NACE INTERNATIONAL

CORROSION
Conference & Expo 2019

CO$_2$ corrosion, H$_2$S corrosion, Organic Acid Corrosion - a Unifying Perspective on Corrosion Mechanisms in Weak Acid Solutions

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ABSTRACT

Recent developments in understanding the mechanism of mild steel corrosion in the presence of carboxylic acids, carbon dioxide, and hydrogen sulfide has challenged the conventional views to corrosion in anoxic environments. Conventionally, the high corrosivity of such environments was associated with the direct reduction of these weak acids. Within the last few years, experimental and theoretical investigations of the electrochemical behavior of these corrosive environments suggest that the buffering effect arising from the dissociation of weak acids at the vicinity of metal surface is the main cause for the observed high corrosivity. These findings suggest that neither carboxylic acids, carbon dioxide, nor hydrogen sulfide are inherently corrosive, they merely exacerbate an existing corrosion process. In this study, the buffering effect is viewed as an inherent property of any weak acid, and it is shown to account for all characteristic behaviors observed in cathodic currents in the cases considered. In order to further elucidate this general property, a comprehensive mathematical model was developed and used to discuss the expected behavior of a hypothetical weak acid depending on the kinetic and thermodynamic properties of its dissociation reaction. The mechanistic findings in the present study is reformed into a generic mechanistic view of corrosion in weak acid solutions. That is 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 acidic solutions.

Key words: Corrosion, Mild steel, Weak acids, Carboxylic acids, Carbon dioxide, Hydrogen sulfide, Cathodic, Mechanism, Polarization, pKa

INTRODUCTION

In order to develop a generic view to the corrosion in the presence of weak acids, a brief review of the literature on the mechanism of corrosion in the presence of weak acids such as organic acids, carbonic acid 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 strong acid solution with the same pH have (without exception) been explained by presuming that the weak acid itself is directly involved in the underlying electrochemical reactions. The argument was that the higher corrosion rates are caused by the "direct reduction" of the weak acid as an additional

electrochemical reaction. Such arguments have been used and slightly modified over decades of research in the field, until more inclusive calculations were introduced that allowed for a detailed account of the effect of homogeneous reactions on the electrochemical response of the system. By doing so in recent years, a major shift in opinion has been made in the current mechanistic understanding of these systems. The present attempt on reforming the existing perspective to *corrosion in weak acid solutions* as one general, and unified topic, stems from this cumulative experience. Following the literature review, a generic mathematical model was developed for the present study. The model was used to demonstrate the extent of the influence of homogeneous chemical reactions on the observed electrochemical behavior of such a corroding system. The results showed that this aspect, which is by definition inherent to all weak acids, is most likely the cause of the higher corrosion rates, not the presumed electrochemical activity of these species.

The case of organic acids

The existing opinions on the mechanism of corrosion in the presence of organic acids is reviewed briefly in the following paragraphs, while a more detailed review of the literature can be found in a recent study dedicated to this subject [1]. The effect of organic acids in aqueous corrosion of mild steel is usually developed using acetic acid 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 commonly justified by presuming that acetic acid is directly reduced at the metal surface [2-6]. In this 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)).

$$Fe_{(aq)}^{2+} + 2e^- \rightleftharpoons Fe_{(s)} \tag{1}$$

$$2H_{(aq)}^+ + 2e^- \rightleftharpoons H_{2\ (g)} \tag{2}$$

$$2HAc_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} + 2Ac_{(aq)}^- \tag{3}$$

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

$$HAc_{(aq)} \rightleftharpoons H_{(aq)}^+ + Ac_{(aq)}^- \tag{4}$$

In more recent years, evidence has 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) [1,7-9]. 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 mass transfer limit of the cathodic 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 towards acetic acid dissociation, therefore, acetic acid acts as an additional source of hydrogen atoms at the metal surface.
This opinion was initially highlighted in 2011 by Amri et al. [7] 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.[8]. The authors investigated the behavior of the cathodic polarization curves in mildly acidic environments, with acetic acid being the only weak acid present in the solution. The polarization curves were obtained on 304 stainless steel in order to eliminate the interference of anodic reactions on the observed cathodic current. 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. This behavior lead to the conclusion that acetic acid is not involved in a charge transfer processes directly, and its main contribution was buffering the surface hydrogen ion concentration, thereby increasing the limiting currents.

However, considering the possible influence of the significant amount of the alloying compounds of 304 stainless steel (~ 20 wt. % Cr, and 10 wt. % Ni) and the passive layer on the electro-activity of the metal surface, the experimental findings on stainless steel may not be presumed valid for mild steel, without further verification. In order to address this shortcomings, Kahyarian et al. [9] investigated the effect of acetic acid directly on the polarization behavior of pure iron and X65 mild steel. Based on the experimental data obtained using rotating disk electrodes and potentiodynamic measurements, the authors showed that acetic acid did not significantly contribute to the charge transfer controlled currents for concentrations up to 1000 ppm. That study was later expanded by extending the environmental conditions and introducing a mechanistic mathematical model of corrosion in the presence of acetic acid, based on the recently developed "buffering effect" mechanism [1]. The experimental data reported in that study was in support of the previous findings by Kahyarian et al. [9] and Tran et al. [8] An example of the results reported by Kahyarian et al. is shown in Figure 1 where the agreement between the results from the model (solely based on H^+ reduction) and the experimental polarization data is demonstrated. The behavior observed in this graph also highlights the inhibitive effect of acetic acid on the polarization response of the system, where increasing the undissociated acetic acid concentration retarded the rate of electrochemical reactions, rather significantly.
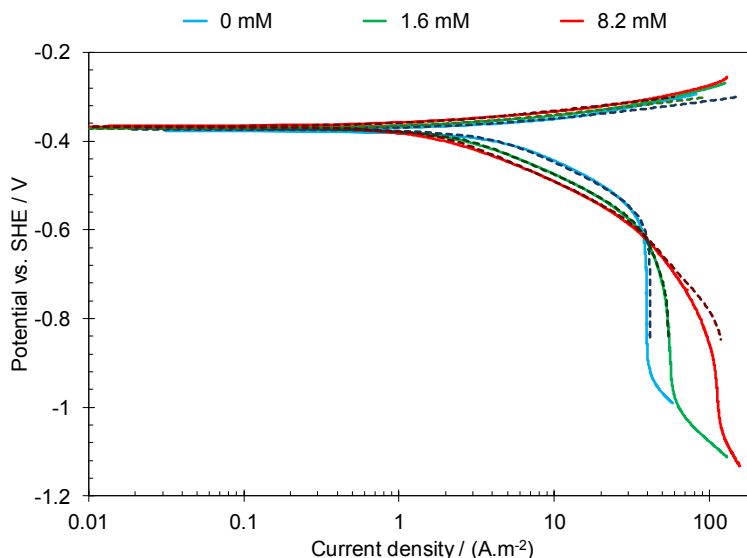

Figure 1. The comparison of the experimental (solid lines) and calculated (dashed lines) polarization curves of X65 mild steel in acidic solutions at pH 3, 30 °C, 0.1 M NaCl, RDE, 2000 rpm. Legend shows the concentration of undissociated weak acid. Data is taken from Kahyarian et al. [1]

Considering the finding in the study by Kahyarian et al. [1], the inconsistent 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 at the vicinity of the metal surface and it's 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 presence of acetic acid, where a synergistic effect between the temperature and acetic acid concentration was observed on corrosion rate [1].

The case of carbon dioxide

CO_2 corrosion of mild steel is perhaps the most common and widely studied corrosion scenario as it concerns the oil and gas industry. A detailed historical review of developments in mechanistic understanding of this corrosion scenario can be found in our earlier studies [10–13]. Similar to the case of organic acids, the classic mechanistic view to CO_2 corrosion associates the higher corrosion rates observed in such systems with the additional carbonic acid and bicarbonate ion reduction reaction:

$$H_2CO_{3(aq)} + e^- \leftrightharpoons HCO_{3(aq)}^- + \frac{1}{2} H_{2(g)} \tag{5}$$

$$HCO_{3(aq)}^- + e^- \leftrightharpoons CO_{3(aq)}^{2-} + \frac{1}{2} H_{2(g)} \tag{6}$$

Additionally the significance of the homogeneous chemical reactions of the CO_2/H_2O system (Reactions (7) through (10)) especially as it relates to the CO_2 hydration has been acknowledged since 1970's [14] and is now well understood.

$$CO_{2(g)} \leftrightharpoons CO_{2(aq)} \tag{7}$$

$$CO_{2(aq)} + H_2O_{(l)} \leftrightharpoons H_2CO_{3(aq)} \tag{8}$$

$$H_2CO_{3(aq)} \leftrightharpoons HCO_{3(aq)}^- + H^+_{(aq)} \tag{9}$$

$$HCO_{3(aq)}^- \leftrightharpoons CO_{3(aq)}^{2-} + H^+_{(aq)} \tag{10}$$

The most recent developments have been focused on the significance of carbonic acid dissociation reaction (Reaction (9)) as compared to electrochemical reduction of this species (Reaction(5)). In recent studies [15–18], it was shown through comprehensive mathematical models, that the limiting currents could be adequately explained even if H_2CO_3 was not considered an electroactive species. This can be understood when considering the local concentration of chemical species at the metal surface, where the homogeneous H_2CO_3 dissociation reaction (Reaction (9)) near the metal surface, followed by electrochemical reduction of the produced H^+ ions, provides a parallel reaction pathway to the direct H_2CO_3 reduction reaction. This observation carries a significant mechanistic implication, because 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 [14,19,20].

Similar to the case of organic acids, an alternative mechanism based on the dissociation of H_2CO_3 at the vicinity of the metal surface has been put forward in a few studies. Linter and Burstein, published one of the earliest articles suggesting that H_2CO_3 is not electrochemically active [21]. The authors developed their arguments based on the polarization curves obtained in N_2-saturated and CO_2 saturated 0.5 M NaCl 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 solutions, leading to the conclusion that H_2CO_3 is not electrochemically active. The findings of Linter and Burstein [21], 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. the fact that at pH 4.0 the cathodic current is dominated by H^+ reduction. In 2008, Remita et al. studied the electrochemical activity of H_2CO_3 using a more quantitative approach [22]. 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 [15–18]. Using the electrochemical kinetic parameters obtained for H^+ reduction in N_2-saturated

solutions, author were able to predict the polarization curves obtained in CO_2 saturated solutions without considering H_2CO_3 as a significant species (absent in their model). Their observation led to the conclusion that H_2CO_3 is not electrochemically active, and the sole effect was claimed to be the buffering effect of H_2CO_3 on surface concentration of H^+. 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[21]. That is the very narrow range of experimental conditions and the fact that at their conditions (pH 4 and 1 bar CO_2) the cathodic currents were dominated by H^+ reduction.

It is important to realize that the clearly demonstrated buffering ability of H_2CO_3 (or any other weak acid) does not exclude the possibility of H_2CO_3 direct reduction, as these are two independent processes. That is the reason why in order to distinguish them, the arguments must be based on the behavior of pure charge transfer controlled currents so that the electrochemical activity of H_2CO_3 can be separated from the chemical equilibria (buffering effect) associated with this species.

In attempt to address the shortcomings of the previous studies, in a more recent study by Tran et al., the authors devised a series of experiments at elevated pressures up to 10 bar CO_2 [23]. At these elevated pressures, the authors were able to investigate the electrochemical activity of H_2CO_3, as the dominant chemical species, with more confidence. Nevertheless, the authors note that even at such high CO_2 partial pressures the charge transfer controlled currents could not be observed on X65 mild steel due to the interference of the anodic reactions at low current densities and the mass transfer limitation at higher end. Therefore, the experiments were conducted on a 304 stainless steel surface. The suppressed anodic current densities on stainless steel surface allowed the charge transfer controlled current densities at the lower range to be clearly observed. The experimental results showed that the presence of H_2CO_3, even when present at significant levels (up to pCO_2=10 bar), did not result in any significant change of charge transfer controlled currents as measured on a stainless steel surface. This observation demonstrated that H_2CO_3 is not electrochemically active, at least not on the surface of stainless steel. The use of stainless steel brings significant uncertainties when comparing the actively corroding mild steel with the passive stainless steel surfaces, as discussed earlier in this manuscript. In an attempt to address this shortcoming, the mechanism of CO_2 corrosion of mild steel was further investigated by Kahyarian et al. [13] In that study, the polarization curves in CO_2 saturated solutions were obtained in a thin channel flow cell that allowed a high flow velocity, elevated pCO_2, and reduced temperatures. Together, these parameters allowed the pure charge transfer controlled currents to be observed clearly. In these studies of the polarization behavior on stainless steel, pure iron and mild steel surfaces, none showed any significant effect of pCO_2 up to 5 bar that could be associated with the direct H_2CO_3 reduction. In a subsequent study [24], the authors expanded the environmental conditions to less acidic solutions of pH 5, in order to further suppress the H^+ reduction contribution to allow for a more accurate discussion on electrochemical activity of H_2CO_3. Figure 2 shows the reported experimental polarization behavior of X65 mild steel at pH 4 and pH 5 and at various CO_2 partial pressures [24]. In such environmental conditions, the charge transfer controlled cathodic currents where observed clearly, as identified by the Tafel behavior just below the open circuit potential. This range of current densities was found to be irresponsive to the increase in pCO_2; a behavior that indicates that the direct reduction of carbonic acid does not occur in any significant extent.

Furthermore, this study showed a rather significant effect of pCO_2 on the rate of the anodic iron dissolution reaction, especially in the transition and pre-passivation ranges. The anodic polarization curves exhibited a consistently increasing rate as the CO_2 partial pressure was increased, suggesting that CO_2 or its related carbonate species may be directly involved in the iron dissolution reaction [24]. The authors concluded that the increased corrosion rates in CO_2 saturated solutions as compared to solutions of strong acid with the same pH, was caused by: the homogeneous chemical reactions of the CO_2/H_2O system that buffer the H^+ concentration at the metal surface –both CO_2 hydration and H_2CO_3 dissociation reactions- and the increased rate of anodic iron dissolution reaction [24].
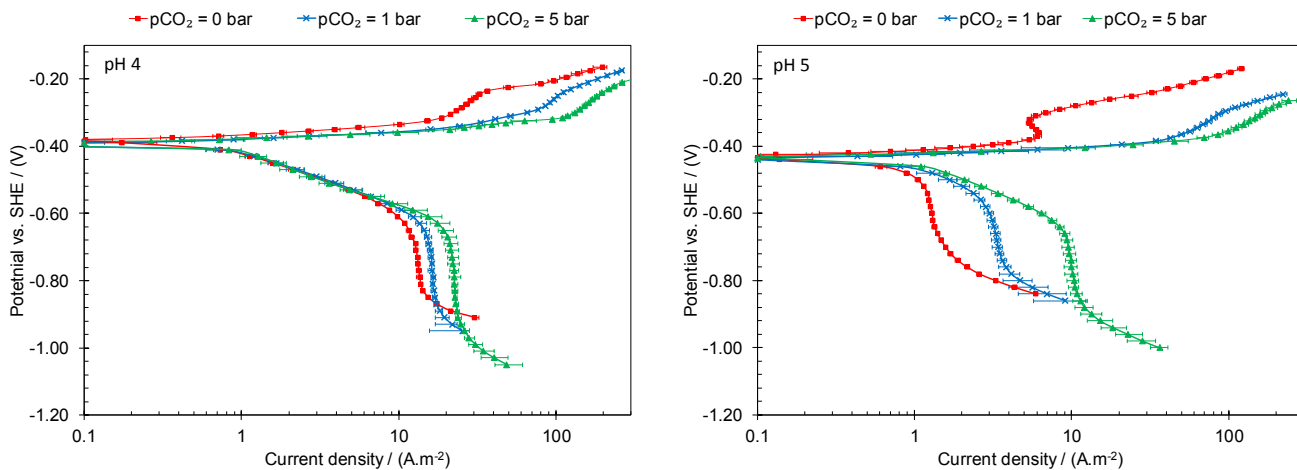
Figure 2. Experimental polarization curves on X65 mild steel surface at 10°C, 11 m.s⁻¹ thin channel flow, 0.1 M NaCl, 0.5 mV.s⁻¹ scan rate. The data at pH 4 and pH 5 are shown the left and the right panels, respectively. The data is taken from Kahyarian et al. [24]

The case of hydrogen Sulfide

The arguments on the electrochemical contribution of H_2S to the cathodic currents can be found in studies as early as 1965, reported by Bolmer[25]. H_2S is believed to be reduced as shown in Reaction (11).

$$H_2S_{(aq)} \rightleftharpoons HS^-{}_{(aq)} + H^+_{(aq)}$$ (11)
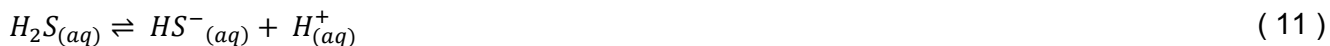
The same direct H_2S reduction reaction was also considered to contribute to the observed polarization cathodic currents obtained in rotating disk experiments by Morris et al.[26] The proposed electrochemical activity of H_2S became an accepted mechanism of corrosion in H_2S systems as seen in several subsequent studies [27–31], even if there was no direct proof for it. 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 H_2S containing solution on a stainless steel surface [32]. The previous reports of the significant effect of H_2S on the limiting current was confirmed in that study. Furthermore, the authors showed that in certain conditions a "double wave" shape appeared in the polarization curves; an observation that was considered as a solid proof for the direct H_2S reduction reaction. The "double wave" was associated with the existence of two electrochemical reactions and their corresponding limiting currents, one being the H^+ and other being the H_2S reduction reaction. In a parallel study[33] , Zheng et al. investigated the mechanism of mild steel corrosion in the presence of H_2S in a wider range of experimental conditions. The effect of H_2S on the limiting current, and the existence of two limiting currents (i.e. the "double wave") was also reported in that study. The authors noted that both limiting currents, associated with the H^+ and H_2S reduction reactions, were the result of mass transfer limitation of the involved reactants. These observations led the authors to conclude that in H_2S containing solutions, the direct reduction of H_2S is a significant cathodic process. Zheng et al. also developed an elementary mechanistic model [10] based on these findings, where a reasonable agreement with the experimental data was reported. In 2017, Esmaeely et al. reported a set of experimental polarization data at pH_2S of 1 bar [34] on a mild steel surface. The reported polarization curves were found to behave similarly to those obtained at lower H_2S partial pressures in earlier studies [33,35]. The authors also used a similar model to that proposed by Zheng et al. [33] to quantify their experimental data.

To date, there seems to be a consensus in the literature that H_2S, unlike acetic acid and carbonic acid, is directly reduced on the metal surface, thus increasing the corrosion rates by increasing the rate of cathodic reactions. These arguments are mostly based on the distinctive behavior of cathodic polarization curves in H_2S 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 H_2S 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, H^+ reduction and H_2S reduction.
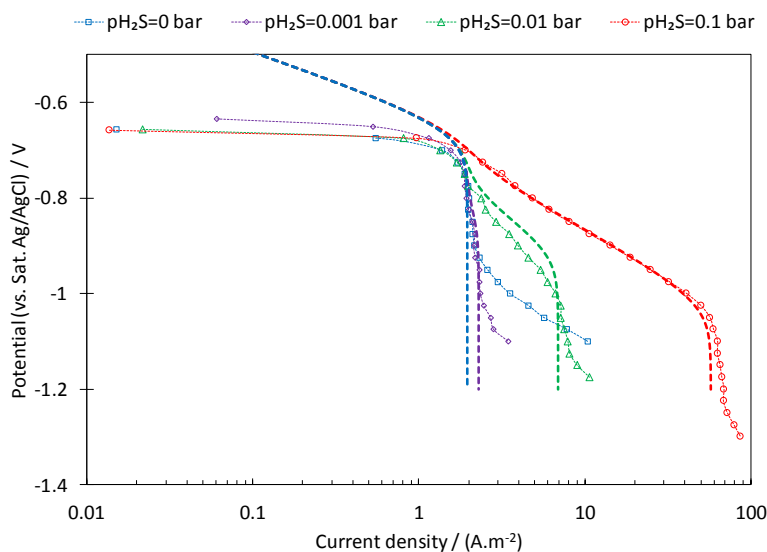

Figure 3. Cathodic polarization curves on X65 mild steel at pH 4, 30°C, 1000 rpm RCE, at various H_2S partial pressures. The data is taken from Kahyarian et al. [36]

However, considering the recent developments in mechanistic understanding of corrosion in the presence of organic acids and carbon dioxide, one may consider that a similar process would be governing the case of hydrogen sulfide as well. While H_2S is physiochemically different from carbonic acid and organic acids, the "buffering effect" is common for all these species as weak acids. Of course, here too there are differences to be expected, where carbonic acid and organic acids are weak acids with relatively low pKa values and very fast dissociation rate constants, while H_2S with pKa of 7 is relatively "weaker" and has slower dissociation rate constant. The recent studies have shown that carbonic acid and organic acids are "strong" buffers, that means they readily dissociate as the surface pH is increased as compared to that in bulk solution [1,9,13,24]. Hence, one may suggest that at the favorable environmental conditions, H_2S would also exhibit the same buffering ability, at least to some extent. This argument was recently examined by Kahyarian et al. [36] in term of theoretical investigation of the cathodic polarization curves, using a comprehensive mathematical model similar to those introduced earlier [1,10,11]. The model was developed with H^+ as the sole cathodic reaction, while the homogeneous chemical reactions of the H_2S/H_2O system were included in calculations. The results from the model were compared to those obtained experimentally as shown in Figure 3. The model predictions, shown as the dotted lines in Figure 3, do not take into account the reduction of water that is only significant in more negative potentials. The good agreement of the model with experimental data, especially the prediction of the "double wave" behavior without considering H_2S as an electro-active species was found to support the underlying "buffering effect" mechanism. Such observations lead the authors to conclude that the buffering effect of H_2S is significant in all the conditions considered and at the same time the direct reduction of H_2S is insignificant, just the same as carbonic acid and carboxylic acids.

From these observations, it appears that a more generic, unifying view to these apparently different corrosion scenarios can be developed. For this purpose, the cathodic polarization behavior of an acidic solution containing a generic weak acid was theoretically studied in the present investigation. This was done by using a mechanistic mathematical model that allowed the homogeneous chemical reactions to be coupled with the mass transfer processes and the H^+ reduction reaction, as described in the following sections.

MATHEMATICAL MODEL

The mathematical model developed in the present discussion is similar to those described in more details in our previous studies [1,10,11]. where H is hydrogen and "A" could be for example: acetate, bicarbonate, carbonate, bisulfide, sulfide, etc., with an equilibrium constant of "K_{HA}", and the dissociation rate constant of "$k_{b,HA}$". As with any weak acid, the dissociation reaction is presumed to occur according to:

$$HA_{(aq)} \rightleftharpoons A^-_{(aq)} + H^+_{(aq)} \tag{12}$$

The present model was used to examine the effect of buffering ability 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 cannot be 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 for this discussion and, hence, 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 seen in below discussions is the result of one single electrochemical reaction: the H^+ reduction.

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

$$H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + H^+_{(aq)} \tag{13}$$

The corresponding mathematical relationships can be expressed as:

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

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

In addition to the equilibrium relationships, the solution speciation has to satisfy the electro-neutrality constraint, shown as Equation (16). At a known solution pH and HA concentration, the solution speciation can be readily obtained based on Equations (14) through (16).

$$\sum_i z_i C_i = 0 \tag{16}$$

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

$$\frac{\partial C_i}{\partial t} = -\nabla . N_i + R_i \tag{17}$$

Equation (17) describes the concentration distribution of species i, where N_i is the flux, and R_i 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) [37], where the terms on the right hand side describe the effect of electro-migration, molecular diffusion, and convective flow, respectively.

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

For an electrochemically one dimensional systems, such as those observed in pipelines and laboratory rotating electrode systems, Equation (17) and Equation (18) can be simplified to Equation (19) and Equation (20). Furthermore, the mobility of ions can be estimated using the Nernst-Einstein relationship ($u_i = D_i/RT$), assuming a dilute solution.

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

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

In the convective term, v_x describes the velocity profile inside the diffusion layer. For example, for the case of a rotating disk electrode (RDE), the analytical solutions for the velocity profile (v_x) and the diffusion layer thickness (δ) are shown as Equation (21), where $a = 0.510$, and Equation (22), respectively [38].

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

$$\delta = \left(\frac{3 D_{lim}}{av} \right)^{1/3} \left(\frac{\omega}{v} \right)^{-1/2} \qquad (22)$$

As mentioned above, the rate of consumption/production of the chemical species via the homogeneous chemical reactions are 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).

$$\sum_{r=1}^{n_r} C_r \rightleftharpoons \sum_{p=1}^{n_p} C_p \qquad (23)$$

$$R_j = k_{f,j} \prod_{r=1}^{n_r} C_r - k_{b,j} \prod_{p=1}^{n_p} C_p \qquad (24)$$

where $k_{f,j}$ and $k_{b,j}$ 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 involving this species, as shown in Equation (25).

$$R_i = \sum_j R_j s_{i,j} \qquad (25)$$

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, and $s_{i,j}$ is the stoichiometric coefficient of species i in reaction j. In addition to concentrations of species, the potential of the solution inside the diffusion boundary layer has to be specified in order to calculate the effect of electro-migration, as seen in Equation (20). This parameter can be obtained by introducing an additional relationship known as the "electro-neutrality" constraint as expressed via Equation (16).

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 appropriate initial and boundary conditions are 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 remains 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 H^+ at the metal surface can be defined as [11,37]:

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

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 $k_{0_{H^+}} = 1.2 \times 10^{-8}$, and the reaction order $m_{H^+} = 0.5$, used in this model, were taken from a recent study by Kahyarian et al. [36]

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

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

$$N_i|_{x=0} = 0 \tag{28}$$

The flux Equations (27) and (28) can be used to describe the boundary conditions for all chemical species at the metal surface. Considering that the N_i appears in these relationships, the solution potential should also be specified at the solution/metal boundary. This can be done similar to that in the governing equations, using the electro-neutrality constraint as described by Equation (16).

RESULTS

In the present document, the buffering effect was discussed as an inherent property of any weak acid, which accounts for the characteristic behaviors observed in cathodic currents in the cases considered previously. The findings based on the individual cases, can be recast into a more generic mechanistic view of *corrosion in weak acid solutions*. This model was used to investigate the effect of the buffering ability of a generic weak acid on the cathodic polarization response of the system.

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 4. Furthermore, these graphs demonstrate how these parameters can influence the characteristic behavior seen in polarization curves. These results demonstrate that any weak acid can significantly influence the electrochemical response of the system, if the conditions favor the dissociation reaction. The buffering effect in some cases merely appears as an increase in the limiting current, in some appears in the form of a "double wave" and in certain conditions has no significant influence. That is indeed all related to the pKa of the weak acid and the pH at the metal surface. That fact is better demonstrated in Figure 5 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 anion are shown in the same graph on the primary vertical axis. As it appears in Figure 5, 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 transfer limitation of the H^+ 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.
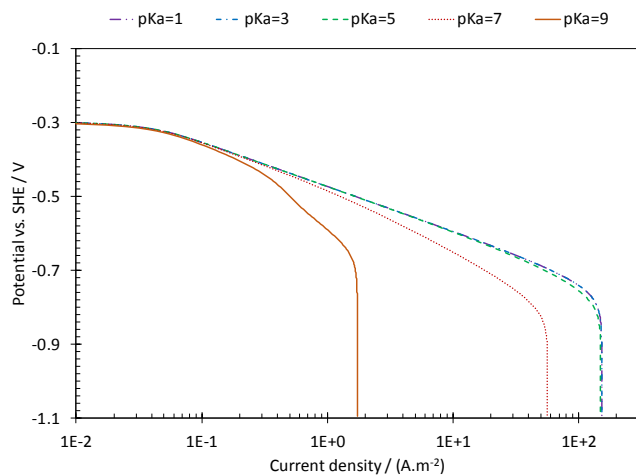
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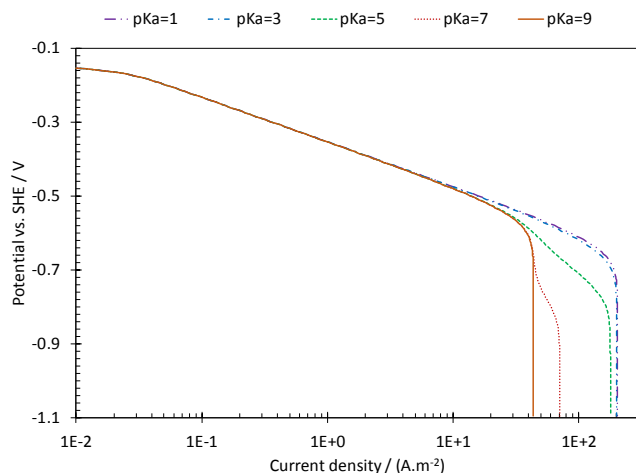
B)
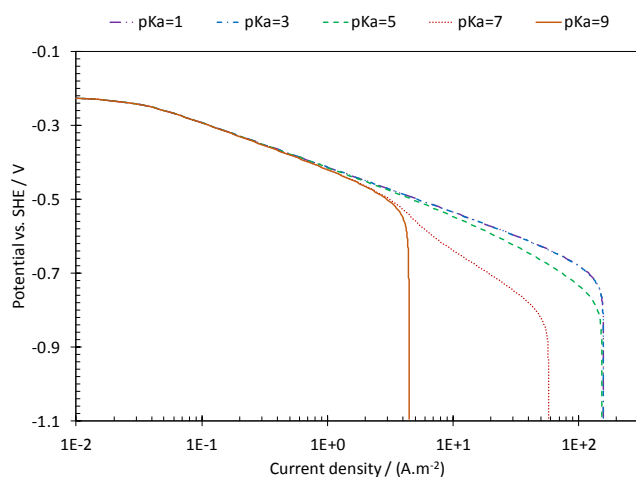
C)

Figure 4. Calculated cathodic polarization curves at 30°C, 2000 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. C) at pH 5.

If we were to condense the discussion to be presented as a high level guideline, it would appear from Figure 5 that the peak of the dissociation reaction (the buffering effect) happens when the surface pH is roughly equal to 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, considering that in the oil and gas transmission pipelines the pH is typically ranging from 4 to 7, the weak acids with pKa of roughly 5 are able readily dissociate when the H^+ limiting current is reached. That results 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 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 limiting current in the presence of these weak acids behaves, for the most part, similar to those of a strong acid 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 deviates significantly from that of strong acids. The observation of a double wave in certain conditions can be considered a characteristic behavior of this group, such as for example is the case of hydrogen sulfide. Bicarbonate ion, and the second dissociation of sulfurous acid and phosphoric acid can also be placed in this group [39].

3. *Non-buffering 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.

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) [1,9,13,24].

The protonation reactions associated with the weak acids of interest in this study are considered to be extremely fast, i.e. diffusion limited [40–42]. That specifies the $k_{b,HA}$ of these reactions to be in a rather narrow range from 10^9 to 10^{11} [40–42]. Hence, one may suggest that the kinetics of dissociation reaction is also represented by the pKa values ($k_{f,HA=}\ k_{b,HA} \times K_{HA}$). 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 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}.

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 electrochemical activity of carboxylic acids, carbonic acid, and hydrogen sulfide. The fact is, amongst the significant species commonly present

in oil and gas production and transmission facilities, the only weak acid that is known to be directly reduced 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 such reactions are impossible, nonetheless, an argument only needs to be made about the rates of these reactions relative to the rather high rate of H^+ and water reduction reactions. If the rate of direct reduction of a weak acid is not significantly higher than that of water (while also taking into consideration their concentrations and not only the reaction rate constants), it should be disregarded.
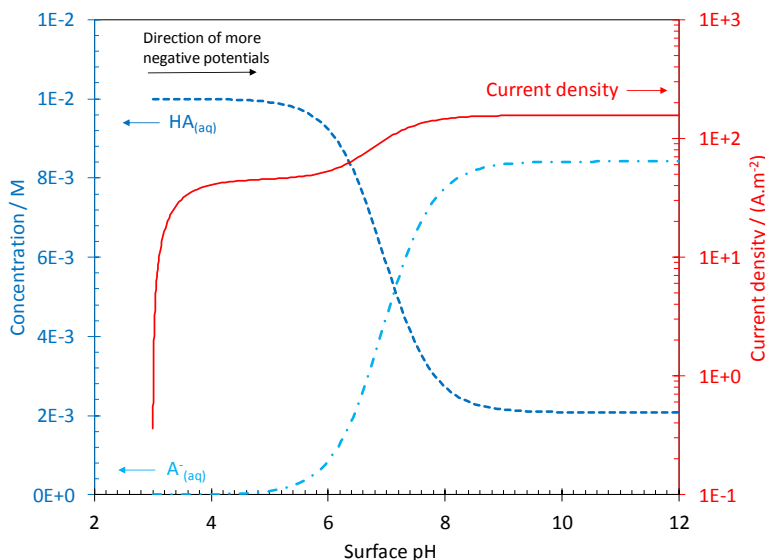

Figure 5. The relationship between the calculated surface pH and the surface concentration of HA and A⁻, on the primary vertical axis, and the calculated current density, on the secondary vertical axis. Conditions: pKa = 7, $k_{b,HA}=10^{10}$, 25°C, 2000 rpm RDE, pH 3, 0.01 M HA, and the potential range from -0.2 to -1.2 V vs. SHE.

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 [1]. In the case of CO_2 corrosion, the carbonate species were found to increase the rate of iron dissolution especially in the transition and pre-passivation ranges [24,43]. 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 [33,35]. At high concentrations, H_2S is believed to replace the hydroxide intermediates, thus increasing the rate of this reaction [33,35]. 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 such systems. Conventionally, such processes 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. An extensive mechanistic investigation on the iron dissolution reaction including the effect of various weak acids is required before it can be fully represented in corrosion rate predictions.

CONCLUSIONS

The study of the recent mechanistic findings in corrosion of mild steel in weak acid solutions, such as carbonic acid, organic acids, and hydrogen sulfide suggest a fundamental change in the mechanistic

view to these corrosion scenarios over the past few years. In these studies, the dissociation of the weak acid is emphasized and introduced as the alternative to the direct electrochemical reduction of weak acid, to account for the extreme corrosivity of such environments. This advancement in understanding is owed to more in depth electrochemical studies and the application of the more comprehensive mathematical models in the analysis of the electrochemical response of the system. Following this trend, <u>a unifying mechanistic view is proposed here that is founded on the buffering ability of weak acids as a generic inherent process</u>. Theoretical analysis using a comprehensive mathematical model showed that the <u>chemical dissociation of weak acids can be held responsible for a wide range of characteristic behaviors seen in cathodic polarization data</u>. That includes the <u>increased limiting currents</u>, the <u>observation of a "double wave"</u>, and an <u>apparent shift in the Tafel region</u>. All of which have been associated with the direct reduction of weak acids at some point in the past. This generic view was further used to categorize the weak acids as *strongly buffering*, *moderately buffering*, and *non-buffering* based on their pKa values to represent their relative "corrosivity". <u>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 non-buffering, and are not expected to have such a deleterious effect.</u>

ACKNOWLEDGEMENTS

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