

Corrosion Mechanisms of Mild Steel in the Presence of Formic Acid and Acetic Acid

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ABSTRACT

The presence of organic acids such as formic acid, acetic acid and propionic acid in oil field brines has been identified as a significant contributor to corrosion of mild steel. Extensive research indicates that corrosion rates of steel are significantly higher in weak acid environments, such as aqueous CO₂ or acetic acid, as opposed to fully dissociated aqueous strong acids at the same pH. A general observation is that the increase in corrosion rate is due to increase in cathodic current, which is due to the partial dissociation of the weak acid. Most corrosion research with respect to aqueous organic acid environments has focused on acetic acid as it is a prevalent organic acid found in oil fields; it is also a good representative for higher molecular weight carboxylic acids with similar acid dissociation constants (K_a) values that may be present, e.g., propionic acid. However, the difference in acidity of formic acid as compared to acetic acid emphasizes the need to establish a mechanistic understanding of the role of operational parameters such as pH, temperature, and/or concentration of undissociated acid concentrations on corrosion behavior. A conventional three electrode glass cell equipped with a rotating disc electrode was used to conduct electrochemical measurements (potentiodynamic sweeps, electrochemical impedance spectroscopy, and linear polarization resistance) on an API 5L X65 steel working electrode in a 1 wt.% NaCl electrolyte maintained at constant pH and temperature. It was confirmed that both formic acid and acetic acid have a similar effect on the cathodic reaction rate, wherein their contribution to the corrosion process is through chemical dissociation, which induces the buffering effect. However, while acetic acid has a slight inhibitive effect on the anodic reaction rate, a similar effect was not observed in the presence of formic acid. The effects of concentration of undissociated acid, temperature, pH, rotational speed, and presence of CO₂ in the environment on corrosion of mild steel were established.

Key words: Organic acid, acetic acid, formic acid, corrosion, electrochemical measurements

INTRODUCTION

Corrosion is a surface phenomenon, which is defined as the deterioration of a material due to chemical and/or electrochemical reactions. The continued interest in understanding corrosion phenomena and devising mitigation methods stems from the potential influence corrosion has on infrastructural damage across diverse industries. The most prevalent forms of corrosion encountered in the oil and gas industry are referred to as sweet and sour, corresponding to aqueous CO_2 and H_2S environments, respectively. The presence of an aqueous phase in these environments leads to the formation of a weak acid which is understood to be detrimental to the service life of carbon steel pipelines, when not properly mitigated.

Corrosion rates of steel have been recorded to be notably higher in weak acid environments as opposed to fully dissociated aqueous strong acids at the same pH.¹ A general observation is that the increase in corrosion rate is due to an increase in cathodic current, which is due to the partial dissociation of the weak acid.² Volatile organic acids such as formic acid, acetic acid, and propionic acid are generally present in oil field conditions, which increase the corrosivity of the sweet and sour environments.³ Acetic acid is one of the most prevalent organic compounds found in oil fields and is considered as representative of carboxylic acids when it comes to corrosion research.⁴ Concentrations of acetic acid up to thousands of ppm have been reportedly measured,⁵ and an increase in the corrosion rate of carbon steel has been observed with acetic acid concentrations as low as 1 mM.⁶

In order to investigate the role of acetic acid on the corrosion mechanisms of mild steel, Kahyarian⁷ implemented an improved experimental procedure using a Rotating Disk Electrode (RDE) glass cell setup, which has a laminar flow profile even at a rotational speed of 2000 rpm. The adopted experimental procedure ensured that the cathodic reaction remained under charge transfer control in the set operating conditions. His research concluded that the direct reduction of acetic acid is insignificant and the increase in cathodic current is a result of the "buffering effect".⁷ As per this mechanism, while hydrogen reduction remains to be the dominant cathodic reaction, chemical dissociation of the weak acid replenishes the hydrogen ions that are consumed during the corrosion process. Corrosion mechanisms of mild steel in other environments such as CO_2 , H_2S , etc., were explained using similar theory because of the similarity in the chemical dissociation properties of weak acids.

While most of the available literature is largely focused on acetic acid because of its predominance in oil fields, the fact that formic acid has a significantly lower pKa (negative base-10 logarithm of K_a) value (stronger acid) as compared to other carboxylic acids indicates that it cannot be grouped under the umbrella of 'Acetic Acid Research' and accentuates the need to study its effect separately (Figure 1).

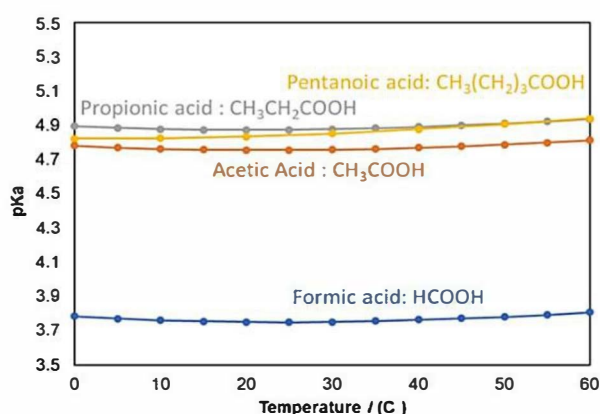


Figure 1: Dissociation constants of organic acids commonly found in oil fields ^{8, 9}

The purpose of this study is to determine the effect of formic acid on corrosion mechanisms to aid in the prediction of corrosion rates of mild steel in upstream oil and gas environments. To achieve this objective,

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targeted experiments over an extended range of operating conditions, at different pH, temperatures, concentrations, rotation speeds, and environments were conducted to establish the effect of each parameter on the corrosion mechanism of mild steel in the presence of formic acid. Further, the corrosion mechanisms of mild steel in the presence of formic acid and acetic acid were compared under selected operating conditions.

EXPERIMENTAL

Equipment

A 2-liter three-electrode glass cell equipped with a rotating disc electrode was used in this study. Electrochemical measurements were conducted in a 1wt% NaCl solution at a rotational speed of 2000 rpm in N₂/CO₂ sparged environments at a constant bulk solution pH. API X65 steel was used as the working electrode material for the current study. Table 1 shows the chemical composition of the working electrode.

Table 1
Chemical composition of the mild steel material (API 5L X65) (in wt.%)

Al	As	C	Co	Cr	Cu	Mn	Mo	Nb	Ni
0.028	0.008	0.05	<0.001	0.252	0.173	1.51	0.092	0.034	0.291
P	S	Sb	Si	Sn	Ti	V	Zr	Fe	
0.004	<0.001	<0.001	0.167	0.002	0.012	0.04	<0.001	balance	

Figure 2 shows the different parts of the experimental setup. An Ag/AgCl electrode was used as the reference, while a platinum mesh was used as the counter electrode. The working electrodes were 5mm diameter disks press fit into Teflon sample holders. The working electrodes were metallographically polished using 600, 800, 1000 and 1200 grit SiC abrasive papers, followed by diamond polishing using 9, 3, and 0.25µm diamond suspensions.

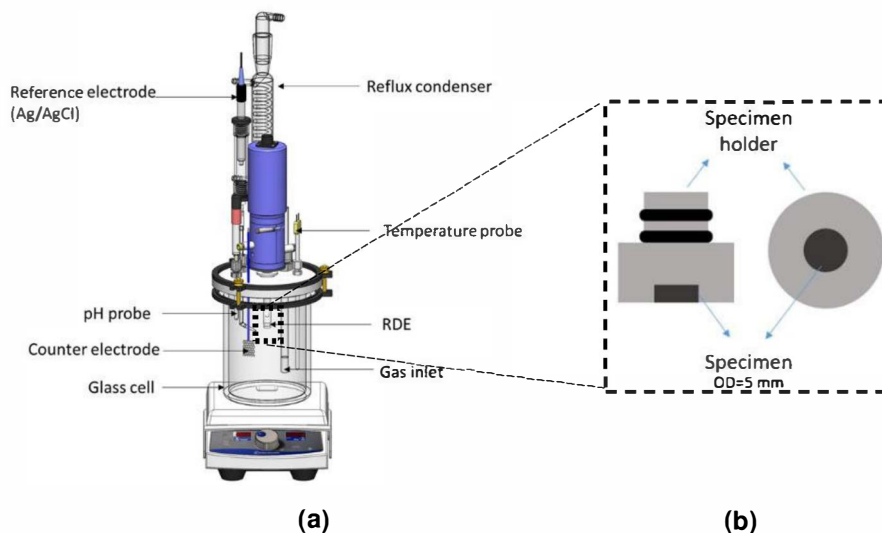


Figure 2: Experimental setup showing (a) glass cell with RDE as working electrode (b) 5mm disk press fit into a Teflon holder.

Test Matrix

The electrochemical experiments were conducted in the presence of organic acids in a 1 wt% NaCl solution de-aerated for 2h with N₂ or CO₂ sparging. The solution was continuously sparged with N₂ or

CO₂ throughout the duration of the experiment. The temperature (30°C, 50°C, or 80°C) and pH (4, 5, or 6) of the test solution were monitored and held constant. The range of experimental parameters used in the current study are shown in Table 2. The test matrices for each experimental set are detailed in the discussion section.

Table 2
Superset of experimental parameters used in the present study

Parameter	Description	
Electrolyte	1 wt% NaCl	
RDE rotation speed (rpm)	1000 – 4000	
Organic Acid (total) (mM)	HAc [†] (0 – 16.67)	HFr [‡] (0 – 39.14)
Organic Acid (total) (ppm)	HAc (0 – 1000)	HFr (0 – 1800)
Fixed pH	4.00 – 6.00 ($\pm$ 0.02)	
Temperature (°C)	30 – 80 ($\pm$ 2)	
Spurge gas	N ₂ or CO ₂	

Electrochemical measurements

The electrochemical measurements were performed using Gamry[§] Potentiostat and conducted twice for each experimental condition. Each experiment consisted of 5 electrochemical tests in specific order: open circuit potential (OCP) + electrochemical cleaning (30 min), OCP + cathodic sweep (55 min), OCP + electrochemical impedance spectroscopy (EIS) (40 min), OCP + linear polarization resistance (LPR) (5 min), and finally OCP + anodic sweep (25 min). An electrochemical cleaning procedure was performed on the working electrode to ensure repeatability of results. This was performed by pulsing currents ($\pm$ 5 A/m², $\pm$ 2 A/m², and $\pm$ 1 A/m² in that order) for 60s at each current, followed by 120s at open circuit potential (OCP), i.e., + 5 A/m² for 60s, followed by -5 A/m² for 60s, followed by 120s at OCP, then repeat the procedure for +2 A/m², etc. After electrochemical cleaning, the OCP was monitored for 20 min until a steady state value was obtained. This was followed by cathodic polarization, EIS, LPR, and anodic polarization, as defined in Table 3. The total duration of each experiment was 4.5 h (2h of de-aeration, sample insertion and 2.5h of electrochemical tests).

Table 3
Parameters for electrochemical measurements

Technique	Parameters	Results
Potentiodynamic Sweeps	Scan Rate: 0.5 mV / s, Sampling period: 1s Cathodic: 0 to -0.55 V (vs. OCP), Anodic: 0 to 0.15 V (vs. OCP)	Mechanisms
Linear Polarization Resistance	Scan Rate: 0.125 mV / s. Polarization range: $\pm$ 5 mV (vs. OCP).	Polarization resistance (Rp)
Electrochemical Impedance Spectroscopy	Frequency range: 10000 Hz ~ 0.1 Hz. Amplitude: 10 mV. DC Potential: 0 vs. OCP	Solution resistance (Rs)

[†] Acetic acid may also be written as its shorthand chemical formula, HAc.

[‡] Formic acid may also be written as its shorthand chemical formula, HFr.

[§] Trade name

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RESULTS

Corrosion mechanisms of mild steel in the presence of formic acid

Electrochemical tests were performed to see the effect of different parameters on the anodic and cathodic mechanisms. Table 4 shows the detailed operational parameters used for each test series. For each of the test series, anodic and cathodic polarization curves were obtained, and these results were corrected for IR drop using R_s obtained from EIS measurements. Corrosion rates were calculated using R_p obtained from LPR, R_s obtained from EIS measurements, and B values of 13.2 mV/dec for tests conducted at 30 °C, 14 mV/dec at 50 °C, and 15.5 mV/dec at 80 °C.

Table 4
Parameters for experiments conducted in N₂ sparged solution

Parameter	HFr concentration				Effect of pH			Effect of rotational speed			Effect of temperature		
Electrolyte	1 wt% NaCl				1 wt% NaCl			1 wt% NaCl			1 wt% NaCl		
RDE rotation speed (rpm)	2000				2000			1000	2000	4000	2000		
Total HFr (mM)	0	0.39	3.91	39.14	3.91	26.38	251.1	3.91			3.91	3.82	3.41
Undissociated HFr (mM)	0	0.14	1.41	14.18	1.41			1.41			1.41		
pH	4.00 ± 0.02				4	5	6	4.00 ± 0.02			4.00 ± 0.02		
Temperature(°C)	30 ± 2				30 ± 2			30 ± 2			30	50	80
Spurge gas	N ₂				N ₂			N ₂			N ₂		

Effect of different undissociated HFr concentrations on corrosion

Figure 3 shows potentiodynamic sweeps of X65 steel in N₂ sparged environment with different concentrations of undissociated HFr in the solution. While there is an increase in the limiting currents with increasing concentration of HFr, the charge transfer part of the cathodic polarization curve remains uninfluenced. This is a clear indication that the hydrogen evolution reaction is the main cathodic reaction and HFr influences the corrosion rate by the “buffering effect”. These results confirm that HFr is not electroactive. HFr is a strong buffer that readily dissociates when needed. It can also be observed that the anodic reaction rates are not significantly influenced by the increase in concentration of HFr.

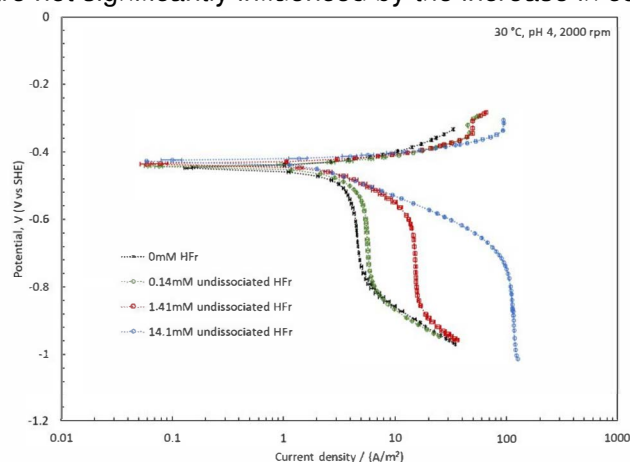


Figure 3: Polarization curves for X65 steel RDE in various concentrations of HFr at pH 4, 2000 rpm, 30°C in N₂ sparged 1 wt% NaCl solution.

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