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Effect of nitrite anions on the rate of iron dissolution in acid electrolytes

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The effect of the concentration of nitrite ions, potential, pH and solution stirring on the dissolution rate of iron was studied. Nitrite ions were shown to accelerate active dissolution. The accelerating action of the oxidant depends on the ratio of the rates of electroreduction at the electrode surface and homogenous chemical reduction in the reaction layer adjacent to the electrode. A possible mechanism of oxidant action on the iron dissolution is considered. The electroreduction process is assumed to generate at the iron surface an activated complex accelerating metal dissolution.

Keywords: *dissolution*, *intermediates*, *iron*, *nitrite*

1. Introduction

Oxygen-containing oxidants, such as sulfite, nitrite and nitrate ions, hydrogen peroxide, and oxygen, play an essential role in the process of metal corrosion in natural environments. Therefore, the determination of the mechanism of their effect on the corrosion behavior of metals is of great interest. In early studies [1, 2], the oxidant was considered only as a cathodic depolarizer shifting the corrosion potential in a positive direction and promoting metal passivation. Many publications are devoted to the study of the passivating effect of the oxidants on metals, but this aspect of the problem is beyond the scope of this work. The interpretation of oxidant effect on the rate of active dissolution of iron and steels varies markedly. For example, the direct involvement of oxidant species in the metal ionization stage [3], the electrocatalytic mechanism involving a stage of oxidation of low-valence metals ions in the diffusion layer [4, 5], the alkalization of the solution layer adjacent to the electrode as a result of oxidant reduction [6] and the interaction between oxidant and adsorbed hydrogen leading to surface activation [7] have been suggested. In recent studies [8–11], the peculiar action of oxidant was associated with the effect of cathodic reduction intermediates on the metal dissolution process. This effect was studied mainly on iron and the model suggested [11] is discussed below.

2. Model for oxidant action on active dissolution of iron

It is widely held that the active dissolution of iron proceeds via its interaction with adsorbed OH^- ions generated during dissociative adsorption of water molecules [2]. It is accepted that the step involving water adsorption is in equilibrium and the quantity of adsorbed OH^- ions depends on the solution acidity. Hence, the rate of iron dissolution (i_a^{eq}) should be inversely proportional to the concentration of hydrogen ions near the electrode surface (C_H^s)

$$i_a^{eq} = Fk_\alpha (C_H^s)^{-r} \exp(F\beta^* E/RT) \qquad (1)$$

where k_α is the rate constant, r is the reaction order with respect to H^+-ions and β^* is the apparent transfer coefficient. In the simplest case with $r = 1$ [12], Equation (1) at constant potential reduces to

$$i_a^{eq} = i_a^0 \ (C_H^0 / C_H^s) \qquad (2)$$

where i_a^0 is the dissolution rate for equal electrode and bulk hydrogen ion concentrations (C_H^0).

Usually, reduction of the oxygen containing oxidant (Ox) involves hydrogen ions [13]

$$\mathrm{Ox} + pH^+ + ne \rightarrow \mathrm{Red} + qH_2O \qquad (3)$$

where p, n, q are stoichiometric coefficients. This means that C_H^s decreases with increasing oxidant concentration (C_{ox}) and the iron dissolution is accelerated according to (2). When the C_{ox} reaches a critical concentration ($C_{ox,c}$) (at which the rate of H^+ ion consumption in reaction (3) is equal to their diffusion flux toward the metal surface) the electrode pH value (pH_s) increases sharply [14].

In the simplest case, when oxidant is reduced at the limiting diffusion current in a concentrated electrolyte, the critical Ox concentration is defined by the stoichiometric diffusion equation [14]

$$C_{ox,c} = D_{HD} C_H^0 / pD_{ox} \qquad (4)$$

where D_{HD} and D_{ox} are the effective diffusion coefficients of proton donors and oxidant, respectively, and p is the number of protons involved in Ox reduction. The value of D_{HD} depends on the buffer action of acid molecules and incompletely dissociated ions [15]. For instance, in 0.5 M sulfate [14]

$$D_{HD} = D_H + 5.1 D_{HSO_4} \qquad (5)$$

where D_H and D_{HSO_4} are the diffusion coefficients of H^+ and HSO_4^- ions, respectively.

If $C_{ox} < C_{ox,c}$, a change in C_H^s with C_{ox} is described by [16]

$$C_H^s = C_H^0 (C_{ox,c} - C_{ox})/C_{ox,c} \quad (6)$$

From (2) and (6), the change in iron dissolution rate with oxidant concentration at constant potential may be written [16] as

$$i_a^{eq} = i_a^0 (C_{ox,c}/(C_{ox,c} - C_{ox})) \quad (7)$$

From (7) it is seen that the plot of the dependence of iron dissolution rate on oxidant concentration is of hyperbolic shape, and a marked increase in i_a^{eq} is observed near the $C_{ox,c}$ value. However, oxidants were found to accelerate iron dissolution, even at C_{ox} significantly below the critical value [8, 9, 17]. The accelerating action of oxidants was explained [11, 18] as an interaction between iron and anode active species (A), formed in the electroreduction process according to the scheme

$$\mathrm{Ox} + n\mathrm{e} \rightarrow \mathrm{Red} + mA_{ads} \quad (8)$$

$$\mathrm{Fe} + A_{ads} \rightarrow \mathrm{Fe}A_{ads} + S \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e} + AS \quad (9)$$

where m is a number of anode active species formed during reduction of one oxidant particle and S is an electrolyte component which de-activates the metal surface. It should be noted that anode active species may be hydroxide ions. In this case the quantity of hydroxide ions on the surface should be in excess of equilibrium.

At constant potential the iron dissolution rate following this scheme (i_a^{ox}) should be directly proportional to the rate of oxidant electroreduction (i_c^{ox}). If oxidant is reduced under limiting diffusion current conditions, we have [11]

$$i_a^{ox} = 2mKi_c^{ox}/n = 2mKFD_{ox}C_{ox}/\delta \quad (10)$$

where K is the ratio of the number of A species interacting with iron to the total number of these species generated in reaction (8) and δ is the diffusion layer thickness. It is obvious that the value of K will decrease with reduction in potential, but this dependence cannot be predicted without knowledge of the nature of the anode active species and the mechanism of their interaction with the metal surface. If the surface coverage of OH_{ads}^- ions (i.e. activated $Fe(OH)_{ads}^-$ complexes) and adsorbed species A is small, the total iron dissolution rate (i_a) in an oxidizing medium is the sum of two partial dissolution processes [16]

$$i_a = i_a^{eq} + i_a^{ox} \quad (11)$$

The dominant dissolution process in the total dissolution of iron is defined by various factors such as oxidant concentration, potential, and solution pH [11].

Oxidant species, such as H_2O_2, CrO_4^-, NO_2^- and others, may be reduced in a homogenous reaction with Fe^{2+} ions in the diffusion layer [11]

$$\mathrm{Ox} + n\mathrm{Fe}^{2+} + p\mathrm{H}^+ \rightarrow n\mathrm{Fe}^{3+} + \mathrm{Red} + q\mathrm{H_2O} \quad (12)$$

In this case, hydrogen ions are consumed and the dissolution rate of iron should increase according (7). However, as reaction (12) proceeds, Ox is replaced by Fe^{3+} as the oxidant, which does not activate the dissolution of iron [17]. If all the oxidant species react in equation (12) before they approach the electrode, the rate of reaction (9) will be $i_a^{ox} = 0$. Thus, the activating action of oxidant and, accordingly, the total iron dissolution rate depends on the completeness of reaction (12). The degree of transformation (12) (if it is not too fast) depends on the values of the diffusion flux of oxidant toward the electrode and Fe^{2+} ions to the bulk electrolyte [19]. Accordingly, convective conditions should influence the dissolution of iron in oxidizing medium.

Hence, to determine the role of oxidant reduction products in the anodic process it is necessary to establish the relation between the rates of the partial electrode reactions proceeding during metal corrosion in the oxidizing media. Nitrite was chosen as the oxidant to be investigated. Its reduction on iron (or steels) is known [20] to produce a number of intermediates which, in principle, may behave as anode active species. To study the activating action of nitrite on the iron dissolution rate, we examined the effect of oxidant concentration, potential, electrolyte acidity and electrolyte stirring.

3. Experimental details

Measurements were made with iron (99.98%) foil with exposed areas 5.5 and 30 cm^2. Just before testing, the specimens were polished on 800 grit emery paper then degreased with acetone. A 0.5 M Na_2SO_4 + 0.03 M H_2SO_4 solution (pH 2.0) was used as a supporting electrolyte and $NaNO_2$ served as additive. The solutions were prepared from distilled water and reagent grade chemicals. In some cases, the solution was saturated with nitrogen monoxide produced by the reaction of copper with concentrated HNO_3 in a separate cell. In several tests the solution was deaereted by bubbling 99.99% purity argon. A propeller agitator was used for stirring the solution. The experiments was carried out at room temperature (20 ± 1 °C).

The polarization curves were potentiodynamically measured from the open circuit potential in the cathodic direction with a potential sweep of $1\,\mathrm{mV\,s^{-1}}$. The iron dissolution rate was calculated using colorimetric analysis of the solution with thiocyanate [21] at $\lambda = 508$ nm.

Colorimetric analysis of the solution for ammonia was carried out with a Nessler's reagent at $\lambda = 480$ nm using a Carl Zeiss Jena "Specol-211" spectrophotometer.

In acidic solutions containing nitrite, HNO_2 decomposes into NO and NO_3^-. At high stirring rate NO evaporates, and the total concentration of oxidant decreases. The decomposition rate of HNO_2

under the experimental conditions was measured from the time-dependent decrease of the diffusion limited cathodic current using an inert Pd electrode at a potential of 0 V (she). The effective concentration of nitrite was determined from the ratio of the actual cathodic current to the initial one.

The dependence of the nitrite reduction rate on rotational speed was determined in the range 660–1300 rpm using a disc electrode of area 1.13 cm^2.

The values of the critical concentrations of oxidants were determined from the dependence of the rate of hydrogen penetration through an iron membrane on the oxidant concentration in a Devanathan penetration cell [22] with a horizontal membrane by the method given in [14]. The membrane area and thickness were 5.5 cm^2 and 0.1 mm, respectively. The anode side of membrane was covered with a palladium layer [23].

The potentials were measured against a Ag/AgCl reference electrode and are reported against the standard hydrogen electrode after correction for ohmic drop. The latter was determined by rectangular pulses of current using a PI-50-1 potentiostat and an S8-13 storage oscillograph.

4. Results and discussion

The dependences of iron dissolution rate on nitrite concentration at constant potential $E = -0.35$ V in stirred and unstirred electrolytes are shown in Fig. 1. With no stirring, i_a became strongly concentration dependent only at oxidant concentrations above 10 mM (curve 1), whereas on stirring (curve 2) this dissolution dependence was nearly linear. However, in both cases i_a reached an upper limit at 12 mM, but i_a was much larger in stirred solution[A].

To understand the activating effect of the nitrite its reduction kinetics were investigated using the balance of external current, the rate of hydrogen evolution, the rate of the ammonia generation, and the dissolution rate of iron. Nitrite was found to completely reduced to ammonia in unstirred solution at potentials between −0.35 and −0.65 V. This is also consistent with the data obtained in [24]. The rates of nitrite reduction and ammonia generation is independent of the potential (Fig. 2a, points 1 and 2); consequently, the reduction of nitrite proceeds under limiting current conditions.

The cathodic polarization curves in base stirred solution and in the solutions with 5 and 15 mM $NaNO_2$ are shown on Fig. 2b (curves 1–3). Using the values of external cathodic current and the rates of iron dissolution, the rates of total cathodic process were calculated (curves 4 and 5). As can be seen , at E −0.35 V the rates of cathodic process coincide well with the rate of ammonia generation (points 6 and 7); hence, in stirred solution nitrite is completely reduced to ammonia. The limiting current measured at $E = -0.44$ V with the disc electrode is a linear function of the square root of the rotation rate and indicates diffusion control.

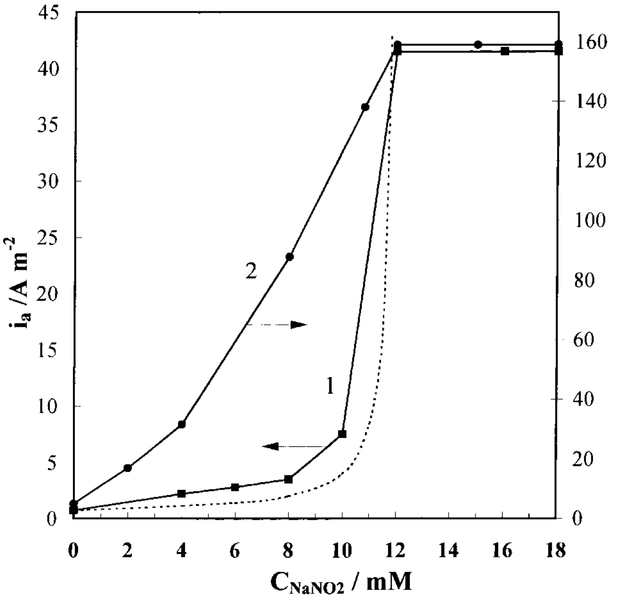

Fig. 1. Rate of the anodic iron dissolution vs $NaNO_2$ concentration in (1) unstirred and (2) stirred electrolytes at a potential of −0.35 V. Dashed line is the dependence calculated from (7).

The diffusive nature of the rate limiting step of nitrite reduction allows us to use equation (4) for the calculation the critical concentration of oxidant. The calculated value $C_{ox,c}$ is equal 11, 9 mM. Above this value the electrode concentration of hydrogen ions and the rate of their discharge should be reduced to zero at any electrode potential and this is confirmed by the dependence of the rate of hydrogen penetration through the membrane (i_p) on nitrite concentration (Fig. 3).

From the determined value $C_{ox,c}$ and Equation (7) the change in iron dissolution rate with nitrite concentration can be calculated (Fig. 1, dashed line); this change is due to an increase in pH_s upon reduction of oxidant. Similar shapes of the calculated and experimental i_a-C_{ox} curves indicate that the increase in pH of the solution layer at the electrode can be regarded as the reason for the acceleration of iron dissolution in unstirred electrolytes. According to the chosen model, alkalization is due to the reaction:

$$\begin{aligned} &6\,Fe^{2+} + HNO_2(NO_2^-) + 7\,H^+ \\ &\quad \rightarrow 6\,Fe^{3+} + NH_4^+(NH_3) + 2\,H_2O \end{aligned} \tag{13}$$

proceeding in the diffusion layer[B]. However, the experimental i_a values exceed those calculated by a

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[A] Stirring increases the iron dissolution rate in solutions free of nitrite. This effect is due to the different rates of oxygen reduction, because in deaerated electrolytes the dissolution rate of iron is almost the same (1.5 and 1.1 A m^{-2} at $E = -0.35$ V with and without stirring, respectively). The influence of oxygen on the iron dissolution rate at constant electrode potential was reported elsewhere [11, 17].

[B] The evidence for reaction (13) proceeding in acidic sulfate solution is given elsewhere [25].

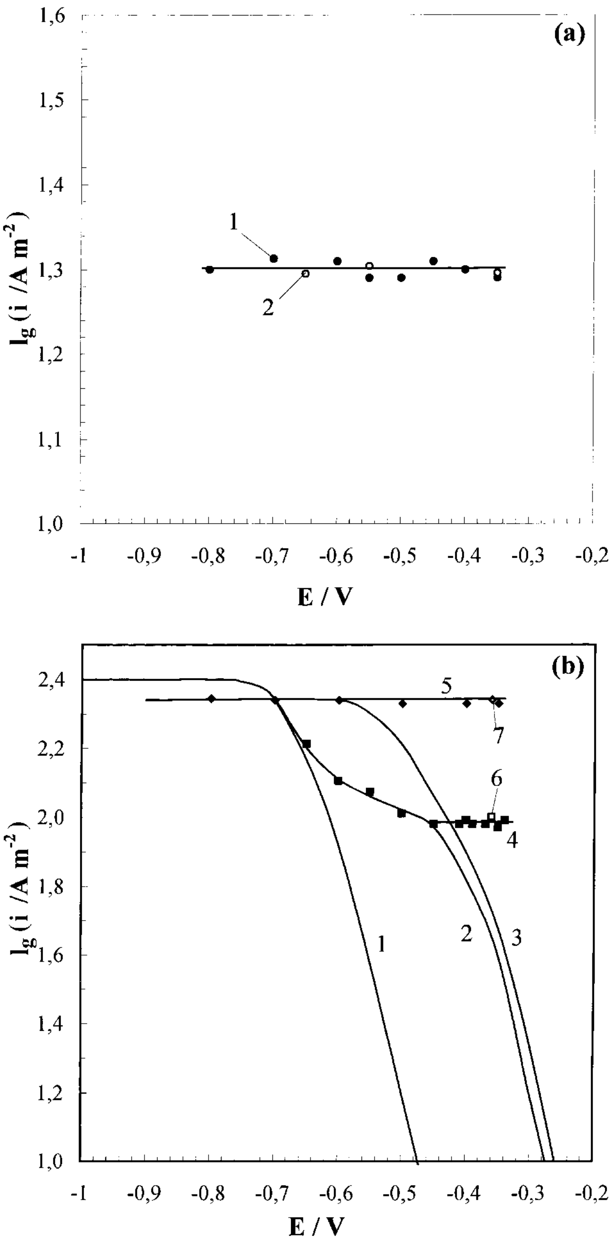

Fig. 2. (a) Rates of (1) nitrite reduction and (2) ammonia generation vs potential in unstirred solution with 10 mM $NaNO_2$. (b) Cathodic polarization curves in (1) stirred base solution and with (2) 5 mM $NaNO_2$ and (3) 15 mM $NaNO_2$. Rates of (4, 5) total cathodic process and (6, 7) ammonia generation vs potential in stirred solution with (4, 6) 5 mM and (5, 7) 15 mM $NaNO_2$.

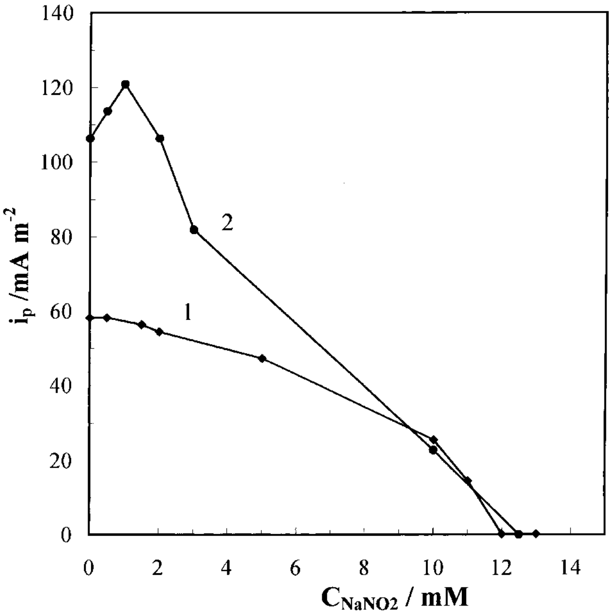

Fig. 3. Rate of hydrogen permeation through an iron membrane vs $NaNO_2$ concentration in unstirred electrolytes at potentials (1) −0.35 and (2) −0.44 V.

factor of 1.5–2.0. Probably, with nitrite the completion of reaction (13) is less than that for H_2O_2, because calculated and experimental curves coincide well in the latter case [16]. Stirring decreases the thickness of the diffusion layer and increases the relative amount of NO_2^- ions which have no time to participate in reaction (13) and, consequently, are reduced at the electrode. During the electroreduction process anode active species should be produced. Therefore, at $C_{ox} < C_{ox,c}$, the experimental values i_a are substantially (up to a factor of 5) greater than the values i_a^{eq} obtained from (7) (Fig. 1, curve 2).

The difference $i_a - i_a^{eq} = i_a^{ox}$ (Fig. 4, curves 1 and 2) is an almost linear function of C_{ox} which confirms the assumption that anode active species are formed in the electroreduction of oxidant. According to (10), the product of m and K can be calculated from the slope di_a^{ox}/dC_{ox}; however, due to reaction (13), only a part of the nitrite diffusing from the bulk of the solution participates in the cathodic reaction at the electrode. Therefore, we can find only an effective value mK^{eff}; since K^{eff} is a function of the ratio of reaction rate (8) to reaction rate (12). In stirred and unstirred solutions, $mK^{eff} = 1.15$ and 0.39, respectively.

It was shown elsewhere [16, 26] that, for the same stirring conditions, but in the absence of chemical interaction between Fe^{2+} ions and Ox (the electroreduction of hydroxylamine or hydrogen peroxide in

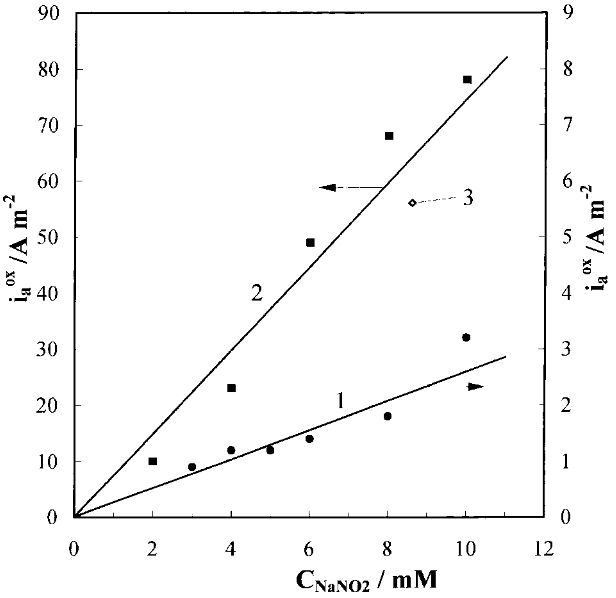

Fig. 4. The value i_a^{ox} vs nitrite concentration in (1) unstirred and (2) stirred electrolytes. Explanation of point 3 is given in the text.

well stirred solutions), the values of K^{eff} are identical and equal to 0.23–0.25. In these cases almost all the oxidant species reduce at the electrode and K^{eff} approaches the theoretical K value which is the upper limit for K^{eff} [18]. It may be assumed that $K^{\mathrm{eff}} \approx K = 0.24\ (\pm 0.1)$ for reduction of nitrite in stirred solution. Therefore, the number of species A appearing for the electroreduction of one particle of nitrite (NO_2^- or HNO_2) can be determined from mK^{eff} in stirred solution. This number is equal to 4.8 ($\pm$0.2). The nature of the species A will be discussed below.

The activating mechanism suggested also explains the dependence of the iron dissolution rate on pH and potential. There is an interesting dependence of the iron dissolution rate on pH at constant nitrite concentration (Fig. 5). With no stirring (curve 1), the lowering of pH from pH 2 (where a nitrite concentration of 12 mM is critical), diminishes i_a by a factor of 10 or more due to the corresponding decrease in the difference between electrode pH and bulk pH. In this case, anode active species are not produced on the metal surface because nitrite is consumed in reaction (13). On the other hand, with stirring (curve 2), the same decrease in bulk pH lowers i_a by no more than one half, while the point i_a, corresponding to pH 1.5, falls on the i_a^{ox} curve (Fig. 4, point 3). This fact correlates with the accelerating action of anode active species produced during oxidant electroreduction.

As for the effect of the potential, according to Fig. 6a at potentials between −0.5 and −0.3 V the dissolution rates without stirring and at overcritical nitrite concentration (15 mM) follow a Tafel line (curve 2). This line, of slope of 100 ($\pm$7) mV, virtually coincides with the one obtained with the buffer solution (NaH_2PO_4 + Na_2HPO_4) at pH 5.2 (dashed line) [27]. Thus, at the overcritical concentrations of oxidant the dissolution of iron should proceed in the same way as in neutral and weakly acidic buffered electrolytes; i_a is likely to be controlled by that part of an electrode area free from iron corrosion products. Here, under stirring, i_a should increase [27] as observed in the case with nitrite (Fig. 1, curves 1 and 2).

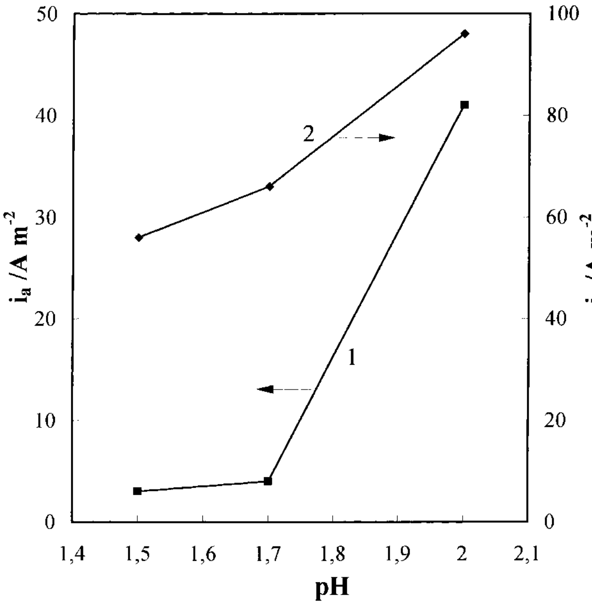

Fig. 5. Effect of pH on the rate of anodic iron dissolution in (1) unstirred and (2) stirred electrolytes at a potential of −0.35 V. The nitrite concentration are (1) 12 and (2) 8 mM.

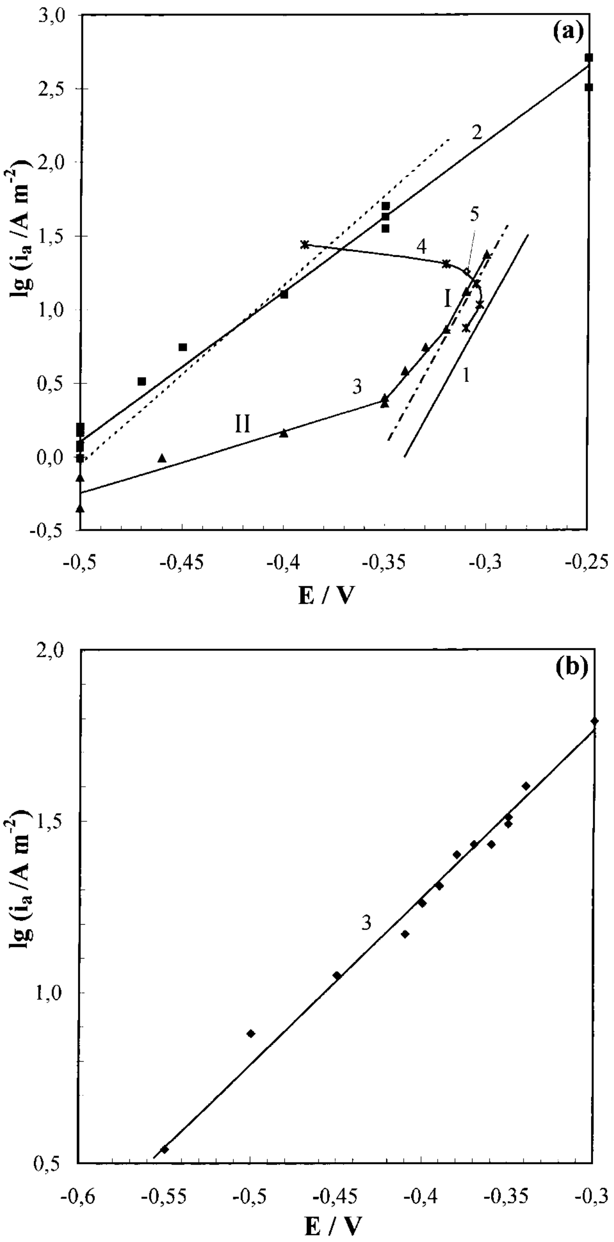

Fig. 6. Effect of the potential on the iron dissolution rates in (a) unstirred and (b) stirred electrolytes. The oxidant concentrations (mM) are (1) 0, (2) 15 $NaNO_2$, (3) 5 $NaNO_2$. Corrosion current as a function of the open circuit potential in the presence of (4) 0–20 mM $NaNO_2$ and (point 5) NO. Dashed and dashed-and-dotted lines are explained in the text.

For an undercritical nitrite concentration (5 mM), the plot of lg i_a vs E (Fig. 6a, curve 3) has two Tafel parts with slopes of 40 mV at $E \geq -0.32$ V (part I) and 230 ($\pm$30) mV at $E < -0.32$ V (part II). The former virtually coincides with the dependence of i_a^{eq} on E (dot-and-dash line) constructed from (7) at $C_{\mathrm{ox}} = 5$ mM using the anodic curve of iron dissolution in the background solution (curve 1). It follows that at a fairly high potential, the accelerating action of the nitrite can only be associated with an increase in pH_s. (At given nitrite concentration calculated pH_s is 2.23.)

Evidently, at a high rate of formation of Fe^{2+} ions, all the oxidant species take part in chemical reaction within the diffusion layer and do not reach the metal surface. At lower potentials, the dissolution rate, and hence the degree of completion of the chemical reaction (13), decreases. As a result, some of the nitrite reduces at the metal, and the plot of i_a vs E deviates from the calculated straight line. Thus, the presence of part II should be attributed to the accelerating effect of the cathodically reduced oxidant.

The dependence of lg i_a on E found in the stirred solution at $C_{ox} = 5\,mM$ (Fig. 6b) provides support for the suggestion above. Since, under stirring, the fraction of cathodically reduced nitrite is larger, the anodic curve of iron dissolution has no part I, and at E ranging from −0.3 to −0.55 V the plot of lg i_a vs E is linear with a slope of 207 (±7) mV. Thus, in the case of oxidant reduction at the surface, the dependence of the metal dissolution rate on the potential has an anomalously high Tafel slope.

The data obtained explain the decrease in the open circuit potential (E_{cor}) of iron in the presence of oxidant in corrosion media [17]. Fig. 6a depicts the dependence of the free corrosion rate on E_{cor} obtained by a "chemical polarization" method, that is, by an increasing of the nitrite concentration in the solution (curve 4). At low C_{ox} the values of E_{cor} fall on the curves E-lg i_a^{eq} calculated for C_{ox}. As the concentration of nitrite increases, so does electrode pH, and the curves E-lg i_a^{eq} shift to lower potentials. Accordingly, E_{cor} decreases. E_{cor} is minimum at $C_{ox,c}$ and, hence, fits curve 2. Further increasing the nitrite concentration does not change the potential or the corrosion rate.

Since reduction of nitrite results in the production of several kinds of species (NO, NH_3, OH^-) which may form activated complexes with the iron surface, let us consider the nature of the species A. If the electrolyte is saturated with nitrogen monoxide, the open circuit potential and the free corrosion current (Fig. 6, point 5) coincide with the curve E_{cor}-lg i_a recorded in the presence of nitrite (curve 4). Consequently, in this case NO causes no specific acceleration (additional in comparison with NO_2^-). An additional activation is also not observed when increasing the concentration of ammonium ions, in solutions with overcritical concentration of nitrite. Under these conditions NH_4^+ ions are converted to NH_3 in the near electrode solution layer. This means that nitrogen-containing products of nitrite reduction have only a slight effect on the iron dissolution, i.e. the products of nitrite reduction accelerating the dissolution of iron are most likely to be the hydroxide ions produced at the electrode surface.

This is confirmed by the calculated number of anode active species, A, formed during reduction of one nitrite particle – 4.8 (±0.2). If the anode active species are the nitrogen-containing compounds this number cannot be larger than 1. In contrast, several OH species (ions or radicals) can be formed in some stages of nitrite reduction.

5. Conclusion

The effect of nitrite concentration, stirring intensity, electrolyte acidity and potential on the dissolution rate of iron was studied. Experimental data are described by a model based on the hypothesis that iron dissolution at constant potential is defined by two factors: the acidity of the solution at the electrode surface and the rate of oxidant electroreduction. The electroreduction process is assumed to generate the species forming an activated complex on the iron surface and thus accelerating dissolution. It is shown that in unstirred electrolytes acceleration of dissolution by the oxidant is mainly due to the increase in pH at the electrode, because the chemical oxidation of Fe^{2+} ions prevents the oxidant from reaching the metal surface. In stirred electrolytes a dependence of iron dissolution rate on the rate of nitrite electroreduction was obtained. The intermediates of oxidant reduction which accelerate iron dissolution are likely to be OH species. The critical oxidant concentrations were determined at which the iron dissolution rate is a maximum. At overcritical concentrations of nitrite the kinetics correspond to iron dissolution in weakly acidic and neutral buffer electrolytes.

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