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MECHANISM OF ANODIC DISSOLUTION AND PASSIVATION OF IRON—I. BEHAVIOR IN NEUTRAL ACETATE BUFFER SOLUTIONS

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Abstract—The kinetics of the anodic dissolution and passivation of Fe have been studied in neutral and slightly acidic acetic acid/sodium acetate buffer solution as a function of the total acetate buffer concentration and pH. The results have been obtained from potential sweep experiments at 5 mV s^{-1} , which corresponds to quasi-steady state conditions. Two anodic peaks were found in the active dissolution region of the voltammogram. A reaction order of -0.7 ± 0.2 with respect to acetate concentration and of 1.4 ± 0.2 with respect to pH has been found for the Tafel region of the first peak; more complicated behavior was found for the remainder of the voltammogram. Galvanostatic cathodic reduction experiments were used to characterize the surface film formed during the anodic sweep. A mechanism is proposed which accounts for the observed reaction orders, and simulates the observed anodic voltammograms in a semi-quantitative fashion. The mechanism provided a simple, physical explanation for the observed negative reaction order with respect to acetate concentration.

Key words: iron, dissolution, acetate, passivation, oxide film.

INTRODUCTION

Over the last three decades, extensive research on the mechanism and kinetics of the anodic dissolution of Fe has been performed. Studies have been made over a wide range of pH's and in many kinds of electrolytes, and a number of different dissolution mechanisms have been proposed. Bockris *et al.*[1, 2] suggested that Fe dissolution in acid solution proceeds according to a consecutive mechanism, with the initial step being the formation of an adsorbed intermediate, *ie* $(\text{FeOH})_{\text{ad}}$, and the rate determining step being the discharge of this intermediate. The general form of this mechanism has been confirmed by many experimental observations[3–14], and other authors [15–17] suggested that the adsorbate was water in acid solution and hydroxyl ion in alkaline solution. Heusler *et al.*[18–20] proposed a catalytic mechanism, where $(\text{FeOH})_{\text{ad}}$ acts catalytically in the initial step of Fe dissolution. Some authors[21–24] observed behavior corresponding to both mechanisms in the same solution; the catalytic mechanism applied to cold-worked Fe surfaces, while the consecutive mechanism applied for annealed surfaces.

Kinetic studies have been made in acid[3, 4, 6, 10, 12, 13, 25–31], neutral[5, 8, 14, 32–36] and alkaline [5, 7, 9, 11, 37–42] solutions, and the influence of the electrolyte species has also been investigated. In acidic chloride solution, the reaction order for Cl^- is not zero; *ie* Cl^- participates in the reaction. However, different values of the reaction order were reported [43–46]. The effects of other anions such as bromide, iodide, acetate, sulfate, sulfide, phosphate and bicarb-

onate have also been investigated[47–53]. In particular, Bech-Nielsen *et al.*[23, 54–57] have performed a series of investigations into the effects of the acetate ion on Fe dissolution.

With regard to the industrial application of corrosion inhibitors, it is clearly important to investigate the effects of the electrolyte species on the corrosion behavior of Fe in neutral solutions. Compared with the detailed research on the effect of corrosive anions such as the halides, very little fundamental knowledge exists on the action of functional groups found in inhibitor formulations. Such functional groups include phosphate, carboxyl, amino, and sulfonate. The present paper presents results on the active dissolution and passivation of Fe in neutral and slightly acid acetic acid/sodium acetate buffer solution, *ie* solutions containing the carboxyl group. A systematic study has been performed to investigate the effect of both pH and acetate concentration, and a mechanism is proposed which provides a semi-quantitative explanation for the results. In addition, the technique of galvanostatic cathodic reduction is used to provide an *in situ* monitor of the presence of surface oxide and/or hydroxide films on the Fe surface as a function of potential.

EXPERIMENTAL

Fe samples were cut from 99.9% + foil of 0.5 mm thickness, supplied by Goodfellow Metals, England. They were polished to 600 grit SiC and were subsequently annealed in vacuum at 850°C for 24 h. The samples were electropolished in 20:1 acetic:perchloric acid before each electrochemical experiment. Thus, the electrode samples should be free from any cold-work effects.

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Acetate buffer solutions were made by mixing equimolar solutions of acetic acid (Aristar, BDH) and sodium acetate (AnalaR, BDH). In the discussion below, [acetate] will refer to the total acetate buffer concentration $[\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]$. $[\text{CH}_3\text{COOH}]$ will be abbreviated [HA] and $[\text{CH}_3\text{COO}^-]$ as $[\text{A}^-]$. The ratio $[\text{HA}]/[\text{A}^-]$ will, of course, vary with pH. The concentration of the various species may be calculated from

$$[\text{HA}] = \frac{10^{-\text{pH}} [\text{acetate}]}{K_a + 10^{-\text{pH}}}$$

$$[\text{A}^-] = [\text{acetate}] - [\text{HA}],$$

where K_a is the equilibrium constant for the dissociation of HA and is given by

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = 1.75 \times 10^{-5}.$$

Solutions were deaerated with nitrogen before use and were quiescent. Experiments were performed at room temperature (20–22°C). Potentials were measured relative to a Hg/Hg₂SO₄/0.15 N Na₂SO₄ reference electrode (0.421 V *vs sce*, 0.661 V *vs she*). All electrodes were galvanostatically reduced at 20 $\mu\text{A cm}^{-2}$ for 300 s to remove the electropolish film before initiating a potential sweep. All sweep experiments were initiated at -1.5 V. A PAR model 173 Potentiostat with a custom modified 276 interface was used as described previously[58]. The potentiostat could be switched from the sweep voltammetry mode to the galvanostatic mode within a few milliseconds.

RESULTS

An anodic direction linear sweep voltammogram at 5 mV s^{-1} of Fe in pH 7, 1 M acetate solution is shown in Fig. 1. A number of anodic peaks are observed; most prominently a small peak at -1.16 V, and a larger peak at -0.88 V, which will be referred to as peak A and peak B, respectively. An extensive range of passivity is observed in this solution, followed by oxygen evolution at high potentials. These two active dissolution peaks have been observed for Fe in many electrolytes, *eg* sulfate[4], carbonate[59–61], and borate[62].

Fig. 1. Anodic sweep voltammograms for Fe at 5 mV s^{-1} in pH 7 solution with [acetate] = 1 M and 0.1 M. Peak A' obtained at [acetate] = 0.1 M is an artifact due to insufficient buffer capacity.

(i) Limitations of the experimental data

In the present work, a systematic investigation of the behavior of Fe in the region of peaks A and B was made as a function of pH and [acetate]. However, it is important to recognize that meaningful results cannot be obtained unless the solution has adequate buffer capacity; this limited the range of pH and [acetate] over which experiments could be performed. Adequate buffer capacity is necessary, since during the cathodic galvanostatic treatment and during the sweep at cathodic potentials, hydrogen is evolved, resulting in a depletion of H^+ at the electrode surface. If the solution has insufficient buffer capacity, this surface pH change will be significant, and will be an uncontrolled parameter in the experiment. Shown in Fig. 1 is an experiment where buffer capacity was insufficient, *viz.* pH 7, 0.1 M [acetate]. This sweep shows three anodic peaks in the region where normally only two are observed. The first peak, labelled A', is an artifact of the polarization-induced basicity near the electrode surface. Peak A' appears when [acetate] < 0.5 M in pH 7 solution and when [acetate] < 0.075 M in pH 6 solution. These solutions have approximately the same buffer index, confirming the origin of peak A' as insufficient buffer capacity. Peak A' disappears at slower sweep rates, indicating that it will not occur if sufficient time is allowed for the surface pH to equilibrate after the cathodic treatment. As a further supporting argument, three peaks are commonly observed in this potential region in strong alkaline solution[38, 39, 63]. In the present paper, results were considered only when buffer capacity was not a problem.

Since the experiments were performed under quiescent conditions, the accumulation of Fe^{2+} at the surface of the electrode is to be expected at high current densities; moreover, it may hydrolyse, resulting in a local acidification at the electrode surface. Furthermore, most experiments were performed at a sweep rate of 5 mV s^{-1} . However, experiments done at slower sweep rates in pH 7 solution indicated that many kinetic parameters, including the Tafel slopes, varied with sweep rate. Therefore, the chosen sweep rate of 5 mV s^{-1} should be considered to correspond to quasi steady-state conditions only. In addition, there is no guarantee that a sweep rate of 5 mV s^{-1} is an equally good approximation to steady-state when the pH and/or [acetate] is varied. While the parameters obtained in this study at 5 mV s^{-1} are probably not rigorous, steady state values, they are comparable to results obtained by many other workers using slow sweeps. Finally, no *IR* compensation was made to the data.

For the above reasons, the data obtained in this work cannot be used in a rigorous, quantitative way. However, it will be shown that a semi-quantitative treatment provides useful information about this important system.

(ii) Effect of acetate buffer concentration

The effect of acetate buffer concentration on the anodic voltammograms of Fe in pH 6 solution is shown in Fig. 2. Significant effects of [acetate] are observed, suggesting that either the acetate anion and/or the undissociated acetic acid is involved in the

Fig. 2. Effect of [acetate] on anodic sweep voltammograms for Fe at 5 mV s^{-1} in pH 6 solution with [acetate] = 1 M and 0.1 M.

reaction. In the Tafel region of peak A, the reaction order with respect to [acetate] (defined as $y_{A,[\text{acetate}]}$) is negative, *ie* the presence of additional [acetate] reduces the reaction rate. However, in the Tafel region of peak B, the results are more complicated. At $\text{pH} \leq 6$, there is a positive reaction order with respect to [acetate], $y_{B,[\text{acetate}]}$, but this reaction order decreases to approximately zero at $\text{pH} 7$. In general, the maximum currents at both peaks A and B ($j_{p,A}$ and $j_{p,B}$) are larger with higher [acetate]. The peak potential for peak A ($E_{p,A}$) is nearly constant as [acetate] is varied, while the peak potential for B ($E_{p,B}$) shifts cathodically with increasing [acetate]. The Tafel slopes calculated from the linear portions of the rising edges of peaks A and B are shown in Fig. 3 as a function of [acetate]. Peak A has a Tafel slope of about 40 mV/decade, while peak B exhibits a higher Tafel slope, about 120 mV/decade. Both Tafel slopes decrease with increasing [acetate]. The effect of [acetate] at $\text{pH} 7$ shows similar trends, except that $E_{p,B}$ as well as $E_{p,A}$ is nearly constant with respect to [acetate].

(iii) Effect of pH

The effect of pH on the anodic voltammograms of Fe in 1 M [acetate] buffer is shown in Fig. 4. The Tafel regions of both peaks A and B clearly indicate that the apparent reaction orders with respect to pH, $y_{A,\text{pH}}$ and $y_{B,\text{pH}}$, are positive. The maximum peak currents, $j_{p,A}$ and $j_{p,B}$, increase with decreasing pH, as shown quantitatively in Fig. 5. In addition $E_{p,A}$ and $E_{p,B}$ change linearly with pH; for 1 M solutions the

Fig. 3. The Tafel slope for peaks A and B as a function of [acetate] of pH 6 solution.

Fig. 4. Effect of pH on anodic sweep voltammograms for Fe at 5 mV s^{-1} in [acetate] = 1 M solution, with pH 6 and 5.

Fig. 5. The maximum current, j_p , at peaks A and B as a function of pH for [acetate] = 1 M and 0.1 M solution.

shift is -76 and $-140 \text{ mV}/(\text{pH unit})$, respectively. The values of these slopes were found to be a function of [acetate], however, changing to $-106 \text{ mV}/(\text{pH unit})$ and $-207 \text{ mV}/(\text{pH unit})$ respectively at [acetate] = 0.1 M. The Tafel slopes for peaks A and B are shown in Fig. 6 for both 1 M and 0.1 M [acetate]. The Tafel slope of peak B seems to show a dependence on [acetate] and pH.

(iv) Calculation of reaction orders

In order to calculate the reaction orders, $y_{A,[\text{acetate}]}$ and $y_{A,\text{pH}}$, values of j_+ , which is the current density at a fixed potential, were obtained by interpolation or extrapolation of the Tafel lines to -1.2 V . This potential was chosen since it was within the Tafel region in most cases. The results are summarized in

Fig. 6. The Tafel slopes for peaks A and B as a function of pH for [acetate] = 1 M and 0.1 M.

Fig. 7. (a) The relationship between j_+ for peak A, extrapolated to a constant potential of -1.2 V, and pH for $[\text{acetate}] = 1$ M and 0.1 M. A reaction order of 1.4 with respect to pH is calculated from the slopes, while the separation of the two lines indicated by the arrow, gives a reaction order of -0.6 ± 0.1 with respect to $[\text{acetate}]$. (b) The relationship between j_+ for peak A, extrapolated to a constant potential of -1.2 V and $[\text{acetate}]$ for a constant pH of 6 , the slope of the line indicates a reaction order of -0.7 with respect to $[\text{acetate}]$.

Fig. 7a. The slope of the lines yields $y_{A, \text{pH}} = 1.4$, while the separation between the lines yields $y_{A, [\text{acetate}]} = -0.6 \pm 0.1$. Some caution is necessary, however, since the Tafel slope depends on $[\text{acetate}]$ and pH (see Figs 3 and 6). Thus, the estimation of $y_{A, [\text{acetate}]}$ will vary depending on the choice of the extrapolation

potential. However, if a different reasonable extrapolation potential (within the linear Tafel region) is chosen for each pH, then $y_{A, [\text{acetate}]}$ is calculated to be -0.7 ± 0.2 , and $y_{A, \text{pH}} = 1.4 \pm 0.2$, in good agreement with the above result for a constant potential of -1.2 V. Another method of calculating $y_{A, [\text{acetate}]}$ is

Table 1. Comparison of experimental parameters with those of Bech-Nielsen[23, 54–57], and the results of the simulation using the model illustrated in Figs 9 and 10 and the constants given in Table 2

Parameter	This work	Bech-Nielsen	Simulation
$y_{A, [\text{acetate}]}$	-0.7 ± 0.2	$-0.7, -1$	-0.60 (pH 7) -0.67 (pH 6)
$y_{B, [\text{acetate}]}$	≈ 0 (pH 7) > 0 ($5 \leq \text{pH} \leq 6$)	$-0.4, -0.2, -0.18$	0.81 (pH 7) 0.56 (pH 6)
$\left(\frac{\partial \log j_{p, A}}{\partial \log [\text{acetate}]}\right)_{\text{pH}}$	$> 0^*$	—	*
$\left(\frac{\partial \log j_{p, B}}{\partial \log [\text{acetate}]}\right)_{\text{pH}}$	0 to 0.45^*	-0.4 to 0.4	0.87 (pH 7) 0.66 (pH 6)
$\left(\frac{\partial E_{p, A}}{\partial \log [\text{acetate}]}\right)_{\text{pH}}$	small*	—	30 (pH 7) 17 (pH 6)
$\left(\frac{\partial E_{p, B}}{\partial \log [\text{acetate}]}\right)_{\text{pH}}$	small, $< 0^*$	0	0 (pH 7) 7 (pH 6)
$y_{A, \text{pH}}$	1.4 ± 0.2	1	1.48 (1 M) 1.62 (0.1 M)
$y_{B, \text{pH}}$	$< 0^*$	-0.2	*
$\left(\frac{\partial \log j_{p, A}}{\partial \text{pH}}\right)_{[\text{acetate}]}$	-0.39 ± 0.1 (1 M) -0.22 ± 0.1 (0.1 M)	-0.5	-0.60 (1 M) -0.53 (0.1 M)
$\left(\frac{\partial \log j_{p, B}}{\partial \text{pH}}\right)_{[\text{acetate}]}$	-0.37 ± 0.1 (1 M) -0.15 ± 0.1 (0.1 M)	-0.5	-0.37 (1 M) -0.44 (0.1 M)
$\left(\frac{\partial E_{p, A}}{\partial \text{pH}}\right)_{[\text{acetate}]}$	-76 (1 M) -106 (0.1 M)	-90	-71 (1, 0.1 M)
$\left(\frac{\partial E_{p, B}}{\partial \text{pH}}\right)_{[\text{acetate}]}$	-140 (1 M) -207 (0.1 M)	$-120, -60$	-68 (1 M) -63 (0.1 M)
Tafel slope peak A	40 to 50	40	39 to 47
Tafel slope peak B	90 to 200	120	125 to 142

*No linear relationship.

shown in Fig. 7b. The slope of a plot of j_+ vs [acetate] at pH 6 also yields a value of -0.7 . Exact numerical values of $y_{B, \text{[acetate]}}$ and $y_{B, \text{pH}}$ cannot be obtained from the voltammetric data, since the Tafel slope depends very strongly on both [acetate] and pH.

Table 1 summarizes the parameters for the acetate system, comparing the results from this work with those obtained by Bech-Nielsen[23, 54–57]. It can be seen that in general there is good agreement. In most cases, the range of values seen in this work is somewhat larger, but this may reflect the greater range of pH and [acetate] utilized in the present work. It should be emphasized that the model developed by Bech-Nielsen gives a value of unity for the reaction order of peak A with respect to pH, $y_{A, \text{pH}}$. Thus, his model cannot account for the value of 1.4 ± 0.2 obtained in the present work. The data of Bech-Nielsen were obtained at more acidic pH, where a sweep rate of 5 mV s^{-1} would be expected to give a reasonable approximation to steady-state conditions. The good agreement between the present parameters and those of Bech-Nielsen provides further support for the assumption of quasi steady-state conditions, as discussed above.

(v) *Galvanostatic cathodic reduction of the film formed during the potential sweep*

Galvanostatic cathodic reduction has been often used to characterize the passive film on Fe. In recent work, this technique was used in acetate buffer solution, and the results compared with those obtained in

the more thoroughly studied borate buffer system[64]. For Fe in pH 7, 1 M [acetate], the arrest structure could be divided into two regions for oxide films formed potentiostatically in the passive region. The first arrest region, referred to as Q_1 , was concluded to result from an Fe_2O_3 (or Fe^{III} -containing) oxide, while the second arrest region, with cathodic charge, Q_2 , corresponded to reduction of Fe_3O_4 or some other Fe^{II} -containing oxide. Both arrests are present for thick passive films, indicating that the oxide consists of two distinct phases. In the present work, this technique was used to characterize the film formed on the Fe surface during the linear potential sweep.

Figure 8a shows the anodic sweep result for pH 7, 1 M [acetate] at 5 mV s^{-1} . Figure 8b shows the cathodic charges in the first and second arrests as a function of the potential at which the anodic sweep was interrupted and galvanostatic cathodic charging at $20 \mu\text{A cm}^{-2}$ begun. It can be seen that as the anodic current rises in the Tafel region of peak A, an arrest corresponding to an Fe^{II} -containing oxide (Q_2) begins to appear, and grows in magnitude through peak A. After the current has decreased in the transition to passivity, the arrest corresponding to the Fe^{III} -containing oxide (Q_1) appears, and increases steadily with potential. There is a maximum in Q_2 during peak B. However, care must be taken in the interpretation of the results for Q_2 in this region, since the large amounts of dissolved Fe^{2+} in the vicinity of the electrode surface may also be reduced in the galvanostatic procedure, and may contribute to the magnitude of Q_2 .

DISCUSSION

(i) *Interpretation of the reaction orders in peaks A and B*

In buffer solutions such as acetate, one could postulate that the anodic dissolution reaction could depend on any of three solution species: OH^- , A^- and HA . The results shown above clearly indicate that both OH^- and either A^- and/or HA participate in the reaction mechanism. It would be of considerable interest to determine whether A^- or HA is the active participant. Normally, this question would be addressed, for example, by holding both $[\text{OH}^-]$ and $[\text{A}^-]$ constant, and varying $[\text{HA}]$. However, in buffer solutions, it is not possible to do this, as $[\text{HA}]$ is not an independent variable under these conditions. Therefore, in the results above, the apparent reaction order with respect to pH and to total acetate concentration, which are the readily observable parameters, were calculated. Nevertheless, it is instructive to consider what the reaction orders would be if A^- or HA was the active participant in the reaction mechanism:

At $\text{pH} \geq 6$, $[\text{HA}]$ is small, and $10^{-\text{pH}} \ll K_a$, thus

$$[\text{HA}] \approx 10^{-\text{pH}} [\text{acetate}] / K_a, \text{ while}$$

$$[\text{A}^-] \approx [\text{acetate}].$$

Thus an observed reaction order of -0.7 ± 0.2 with respect to [acetate] implies the following three possibilities: (1) -0.7 is the reaction order with

Fig. 8. (a) Experimental anodic sweep voltammogram for Fe at 5 mV s^{-1} in pH 7 solution with [acetate] = 1 M. (b) The cathodic charges corresponding to the two stages in the galvanostatic ($20 \mu\text{A cm}^{-2}$) cathodic reduction profile. The potential was swept to a given value at 5 mV s^{-1} , and then the galvanostatic reduction was started. The charge Q_1 refers to the reduction of a Fe^{III} -containing oxide, while Q_2 refers to reduction of a Fe^{II} -containing oxide.

respect to $[A^-]$, (2) -0.7 is the reaction order with respect to $[HA]$, or (3) -0.7 is the sum of the reaction orders with respect to $[HA]$ and with respect to $[A^-]$. For constant [acetate], the observed reaction order with respect to pH is 1.4 ± 0.2 . In this case, $[HA]$ varies exponentially with pH, according to the equation above, while $[A^-]$ is approximately independent of pH. Thus, if possibility (1) is correct, then the relevant reaction orders are 1.4 with respect to pH and -0.7 with respect to $[A^-]$, while if possibility (2) is correct, then the reaction orders are $-0.7 + 1.4 = 0.7$ (by addition of the exponents) with respect to pH and -0.7 with respect to $[HA]$. Therefore, it is clear that the reaction order with respect to pH depends on which of A^- or HA is the active participant in the anodic dissolution reaction.

(ii) Reaction mechanism

The mechanism presented below was designed to qualitatively model the experimental anodic voltammograms over the wide range of [acetate] and pH

used in this work. The approach is an expansion of that used by El Miligy *et al.*[65], however it has been made much more general by allowing for the surface adsorption of numerous types of acetate-containing species as well as hydroxyl-containing species. In simple terms, the model proposed here accounts for the effect of [acetate] on the experimental results by postulating that there is competitive formation between acetate-containing adsorbed species such as $(FeA)_{ad}$ and the corresponding hydroxyl-containing species. Passivation is assumed to be conferred by a $Fe(OH)_3$ -oxide phase, which can be formed only by oxidation of $[Fe(OH)_2]_{ad}$. The various equilibria considered in the mechanism are shown schematically in Fig. 9. The arrows indicating equilibria have a large arrow in the direction which the equilibrium would be shifted for large values of K , the equilibrium constant. A complete listing of the reactions considered in the model is shown in Fig. 10.

The first step is the adsorption of H_2O or HA in the undissociated form on the Fe surface. Within the framework of the reaction scheme shown in Fig. 9, it

Fig. 9. A schematic of the equilibria considered in the proposed reaction mechanism. The species considered are enclosed in boxes, and are assigned a surface coverage θ_i , $i = 1$ to 8. The arrows connecting the boxes refer to the equilibria which are assumed to exist between the various species. The larger arrow indicates the direction in which the reaction would be shifted for a large value of the equilibrium constant, K_i , $i = 1$ to 6, 9 to 15.

Fig. 10. Equilibrium reactions (equations 1–6, 9–15) and rate determining steps (rds, equations 7, 8, 16–18) considered in the proposed mechanism, shown schematically in Fig. 6. Fe_s represents an iron atom in the metallic substrate. The equilibrium constant K_i is given by k_i/k_{-i} for $i = 1-6, 9-15$.

is difficult to obtain an apparent reaction order $y_{\text{A}, \text{pH}}$ of greater than unity if the first step was postulated to be the adsorption of A^- on the Fe surface. The experimental value of $y_{\text{A}, \text{pH}}$ is 1.4 ± 0.2 , thus the adsorption of HA was chosen for the first step. This approach was also supported by recent FT-*ir* work on Pt and Au which indicates that the undissociated acetic acid is the species adsorbed on these surfaces, even at neutral pH [66–68].

For all of the other equilibria where HA or A^- is required as a reactant, *ie* reactions 6, 10, 12, 13 and 14, the model has been formulated so that the undissociated acetic acid is the formal reactant. However, it should be noted that this distinction will not change the outcome of any simulation; if A^- was chosen as the reactant, then the equilibrium constant in that case would be the same as the equilibrium constant in the case of HA being the reactant, but divided by a factor of K_{a} . It is also apparent that use of the model does not require one to distinguish between the various possibilities for the exact reaction orders with respect to $[\text{A}^-]$, $[\text{OH}^-]$ and $[\text{HA}]$ as discussed in the section above. Since the equilibria between these three species are incorporated into the equations of the model, the results of a simulation are the experimentally observable quantities of the apparent reaction orders with respect to pH and [acetate].

The initial steps in the model for the hydroxyl-containing species correspond to the consecutive

mechanism[4, 21, 65], and analogous reactions were chosen for the acetate-containing species. This approach was taken because the Tafel slope in peak A was approximately 40 mV/decade, and because the annealed and electropolished electrodes were expected to be free of cold work effects. In addition to the equilibria shown in Fig. 9, six additional reactions are chosen as rate determining steps (rds). They are listed at the bottom of Fig. 10. Reactions 7 and 17 are identical to those chosen by El Miligy *et al.*[65], while reaction 16 is accelerated by HA instead of by A^- as chosen by those authors. The addition of reaction 18 was necessary in order to provide a satisfactory fit to the experimental data. In reactions 17 and 18, Fe_s represents an iron atom in the metallic substrate. As discussed by El Miligy *et al.*[65], such reactions are needed to produce the extra anodically-driven dissolution path which becomes important in peak B.

Of course, not all of the equilibria in Fig. 9 need result in substantial amounts of coverage by a specific species. For example, it is possible to obtain $\theta_8 \approx 0$ by choosing $K_{11} \gg K_{12}$, with K_{13} large. Similarly, it can be easily seen that not all equilibrium constants are independent. For example, $K_3 = K_4/K_5K_6$. The constants K_1 , K_4 , K_5 , K_6 , K_9 , K_{10} , K_{12} and K_{15} were chosen as the independent parameters for modelling purposes, while the other equilibrium constants were then fixed by the values of the independent parameters.

Some conclusions can be drawn from inspection of the reaction model. Since there are complex equilibria controlling the coverages of the various species, it is not possible to quantitatively predict the coverages of two linked species by consideration of that single equilibrium reaction alone, since a shift in any one equilibrium resulting from a change in [acetate] or pH will result in coverages other than those directly linked by that specific equilibrium constant. Nevertheless, the relative coverages of two linked species will be affected in the way that would be predicted by an examination of the single equilibrium reaction. The coverages of acetate-containing adsorbed species will be increased relative to those of hydroxyl-containing species as [acetate] is increased. For example, an increase in [acetate] will result in a relative decrease in the coverage θ_3 , compared to θ_4 . Since the currents from reactions 7 and 8 occur in the same potential region (as both involve the same number of electrons overall) a proper choice of K_6 , k_7 and k_8 (so that reaction 7 is dominant) will result in an overall negative reaction order with respect to [acetate].

Spreadsheet (Excel on a Macintosh computer) simulations of the above mechanism were performed. The procedure for writing down the kinetic equations followed that given by El Miligy *et al.*[65]. Langmuir isotherm conditions were assumed, and a charge-transfer coefficient α of 0.5, and a temperature T of 298 K, were used. Only two dimensional coverage was assumed, *ie* the sum of all coverages is unity. The potentials were converted from the hydrogen scale (in which the simulation was done) to the $\text{Hg}/\text{Hg}_2\text{SO}_4/0.15 \text{ N Na}_2\text{SO}_4$ scale by subtracting 0.661 V. The parameters were adjusted to give a reasonable correspondence ($\pm 40\%$) with the peak currents for pH between 5 and 7, and [acetate] between 0.1 and 2.5 M.

Fig. 11. Simulated anodic sweep voltammograms for Fe in pH 6 solution with [acetate] = 1 M and 0.1 M. The constants shown in Table 2 were used in the simulation.

Fig. 13. Simulated values of j_+ for peak A, extrapolated to a constant potential of -1.2 V, as a function of pH for [acetate] = 1 M and 0.1 M. The constants shown in Table 2 were used in the simulation.

In addition, the parameters were adjusted to give an appropriate appearance to the relative positions of the curves for 1 M and 0.1 M, pH 6 and for 1 M, pH 6 and pH 5 pairs as shown in Figs 2 and 4. The corresponding simulated data are shown in Figs 11 and 12, and the values of the rate and equilibrium constants used in the simulation are given in Table 2. Clearly, this procedure will not result in an optimum fit to the data, such as would be obtained from a non-linear least squares analysis, but as the objective was to obtain a semi-quantitative fit to the data, such analysis was not attempted. For reasons which will be explained below, the model is also capable of further refinement to better fit the data. It is recognized that because of the limitations of the experimental data (as described above), particularly the quasi steady-state

Fig. 12. Simulated anodic sweep voltammograms for Fe in pH 6 and pH 5 solution with [acetate] = 1 M. The constants shown in Table 2 were used in the simulation.

approximation, the individual values of the rate and equilibrium constants are not expected to have any quantitative meaning. Moreover, because of the large number of kinetic parameters, compared to the experimental parameters, it is likely that an equally good fit to the data could have been obtained with a quite different set of values for the model parameters. Thus, no interpretation of the model parameters will be made. Nevertheless, it is believed that the coverages, θ_i , calculated using the model, have some semi-quantitative meaning and can be used to predict trends in the data with respect to solution parameters such as [acetate] and pH.

Shown in Table 1 are the values of the kinetic parameters obtained with the constants of Table 2. Although these parameters could, in theory, be calculated from partial differentiation of the derived equations, such an approach is very time consuming in practice. Therefore, the parameters were obtained from a series of simulated curves under various conditions. It can be seen that there is rather good agreement between the simulated and experimental data. Most importantly, the experimental reaction orders with respect to pH and [acetate] are very well reproduced by the model as seen by comparing the simulation in Fig. 13 with the data in Fig. 7a. In contrast to the model proposed by Bech-Nielsen [23, 54–57, 69], the model used in the present simulation provides a simple physical explanation for the observed dependencies of the reaction order with respect to solution species. The model easily accounts for non-unit reaction orders and could also describe the data of Bech-Nielsen.

Table 2. Values of the rate and equilibrium constants used in the simulation using the model illustrated in Figs 9 and 10

Independent equilibrium constants		Derived equilibrium constants		Rate constants for rds	
K_1	1500	K_2	1.17×10^6	k_7	2.9×10^{-5}
K_4	700	K_3	778	k_8	5×10^{-4}
K_5	0.6	K_{11}	105	k_{16}	1×10^{-10}
K_6	1.5	K_{13}	52.5	k_{17}	6×10^{-7}
K_9	20	K_{14}	0.286	k_{18}	1×10^{-7}
K_{10}	70				
K_{12}	2				
K_{15}	1×10^{-4}

Fig. 14. The maximum current, j_p , at peaks A and B as a function of pH for $[\text{acetate}] = 1 \text{ M}$ and 0.1 M solution, as calculated from the model using the constants given in Table 2.

Figure 14 shows simulated values of $j_{p,A}$ and $j_{p,B}$ for $[\text{acetate}] = 1 \text{ M}$ and 0.1 M as a function of pH. The corresponding experimental data is shown in Fig. 5. As can be seen, there is quite good agreement between the two figures, particularly with regard to the trends of j_p . Overall, it is clear that the model provides a good, semi-quantitative fit to the data, and reproduces most of the experimental kinetic parameters. The only portion of the experimental curves which are not reasonably well represented by the present model is the transition between peak B and the onset of passivation. The experimentally observed transition is much steeper than that in the model, and the model fails to reproduce the dependence on $[\text{acetate}]$ in this region. Consequently, the results for $E_{p,B}$

are not particularly good. At least two reasons are apparent for this discrepancy. First, as discussed by El Miligy *et al.*[65], the equilibrium represented by K_{15} may not be a good description of the passivation process. These authors suggest several other sub-steps to replace the equilibrium K_{15} , which result in a more abrupt transition between peak B and the passive region. A second explanation of the discrepancy follows from experimental results which will be discussed below.

The coverages of the various species as a function of potential, calculated from the model for pH 6, 1 M and 0.1 M solutions are shown in Fig. 15. The coverage of Fe^0 species (θ_1 and θ_2) begins to decrease immediately with increasing potential. Coverage with Fe^I species (θ_3 and θ_4) then increases, goes through a maximum and then decreases, to be replaced by coverage with Fe^{II} species (θ_5 and θ_6). Finally, the Fe^{II} species are replaced by the oxide phase (Fe^{III} , θ_7), the coverage of which increases to unity. As would be expected, the relative coverage with species which include adsorbed acetate (θ_2 , θ_4 and θ_6) increases with increasing $[\text{acetate}]$, compared to the coverage by species which contain no acetate (θ_1 , θ_3 , and θ_5). The coverage θ_8 was negligible for all pHs and $[\text{acetate}]$ for the values of the constants used. No assumption was made about the surface coverage of bare Fe, but it turned out to be negligible in the potential region of interest.

Experimental determination of some of the surface coverages could, in principle, be made using the galvanostatic cathodic reduction procedure illustrated in Fig. 8. Unfortunately, it is difficult to quantify the exact coverages corresponding to the quantities of cathodic charge because the reduction efficiency for an oxide such as $\text{Fe}(\text{OH})_2$ in acetate solution is not known. Nevertheless, it is apparent that there is a strong correlation between Q_2 and the coverage θ_5 (or θ_6) and between Q_1 and the coverage θ_7 . These results provide direct, *in situ* electrochemical evidence for the coverage of the surface by a Fe^{II} -containing oxide during the active dissolution in peak A, and thus provide support for the proposed model. The striking difference between the model calculation and the experimental results is that Q_2 does not decrease as Q_1 increases, in other words, experimentally, the Fe^{III} -containing oxide is formed on top of the Fe^{II} -containing oxide, rather than replacing the lower oxide. This illustrates an important limitation of the model; the maximum coverage is assumed to be unity, thus, the model cannot account for a true phase oxide. Therefore, it is not expected that the model will satisfactorily describe the transition between peak B and passivation.

SUMMARY

Potential sweep experiments, coupled with galvanostatic cathodic reduction, have been used to study the kinetics of the dissolution and passivation of Fe in acetate solutions. Results similar to those obtained previously by Bech-Nielsen were obtained for the various kinetic parameters, although results from this study were obtained at a greater range of pH and concentration. A significant difference was the

Fig. 15. The surface coverages, θ_i , $i = 1$ to 8, calculated from the model for (a) pH 6, $[\text{acetate}] = 1 \text{ M}$, and (b) pH 6, $[\text{acetate}] = 0.1 \text{ M}$. θ_8 is negligible for all $5 \leq \text{pH} \leq 7$ and $0.1 \leq [\text{acetate}] \leq 2.5 \text{ M}$. The constants shown in Table 2 were used in simulation.

observation of a non-unit reaction order of 1.4 ± 0.2 with respect to pH in the Tafel region of the first anodic peak. A negative reaction order with respect to the total acetate concentration was found in the same region. A mechanism was proposed which accounts for these reaction orders, and provides a semi-quantitative fit to the experimental data. The first steps were postulated to be the adsorption of undissociated acetic acid and water on the Fe surface. The negative reaction order with respect to total acetate concentration arises from a competitive formation between $(\text{FeA})_{\text{ad}}$ and $(\text{FeOH})_{\text{ad}}$. It is this $(\text{FeOH})_{\text{ad}}$ intermediate which is the reactant in the dominant rate-determining step in the Tafel region of the first anodic peak. In other words, the acetate must be desorbed from the surface in order to yield anodic current in the Tafel region of peak A. The requirement for this desorption results in the negative reaction order.

REFERENCES

1. J. O'M. Bockris, D. Drazic and A. R. Despic, *Electrochim. Acta* **4**, 325 (1961).
2. J. O'M. Bockris and D. Drazic, *Electrochim. Acta* **7**, 293 (1962).
3. I. Epelboin and M. Keddam, *J. electrochem. Soc.* **117**, 1052 (1970).
4. D. Geana, A. A. El Miligy and W. J. Lorenz, *Corros. Sci.* **13**, 505 (1973); **14**, 657 (1974).
5. S. Asakura and K. Nobe, *J. electrochem. Soc.* **118**, 13, 19 and 536 (1971).
6. J. Bessone, L. Karakaya, P. Lorbeer and W. J. Lorenz, *Electrochim. Acta* **22**, 1147 (1977).
7. P. Doig and P. E. J. Flewitt, *Corros. Sci.* **17**, 369 (1977).
8. M. Erbil and W. J. Lorenz, *Werkst. Korros.* **29**, 505 (1978).
9. R. S. S. Guzmán, J. R. Vilche and A. J. Arvia, *Electrochim. Acta* **24**, 395 (1979).
10. P. Lorbeer and W. J. Lorenz, *Corros. Sci.* **20**, 405 (1980); *Electrochim. Acta* **25**, 375 (1980).
11. D. M. Drazic and C. S. Hao, *Electrochim. Acta* **27**, 1409 (1982).
12. H. Bala, *Electrochim. Acta* **29**, 119 (1984).
13. D. R. MacFarlane and S. I. Smedley, *J. electrochem. Soc.* **133**, 2240 (1986).
14. E. B. Castro, S. G. Real, R. H. Milocco and J. R. Vilche, *Electrochim. Acta* **36**, 117 (1991).
15. G. M. Florianovich, L. A. Sokolova and Ya. M. Kolotykin, *Electrochim. Acta* **12**, 879 (1967).
16. G. Eichkorn, W. J. Lorenz, L. Albert and H. Fischer, *Electrochim. Acta* **13**, 183 (1968).
17. K. Schwabe, H. D. Zushke and M. Time, *Zashch. Metal.* **10**, 491 (1974).
18. K. E. Heusler, *Z. Elektrochem.* **62**, 582 (1958).
19. W. Allgaier and K. E. Heusler, *Z. Phys. Chem.* **98**, 161 (1975).
20. B. Follmer and K. E. Heusler, *J. electroanal. Chem.* **180**, 77 (1984).
21. F. Hilbert, Y. Miyoshi, G. Eichkorn and W. J. Lorenz, *J. electrochem. Soc.* **118**, 1919, 1927 (1971).
22. V. H. Rossow, G. Eichkorn and W. J. Lorenz, *Werkst. Korros.* **25**, 86 (1974).
23. G. Bech-Nielsen, *Electrochim. Acta* **19**, 821 (1974); **20**, 619 (1975).
24. H. Worch and W. Forker, *Electrochim. Acta* **35**, 163 (1990).
25. C. Voigt, *Electrochim. Acta* **13**, 2037 (1968).
26. G. Bech-Nielsen, *Electrochim. Acta* **18**, 671 (1973); **27**, 1383 (1982).
27. G. J. Bignold and M. Fleischmann, *Electrochim. Acta* **19**, 363 (1974).
28. I. Epelboin, C. Gabrielli, M. Keddam and H. Takenouti, *Electrochim. Acta* **20**, 913 (1975).
29. B. Bechet, I. Epelboin and M. Keddam, *J. electroanal. Chem.* **76**, 129 (1977).
30. H. Schweickert, W. J. Lorenz and H. Friedburg, *J. electrochem. Soc.* **127**, 1693 (1980).
31. M. Keddam, O. R. Mattos and H. Takenouti, *J. electrochem. Soc.* **128**, 257, 266 (1981).
32. K. E. Heusler and L. Fischer, *Werkst. Korros.* **27**, 697 (1976).
33. K. Ogura and T. Majima, *Electrochim. Acta* **23**, 1361 (1978).
34. M. A. Morsi, Y. A. Elewady, P. Lorbeer and W. J. Lorenz, *Werkst. Korros.* **31**, 108 (1980).
35. F. Mansfeld, M. W. Kendig and S. Tsai, *Corros. Sci.* **22**, 455 (1982).
36. G. T. Burstein and G. W. Ashley, *Corrosion* **39**, 241 (1983).
37. R. D. Armstrong and I. Baurhoo, *J. electroanal. Chem.* **34**, 41 (1972); **40**, 325 (1972).
38. D. D. MacDonald and D. Owen, *J. electrochem. Soc.* **120**, 317 (1973).
39. D. D. MacDonald and B. Roberts, *Electrochim. Acta* **23**, 557, 781 (1978).
40. L. D. Burke and M. E. G. Lyons, *J. electroanal. Chem.* **198**, 347 (1986).
41. C. Chanson, P. Blanchard, A. Wattiaux and J.-C. Grenier, *J. electrochem. Soc.* **136**, 3690 (1989).
42. J. Wilinski, J. Flis and P. Kedzierski, *Br. Corros. J.* **25**, 184 (1990).
43. E. McCafferty and N. Hackerman, *J. electrochem. Soc.* **119**, 999 (1972).
44. N. A. Darwish, F. Hilbert, W. J. Lorenz and H. Rossow, *Electrochim. Acta* **18**, 421 (1973).
45. H. C. Kuo and K. Nobe, *J. electrochem. Soc.* **125**, 853 (1978).
46. M. Mogensen, G. Bech-Nielsen and E. Maahn, *Electrochim. Acta* **25**, 919 (1980).
47. J. G. N. Thomas, T. J. Nurse and R. Walker, *Br. Corros. J.* **5**, 87 (1970).
48. D. W. Shoesmith, P. Taylor, M. G. Bailey and B. Ikeda, *Electrochim. Acta* **23**, 903 (1978).
49. V. S. Muralidharan and K. S. Rajogopalan, *Electrochim. Acta* **23**, 1297 (1978).
50. G. T. Burstein and D. H. Davies, *Corros. Sci.* **20**, 1143 (1980).
51. Z. A. Foroulis, *Werkst. Korros.* **31**, 463 (1980).
52. A. Frignani, M. Tassinari and G. TrabANELLI, *Electrochim. Acta* **34**, 1259 (1989).
53. O. E. Barcia and O. R. Mattos, *Electrochim. Acta* **35**, 1003 (1990).
54. K. A. Christiansen, H. Høeg, K. Michelsen, G. Bech-Nielsen and H. Nord, *Acta Chem. Scand.* **15**, 300 (1961).
55. H. Nord, C. E. Foverskov and G. Bech-Nielsen, *Acta Chem. Scand.* **18**, 681 (1964).
56. H. Nord and G. Bech-Nielsen, *Electrochim. Acta* **16**, 849 (1971).
57. G. Bech-Nielsen, *Electrochim. Acta* **23**, 425 (1978).
58. J. A. Bardwell, B. MacDougall and M. J. Graham, *J. electrochem. Soc.* **135**, 413 (1988).
59. C. M. Rangel, I. T. Fonseca and R. A. Leitão, *Electrochim. Acta* **31**, 1659 (1986).
60. C. M. Rangel, R. A. Leitão and I. T. Fonseca, *Electrochim. Acta* **34**, 255 (1989).
61. E. B. Castro, J. R. Vilche and A. J. Arvia, *Corros. Sci.* **32**, 37 (1991).
62. M. E. Vela, J. R. Vilche and A. J. Arvia, *J. appl. Electrochem.* **16**, 490 (1986).
63. A. Hugot-Le Goff, J. Flis, N. Boucherit, S. Joiret and J. Wilinski, *J. electrochem. Soc.* **137**, 2684 (1990).

64. K. Takahashi, B. MacDougall and M. J. Graham, *J. electrochem. Soc.* **137**, 3023 (1990).
65. A. A. El Miligy, D. Geana and W. J. Lorenz, *Electrochim. Acta* **20**, 273 (1975).
66. A. Wieckowski, J. Sobkowski, P. Zelenay and K. Franaszczuk, *Electrochim. Acta* **26**, 1111 (1981).
67. D. S. Corrigan, E. K. Krauskopf, L. M. Rice, A. Wieckowski and M. J. Weaver, *J. phys. Chem.* **92**, 1596 (1988).
68. E. K. Krauskopf and A. Wieckowski, *J. electroanal. Chem.* **271**, 295 (1989).
69. G. Bech-Nielsen, *Electrochim. Acta* **21**, 627 (1976).