

Investigation of the Electrochemical Mechanisms for Acetic Acid Corrosion of Mild Steel

Thu Tran,^{†*} Bruce Brown,^{*} Srdjan Nešić,^{*} and Bernard Tribollet^{**}

ABSTRACT

Acetic acid (CH_3COOH) is recognized as an important factor in mild steel corrosion. Similar to carbonic acid (H_2CO_3) present in carbon dioxide (CO_2)-saturated aqueous environments, acetic acid is a weak acid, which partially dissociates with the equilibrium being a function of pH and the solution temperature. Stronger than carbonic acid (pK_a 4.76 vs. 6.35 at 25°C), acetic acid is the main source of hydrogen ions when the concentration of each acid is the same. Based on many different studies, it is agreed that acetic acid enhances the corrosion rate of mild steel by accelerating the rate of the cathodic (reduction) reaction. However, the electrochemical mechanism of acetic acid reduction at the metal surface is still being debated. One possibility is for the undissociated acetic acid to provide additional hydrogen ions by dissociation near the metal surface. In that case the main cathodic reduction is hydrogen ion reduction, and this mechanism is commonly referred to as a "buffering effect." If, in addition to this pathway for hydrogen evolution, there is a reduction of the adsorbed undissociated acetic acid at the metal surface, the mechanism is known as "direct reduction." In the present study, electrochemical techniques were used to investigate the effect of acetic acid on the cathodic reaction mechanism. It was found that the presence of acetic acid affects only the overall cathodic limiting current, but had no significant effect on the cathodic charge-transfer current. The latter was found to respond only to a change of

pH. It was therefore concluded that the buffering effect mechanism is correct.

KEY WORDS: acetic acid, cathodic reaction, mild steel corrosion

INTRODUCTION

The presence of organic acids found in produced water was reported as a severe concern in mild steel pipeline corrosion in the oil and gas industry.¹⁻⁴ In 1944, Menaul³ reported the presence of 250 ppm of organic acids in the Katy field near Katy, Texas. Since then, the detrimental effects of organic acids on mild steel corrosion were confirmed in the so-called bottom-of-the-line corrosion, as a result of produced water, as well as in top-of-the-line corrosion arising from water condensation. Typical aqueous concentrations of organic acids reported in the field are of the order of 100 ppm, while in some cases, up to 3,000 ppm of organic acids was reported.⁴ Among organic acids, acetic acid (CH_3COOH , or HAc) is known as the dominant, low-molecular weight organic acid found in produced fluids (usually about 50% to 90% of the total organic acids).⁵

In the past few decades, a number of studies⁴⁻¹¹ have been dedicated to investigating the effect of HAc on mild steel corrosion in aqueous environments. Similar to the carbonic acid (H_2CO_3) found in carbon dioxide (CO_2)-saturated aqueous solutions, HAc is a weak acid, which partially dissociates (Reaction [1]) to an extent that is governed by pH and the solution temperature.

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where K_a is the equilibrium constant, defined as:

$$K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} \quad (2)$$

Stronger than carbonic acid (pKa 4.76 vs. 6.35 at 25°C), HAc is the main source of hydrogen ions when the concentration of each acid is the same. According to most mechanistic studies,⁶⁻¹¹ HAc enhances the corrosion rate of mild steel by accelerating the rate of the cathodic hydrogen evolution reaction. However, the exact mechanism remains controversial. In a mechanism referred to as “buffering effect,” HAc dissociates and provides an additional source of free hydrogen ions near the steel surface, and the only cathodic reaction remains to be reduction of hydrogen ions. The alternative possibility is that the adsorbed undissociated HAc molecule is reduced at the surface (in addition to any reduction of free hydrogen ions); this mechanism is called “direct reduction.” These two mechanisms are reviewed in detail below.

Buffering Effect

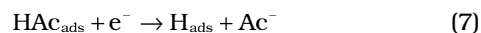
In this scenario, the role of HAc is to act as a “buffer” and provide more hydrogen ions when they are consumed by the corrosion reaction at the surface. This mechanism is termed the “buffering effect.” There, it is shown that HAc dissociates to give hydrogen ions and acetate ions (Reaction [3]); hydrogen ion diffuses from the bulk to the metal surface and adsorbs (Reaction [4]), where it is reduced to form a hydrogen atom (Reaction [5]), just like it happens with strong acids.



By conducting a series of potentiodynamic sweeps on a rotating cylinder electrode at pH 4, George and co-workers⁸⁻⁹ suggested the validity of the buffering effect mechanism. According to George’s study,⁸ only the cathodic limiting current is significantly accelerated in the presence of HAc, while the anodic reaction is slightly retarded. He argued that if HAc was directly reduced at the surface, the corrosion current density would increase proportionally with increasing HAc concentrations, which was not observed in his experimental data. Therefore, the author suggested that the role of HAc is to be a “reservoir” providing hydrogen ions as needed to feed the cathodic reaction. However, in a subsequent paper,¹⁰ the same authors proposed a different mechanism—“direct reduction” of HAc.

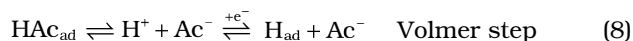
Direct Reduction

In the so-called “direct reduction” of HAc, the reactions ([3] through [5]) underlying the buffering effect mechanism are assumed to be still valid. In addition, according to this mechanism, HAc is also adsorbed on the metal surface (Reaction [6]) and reduced “directly” according to Reaction (7).



This mechanism was favored by other authors as well⁶⁻⁷ and used to explain a high corrosion rate of mild steel in the presence of HAc. Garsany, et al.,⁶ studied the role of acetate ion on the corrosion rate of carbon steel in a CO₂ environment using a rotating disk electrode. Their voltammograms showed two “waves,” apparently resulting from the reduction of free hydrogen ions and the direct reduction of HAc. However, the authors also pointed out that because of the fast dissociation of HAc, it is very difficult to experimentally distinguish between the direct reduction of HAc and that of hydrogen ions. Matos, et al.,⁷ used square wave voltammetry and observed two different peaks on a platinum microdisk working electrode, suggesting the reduction of both free hydrogen ions and HAc.

Amri, et al.,¹¹ proposed a mechanism that suggested that the dissociation of adsorbed HAc is followed by a Volmer-Heyrovsky step:



In any case, all these mechanisms are identical from a thermodynamic point of view: the beginning and end of the process are the same. The difference is in the pathway and, consequently, the kinetics.

It should be noted that the anodic reaction that occurs at the same time at the metal surface, to balance the charge, is the dissolution of iron:



Hypothesis and Objective

It remains important to distinguish these two principal mechanisms in HAc corrosion of mild steel, not least because the corrosion rate behavior and prediction depends strongly on the adopted pathway. If direct reduction of HAc occurs at the steel surface, the corrosion rate would steadily increase with the increasing HAc concentration (at the same pH), irrespective of the rate-controlling step (charge or mass-transfer control) (schematic in Figure 1). This is due to an increase of both the charge and mass-transfer

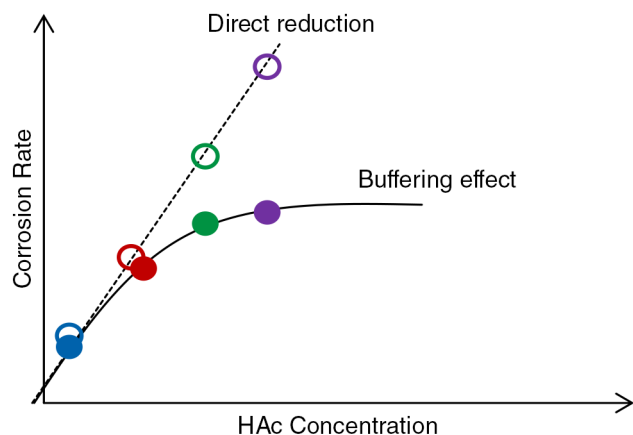


FIGURE 1. Illustration of corrosion rate change as a function of acetic acid concentration for direct reduction and buffering effect mechanism.

limiting currents with increasing HAc concentration (as shown schematically in Figure 2). However, if the only cathodic reaction that happens at the metal surface is the reduction of hydrogen ions, as proposed by the buffering effect, the corrosion rate will stop increasing beyond a certain HAc concentration (schematic in Figure 1). This happens when the cathodic reaction rate control shifts from mass transfer (which responds to HAc concentration) to charge transfer of hydrogen ions, which is insensitive to HAc concentration, as shown in the schematic in Figure 3.

The brief review of critical literature above shows that, so far, the answer to this dilemma is not clear. Therefore, the objective of the present work was to provide additional empirical evidence that could help determine whether the direct reduction of HAc occurs or not. Furthermore, a study leading to an improved understanding of HAc corrosion mechanisms will provide a good starting point for a similar analytical approach to be applied to study CO₂ corrosion mechanism, where experimentation is more difficult. There, it is similarly debated whether the weak carbonic acid acts as a reservoir of hydrogen ions¹²⁻¹⁴ (buffering effect) or can be reduced directly at the steel surface.¹⁵⁻¹⁸

EXPERIMENTAL PROCEDURES

Method

In the previous corrosion studies carried out by George,⁸ and others, it has been difficult to resolve this issue since the charge-transfer region for the hydrogen ion reduction overlaps with the region where the dominant reaction is anodic dissolution of iron (for example, George⁸ used X65 pipeline steel [UNS K03014]⁽¹⁾). This led to a choice of a different substrate

⁽¹⁾ UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

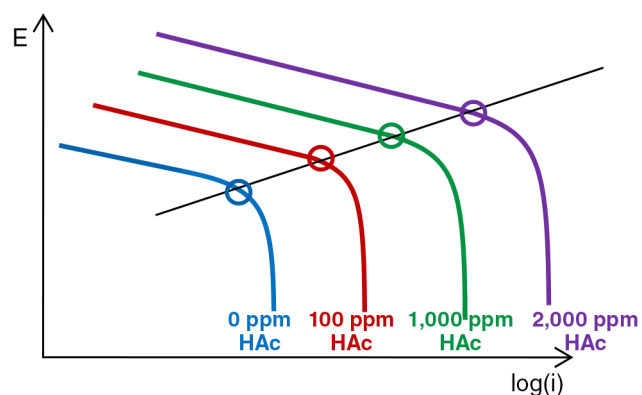


FIGURE 2. Illustration of cathodic behavior if direct reduction of acetic acid occurs at the surface, with points indicating the intersection between the anodic line and the cathodic line.

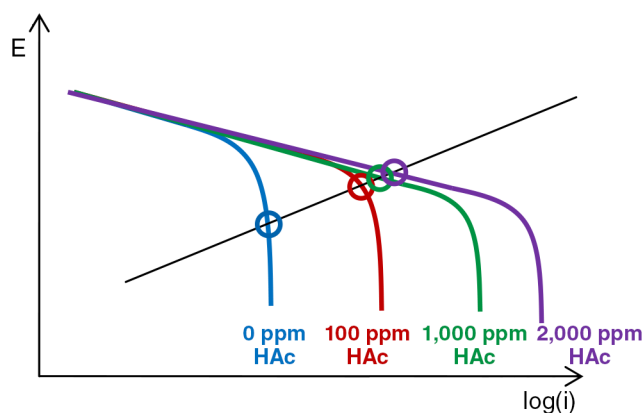


FIGURE 3. Illustration of cathodic behavior if buffering effect mechanism were correct, with points indicating the intersection between the anodic line and the cathodic line.

in the current work for the study of HAc reduction mechanisms. After trying out several noble metals (platinum and gold), the best and most consistent results were obtained by using a passive metal—a stainless steel (SS) Type 304 (UNS S30400) electrode. The charge-transfer current arising from reduction of hydrogen ions on SS304 could be examined without interference from the iron dissolution reaction. An additional benefit of using a passive stainless steel electrode rather than one made from a noble metal is that the former could be considered to be more alike to a mild steel surface, and the strong catalytic effects of hydrogen reduction seen on noble metals can be avoided. As Figure 4 shows, a reasonably good agreement was obtained between the cathodic reactions (where they did overlap) obtained on the two steels (SS304 and X65) under the same environmental conditions. Based on this result, it was assumed that the mechanism of the HAc cathodic reaction on mild steel can be revealed by examining the behavior of the same reaction on stainless steel at comparable conditions.

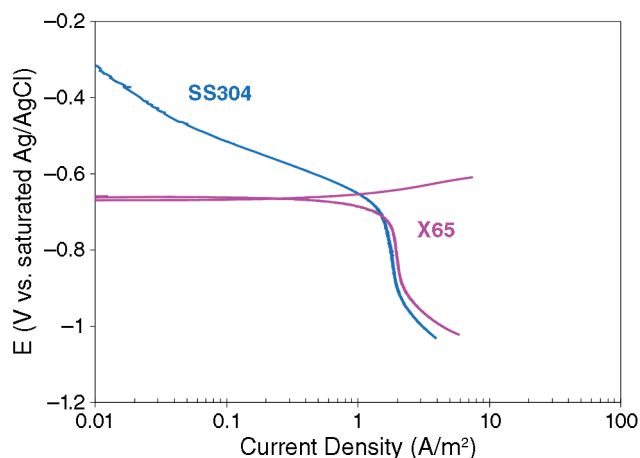


FIGURE 4. Comparison of cathodic sweeps obtained on SS304 stainless steel and X65 mild steel at 25°C, pH 4.0, aqueous solution saturated with N_2 with 3 wt% NaCl, 0 ppm HAC, RCE rotating speed 1,000 rpm.

Procedure

Both a rotating disk electrode (RDE) and a rotating cylinder electrode (RCE) were used in present work. The RDE operates under a well-defined laminar flow regime and is a common setup that is used to examine electrochemical reaction mechanisms.^{14,19}

The RCE typically operates under very turbulent flow conditions and is a standard tool that is used to investigate flow-sensitive corrosion.^{8-10,16} In both of these cases, well-defined mass-transfer correlations exist.^{16,19} In the present study, both the RDE and the RCE were used to establish the validity of the conclusions across a broad range of flow and mass-transfer conditions.

Experiments were conducted in a 150-mL glass cell for the RDE and a 2-L glass cell for the RCE, using a standard three-electrode setup.¹⁶ The glass cell was filled with 3 wt% NaCl aqueous electrolyte. Before each experiment, the solution was purged with nitrogen for at least 2 h to achieve electrolyte deoxygenation.

As a result of the dissociation, the added acid is present as either undissociated HAC or acetate ion Ac^- (Reaction [1]). Therefore, the total amount of acetic acid added to the glass cell, $[HAC_{tot}]$, can be calculated from the desired undissociated acetic acid concentration, $[HAC]$, using the equilibrium expression (Equation [2]), constant K_a , and the desired pH (hydrogen ion concentration $[H^+]$):

$$[HAC_{tot}] = [HAC] \left(1 + \frac{K_a}{[H^+]} \right) \quad (11)$$

where K_a is a function of temperature T_K (in Kelvin).²⁰

$$K_a = 10^{(-6.66104 - 0.001349 \times T_K + 2.37856 \times 10^{-5} \times T_K^2)} \quad (12)$$

In this work the HAC concentration mentioned refers to the undissociated HAC concentration, $[HAC]$, unless otherwise stated.

To achieve the desired pH at a given HAC concentration, the pH was adjusted by adding deoxygenated hydrochloric acid (HCl) or sodium hydroxide (NaOH). Before immersion into the test solution, the stainless steel electrodes were polished using 150, 400, and 600 grit silicon carbide (SiC) paper and then washed with isopropyl alcohol (C_3H_8O) and air dried.

The electrochemical tests started when the measured corrosion (open-circuit potential, OCP) potential stabilized within ± 5 mV over at least 2 min. The OCP was always found to be in the range between -250 mV and -450 mV with respect to the saturated silver/silver chloride (Ag/AgCl) electrode. The electrochemical impedance spectroscopy (EIS) measurements were conducted by applying an oscillating potential of ± 10 mV around the OCP using a frequency range from 10,000 Hz to 0.01 Hz to get the solution resistance. For the cathodic sweeps, the working electrode was polarized from the OCP in the negative direction using a scan rate of 0.2 mV/s. The cathodic sweeps are corrected by knowing the measured solution resistance from EIS.

RESULTS AND DISCUSSION

As hypothesized above, if the “buffering effect” mechanism is correct, the following processes occur:

- dissociation of HAC to form hydrogen ions and acetate ions (Reaction [3])
- transport of hydrogen ions (Reactions [4]) from the bulk to the metal surface
- reduction of hydrogen ions at the metal surface (Reaction [5])
- dissolution of iron to release ferrous ions (Reaction [10])

In this mechanism, the role of HAC is to be a reservoir of hydrogen ions. HAC provides hydrogen ions via dissociation as they are consumed at the metal surface. As a result, the ability of HAC to provide more hydrogen ions will increase with HAC concentration, leading to an increase of the limiting currents. The “buffering effect” mechanism does not account for the direct reduction of HAC at the metal surface. Consequently, there should be no effect of HAC on the charge-transfer current, which is a consequence of electrochemical reactions occurring at the metal surface.

On the other hand, if HAC is directly reduced at the steel surface, the charge-transfer current will increase with increasing HAC concentration. The limiting current will also increase when more HAC is present, as a result of its ability to dissociate and provide hydrogen ions.

Therefore, the key difference between the “buffering effect” and the “direct reduction” mechanism is

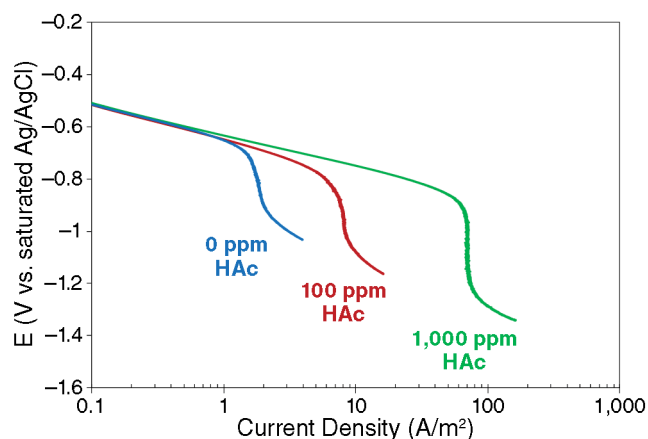


FIGURE 5. Comparison of potentiodynamic sweeps obtained using a SS304 for different undissociated acetic acid concentrations at 25°C, pH 4.0, aqueous solution saturated with N_2 , 3 wt% NaCl, RCE rotating speed 1,000 rpm.

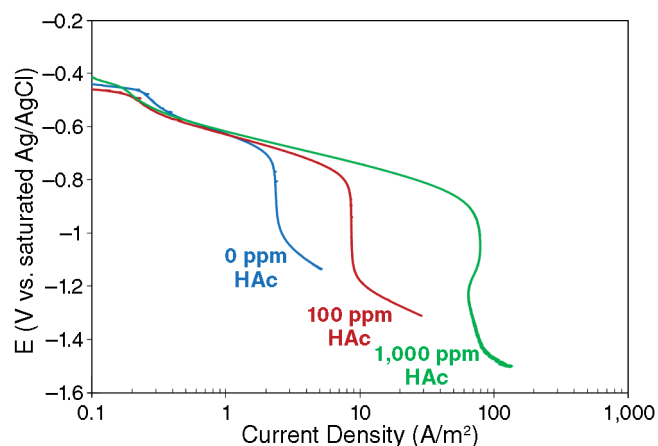


FIGURE 6. Comparison of potentiodynamic sweeps obtained using a SS304 for different undissociated acetic acid concentrations at 25°C, pH 4.0, aqueous solution saturated with N_2 , 3 wt% NaCl, RDE rotating speed 1,000 rpm.

based on how the charge-transfer current responds to a change of HAc concentration. Therefore, cathodic polarization was performed at a fixed pH (constant hydrogen ion concentration) at different HAc concentrations to determine if the presence of HAc affects the charge-transfer current. If the charge-transfer current responds to the change of HAc concentration, the direct reduction of HAc has to be considered (Figure 2). Conversely, if the charge-transfer current remains the same despite the change of HAc concentration, the “buffering effect” mechanism is correct (Figure 3).

Potentiodynamic Sweeps

Potentiodynamic sweeps were performed at a constant pH to investigate the effect of HAc concentration on the charge-transfer current. Figures 5 and 6 show the cathodic reaction rate on stainless steel at different concentrations of HAc at pH 4 by using a rotating cylinder electrode (RCE) and a rotating disk electrode (RDE), respectively. Indeed, at pH 4, an increase of HAc concentration only affects the limiting current, arising from mass transfer, but has no influence on the charge-transfer current (Figures 5 and 6). The same result was obtained in a laminar and turbulent flow regime (using the RDE and RCE, respectively).⁽²⁾ This indicates that, besides the reduction of hydrogen ions, there are no other significant cathodic reactions occurring at the metal surface. Similar results were observed at pH 3 (Figure 7), where, again, the HAc concentration has no effect on the charge-transfer current. In other words, under all these conditions, HAc acts primarily as a source of hydrogen ions, which only causes an increase in the

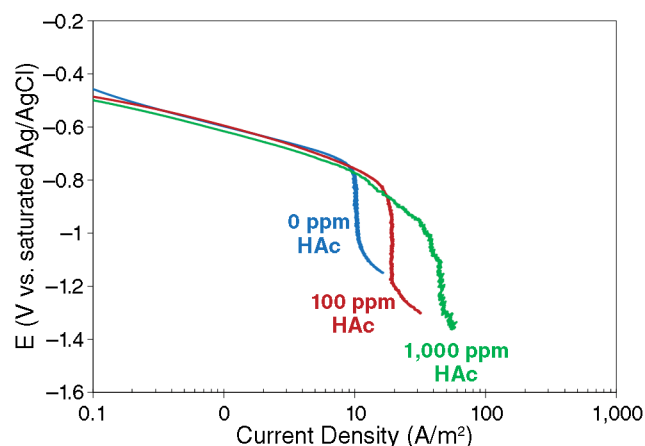


FIGURE 7. Comparison of potentiodynamic sweeps obtained using a SS304 for different undissociated acetic acid concentrations at 25°C, pH 3.0, aqueous solution saturated with N_2 , 3 wt% NaCl, RCE rotating speed 1,000 rpm.

mass-transfer-controlled limiting current for hydrogen evolution.

Since hydrogen ions appear to be the only cathodic reactants, the change of hydrogen ion concentration should affect the charge-transfer current. Indeed, Figures 8 and 9 show a change of charge-transfer current when pH changes. This was observed irrespective of whether HAc was present or not. In both cases, a higher charge-transfer current is expected when pH decreases (i.e., the hydrogen ion concentration increases). This result confirms that hydrogen ions are the main cathodic reactant in the systems studied in this work.

The charge-transfer current density can be calculated as a function of potential (Equation [13]):

$$i_{\alpha(H^+)} = i_{0(H^+)} \times 10^{\frac{\eta}{bc}} \quad (13)$$

⁽²⁾ The results on the RCE were conducted at Ohio University (Athens, Ohio) while the results on the RDE were obtained at the University of Pierre and Marie Curie (Paris, France) using slightly different experimental arrangements, which further reinforces the validity of the results.

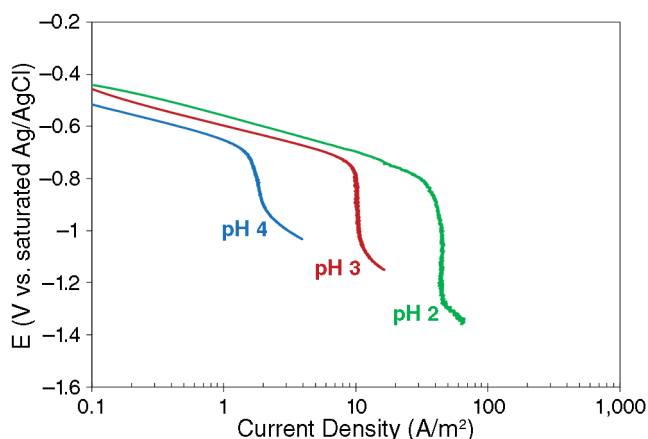


FIGURE 8. Comparison of potentiodynamic sweeps obtained using a SS304 for different pH at 25°C, aqueous solution saturated with N_2 , 0 ppm HAc with 3 wt% NaCl, RCE rotating speed 1,000 rpm.

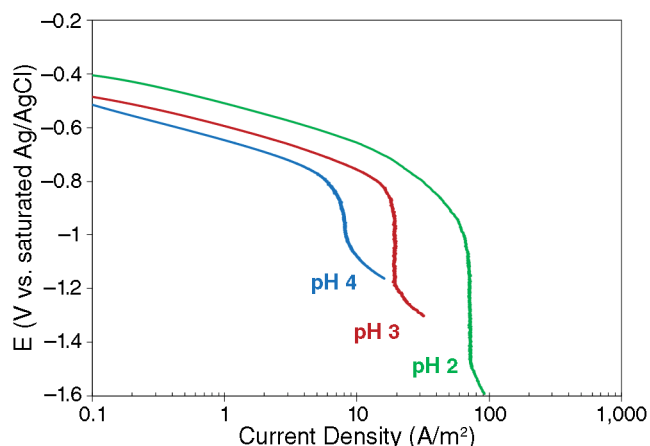


FIGURE 9. Comparison of potentiodynamic sweeps obtained using a SS304 for different pH at 25°C, aqueous solution saturated with N_2 , 100 ppm HAc with 3 wt% NaCl, RCE rotating speed 1,000 rpm.

TABLE 1

Comparison Between Calculated and Measured Limiting Currents at pH 4 Using Rotating Cylinder Electrode

HAc Concentration (ppm)	i_{lim} Calculated (A/m^2)	i_{lim} Measured (A/m^2)
0	1.5	$1.7 \pm 10\%$
100	8.5	$8 \pm 10\%$
1,000	70.4	$70 \pm 10\%$

TABLE 2

Comparison Between Calculated and Experimental Limiting Currents at pH 3 Using Rotating Cylinder Electrode

HAc Concentration (ppm)	i_{lim} Calculated (A/m^2)	i_{lim} Measured (A/m^2)
0	15	$11 \pm 10\%$
100	22	20
1,000	84	$50 \pm 10\%$

where η is the overpotential, b_c is the cathodic Tafel slope, and $i_{0(H^+)}$ is the exchange current density for hydrogen reduction.

According to Bockris and Reddy,²¹ $b_c = 0.118$ V at 25°C. The results from Figures 5 through 9 agree well with this value. Bockris and Reddy²¹ also predicted that the charge-transfer current density in Equation (13) depends on the pH:

$$\frac{\partial \log i_{\alpha(H^+)}}{\partial pH} = -0.5 \quad (14)$$

As shown in Figure 8, the measured charge-transfer current increased approximately with a factor of three when pH decreased one unit. This result

agreed well with Bockris's Equation (14) and agreed with Stern's finding.²²

While the charge-transfer current is only a function of pH, the limiting current changes accordingly to both pH and HAc concentration. The limiting current arising from the diffusion of hydrogen ions to the metal surface, $i_{lim(H^+)}^d$, can be written as:

$$i_{lim(H^+)}^d = k_m F [H^+]_b \quad (15)$$

where F is Faraday's constant, $[H^+]_b$ is the concentration of hydrogen ions in the bulk, and k_m is the mass-transfer coefficient, which for an RCE can be calculated from the Eisenberg, et al., correlation:²³

$$Sh = \frac{k_m d}{D_{H^+}} = 0.0791 \times Re^{0.7} \times Sc^{0.356} \quad (16)$$

where D_{H^+} is the diffusion coefficient for H^+ ions, and d is the specimen diameter.

In the case of a pure limiting mass-transport current on a RDE, the limiting current can be directly predicted by Equation (17) given by Levich:¹⁹

$$i_{lim(H^+)}^d = 0.62 F [H^+]_b D_{H^+}^{2/3} \nu^{-1/6} \Omega^{1/2} \quad (17)$$

where F is Faraday's constant, D_{H^+} is the H^+ diffusion coefficient, ν is the kinematic viscosity, and Ω is the angular rotation speed of the electrode. The limiting current value obtained on the RDE in the case of N_2 -saturated solution without acetic acid (Figure 6) agreed well with Equation (17).

The limiting current arising from diffusion of HAc to the metal surface, $i_{lim(HAc)}^d$, can be calculated in a similar fashion. If we assume that the two limiting currents are additive, Tables 1 and 2 show the comparison between the calculated and measured limiting

currents as a function of HAC concentration at pH 4 and pH 3 in the case of a RCE. The calculated limiting currents are in a reasonably good agreement with the measured limiting currents at pH 4, which are also consistent with George's work.⁸ The calculated limiting currents at pH 3 agree well with the measured limiting currents at low HAC concentration but slightly overpredict at high HAC concentration.

CONCLUSIONS

- ❖ The dominant cathodic reaction mechanism related to the reduction of acetic acid on steel is the so-called "buffering effect."
- ❖ The presence of acetic acid only affects the cathodic limiting current due to the ability of acetic acid to provide the hydrogen ions by dissociation, when the latter are consumed at the metal surface.
- ❖ Acetic acid has no influence on the charge-transfer cathodic current since no direct reduction of acetic acid can be detected. Hydrogen ions are the only cathodic reactants reduced at the metal surface. A change of pH leads to a change of the cathodic charge-transfer current, as expected.
- ❖ Experimental results are in agreement with theoretical calculations, which are based on the "buffering effect" mechanism.

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