

Effect of Acridine and Myristic Acid on CO₂ Corrosion During Intermittent Oil/Water Wetting

Neda Norooziasl, David Young, Bruce Brown, Marc Singer
Institute for Corrosion and Multiphase Technology, Ohio University
342 W State Street
Athens, Ohio, 45701
USA

ABSTRACT

The effect of a paraffinic model oil containing select surface-active compounds (myristic acid and acridine) on CO₂ corrosion with and without intermittent wetting has been studied. Observations have shown that the presence of myristic acid in the oil phase has no effect on corrosion behavior due to its lack of partitioning in the water phase. However, after direct contact between the oil phase containing myristic acid and the metal surface, there was a significant decrease in the corrosion rate. This phenomenon gradually diminished at pH 4.0 but was more persistent at pH 6.5. The presence of acridine in the oil phase was shown to have a strong inhibitive effect at pH 4.0, even during the partitioning step. However, there was no inhibitive effect conferred by the presence of acridine on the corrosion rate at pH 6.5. An experimental methodology was developed that facilitated improved simulation of the effect of intermittent oil/water wetting on CO₂ corrosion. The electrochemical current response during the oil/water intermittent wetting cycles showed that persistency of model oil (without surface active compounds) on the mild steel surface is only a matter of seconds. Corrosion rate measurements showed that the presence of myristic acid renders the oil layer more persistent after intermittent wetting as compared to one-time direct contact.

Key words: CO₂ corrosion, carbon steel, oil/water intermittent wetting, oil film, naturally occurring surface-active compounds

INTRODUCTION

Pipelines are the most effective way to transport oil and natural gas, particularly for their bulk transmission over long distances^{1,2}. Corrosion in oil and gas pipelines occurs because of the presence of dissolved corrosive gases, such as CO₂ and/or H₂S, in reservoir derived brine, and contact between this brine and the steel surface. The oil phase by itself does not cause corrosion and can even inhibit corrosion^{3,4,5,6}. In fact, many surface-active compounds naturally exist in crude oils⁷. Crude oils can be defined as naturally occurring liquid mixture of hydrocarbons (83 wt.%–87 wt.% of carbon, 10 wt.%–14 wt.% of hydrogen) containing derivatives of nitrogen (0.1 wt.%–2.0 wt.%), oxygen (0.05 wt.%–1.5 wt.%), sulfur (0.05 wt.%–6.0 wt.%), metals (less than 1000 ppm), and other elements^{8,9}. Some chemical compounds native to crude oils identified as surface-active compounds have an ability to preferentially adsorb at

steel-water, steel-oil, and oil-water interfaces, thereby altering the wetting and corrosion properties of steel surfaces¹⁰. Therefore, if the water phase in a pipeline was entirely entrained by the hydrocarbon phase, instead of flowing at the bottom, no corrosion problems are expected to occur. Therefore, it is important to determine whether the pipe internal surface is wetted by oil or water depending on the fluid properties and the operating flow rates¹⁰. This knowledge can help decrease economic costs and mitigate the potential for adverse environmental impacts caused by leakage from corroding tubular steels.

In oil-water flow through a horizontal pipeline at low rates, the water phase flows as a separate layer at the bottom of the pipe. This corresponds to a stratified flow regime because gravitational force dominates over turbulent force. By increasing the flow rate inside the pipeline, the turbulent energy increases and, as a result, the water phase becomes gradually entrained as droplets in the oil phase¹¹. An example of this can be seen through research conducted with 10% and 1% water cuts as shown in Figure 1: in the image on the left, a separate layer of water on the bottom half surface of the pipe is observed, and in the image on the right the water phase is mostly observed in the form of droplets. Therefore, water may not always wet the bottom surface of the pipe completely, leading to very different corrosion rates depending on the operating scenarios. The measurement of iron count in this example showed the corrosion rate was about 10 times higher when the water content was increased from 1 to 10% while other conditions were kept constant¹².

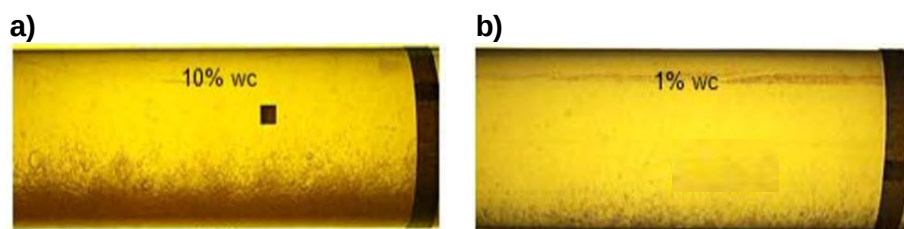


Figure 1. Images of horizontal flow patterns of oil/water flow (LVT-200 & water) at mixture liquid velocity of 1.0 m/s for: a) 10% water cut; and b) 1% water cut¹².

The water phase is typically entrained by the hydrocarbon phase when the water content is low, as a result the oil phase wets the internal surface of the pipe, and there would be no corrosion problem. By increasing the water content, water breakout may occur, consequently, water may more easily wet the surface of the pipe, and corrosion is possible^{13,14,15}. Considering that production flow rates can vary significantly during the life of pipeline systems, different flow patterns can be expected in which oil and water can alternately wet the pipe internal surface. This phenomenon is identified as “intermittent wetting”¹⁶. Flow rate and water cut can affect the degree of intermittent wetting¹⁵. This phenomenon can influence the corrosion mechanism of the metal surface, which may differ from those commonly accepted for aqueous corrosion (*i.e.*, full water wetting)^{6,17,18}. Consequently, wetting condition of the metal surface is a key parameter to predict corrosion behavior^{19,20,21,22}, and it is important to know the relation between wetting of the surface and corrosion processes^{23,24,25}.

EXPERIMENTAL PROCEDURE

Materials and Chemicals

The metal specimens were carbon steel X65 specimens used for electrochemical measurements. The composition of crude oils is complicated and contains many different chemical compounds. Therefore, model oils containing select dissolved species were used to simulate crude oil behaviors in order to isolate their influence. In this study, LVT-200 model oil, which is a hydrotreated light distillate petroleum fraction²⁶, was used with and without the addition of 0.1 wt.% of two different surface-active compounds, myristic acid and acridine, in the conducted experiments. However, acridine is not soluble in LVT-200

due to the oil's low aromaticity. Therefore, acridine was dissolved in a 60:40 weight ratio of LVT-200 and Aromatic-200. Aromatic-200 model oil contains a complex mixture of aromatic hydrocarbons which are mostly derivatives of naphthalene²⁷. Myristic acid and acridine are representative of oxygen and nitrogen containing compounds, respectively, which naturally exist in crude oils. Further, the surfactants concentration used in this study are in the common range of naturally occurring compounds concentration in crude oils. The molecular structures of these surface-active species are shown in Figure 2. Note the amphiphilic character of myristic acid, and the aromaticity of acridine. Myristic acid has a low solubility in water, however acridine is soluble in water at low pH values²⁵.

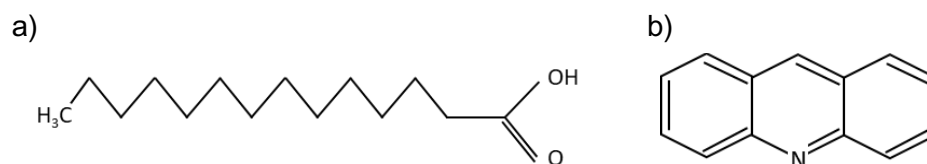


Figure 2. Molecular structures of; a) myristic acid; and b) acridine.

Experimental Apparatus and Procedure

Experiments were performed in a standard three electrode glass cell with an X65 carbon steel rotating cylinder electrode (RCE) working electrode, a platinum-coated titanium mesh counter electrode, and an Ag/AgCl (KCl saturated) reference electrode. Before each experiment, the RCE was sequentially polished with 400 and 600 grit silicon carbide abrasive papers, cleaned with isopropanol in an ultrasonic bath, and air-dried. Both oil and water solutions were deoxygenated for 1 hour by sparging with CO₂ before the introduction of the working electrode. After the RCE was inserted into the glass cell, a pre-corrosion test was conducted to determine whether the initial corrosion rate was close to the blank test corrosion rate to ensure no contamination occurred from the previous test. Linear polarization resistance (LPR) measurements were taken using a Gamry potentiostat. To minimize the noise in electrochemical measurements caused by CO₂ sparging, the sparge tube was retracted into the headspace during data acquisition. The solution was sparged with CO₂ throughout the test to prevent air (oxygen) ingress and to saturate the test solution with CO₂. The pH was adjusted by adding deoxygenated hydrochloric acid or sodium bicarbonate solution during each experiment. The experiments were performed using two different procedures: one-time direct contact or intermittent wetting.

- I. One-time direct contact: The main glass cell was connected to a separate side glass cell used to change the level of the water phase in the main glass cell, enabling immersion of the specimen in oil and water, alternately. A schematic of this setup is shown in Figure 3. In this method, the experiments were performed in four steps:
 1. Pre-corrosion: The polished specimen was immersed in the water phase.
 2. Partitioning: 0.3 liters of an oil layer containing a surface-active compound was added to the top of the water phase. The polished specimen remained immersed in the water phase and rotated for one hour at 1000 rpm. Corrosion rate by LPR was measured every 20 minutes.
 3. Direct inhibition by oil: The water was drained from the side port of the glass cell until the polished specimen was immersed into the oil phase and rotation continued for one hour at 1000 rpm.
 4. Persistency: After immersion in the oil layer, fresh brine, prepared and sparged in the side glass cell, was gravity fed into the main glass cell so that the specimen was returned to the water phase. Corrosion rate by LPR was measured every 20 minutes until reaching a stable value.

A schematic of the procedure for these experiments is shown in Figure 4. The test matrix used to study the effect of direct contact with oil on corrosion rate is presented in Table 1.

1. Hot plate
2. Reference electrode
3. Temperature probe
4. Counter electrode
5. Rotator
6. Gas inlet
7. pH probe
8. Luggin capillary
9. Working electrode

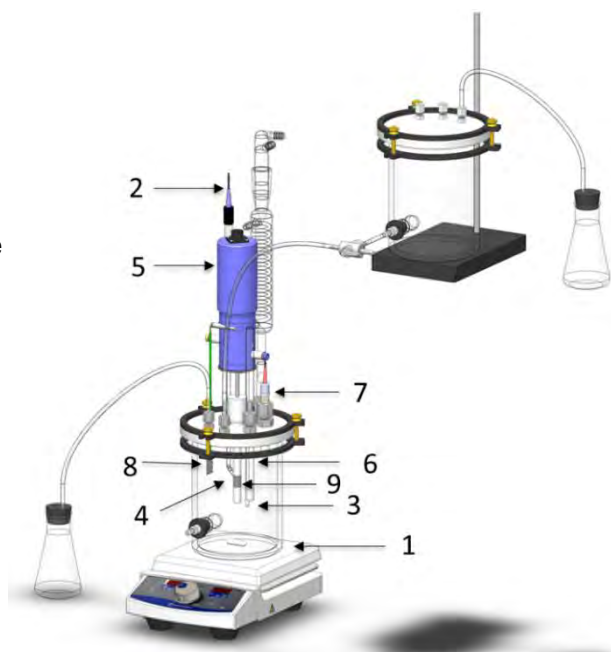


Figure 3. Schematic of main and side glass cells. The side glass cell is located on a shelf above the main cell.

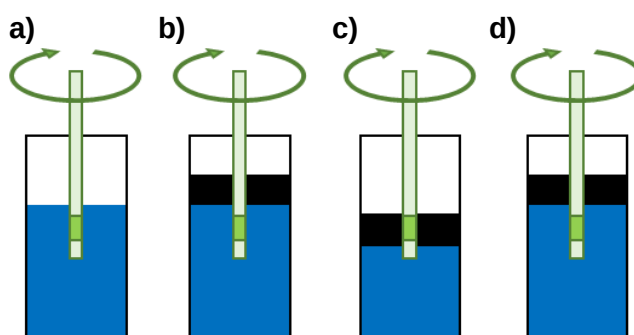


Figure 4. Procedure of one-time direct contact experiments: a) pre-corrosion; b) partitioning; c) direct inhibition by oil; and d) persistency.

Table 1. Test matrix to study the effect of one-time direct contact with oil on corrosion rate.

Parameter	Conditions
Material	X65
Solution	1 wt.% NaCl/model oil (15% of total liquid)
Model oil	LVT-200 (for myristic acid), 60:40 weight ratio of LVT-200 and Aromatic-200 (for acridine)
Surface-active compounds	Myristic acid, acridine (0.1 wt.% of oil phase)
Wetting regime	Direct contact with oil
Temperature	30°C
CO ₂ partial pressure	0.96
pH	4.0, 6.5
Experimental equipment	RCE, Glass cell
Electrochemical measurements	OCP, LPR, EIS, potentiodynamic

- II. **Intermittent wetting:** The electrochemical glass cell was connected to another reservoir glass cell to change the level of the water phase in the main glass cell, enabling placement of the specimen in oil and water, alternately. These two glass cells are connected to each other using a pump with two solenoid valves. A simple schematic of the intermittent wetting setup is shown in Figure 5. Experiments were performed therein in four steps as well, with the third step being different from the previous method. In this method, the “inhibition by oil” step consisted of alternating between oil wetting and water wetting instead of direct continuous contact with oil in order to facilitate improved simulation of intermittent wetting. The intermittent wetting step includes two sub-steps:
- Oil wetting step: Brine is pumped from the electrochemical cell to the reservoir cell to lower the oil layer, so the oil layer completely surrounds the specimen surface.
 - Water wetting step: Brine is pumped from the reservoir cell back to the electrochemical cell to lift the oil layer well above the specimen surface.

The wetting periods were initially repeated every 30 seconds for at least one hour. Since LPR measurements could not be performed during the intermittent wetting cycles (a cycle duration is too short to allow collection of LPR data), a different method had to be used to assess the corrosion response. To do so, the electrode potential was held at an arbitrary anodic potential of +60 mV vs. OCP, and the current response was collected. It is understood that the measured current does not correspond to the natural corrosion rate of the specimen, however, it can give indication on whether or not corrosion occurs.

Most of the experiments were performed considering wetting periods that were repeated every 60 seconds for one hour. 60 seconds cycles proved to be more practical than 30 seconds and yielded no significant difference on the results. For this sets, LPR was performed after the cyclic wettings. A schematic picture of the procedure for these experiments is shown in Figure 6. The test matrix used to study the effect of intermittent contact with oil on corrosion rate is presented in Table 2.

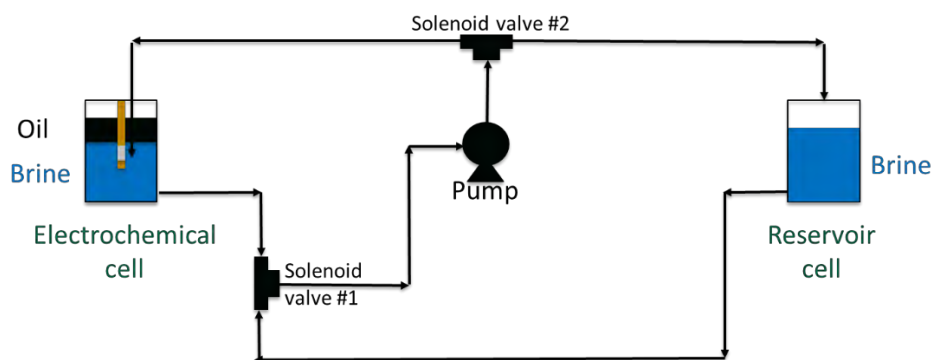


Figure 5. A simple schematic of the intermittent wetting setup.

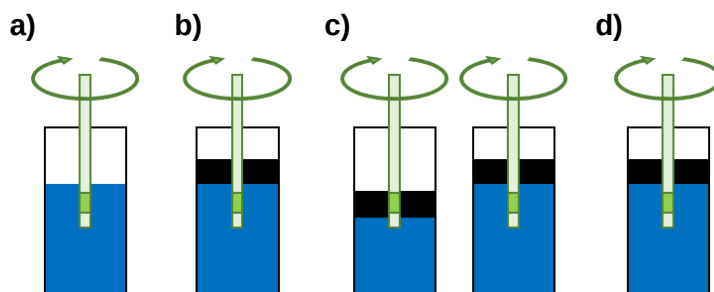


Figure 6. Procedure of intermittent wetting experiments: a) pre-corrosion; b) partitioning; c) oil/water intermittent wetting; and d) persistency.