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The Unified Mechanism of Corrosion in Aqueous Weak Acids Solutions: A Review of the Recent Developments in Mechanistic Understandings of Mild Steel Corrosion in the Presence of Carboxylic Acids, Carbon Dioxide, and Hydrogen Sulfide

Aria Kahyarian,^{‡,*} Bruce Brown,^{*} and Srdjan Nešić^{*}

The recent developments in mechanistic understandings of mild steel corrosion in the presence of carboxylic acids, carbon dioxide, and hydrogen sulfide, when placed side by side, reveal a simple, universal mechanism despite all the differences conventionally presumed for these corroding systems. These findings are recast into a generic mechanistic view of corrosion in aqueous weak acid solutions herein. In this mechanism, the buffering effect resulting from the chemical dissociation reaction inside the boundary layer, is highlighted as an inherent property of all weak acids. The validity of this mechanism was further examined through mathematical experimentation based on a comprehensive mechanistic model. It is shown that this mechanism is able to account for a wide range of characteristic behavior of cathodic currents, including those previously associated with the direct reduction reactions. The results are ultimately presented as a simple and generic categorization of weak acids based on their pK_a values to serve as a basis to assess the detrimental effect of any weak acid on mild steel corrosion in aqueous acidic solutions.

KEYWORDS: carbon dioxide, carboxylic acids, cathodic, hydrogen sulfide, mechanism, mild steel, polarization, weak acids

INTRODUCTION

In order to develop a broad view of corrosion in the presence of weak acids, a review of the more recent literature on the mechanism of corrosion in the presence of carboxylic acids, carbon dioxide, and hydrogen sulfide is necessary. In all cases, the historical developments show a similar trend. The higher corrosion rates of mild steel in the solution of different weak acids as compared to those seen in the strong acid solutions with the same pH (without exception) had previously been explained by presuming that the weak acid itself is directly involved in the underlying electrochemical reactions.¹⁻⁶ The argument was that the higher corrosion rates are caused by the higher cathodic currents from "direct reduction" of the weak acid as an additional electrochemical reaction.¹⁻⁶ Such arguments have been used and slightly modified over decades of research in the field. Nevertheless, recent developments in understanding of the mechanism of mild steel corrosion in the presence of carboxylic acids, carbon dioxide, and hydrogen sulfide have challenged the conventional views to mild steel corrosion in such anoxic environments.⁷⁻⁸ Recently, the experimental and theoretical investigations of the electrochemical behavior of these corrosive

environments suggest that the "buffering effect" arising from dissociation of weak acids at the vicinity of metal surface (the boundary layer) is the main cause for the observed high corrosivity.⁷⁻¹³ These findings suggest that neither carboxylic acids, carbon dioxide, nor hydrogen sulfide are inherently corrosive in their undissociated form, and they merely exacerbate an existing corrosion process driven by the hydrogen ion reduction. Considering these recent developments and the observed similarities among various corrosion scenarios, it is natural at this point to seek a simpler, more generic mechanism that could represent all of these individual cases. The purpose of this article is to present the *corrosion in aqueous weak acid solutions* as one general and unified topic, founded on the cumulative experience obtained in the last decade in this field of study.

In the following, recent developments in mechanistic understanding of corrosion in the presence of carboxylic acids, carbon dioxide, and hydrogen sulfide are reviewed briefly, and their differences and similarities are highlighted. Following the literature review, a generic mathematical model was developed to demonstrate the extent of the influence of homogeneous chemical reactions on the

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[‡] Corresponding author. E-mail: ak702711@ohio.edu

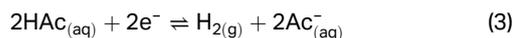
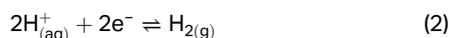
^{*} Institute for Corrosion and Multiphase Flow Technology, Department of Chemical and Biomolecular Engineering, Ohio University, Athens, Ohio, 45701.

observed electrochemical behavior of such corroding systems.

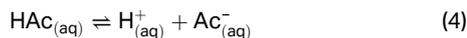
1.1 | The Case of Carboxylic Acids

The existing opinions on the mechanism of corrosion in the presence of carboxylic acids is reviewed briefly in the following paragraphs, while a more detailed review of the earlier literature can be found in a recent study dedicated to this subject.⁹ The effect of organic acids in aqueous corrosion of mild steel is usually discussed using acetic acid (referred to as HAc in the following) as the representative of this group. That is due to its prevalence in industrial applications and the expected similarities in the behavior of the short chain carboxylic acids.

The increased corrosion rates in the presence of acetic acid were conventionally justified by presuming that acetic acid is directly reduced at the metal surface.¹⁴⁻¹⁸ In that corrosion mechanism, the anodic iron dissolution (Reaction [1]) is accompanied by two parallel cathodic reactions, namely, hydrogen ion reduction (Reaction [2]) and the direct reduction of the undissociated acetic acid (Reaction [3]).



The undissociated acetic acid is present in the solution according to the partial dissociation equilibria as shown below:



In the recent years, evidence have been mounting that suggests acetic acid is not a significant electroactive species and its sole contribution to cathodic currents is through the homogeneous Reaction (4).^{9-10,19-20} In this mechanistic view, acetic acid acts merely as a hydrogen ion carrier in the solution and its presence only leads to an increase in the cathodic limiting currents. This mechanism points to the fact that at mass transfer limiting current, where the surface pH is increased, the chemical equilibrium of acetic acid (Reaction [4]) shifts toward dissociation, therefore, acetic acid acts as an additional source of hydrogen atoms inside the boundary layer.

This mechanistic view was initially highlighted in 2011 by Amri, et al.,¹⁹ in their study on the effect of acetic acid on the top of the line corrosion of X65 mild steel. However, the first systematic investigation of the subject was published in 2014 by Tran, et al.²⁰ The authors investigated the behavior of the cathodic polarization curves in mildly acidic environments. The polarization curves were obtained on Type 304 (UNS S30400⁽¹⁾) stainless steel due to the experimental difficulties in observing the cathodic currents on mild steel. Using this approach, the authors were able to show that the concentration of acetic acid does not affect the charge transfer controlled portion of the cathodic sweeps. That led the authors to conclude acetic acid was not directly involved in a charge transfer process on stainless steel surface.

⁽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.

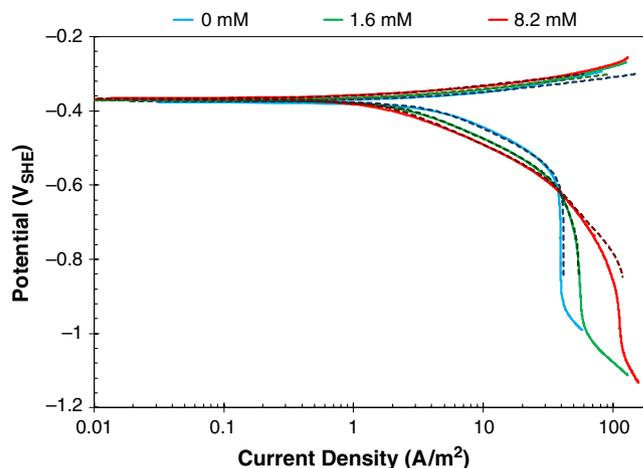


FIGURE 1. The comparison of the experimental (solid lines) and calculated (dashed lines) polarization curves based on the buffering effect mechanism for X65 mild steel in acidic solutions at pH 3, 30°C, 0.1 M NaCl, RDE, 2,000 rpm. The legend shows the concentration of undissociated acetic acid. Data are taken from Kahyarian, et al.⁹

In order to address the concerns arising from using a passive stainless steel surface in the mechanistic study of cathodic currents, Kahyarian, et al.,¹⁰ investigated the electrochemical activity of acetic acid on pure iron and X65 mild steel. Based on the experimental data obtained using rotating disk electrodes and potentiodynamic measurements, the authors showed acetic acid did not significantly contribute to the charge transfer controlled currents at concentrations up to 1,000 ppm. That study was later expanded by extending the environmental conditions and introducing a mechanistic mathematical model of corrosion, based on the recently developed “buffering effect” mechanism.⁹ The experimental data and mathematical simulations reported in that study⁹ were in support of the previous findings by Kahyarian, et al.,¹⁰ and Tran, et al.²⁰

Figure 1 demonstrates the typical polarization behavior of acetic-acid-containing solutions on mild steel surface and the agreement found with the results from the model based on the buffering effect mechanism with hydrogen ion reduction being the sole cathodic reaction. The behavior observed in this graph also highlights the inhibitive effect of acetic acid, where increasing the undissociated acetic acid concentration retarded the rate of electrochemical reactions, rather significantly. Considering the finding in the study by Kahyarian, et al.,⁹ the inconsistency in the previous reports on the effect of acetic acid concentration on the observed corrosion rates were explained by the counteracting effects of acetic acid on the electrochemical response of the system. Those are: the ability of acetic acid to increase the cathodic limiting current through chemical dissociation inside the boundary layer, and its inhibitive effect on charge transfer reactions by adsorption onto the metal surface. The effect of temperature was also investigated and shown to be of particular significance for corrosion in the presence of acetic acid, where a synergistic effect between the temperature and acetic acid concentration on corrosion rates were observed.⁹ The validity of buffering effect as the governing mechanism in the acetic acid corrosion of mild steel was further verified by comparing the predicted corrosion rates based on this mechanism with the experimental data. The results of such comparison in a rather wide range of environmental and chemical conditions can be seen in the parity graph in Figure 2, where a good agreement was observed.

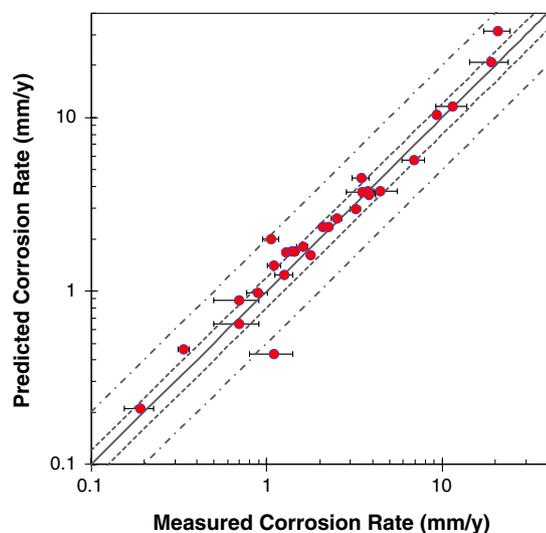
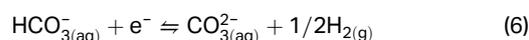
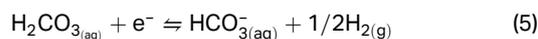


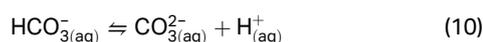
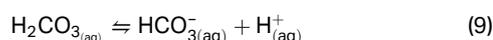
FIGURE 2. Comparison of the predicted corrosion rates based on the buffering effect mechanism with experimental results for acetic acid corrosion of mild steel obtained in a wide range of environmental conditions. $22^{\circ}\text{C} < T < 60^{\circ}\text{C}$, $2 < \text{pH} < 5$, $0 \text{ mM} < C_{t,\text{HAc}} < 16.6 \text{ mM}$, $125 \text{ rpm} < \text{rotation speed} < 2,000 \text{ rpm}$. Dashed lines and the dotted dashed lines represent 20% and one fold deviation, respectively. Error bars are based on the standard deviation of at least three repeats. Data are taken from Kahyarian, et al.⁹

1.2 | CO_2 Corrosion: The Case of Carbonic Acid

CO_2 corrosion of mild steel is perhaps the most common and widely studied corrosion scenario as far as it concerns the oil and gas industry. A detailed historical review of developments in the mechanistic understanding of this corrosion scenario can be found in earlier studies.^{1,8,21–22} Similar to the case of organic acids, the classic mechanistic view of CO_2 corrosion associates the higher corrosion rates observed in such systems with the additional carbonic acid and bicarbonate ion reduction reactions, depending on their bulk concentrations and the solution pH:



Additionally the significance of the homogeneous chemical reactions of the $\text{CO}_2/\text{H}_2\text{O}$ system (Reactions [7] through [10]), specifically the CO_2 hydration reaction, has been acknowledged since the 1970s.²³



The most recent developments have been focused on the significance of carbonic acid dissociation reaction (Reaction [9]) as compared to the electrochemical reduction of this species (Reaction [5]). In recent studies,^{2,24–26} it was shown

through comprehensive mechanistic mathematical models, that the limiting currents could be adequately explained even if carbonic acid was not considered an electroactive species, similar to that for the case of acetic acid. This can be understood when considering the local concentration of chemical species at the metal surface, where the homogeneous carbonic acid dissociation reaction (Reaction [9]) inside the boundary layer followed by electrochemical reduction of the produced hydrogen ions, provides a parallel reaction pathway to the direct carbonic acid reduction reaction. This observation carries a significant mechanistic implication as it undermines the previous commonly accepted mechanistic arguments, which were developed based on the analysis of cathodic polarization behavior at or close to limiting currents.^{23,27–28}

Similar to the case of acetic acid, an alternative mechanism highlighting the dissociation of carbonic acid inside the boundary layer has been put forward in a few studies. Linter and Burstein published one of the earliest articles suggesting that the direct carbonic acid reduction is not occurring to any significant extent in certain environmental conditions.²⁹ The authors developed their arguments based on the polarization curves obtained in N_2 -saturated and CO_2 -saturated solutions at pH 4.0 with additional potassium hydrogen phthalate buffer. Using this approach, the authors were able to observe the charge transfer controlled current densities for both N_2 -saturated and CO_2 -saturated solutions. The results showed no significant increase in this range of current densities when comparing the two cases, leading to the conclusion that carbonic acid is not electrochemically active. The findings of Linter and Burstein²⁹ did not gain much attention over the years, perhaps due to the concerns arising from the limited environmental conditions covered in their study—i.e., at pH 4.0 and 1 bar (100 kPa) pCO_2 the cathodic current is dominated by hydrogen ion reduction. In 2008, Remita, et al., studied the electrochemical activity of H_2CO_3 using a more quantitative approach.¹² The authors conducted a series of experiments in N_2 -saturated and CO_2 -saturated solutions at pH ~ 4 using a rotating disk electrode experimental apparatus. Their arguments were based on a comprehensive mathematical model, similar to those discussed elsewhere.^{2,24–26} Using the electrochemical kinetic parameters obtained for hydrogen ion reduction in N_2 -saturated solutions, authors were able to predict the polarization curves obtained in CO_2 -saturated solutions without considering carbonic acid as a significant species (absent in their model). Their observation led them to conclude that carbonic acid is not electrochemically active, and the sole effect was claimed to be the buffering effect of carbonic acid on the surface concentration of hydrogen ion. It is worthwhile to mention that the arguments used in this study suffer from the same shortcomings as those in the study by Linter and Burstein.²⁹ That is the very narrow range of experimental conditions and the fact that at those conditions (pH 4 and 1 bar CO_2), even in the classic mechanistic view with direct carbonic acid reduction, the contribution of this species to cathodic currents was believed to be very small as compared to that from hydrogen ions. Hence, their conclusions could not be assumed valid for the conditions with significantly higher carbonic acid concentrations (higher pCO_2).

It is important to realize that the clearly demonstrated buffering ability of carbonic acid (or any other weak acid) does not exclude the possibility of the direct reduction reaction, as these are two independent processes. That is the reason why the arguments developed to evaluate the significance of carbonic acid reduction must be based on the behavior of pure charge

transfer controlled currents so that the electrochemical activity of this species can be distinguished from the influence of the chemical equilibria (buffering effect).

In an attempt to address this shortcoming, the mechanism of CO₂ corrosion of mild steel was further investigated by Kahyarian, et al.⁸ In that study, the polarization curves in CO₂-saturated solutions were obtained in a thin channel flow cell (TCFC) that allowed a high flow velocity, elevated pCO₂, and reduced temperatures. Together, these conditions allowed the pure charge transfer controlled currents to be observed clearly. The investigation of polarization behavior on stainless steel, pure iron, and mild steel surfaces in that study did not show any indications of direct carbonic acid reduction at pCO₂ up to 5 bar (100 kPa). That led the authors to conclude that the buffering effect is the governing mechanism for the contribution of carbonic acid to cathodic currents. In subsequent studies,^{7,30} this mechanism was confirmed to remain valid in extended environmental conditions of pH range from 4 to 6 and CO₂ partial pressures up to 15 bar (1,500 kPa). Figure 3 shows the reported experimental polarization behavior of X65 mild steel at pH 4 and pH 5 and at various CO₂ partial pressures alongside the results obtained from a mechanistic model introduced by the authors.³⁰ The model was developed with hydrogen ion reduction as the sole cathodic reaction, while the effect of homogeneous chemical reactions, turbulent flow mixing, and non-ideal solution properties were accounted for mechanistically.³⁰ The agreement of the model with experimental cathodic polarization curves further supports the underlying mechanisms used in its development.³⁰

Furthermore, these studies showed a rather significant effect of pCO₂ on the rate of the anodic iron dissolution reaction, especially in the transition and prepassivation ranges.^{7,30-31} The anodic polarization curves exhibited a consistently increasing rate as the CO₂ partial pressure was increased, suggesting that CO₂ or its related carbonate species may be directly involved in the iron dissolution reaction.^{7,30-31} The authors concluded that the increased corrosion rates in CO₂-saturated solutions, as compared to solutions of strong acid with the same pH, were caused by the homogeneous chemical reactions of the CO₂/H₂O system that buffer the hydrogen ion concentration at the metal surface (both CO₂ hydration and carbonic acid dissociation reactions), as well as the increased rate of the anodic iron dissolution reaction.^{7-8,30-31}

1.3/CO₂ Corrosion: The Case of Bicarbonate Ion

The conventional mechanistic view of CO₂ corrosion assumes that bicarbonate ion is also electrochemically active (similar to carbonic acid) according to Reaction (6).^{1,3,22,28,32-33} This reaction was believed to be significant in the near-neutral and mildly alkaline pH range. However, the recent developments in mechanistic understanding of the role of carbonic acid raised questions about the significance of the direct bicarbonate ion reduction and the role of its corresponding dissociation reaction in cathodic currents. Such concerns have been addressed recently by Kahyarian.³⁰ The author showed that at pH 6 and elevated CO₂ partial pressures the limiting current was dominated by the contribution from the bicarbonate ion. The reported polarization curves, as shown in Figure 4, include two partially separated limiting currents.³⁰ The first limiting current is believed to be the result of hydrogen ion reduction reaction buffered by carbonic acid; the same governing mechanism as that seen in the limiting currents obtained at lower pH values (i.e., as seen in Figure 3).³⁰ The second limiting current observed at pH 6 was associated with the presence of a high concentration of the bicarbonate ion.³⁰

In mechanistic studies of corrosion in the presence of weak acids, it has been common to readily associate the observation of a second limiting current with the direct reduction of a weak acid. This was done previously for the case of aqueous hydrogen sulfide,^{5-6,34} even though that is now known not to be true as discussed in the following section.³⁵ For the case of bicarbonate ion, the authors³⁰ argued that with the high concentration of this species (about 0.1 M) at pH 6 and 15 bar CO₂, the limiting current resulting from bicarbonate ion direct reduction should be one to two orders of magnitude higher than what was observed experimentally.³⁰ Therefore, the significantly lower limiting currents observed in this case suggest that the appearance of this secondary wave is due to kinetically controlled chemical buffering of hydrogen ion by the bicarbonate ion dissociation, rather than an additional reduction reaction. The distinction of the two mechanisms, "buffering effect" and "direct reduction," is in this sense easier for the case of bicarbonate ion as compared to the case of carbonic acid. With the high pKa and the slow dissociation rate constant, at the limiting current condition the surface concentration of bicarbonate ion remains at an appreciable level. That leads to lower limiting currents as compared to the case if the species was completely consumed

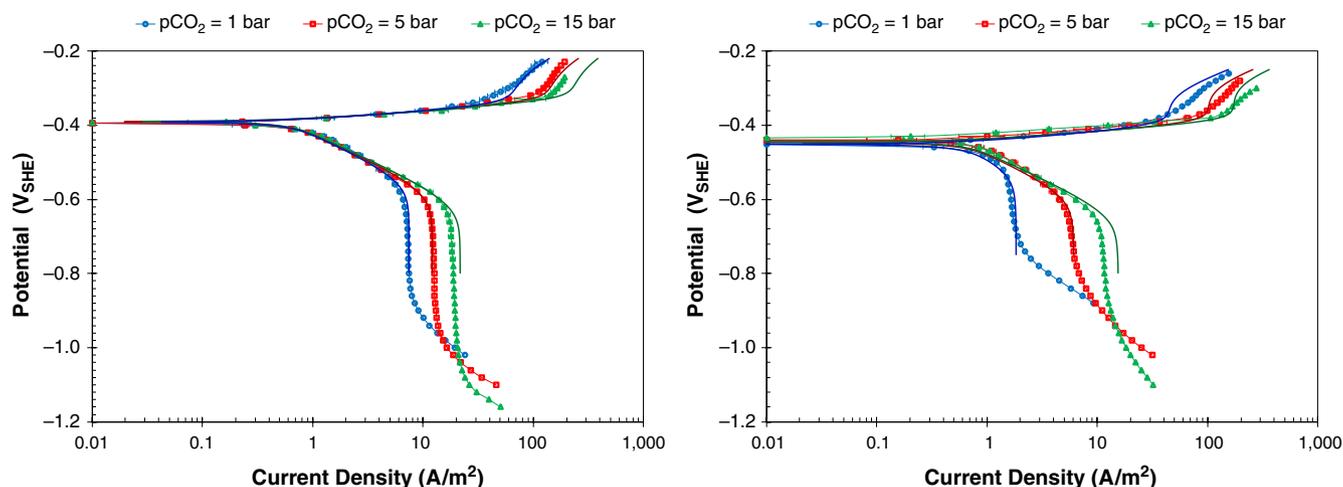


FIGURE 3. The comparison of the experimental polarization curves and the simulated data based on buffering effect mechanism for CO₂-containing system, obtained on API 5L X65 mild steel at 10°C, 0.1 M NaCl, 4.4 m/s flow velocity, at pCO₂ of 1, 5, and 15 bar. (a) pH 4, and (b) pH 5. The error bars show the standard deviation of at least three repeated experiments. The data are taken from Kahyarian.³⁰

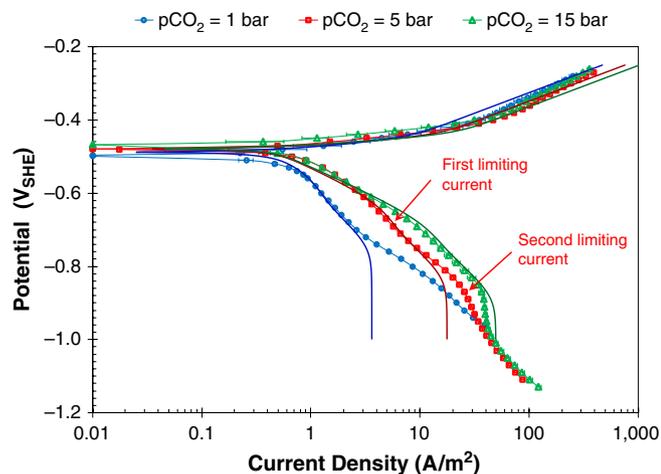


FIGURE 4. The comparison of the experimental polarization curves and the simulation data based on the buffering effect mechanism for CO_2 -containing system, obtained on API 5L X65 mild steel at 10°C , 0.1 M NaCl , 4.4 m/s flow velocity, at $p\text{CO}_2$ of 1, 5, and 15 bar, at pH 6. The error bars show the standard deviation of at least three repeated experiments. The data are taken from Kahyarian.³⁰

through an electrochemical reaction. The significance of bicarbonate ion dissociation reaction and its corresponding second limiting current was further validated through a mathematical simulation of polarization curves. As shown in Figure 4, the predicted cathodic polarization curves based on the model developed with hydrogen ion reduction as the sole cathodic reaction can readily predict the second limiting current resulting from buffering effect of bicarbonate ion with good accuracy, when the homogeneous chemical reactions are properly incorporated into the model.

The above-mentioned mechanism of CO_2 corrosion as it relates to the carbonic acid and bicarbonate ion contribution to cathodic currents was further evaluated by comparing the experimental and predicted corrosion rates.³⁰ The results as illustrated in the parity graph of Figure 5 showed

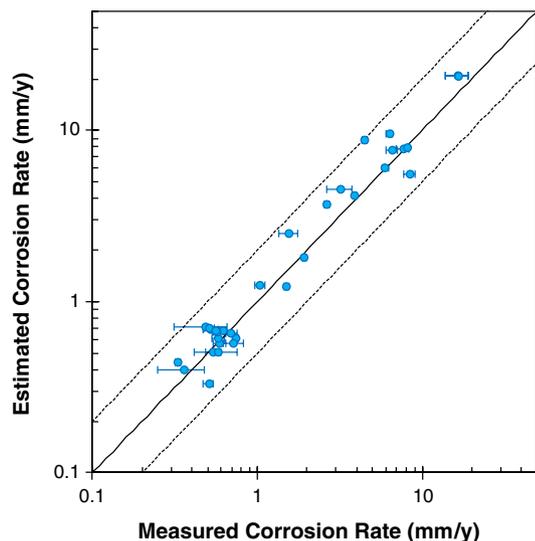
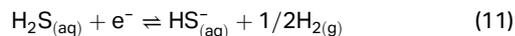


FIGURE 5. Parity graph of the corrosion rate data and the estimated values for CO_2 corrosion of mild steel based on the buffering effect mechanism at $0 < p\text{CO}_2 < 15\text{ bar}$, $4.0 < \text{pH} < 6.0$, $10^\circ\text{C} < T < 40^\circ\text{C}$, flow = 4.4 m/s and 12.9 m/s . The dashed lines represent a two-fold error limit. The data were taken from Kahyarian.³⁰

a reasonable agreement in a rather wide range of parameters, where almost all data points fell within a band denoting a factor of two-fold difference between calculated and experimental values.

1.4 | The Case of Hydrogen Sulfide

The arguments on the electrochemical contribution of hydrogen sulfide to cathodic current can be found in studies as early as 1965, reported by Bolmer.³⁶ Hydrogen sulfide was believed to be reduced directly as shown by Reaction (11).



The direct hydrogen sulfide reduction reaction was also considered to contribute to the observed polarization cathodic currents obtained in rotating disk experiments by Morris.³⁷ The proposed electrochemical activity of hydrogen sulfide became an accepted mechanism of corrosion in such systems as seen in several subsequent studies.³⁸⁻⁴² Nevertheless, a systematic investigation of this mechanistic aspect was not done until more recent years. In 2013, Kittel, et al., investigated the cathodic polarization curves of a hydrogen sulfide containing solution on stainless steel surface.⁶ The previous reports on the significant effect of hydrogen sulfide on the limiting current were believed to remain valid in that study. Furthermore, the authors showed that in certain conditions a “double wave” shape appears in polarization curves, an observation that was considered as proof for the direct hydrogen sulfide reduction reaction. The observation of the double wave was associated with the existence of two electrochemical reactions and their corresponding limiting currents, one being the hydrogen ion reduction and other being the hydrogen sulfide reduction reaction. In a parallel study,⁵ Zheng, et al.,⁴³ investigated the mechanism of mild steel corrosion in the presence of hydrogen sulfide in a wider range of experimental conditions. The effect of hydrogen sulfide on the limiting current and the existence of two limiting currents (i.e., the double wave) were also reported in that study. The authors noted that both limiting currents, associated with the hydrogen ion and hydrogen sulfide reduction reactions, were the result of mass transfer limitation of the involved reactants. These observations led the authors to conclude that in hydrogen sulfide containing solutions, the direct reduction of hydrogen sulfide is a significant cathodic process. In 2017, Esmaeely, et al., reported a set of experimental polarization data at pH_2S of 1 bar on a mild steel surface.⁴⁴ The reported polarization curves were found to behave similarly to those obtained at lower pH_2S in earlier studies.⁵⁻⁶

Until recently, there seemed to be a consensus in the literature that hydrogen sulfide, unlike acetic acid and carbonic acid, is directly reduced on the metal surface, thus increasing the corrosion rate by increasing the rate of cathodic reactions. These arguments are mostly based on the distinctive behavior of cathodic polarization curves in hydrogen sulfide containing solutions, as compared to the behavior observed in the solutions of strong acids or those in the presence of other weak acids such as carboxylic acids and carbonic acid. One of the main indicators of direct reduction of hydrogen sulfide is believed to be the observation of a double wave in cathodic polarization curves, which is commonly taken as proof of two parallel cathodic reactions, hydrogen ion reduction and hydrogen sulfide reduction.⁵⁻⁶

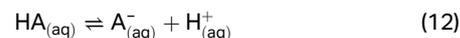
THE UNIFIED MECHANISM OF CORROSION IN AQUEOUS SOLUTIONS OF WEAK ACIDS

The brief review of the recent literature as presented above reveals a simple repetitive mechanistic pattern of the uniform corrosion in aqueous solutions containing carboxylic acids, carbonic acid, bicarbonate ion, and hydrogen sulfide. That includes the two fundamental electrochemical reactions driving the corrosion process, metal dissolution and hydrogen ion reduction, coupled with homogeneous chemical reactions inside the boundary layer. The conventional complex set of cathodic reactions associated with such species is shown to be merely the result of misinterpretation of the experimental data that have been repeated in the literature for decades.

Building on this cumulative knowledge, in this study all such systems are grouped under a one generic corrosion scenario: *corrosion in aqueous weak acid solutions*. In that sense, all of these systems are merely different branches with one unified fundamental underlying mechanism. The characteristic feature of this group is the interaction of the homogeneous dissociation reactions inside the boundary layer with the hydrogen ion reduction reaction. In this section the various expected polarization behavior from this mechanistic view is studied to show how the apparently different behaviors observed, for example, in the case of acetic acid can be explained with the same mechanism as that governing the hydrogen sulfide corrosion. For this purpose, the cathodic polarization behavior of an acidic solution containing a generic weak acid was theoretically studied using a mechanistic mathematical model.

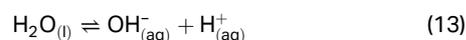
2.1 | Mathematical Model

The mathematical model developed in the present discussion is similar to those described in more detail in previous studies.^{1,9,21} The model is developed for a generic weak acid "HA," where H⁺ is hydrogen ion and "A⁻" is the corresponding conjugate base, e.g., acetate, bicarbonate, carbonate, bisulfide, sulfide, etc., with an equilibrium constant of "K_{HA}," and the association rate constant of "K_{b,HA}." As with any weak acid, the dissociation equilibrium is presumed to occur according to:



The present model was used to examine the effect of chemical dissociation reaction of a given weak acid on the cathodic polarization behavior of the system. Therefore, the weak acid is not considered to be electrochemically active, i.e., it is not directly reduced. The water reduction reaction, only significant in lower potentials, has no major contribution to the corrosion current at typical pH values and environmental conditions of interest in this discussion, hence, it is not included in the model. Furthermore, in order to keep the focus on the behavior of cathodic currents and allow for better observation of the electrochemical response of the system, the iron dissolution reaction was not included in the present model. Therefore, the electrochemical response of the model as described below is the result of a single electrochemical reaction: H⁺ reduction.

Speciation in the bulk solution can be obtained by simple equilibrium calculation based on the dissociation Reaction (12) and that of water as shown via Reaction (13).



However, considering the recent developments in mechanistic understanding of corrosion in the presence of carboxylic acids and carbon dioxide, one may consider that a similar process would be governing the case of hydrogen sulfide as well. While hydrogen sulfide is physicochemically different from carbonic acid and carboxylic acids, the buffering effect is common for all of these species as weak acids. Of course, there are differences to be expected, where carbonic acid and carboxylic acids are weak acids with relatively low pK_a values and very fast dissociation rate constants, while hydrogen sulfide with pK_a of 7 is relatively "weaker" and has a slower dissociation rate constant. As briefly reviewed above, the recent studies have shown that carbonic acid and carboxylic acids are "strong" buffers, that means they readily dissociate as the surface pH is increased as compared to that in bulk solution.^{8-10,45} On the other hand, the double wave behavior observed for the case of bicarbonate ion suggests that the observation of a secondary limiting current is not conclusive evidence for the direct reduction of the weak acid.³⁰ Hence, one may suggest that at the favorable environmental conditions, hydrogen sulfide would also exhibit the same buffering ability, at least to some extent. This argument was recently examined by Kahyarian and Nešić¹¹ in terms of theoretical investigation of the cathodic polarization curves, using a comprehensive mathematical model similar to those introduced earlier.^{1,9,21} Once again, the hydrogen sulfide corrosion model was developed with hydrogen ion reduction as the sole cathodic reaction, while the homogeneous chemical reactions of the H₂S/H₂O system were included in calculations. The results from the model were compared to those obtained experimentally (Figure 6). The model predictions in that study, shown as the dotted lines in Figure 6, do not take into account the reduction of water which is only significant at more negative potentials. The good agreement of the model with experimental data, especially the prediction of the double wave behavior without considering hydrogen sulfide as an electroactive species, was found to support the underlying buffering effect mechanism. The authors therefore concluded that the buffering effect of hydrogen sulfide is significant in all considered conditions and at the same time the direct reduction of hydrogen sulfide is insignificant, just the same as carbonic acid and carboxylic acids.³⁰

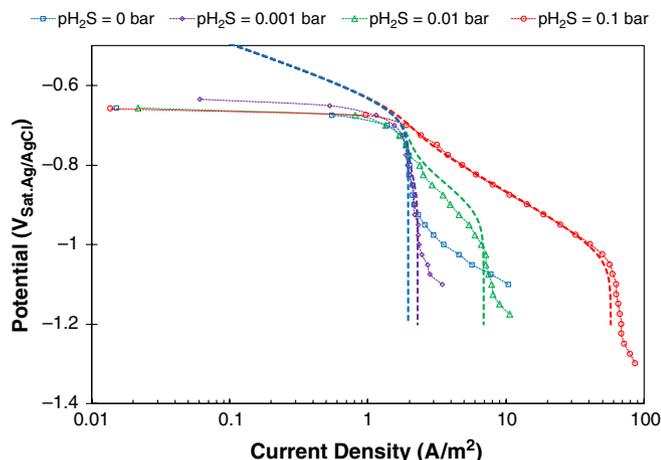


FIGURE 6. Predicted (dashed lines) cathodic polarization curves based on buffering effect mechanism and experimentally obtained curves (points) on X65 mild steel at pH 4, 30°C, 1,000 rpm RCE, at various H₂S partial pressures. The data are taken from Kahyarian and Nešić.¹¹

The corresponding mathematical relationships can be expressed as following, where C_i represents the concentration of species i (M), and K_j is the equilibrium constant of chemical equilibrium j :

$$\frac{C_{A^-}_{(aq)} \cdot C_{H^+}_{(aq)}}{C_{HA(aq)}} = K_{HA} \quad (14)$$

$$C_{OH^-}_{(aq)} \cdot C_{H^+}_{(aq)} = K_w \quad (15)$$

In addition to the equilibrium relationships, the solution speciation has to satisfy the electroneutrality constraint, shown as Equation (16), where z_i is the charge of species i . At a known solution pH and HA concentration, the solution speciation can be readily obtained based on Equations (14) through (16).

$$\sum_i z_i C_i = 0 \quad (16)$$

The concentration distribution of the involved chemical species can be expressed based on the mass-conservation law, known as the Nernst-Planck Equation:

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot N_i + R_i \quad (17)$$

Equation (17) describes the concentration distribution of species i , where t (s) is time, N_i ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$) is the flux, and R_i ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-3}$) is the source term that includes the consumption/production of species i through homogeneous chemical reactions. The flux of any given species can be described through Equation (18),⁴⁶ where the terms on the right-hand side describe the effect of electromigration, molecular diffusion, and convective flow, respectively.

$$N_i = -z_i u_i F C_i \nabla \phi - D_i \nabla C_i + v C_i \quad (18)$$

In Equation (18), u_i ($\text{mol}\cdot\text{m}^2\cdot\text{s}^{-1}\cdot\text{V}^{-1}\cdot\text{C}^{-1}$) is the mobility of the ionic species, ϕ (V) is the electric potential inside the solution, v ($\text{m}\cdot\text{s}^{-1}$) is the convective velocity, and other parameters have their common electrochemical meaning. For electrochemically one-dimensional systems, such as those observed in pipelines and laboratory rotating electrode systems, Equations (17) and (18) can be simplified to Equations (19) and (20). Furthermore, the mobility of ions can be estimated using the Nernst-Einstein relationship, $u_i = D_i/RT$, with R ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) being the universal gas constant and T (K) being the absolute temperature, assuming a dilute solution.

$$N_i = -D_i \frac{\partial C_i}{\partial x} - \frac{z_i D_i F C_i}{RT} \frac{\partial \phi}{\partial x} + v_x C_i \quad (19)$$

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial}{\partial x} \frac{\partial C_i}{\partial x} + \frac{\partial}{\partial x} \left(\frac{z_i D_i F C_i}{RT} \frac{\partial \phi}{\partial x} \right) - v_x \frac{\partial C_i}{\partial x} + R_i \quad (20)$$

In the convective term, v_x describes the velocity profile inside the diffusion layer. For example, in the case of a rotating disk electrode (RDE), the analytical solutions for the velocity profile (v_x) are shown as Equation (21), where $a = 0.510$, ω is the angular velocity (rad/s), ν (m^2/s) is the kinematic viscosity, and x (m) is the distance from the electrode surface. The diffusion layer thickness (δ) can be obtain via Equation (22).⁴⁷

$$v_x = -a\omega \left(\frac{\omega}{\nu} \right)^{1/2} x^2 \quad (21)$$

$$\delta = \left(\frac{3D_i}{a\omega} \right)^{1/3} \left(\frac{\omega}{\nu} \right)^{-1/2} \quad (22)$$

As mentioned above, the rate of consumption/production of the chemical species via homogeneous chemical reactions is incorporated in these calculations through the R_i term in Equation (20). The rate of chemical reaction j , presented in the form of Reaction (23) is expressed as Equation (24).



$$R_j = k_{fj} \prod_{r=1}^{n_r} C_r - k_{bj} \prod_{p=1}^{n_p} C_p \quad (24)$$

where k_{fj} and k_{bj} are the reaction rate constants of the forward and backward reactions. For each chemical species, R_i is the sum of the rates corresponding to all j chemical reactions (with rate of R_j) involving this species as shown in Equation (25), with s_{ij} being the stoichiometric coefficient of species i in reaction j .

$$R_i = \sum_j R_j s_{ij} \quad (25)$$

In Equation (25), the rate of reaction where species i is produced is expressed as a positive value, and when it is consumed as a negative value. In addition to concentrations of species, the electric potential inside the solution has to be specified in order to calculate the effect of electromigration, as seen in Equation (20). This parameter can be obtained by introducing an additional relationship based on the "electroneutrality" constraint as expressed via Equation (16), as discussed in details elsewhere.^{1,21}

The concentration distribution of the chemical species, including those at the metal surface (required for calculating the rate of electrochemical reactions) can be obtained based on the Nernst-Planck equation if initial and boundary conditions are properly defined. At the initial time ($t = 0$), it can be assumed that the bulk solution comes into contact with the metal surface. Hence, the concentrations of the chemical species are constant known values over the whole spatial axis ($x \geq 0$), defined by the chemical equilibria of the solution. Furthermore, at the bulk solution boundary, where $x = \delta$, the concentration of chemical species remain unchanged at all times ($t \geq 0$).

The boundary condition at the metal/solution interface is defined by the flux of the chemical species based on electrochemical reactions. As mentioned above, the only electrochemical reaction considered in this model is H^+ reduction. Therefore, the flux of hydrogen ion at the metal surface can be defined as following, where i_{H^+} is the cathodic current density of hydrogen ion reduction.^{21,46}

$$N_{H^+}|_{x=0} = \frac{i_{H^+}}{F} \quad (26)$$

Due to the negligible concentration of H_2 in the solution, no significant contribution of the hydrogen oxidation reaction over the potential range of interest is expected. Hence, the

cathodic current density resulting from hydrogen ion reduction was calculated in the form shown in Equation (27). The kinetic parameters, including the transfer coefficient $\alpha_{H^+} = 0.5$, the reaction rate constant $k_{0H^+} = 1.2 \times 10^{-8}$, and the reaction order $m_{H^+} = 0.5$ used in this model are based on the values obtained experimentally at similar conditions and pH range in a recent study by Kahyarian, et al.⁴⁸

$$i_{c,H^+} = -n_{H^+} F k_{0H^+} C_{H^+}^S m_{H^+} e^{\left(\frac{-\alpha_{H^+} n_{H^+} F (E_{app} - E_{0H^+})}{RT}\right)} \quad (27)$$

For other, non-electroactive species, the flux at the metal surface is zero:

$$N_i|_{x=0} = 0 \quad (28)$$

The flux Equations (27) and (28) can be used to describe the boundary conditions for all chemical species at the metal surface. Considering that N_i appears in these relationships, the solution potential should also be specified at the solution/metal boundary. This can be done similarly to that in the governing equations, using the electroneutrality constraint.

The resulting governing equations and boundary conditions described above form a set of nonlinear, coupled partial differential equations. These equations can be solved numerically as detailed in earlier publications^{1,7,21,35} to obtain the concentration of the chemical species and electric potential inside the boundary layer, as well as the current potential response of the system.

RESULTS AND DISCUSSION

The intent of the present discussion is to explore and illustrate the effect that weak acids have on cathodic currents, in the broad scope of the corrosion in aqueous weak acid solutions. The dissociation equilibrium by definition is an inherent property of all weak acids. Naturally, in an environment where the solution pH is altered by an external stimulus, the equilibrium shifts in response. In corroding systems of this discussion, the hydrogen ion reduction is the external force that drives the pH inside the boundary layer higher than the bulk solution under mass transfer limited conditions, leading to the shift of chemical equilibrium toward dissociation—"buffering" the surface concentration of the hydrogen ion. Nonetheless, the extent of this buffering effect, and hence the behavior of cathodic currents, is strongly dependent on the nature of the weak acid, represented by its pKa and dissociation kinetics, the environmental conditions, and the bulk pH. This effect is studied systematically by mathematical experimentation using the mechanistic model developed in the previous section.

The significance of the bulk pH and the pKa of the weak acid on the extent of its buffering ability is readily seen in Figure 7. The effect of weak acid presence in the solution at pH 3 is shown in Figure 7(a). The cathodic current for the case of weak acid with pKa of 1 shows an increased limiting current resulting from its buffering ability, while the cathodic current prior to the limiting current do not show any deviations as compared to that expected from hydrogen ion reduction. The weak acids with pKa up to 5 still demonstrate a strong buffering ability as seen from the increased limiting currents. However, in this case the cathodic currents prior to the limiting current show a gradual shift toward higher apparent Tafel slopes. It should be noted that this range of cathodic currents with increased apparent Tafel slope do not represent a charge transfer controlled range, as the

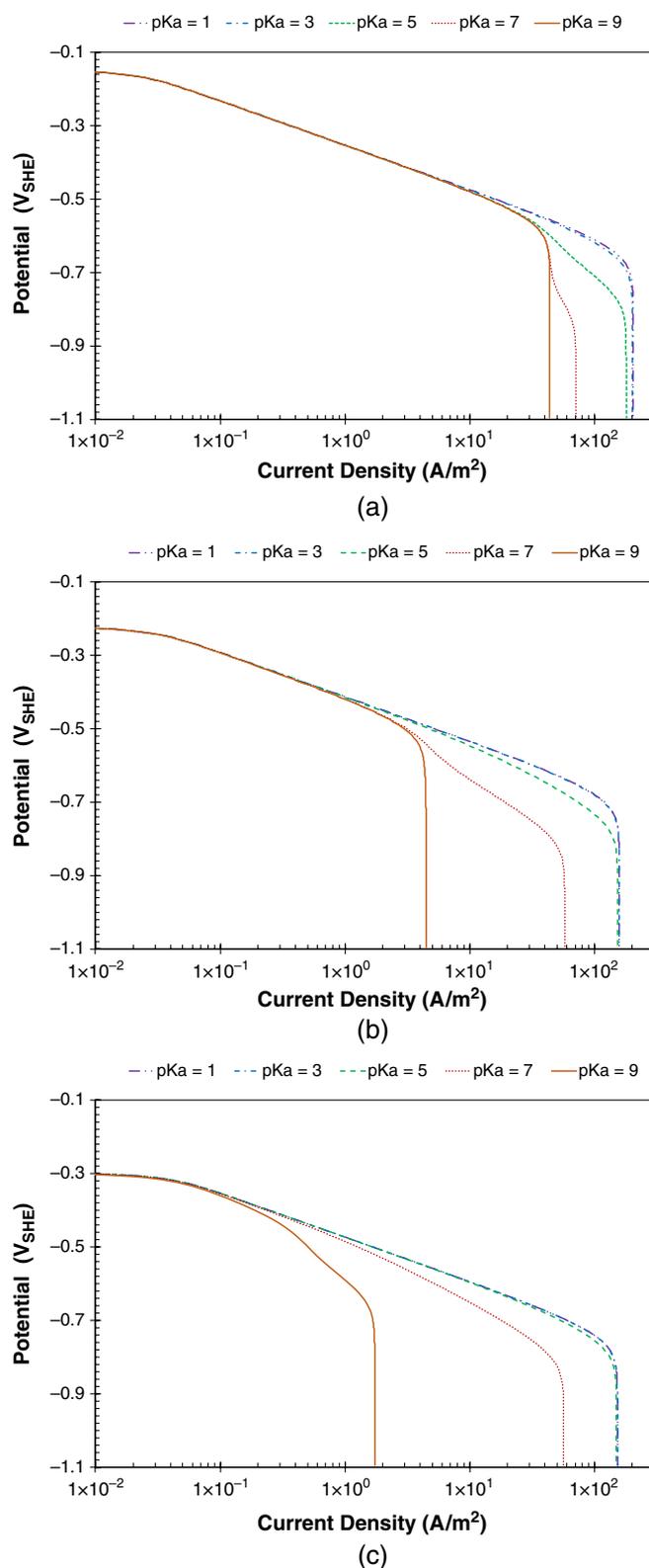


FIGURE 7. Calculated cathodic polarization curves at 30°C, 2,000 rpm RDE, for a hypothetical weak acid with pKa ranging from 1 to 9 and $k_{b,HA} = 10^{10}$. (a) At pH 3, (b) at pH 4, and (c) at pH 5.

surface concentration of the hydrogen ion is under a mixed control of both the charge transfer and the homogeneous dissociation reactions. Moving toward higher pKa values,

the weak acid with pKa of 7 shows a distinct double wave behavior with lower buffering ability as seen from the decreased magnitude of the limiting current. At the end of this spectrum, weak acids with pKa of 9 are behaving as an inert species, where the cathodic current is only due to the hydrogen ion reduction and the limiting current is that of hydrogen ion mass transfer. At pH 4, as shown in Figure 7(b), a similar trend is observed, but with a shift in the corresponding pKa values. Here, the weak acids with pKa as high as 3 readily dissociate, leading to an increased limiting current. The double wave for weak acids with pKa of 7 is no longer observed clearly as compared to that at pH 3, giving its place to an extended range of currents with an increased apparent Tafel slope. The weak acids with pKa of 9 remain inactive at this condition. This trend is continued at pH 5 as illustrated in Figure 7(c), but with a major difference in the behavior of the weak acids with higher pKa. At such conditions the weak acids with pKa as high as 9 do have the favorable conditions to exhibit some buffering ability, as seen from the appearance of a characteristic double wave shape in the cathodic current and the increase in the limiting current in this condition.

The results presented above illustrate how weak acids, depending on their pKa and the solution pH, can influence the characteristic behavior seen in polarization curves. Any weak acid can alter the electrochemical response of the system, if and only if the conditions favor its dissociation reaction. The buffering effect in some cases appears merely as an increase in the limiting current, in some cases appears in the form of a shift in the Tafel slope and ultimately can lead to appearance a double wave, and in certain conditions has no notable influence.

The dynamics of this process is better demonstrated in Figure 8 for a weak acid with pKa of 7 at bulk pH of 3, where the cathodic current is shown on the secondary axis, versus the calculated surface pH on the horizontal axis. The surface concentration of the weak acid and its conjugate base are shown in the same graph on the primary vertical axis. As it appears in Figure 8, at low current densities, under charge transfer control, the surface pH and the concentration of the weak acid and its anion remain unchanged. As the mass

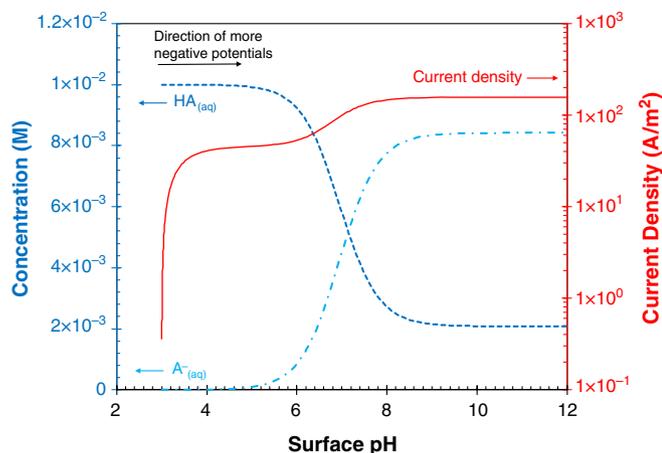


FIGURE 8. The relationship between the calculated surface pH and the surface concentration of HA and A^- , on the primary vertical axis, and the calculated current density, on the secondary vertical axis with buffering effect as the governing mechanism. Conditions: $pK_a = 7$, $k_b, HA = 10^{10}$, $25^\circ C$, 2,000 rpm RDE, pH 3, 0.01 M HA, and the potential range from $-0.2 V_{SHE}$ to $-1.2 V_{SHE}$.

transfer limitation of the hydrogen ion is reached, the surface pH increases, which gradually favors the dissociation of HA. The second wave is therefore associated with the buffering effect of the weak acid and its corresponding limiting current is defined either by the mass transfer limitation of this species or its dissociation kinetics.

If this discussion were condensed to be presented as a high level guideline, it would appear from Figure 8 that the peak of the dissociation reaction (the buffering effect) happens when the surface pH is equal to the pKa of the weak acid (i.e., a condition when the concentration of the weak acid and its anion are equal). On the other hand, when the H^+ mass transfer limited current density is reached, the surface pH is about one or two units higher than that of the bulk solution. With this in mind and considering that the pH of the brine in oil and gas transmission pipelines typically ranges from 4 to 7, weak acids with a pKa of up to ~ 5 are able to readily dissociate when the H^+ limiting current is reached. This would result in increased limiting currents and increased corrosion rates commonly seen in such conditions. The weak acids with higher pKa values require the corrosion current to be "deeper" in the limiting current region, so that the surface pH is much higher than in the bulk solution, in order to show their buffering ability. At the very end of the spectrum are the weak acids with such a high pKa that they never find themselves in the favorable condition to exhibit any significant buffering ability in practical conditions. Therefore, considering the typical conditions related to corrosion in oil and gas industry, one can categorize weak acids into three groups:

1. **Strongly buffering weak acids:** weak acids with pKa below 5, which readily dissociate when the mass transfer limiting current of H^+ is reached. The cathodic current in the presence of these weak acids behaves, for the most part, similar to those of a strong acid but with an increased limiting current. Carbonic acid and most short chain carboxylic acids fall within this group.
2. **Moderately buffering weak acids:** weak acids with pKa between 5 and 11, which are still able to exhibit a significant buffering ability. Nevertheless, depending on the environmental condition and the solution pH, the extent of this buffering effect may vary. The cathodic polarization behavior in the presence of such weak acids, including the apparent Tafel slope, could deviate notably from that observed in strong acid solutions. The observation of a double wave in certain conditions can be considered a characteristic behavior of this group, such as the case of hydrogen sulfide. Bicarbonate ion and the second dissociation of sulfurous acid and phosphoric acid can also be placed in this group.⁴⁹
3. **Nonbuffering weak acids:** weak acids with pKa values above 11 generally do not encounter favorable conditions for their dissociation to occur to any significant extent, at least when it comes to the typical conditions considered here. This is even more true when considering that the water reduction reaction overwhelms any possible effect that such species may have on the surface concentration of H^+ . Bisulfide ion and water can be considered as examples of such species.

3.1 | Effect of Dissociation Kinetics

The above categorization based on pKa values is a thermodynamic measure to gauge the expected buffering ability for a given weak acid. The kinetics of the dissociation reaction is also an important factor in defining the extent of dissociation.

In the cases of acetic acid and carbonic acid, it was shown that the rate of dissociation is very fast, which allows these weak acids to fully dissociate when the thermodynamic conditions are satisfied (e.g., under mass transfer limiting conditions).^{8-10,45}

The protonation reactions (recombination of the hydrogen ion with the conjugate base) associated with weak acids of interest in this study are known to be extremely fast, i.e., diffusion limited.⁵⁰⁻⁵² That specifies the $k_{b,HA}$ of these reactions to be in a rather narrow range from 10^9 to 10^{11} .⁵⁰⁻⁵² Hence, at a high level discussion, one may suggest that the kinetics of dissociation reaction is also represented by the pKa values ($k_{f,HA} = k_{b,HA} \times K_{HA}$) considering that the value of $k_{b,HA}$ is roughly defined for all such reactions. That is, the lower pKa values correspond to dissociation reactions with large kinetic rate constants. As pKa values increase, for the case of moderately buffering weak acids, the kinetic rate constant of the dissociation reaction decreases, which limits the extent of dissociation of such weak acids. The buffering effect as seen in the case of bicarbonate ion is an example of this kinetically limited scenario.³⁰ The species, which are already thermodynamically categorized as non-buffering weak acids, also have very slow dissociation reactions. An example of this is water with a dissociation rate constant in the order of 10^{-3} .

3.2 | Direct Reduction Reactions

While the buffering ability of weak acids is at this point well understood, their electrochemical properties are a subject that needs to be investigated on a case-by-case basis. The findings of recent studies discussed above suggest that there is no indication for significant cathodic electrochemical activity of carboxylic acids, carbonic acid, bicarbonate ion, and hydrogen sulfide on steel surface. The fact is, among the significant species commonly present in oil and gas production and transmission facilities, the only weak acid that is known to be directly reduced on steel surface with certainty is water. Water is present in these systems as the solvent at an extreme concentration, and even at this level the water reduction reaction is not considered as a significant player in acidic corrosion of mild steel. Therefore, the direct reduction of weak acids to hydrogen at the metal surface, at the concentrations typically encountered in the oil and gas industry, appear to be generally an insignificant factor. One cannot state with absolute certainty that reduction of weak acids to hydrogen or other chemical compounds are impossible on steel surface. Nonetheless, arguments on the significance of these reduction reactions is matter of faradic efficiency relative to the rather high rate of hydrogen ion and water reduction reactions. If the rate of weak acid reduction is not notably higher than that of water reduction, that reaction would not be of any importance in acidic steel corrosion context and can be disregarded.

3.3 | The Effect of Weak Acids on Iron Dissolution Reaction

In addition to their influence on the cathodic currents, weak acids have been found to alter the kinetics of the iron dissolution reaction in different ways, depending on the species. Acetic acid was found to decrease the rate of electrochemical reactions by adsorbing on the metal surface.⁹ In the case of CO₂ corrosion, the carbonate species were found to increase the rate of iron dissolution especially in the transition and prepassivation ranges.^{31,45} Hydrogen sulfide was also found to influence the rate of this reaction, and reduce the rate of iron dissolution at low concentrations, in a similar way as

was seen for acetic acid.^{5,44} At high concentrations, hydrogen sulfide is believed to replace the hydroxide intermediates, thus increasing the rate of this reaction.^{5,44} Such effects were to some extent quantified. Nevertheless, the effect of weak acids on the mechanism of iron dissolution remains one of the least understood aspects of the corrosion process in these systems. Conventionally weak acids were believed to have a negligibly small impact on the overall observed corrosion rates. However, the findings in the present study, especially when considering that weak acids are not significantly reduced at the metal surface, puts the effect of these species on the iron dissolution reaction under the spotlight. That is expected to account for majority of the deviations observed in the predicted corrosion rates, highlighting the need for extensive mechanistic investigation on the iron dissolution reaction including the effect of various weak acids before it can be fully represented in corrosion rate predictions.

CONCLUSIONS

> A brief review of the recent mechanistic findings in corrosion of mild steel in aqueous weak acid solutions, such as carbonic acid, carboxylic acids, and hydrogen sulfide shows a fundamental change in the mechanistic view to these corrosion scenarios over the past few years. Following this trend, a unifying mechanistic view is proposed here that is founded on the buffering ability of weak acids as a generic inherent property. Theoretical analysis using a comprehensive mathematical model showed that the chemical dissociation of weak acids can be held responsible for a wide range of characteristic behaviors seen in cathodic polarization data. That includes the increased limiting currents, the observation of a "double wave," and an apparent shift in the Tafel region. This generic view was further used to categorize the weak acids as *strongly buffering*, *moderately buffering*, and *nonbuffering* based on their pKa values to represent their relative significance in the corrosion process. The strongly buffering weak acids such as organic acids and carbonic acids are prone to readily get involved in the corrosion process, while moderately buffering species like hydrogen sulfide and bicarbonate ions require certain environmental conditions, usually high pH values, to demonstrate such behavior. On the other end of the spectrum, weak acids like water and bisulfide ions are categorized as nonbuffering and are not expected to have such a deleterious effect.

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