrease in the pH of the solution shifted the anodic polarization curves of nickel towards more active direction with a Tafel slope always remaining at 120 ± 10 mV decade^{-1}. This indicates that decreasing the pH of the solution increases the rate of the anodic reaction.[20]

The reaction order at a constant Cl$^-$ ion concentration with respect to the hydrogen ion concentration for nickel dissolution is determined from plots of current density versus concentration of hydrogen ions on a double logarithmic scale, at constant potentials (E = −160 and −120 mV) lying in the Tafel region. Figure 3 shows that:

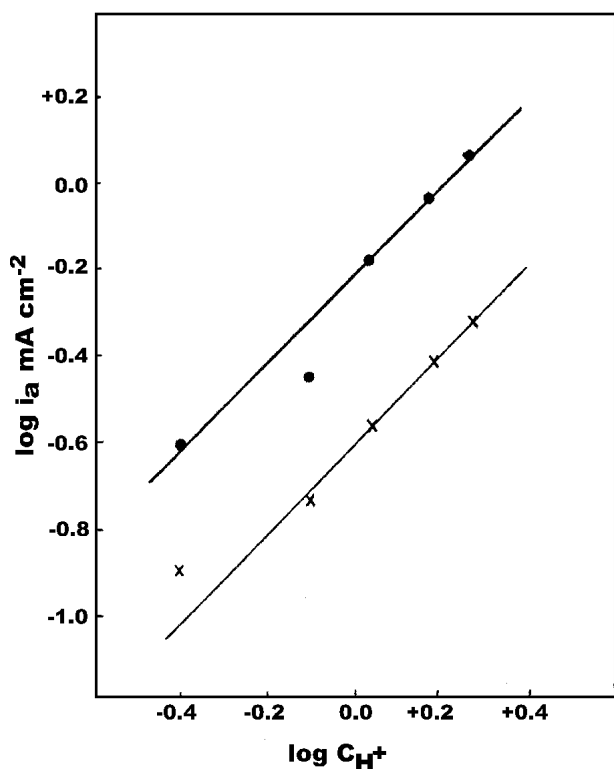$$\left(\frac{d \log i_a}{d \log [H^+]} \right)_{E[Cl^-]} = 1.0 \qquad \text{(Eq 2)}$$
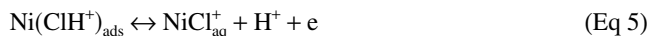
Fig. 3 Reaction order plot with respect to hydrogen ion concentrations for nickel dissolution at potentials (x) −160 and (•) −120 mV

The following mechanism is proposed for the dissolution of the nickel anode in acidic chloride solution:

$$Ni + Cl^- \leftrightarrow Ni(Cl)_{ads} + e \tag{Eq 3}$$

$$Ni(Cl)_{ads} + H^+ \leftrightarrow Ni(ClH^+)_{ads} \tag{Eq 4}$$

$$Ni(ClH^+)_{ads} \leftrightarrow NiCl^+_{aq} + H^+ + e \tag{Eq 5}$$

A same mechanism was also proposed by Darwish et al.[21] for the dissolution of iron in acidic chloride solutions. In the above mechanism the rate-determining step (Eq 4) is not electrochemical, but is a chemical adsorption step that forms a kind of ion pair at the electrode surface.[21] If, however, the adsorbed intermediate (NiCl)$_{ads}$ follows the Temkin adsorption behavior, the current density-potential relationships for the electrochemical adsorption step (Eq 3) would be:[21,22]

$$i_1 = k_1 \cdot (1 - \theta) \cdot [Cl^-] \cdot \exp\left(\frac{\alpha_1 FE}{RT}\right) \cdot \exp\{-\beta_1 f(\theta)\} \tag{Eq 6}$$

and

$$i_{-1} = -k_{-1} \cdot \theta \cdot \exp\left(-\frac{(1 - \alpha_1)FE}{RT}\right) \cdot \exp\{(1 - \beta_1)f(\theta)\} \tag{Eq 7}$$

where θ is the surface coverage of the adsorbed intermediate, $Ni(Cl)_{ads}$, α and β are the electrochemical and the chemical

transfer coefficients, respectively, and f is the correlation function between the free enthalpy of adsorption and the degree of surface average θ.

For Temkin adsorption, $0.2 < \theta < 0.8$. Therefore, the variation in the pre-exponential terms $1-\theta$ and θ are negligible and can be combined with the constants k_1 and k_{-1}, respectively.[22] Equations 6 and 7 become:

$$i_1 = k'_1 \cdot [Cl^-] \cdot \exp\left(\frac{\alpha_1 FE}{RT}\right) \cdot \exp\{-\beta_1 f(\theta)\} \tag{Eq 8}$$

and

$$i_{-1} = -k'_{-1} \cdot \exp\left(-\frac{(1 - \alpha_1)FE}{RT}\right) \cdot \exp\{(1 - \beta_1)f(\theta)\} \tag{Eq 9}$$

For quasi-equilibrium conditions of reaction (Eq 3) it follows that $i_1 = i_{-1}$. From this expression it follows that:

$$\exp[f(\theta)] = \left(\frac{k'_1}{k'_{-1}} \cdot [Cl^-] \cdot \exp\left\{\frac{FE}{RT}\right\}\right) \tag{Eq 10}$$

Equation 10 can be transformed to:

$$\exp\{(1 - \beta_1)f(\theta)\} = \left\{\left(\frac{k'_1}{k'_{-1}}\right)^{(1-\beta_1)} \cdot [Cl^-]^{(1-\beta_1)} \right.$$
$$\left. \cdot \exp\left\{\frac{(1 - \beta_1)FE}{RT}\right\}\right\} \tag{Eq 11}$$

For the rate determining chemical step (Eq 4), the respective current density could be shown by the following equation:

$$i_2 = k_2 \cdot \theta \cdot [H^+] \cdot \exp\{(1 - \beta_2)f(\theta)\} \tag{Eq 12}$$

Assuming $\beta_1 = \beta_2 = \beta$ and substituting Eq 11 in Eq 12 yields:

$$i_2 = k_2 \cdot \left(\frac{k'_1}{k'_{-1}}\right)^{(1-\beta)} \cdot \theta \cdot [H^+] \cdot [Cl^-]^{(1-\beta)} \cdot \exp\left\{\frac{(1 - \beta)FE}{RT}\right\} \tag{Eq 13}$$

and by combining all the constants k_1, k_{-1}, and k_2 in K, Eq 13 becomes:

$$i_2 = K \cdot \theta \cdot [H^+] \cdot [Cl^-]^{(1-\beta)} \cdot \exp\left\{\frac{(1 - \beta)FE}{RT}\right\} \tag{Eq 14}$$

On differentiating E in Eq 14 with respect to log i, we get

$$\left(\frac{dE}{d \log i}\right)_{[H^+],[Cl^-]} = \frac{2.303\, RT}{(1 - \beta)F}\left[1 - \frac{d \log \theta}{d \log i}\right] \tag{Eq 15}$$

By assuming that the variation of θ with the current density to be quite small, the differential term $(d \log \theta)/(d \log i)$ is negligible with respect to one.[21] Under these conditions the anodic Tafel slope at temperature = 298 °K and $\beta = 0.5$, becomes:
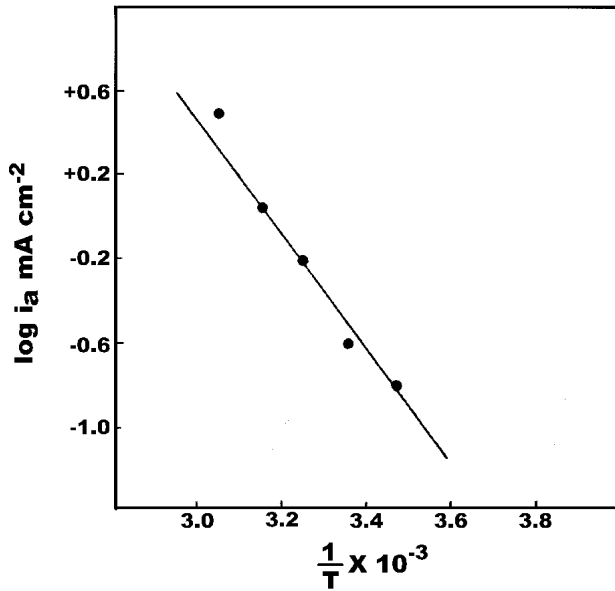
Fig. 4 Arrhenius plot of anodic polarization of nickel in 1 M HCl solutions at constant potential (E = −120 mV)

$$b = \left(\frac{d\,E}{d\log i}\right)_{[H^+],[Cl^-]} = \frac{2.303\,RT}{(1-\beta)F} = +120\,mV \qquad (Eq\ 16)$$

and the electrochemical reaction orders with respect to chloride and hydrogen ions are found to be the same as in Eq 1 and 2, respectively.

Thus, the proposed mechanism predicts values of 120 mV decade^{-1}, 1.0 and 0.5 for the anodic Tafel slope, the reaction order with respect to the hydrogen ion and to the chloride ion concentration, respectively. Note that these computed values are in good agreement with the experimental data obtained.

3.3 Effect of Temperature

The effect of temperature on the anodic polarization of nickel in 1 M HCl solutions was further investigated. The anodic polarization curves are shifted into the more active direction and the slope of the Tafel lines decreases very slightly with increasing the temperature. This indicates that the rise in temperature enhances the anodic dissolution of the nickel.[23] The curve of Fig. 4 represents the Arrhenius plots of log i_a versus 1/T in the temperature range 15-55 °C, at constant potential (E = −120 mV) lying in the Tafel region according to the following equation:

$$\left(\frac{d\log i_a}{d\,T^{-1}}\right)_E = \frac{\Delta H}{2.303\,R} \qquad (Eq\ 17)$$

The calculated value for activation energy ΔH, was found to be 12 kcal. mol^{-1}. This value is in agreement with that obtained by Piatti et al.[24] of 13 ± 3 kcal · mol^{-1} during the studies of anodic dissolution of pure nickel in acidic chloride solutions for the pH range 0.5-6.5 and temperature between 25-60 °C, using steady-state potentiostatic technique.
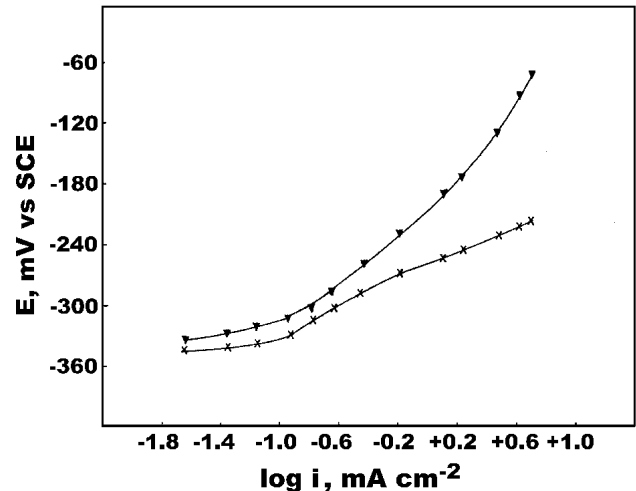

Fig. 5 Anodic polarization of nickel in 1 M HCl solution under (▼) stagnant and (x) stirred conditions

3.4 Effect of Stirring

To show whether the behavior of Ni is affected by stirring of the solution, two anodic polarization experiments were made in deaerated 1 M HCl under stagnant and stirring conditions at 25 °C. From the results shown in Fig. 5, the polarization curve under stirring conditions is clearly shifted to the more active direction than that obtained under the stagnant state. This could be possibly attributed to the destruction of the oxide film formed on the metal surface upon stirring and the subsequent increase in the rate of metal dissolution.[25]

3.5 Effect of Aeration

To examine the role of the presence of oxygen in the process of passivation and/or metal dissolution, the anodic polarization of the nickel electrode was studied in 1 M HCl solutions saturated with oxygen gas, nitrogen gas, and /or naturally aerated at 25 °C. Results shown in Fig. 6 show that, at the same current density, the potential becomes positive in the solution saturated with oxygen gas compared with that reported in a naturally aerated solution and both potentials are more positive than that recorded in the deaerated solution. Therefore, it is easy to conclude that the presence of oxygen assists the passivation process and consequently delays the dissolution of the metal.[25]

3.6 Effect of Organic Inhibitors

The effect of additions of various concentrations of some organic N-containing compounds such as aniline, o-anisidine, m-anisidine, and p-anisidine on the anodic polarization of nickel in 1 M HCl solutions at 25 °C was also investigated. The influence of these compounds on the cathodic polarization of nickel in 1 M HCl solutions was previously carried out.[26] Figure 7 shows the current density-potential relationships for anodic polarization of nickel in 1 M HCl solutions in the presence and absence of the p-anisidine as an example of the studied compounds. Clearly, increasing the concentration of the
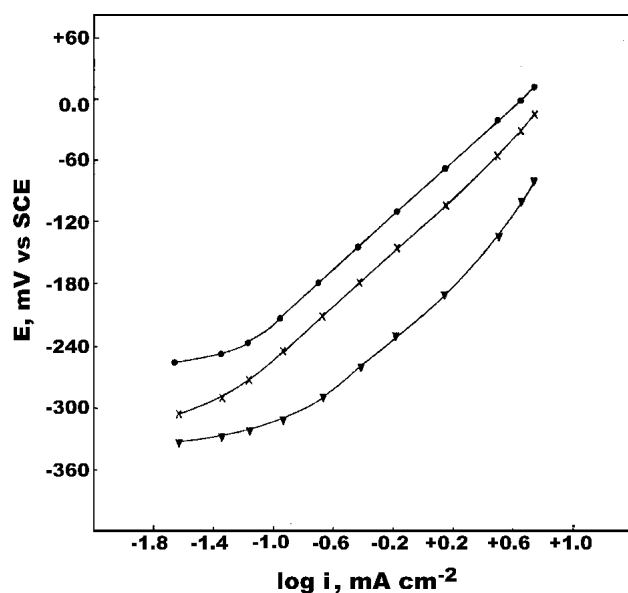
Fig. 6 Anodic polarization of nickel in (•) oxygen saturated, (▼) nitrogen saturated, and (x) naturally aerated 1 M HCl solutions
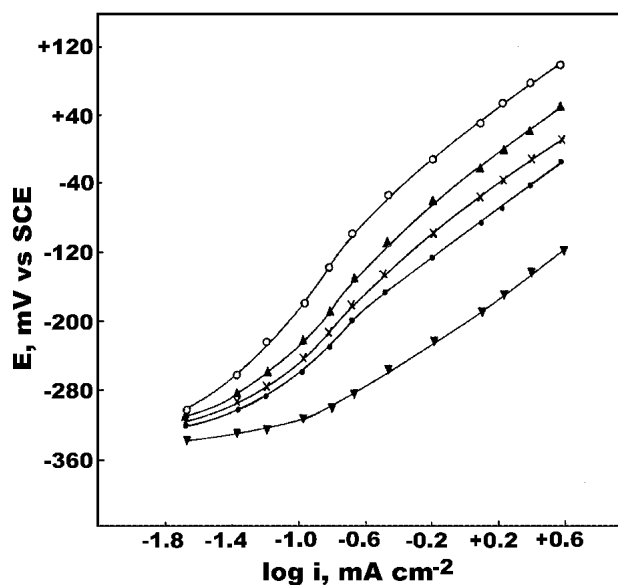

Fig. 7 Effect of different concentration of p-anisidine on the anodic polarization of nickel in 1 M HCl solution: (▼) 0.0, (•) 1×10^{-4}, (x) 5×10^{-4}, (▲) 5×10^{-3} and (○) 1×10^{-2} M

Table 1 Surface Coverage (θ) and Percent Inhibition (%I.E.) of the Anodic Process by the Various Inhibitors, as Estimated From the Tafel Plots at Constant Potential (−120 mV vs SCE)

Concentration	Aniline		O-anisidine		M-anisidine		P-anisidine	
	θ	%I.E.	θ	%I.E.	θ	%I.E.	θ	%I.E.
1×10^{-4}	0.56	56	0.63	63	0.72	72	0.80	80
5×10^{-4}	0.60	60	0.72	72	0.82	82	0.86	86
5×10^{-3}	0.79	79	0.82	82	0.86	86	0.91	91
1×10^{-2}	0.83	83	0.87	87	0.90	90	0.95	95

additive shifted the polarization curves toward the more positive direction. The Tafel slope remains around 120 ± 10 mV decade^{-1} and did not change appreciably on adding the examined inhibitors. The shift in the potential toward the more positive direction and the approximately constant values of the anodic Tafel slopes suggests that the inhibition action of such compounds occurs by simple blocking of the electrode surface through adsorption. The nearly constant values of the anodic Tafel slopes indicate that the presence of such inhibitors does not affect the mechanism of nickel dissolution.[27] Some authors for the inhibition of nickel have previously found similar behavior in different aggressive media by using some organic inhibitors.[28,29].

The surface coverage (θ) or the percentage of inhibition (%I.E.) at constant potential (E = −120 mV) lying in the anodic Tafel region was determined from the following:

$$\theta = 1 - \frac{i_2}{i_1} \qquad \text{(Eq 18)}$$

and

$$\%\text{I.E.} = \left(1 - \frac{i_2}{i_1} \right) \times 100 \qquad \text{(Eq 19)}$$

where i_1 and i_2 are the current density, in mA cm^{-2}, reported in absence and in presence of inhibitors, respectively. Table 1 gives values for the surface coverage (θ) and percentage inhibition (%I.E.) as functions of the concentration of the various inhibitors. The values for the surface coverage (θ) were found to fit with the Temkin isotherm[30] as shown in Fig. 8 and according to the following equation:

$$\theta = \frac{1}{\gamma} \ln B^* C \qquad \text{(Eq 20)}$$

where B* is the value of Langmuir constant, γ is a constant depending on intermolecular interactions in the adsorption layer and on the heterogeneity of the surface, and C is the bulk concentration of the adsorbate. As shown in Fig. 8, the surface coverage (θ) changes almost linearly with the concentration of the inhibitors. Accordingly, in the presence of one and the same inhibitor concentration, the inhibition efficiency increases in the following order: aniline < m-anisidine < o-anisidine < p-anisidine.

Generally, it has been assumed that the first stage in the mechanism of inhibition is the adsorption of the inhibitors onto the metal surface. Adsorption at the electrode-solution interface depends on the chemical structure of the inhibiting mol-
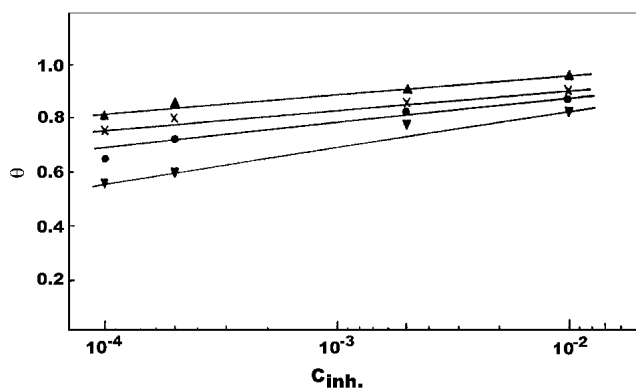
Fig. 8 Variation of the degree of inhibition of the anodic process with different concentration of the inhibitor in 1 M HCl solutions at constant potential (E = −120 mV), (▼) aniline, (•) m-anisidine, (x) o-anisidine, and (▲) p-anisidine

Fig. 9 Molecular structure of inhibitors

ecule, solution composition, nature of the metal surface, temperature, and the electrochemical potential at the metal-solution interface.[31] The variation of inhibition efficiency from one compound to another depends mainly on the type and number of the substitute present.[31] On the other hand, the inhibition efficiency of a given compound depends on the number of centers of adsorption and on the charge density of the inhibitor. In the case under consideration, all the studied compounds have the same center of adsorption, which is the −NH₂ group. Therefore, the performance of aniline and the other derivatives in 1 M HCl solutions as inhibitors can be explained in terms of the chemical structure of their molecules in solution. Thus, in aqueous acidic solution these compounds exist either as neutral molecules or in the cationic forms. As neutral molecules these compounds could be adsorbed on the metal surface via a chemisorptions mechanism, involving the displacement of water molecules from the metal surface and the sharing of electrons between their nitrogen atoms and the metal surface.[32] The present results show that the anisidine compounds (o-, m-, and p-) are more effective as inhibitors than the parent compound (aniline). The enhanced efficiency of these derivatives could be attributed to the presence of an electron-releasing group (e.g., −OCH₃) in the aniline ring (Fig. 9).

The inhibition action with o- and p-anisidine was found to be more efficient than that caused by m-anisidine. This could be attributed to the mesomeric (+M) effect of the −OCH₃ group on the −NH₂ group in the o- and p-positions, which is more effective than in the m-position. The electron density on the central group (−NH₂ group) in m-anisidine is less than that in o- and p-anisidine. On the other hand, the lower inhibition value for o-anisidine than for p-anisidine may be attributed to the steric hindrance effect in o-anisidine molecules.[26,33]

The adsorption of aniline and its derivatives as anilinium cations on the metal surface cannot be excluded. Thus, specifically absorbed Cl⁻ ions create excess negatively charged sites on the metal surface towards the solution side.[34] These negative sites could attract more of the positively charged anilinium cations, leading to the pronounced inhibition of Ni corrosion.[34].

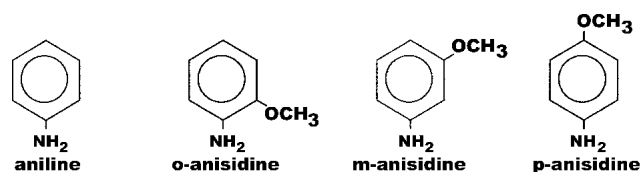## 4. Conclusions

The different factors affecting the anodic dissolution of nickel in hydrochloric acid were studied. Such factors were acid concentration, pH, temperature, stirring, aeration, and addition of aniline and some of its derivatives (o-, m-, and p-anisidine). It was found that:

- Increasing acid concentration causes an increase in the anodic dissolution of nickel.
- Raising the temperature enhances the anodic dissolution of Ni. The activation energy, ΔH, for the dissolution process was found to be 12 kcal · mol⁻¹, which is in good agreement with previous results.
- Stirring of the solution shifts the polarization curves to the more active direction and accounts for increased dissolution. On the other hand, presence of oxygen gas shifts the polarization curves to the more positive direction indicating increased tendency for passivation.
- Addition of aniline and its derivatives to 1 M HCl solutions inhibits nickel dissolution. These compounds act by way of adsorption mechanism.

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