Role of Interfacial Chemistry on Wettability and Carbon Dioxide Corrosion of Mild

Steels

A dissertation presented to

the faculty of

the Russ College of Engineering and Technology of Ohio University

In partial fulfillment

of the requirements for the degree

Doctor of Philosophy

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April 2017

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This dissertation titled

Role of Interfacial Chemistry on Wettability and Carbon Dioxide Corrosion of Mild

Steels

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ABSTRACT

BABIC, MARIJAN, Ph.D., April 2017, Chemical Engineering

Role of Interfacial Chemistry on Wettability and Carbon Dioxide Corrosion of Mild Steels

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Internal corrosion of oil and gas pipelines made from mild steel is a commonly encountered problem in the oil and gas industry. It is frequently associated with the presence of water that wets the steel surface and carbon dioxide which produces corrosive species in a water phase. This study addresses four aspects related to the role of interfacial chemistry on wetting and corrosion:

- Effect of crude oil foaming on corrosion inhibition.
- Effect of oil on foams produced by corrosion inhibitors and subsequent corrosion inhibition.
- Effect of ionization of naturally present crude oil compounds on wetting and corrosion inhibition.
- Effect of residual carbide corrosion products on steel wettability and wetting.

The effect of crude oil foaming on corrosion inhibition was investigated with model compounds chosen to represent polar compounds in real crudes with dual foam-forming and corrosion inhibition properties; the investigations were performed in a small scale experimental apparatus. It was found that corrosion inhibition properties of oils were unaffected by the foaming process.

The effect of oil on inhibitor-induced foaming was studied in small scale tests with an imidazoline-type corrosion inhibitor and two oils of different chemical composition. The results showed that the hydrocarbon oil can suppress foam generation, effectiveness of corrosion inhibitor can be partially preserved when the layer of oil is in the contact with a foaming aqueous solution.

The influence of pH on corrosion inhibition by polar crude oil compounds on their corrosion inhibition and wetting properties was determined using a model oil. Experiments were again performed using an in-house designed and built apparatus for wetting measurements in dynamic conditions. It was shown that pH can significantly alter the corrosion and wetting properties of steel by ionizing crude oil polar compounds.

In the last segment of the study the wettability of corroded surfaces was investigated. It was found that carbide layers were more hydrophobic compared to the initial steel surface. However, the water which stays entrapped within the porous carbide layer creates confined aqueous environments that have the potential to significant affect corrosion. DEDICATION

To my family and friends

for their love, care and support during this journey

ACKNOWLEDGMENTS

I would like to thank many people who in a distinct way contributed during the process of making this dissertation. At first, I am thankful and forever indebted to my advisor and chair of my dissertation committee, Dr. Srdjan Nesic for his guidance, understanding and support during my Ph.D. studies. His understanding of the 'philosophy of nature' inspired me to think 'out of the box' and encouraged me during my work. I would also like to extend this appreciation to Prof. Savas Kaya, Prof. Monica Burdick, Prof. David Ingram, and Dr. Katherine Cimatu for serving on my PhD committee. I am forever thankful to my coworkers in the Water Wetting JIP; Dr. Sonja Richter, for sharing her knowledge and expertise, for being patient, supportive and intuitive; and Dr. Kok Eng Kee for the thoughtful advice, 'endless' dialogues and encouragement during the 'hard times'. Special thanks to Dr. David Young, Dr. Luciano Paolinelli, Dr. Gheorghe Bota and Dr. Amr Saleh for their support to bring this dissertation to an end. I would like to extend my sincere gratitude to ICMT affiliates, Dr. Fernando Farelas, Dr. Bruce Brown, Dr. Winston Robbins, Dr. Marc Singer and Dr. Yoon-Seok Choi for their advice and useful discussions. I express my special appreciation to ICMT employees Rebecca Gill, Albert Schubert, Phillip Bullington, Cody Shafer, Alexis Barxias, Steve Upton, and Daniel Cain for their administrative and technical support in the laboratory work. Finally, I would like to express my gratitude to all fellow students from the ICMT, my former officemates and guys from the 'Isle of Awesomeness' for their friendship, help and encouragement. A special place in my heart have faculty and students of the Ohio University School of Film who were in their unique way part of these graduate studies.

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CHAPTER 1: INTRODUCTION

"Interface, of the resonant interval as 'where the action is', whether chemical, psychic or social, involves touch."

M. McLuhan & E. McLuhan

Interfaces are places where phases meet. In this context the word *phase* does not refer to state (gas, liquid or solid) but to separate entities (components) within the system. Although McLuhans referred to philosophical concepts, several words from their quote are applicable to what is discussed in this dissertation [1]. Wetting and corrosion are both processes that involve surfaces and interfaces. In general, wetting is defined as the action in which one liquid spreads over the surface of a solid or another immiscible liquid [2]. Likewise, corrosion is a process which happens at the surface of the material due to contact with its environment [3]. This chapter introduces basic concepts related to wetting and corrosion in the oil and gas pipelines.

Foundations

Pipeline transmission is the dominant method for conveying crude oils and natural gases. This is particularly cost effective for transporting large amounts of fluids over long distances. In the oil and gas industry, pipelines and tubulars are utilized for transmission of a range of fluids associated with various stages of production and processing [4], [5]. Examples include lines for injection of water or carbon dioxide into rock formations, casings and downhole tubulars which carry fluids from wells to the surface, production pipelines which transport oil, gas and other fluids from the wellheads to separation

facilities then onwards and, finally, transmission pipelines that transport purified oil, gas and petrochemicals products from refineries (Figure 1) [6].



Figure 1 – Schematic representation of typical pipeline usage for extraction and processing of crude oils. Adapted from reference [6].

Various metallic alloys are utilized as pipeline construction materials. However, due to the balance between mechanical properties and cost, carbon steels are always the first choice insofar as they can meet technical requirements [7], [8]. In particular, carbon steels with low content of carbon and other alloying elements are commonly employed because of their suitable mechanical properties and ease of use for pipeline fabrication, e.g., for welding. Those steels are sometimes termed 'mild' owing to their low carbon content, which generally does not exceed 0.3 wt.%, and excellent formability characteristics [9].

Carbon steel is, like other materials, prone to degradation caused by interactions with the environment, especially corrosion. Corrosion which can occur at internal and external pipeline surfaces presents a serious problem to pipeline integrity [10]. According to one report, about 68% of all energy related pipeline failures in the Canadian province of Alberta were attributed to corrosion, which predominantly occurred on internal surfaces. Internal corrosion was responsible for 57% of failures in water pipelines, 51% of production pipelines, 21% of oil transmission lines and 53% of natural gas pipelines. In total, 55% of failures in all pipelines combined were due to internal corrosion [11].

Corrosion attack can appear in several forms. In uniform (general) corrosion sections of pipeline corrode at a relatively even rate, while in various forms of localized corrosion such as pitting, underdeposit or crevice corrosion, as well as various forms of environmentally assisted cracking, corrosion attack is spatially confined and notably more intense compared to adjacent areas [3], [10]. In most cases corrosion of carbon steel pipelines is an electrochemical process. Alongside solely electrochemical processes, degradation can be the result of combined electrochemical-mechanical and/or microbiological processes. In the former case, named erosion-corrosion, deterioration is caused by dispersed solid particles which collide with the pipe wall. The latter, termed Microbiologically Influenced Corrosion (MIC), is governed by bacteria [6], [12], [13].

In pipelines, electrochemical corrosion occurs due to the two key factors are prerequisites for internal electrochemical corrosion processes in pipelines:

- The presence of water at the internal surface of the pipe.
- Dissolved chemical species that react with iron surface.

The presence of water and corrosive species in pipelines does not necessarily lead to corrosion. Corrosion occurs only if water with dissolved corrosive chemical species wets

the steel surface. This condition is not always satisfied, considering the fact that pipelines carry oil, water and gas phases and that all three can contact and/or wet, certain areas of the internal pipe wall. Areas of the steel which are not wetted with water do not corrode [14], [15]. Naturally present chemical species dissolve therein, generating acid that reacts with iron in the formed aqueous conditions at the steel surface [7], [15]; the environment is typically anoxic. Water and corrosive chemical species such as CO₂, H₂S and organic acids are omnipresent in upstream oil and gas pipelines [16].

Motivation

Current understanding of relevant interfacial phenomena mostly accounts for the chemical and physical alteration of the water-steel surface since the corrosion process takes place at that interface. This also relates to precipitation of corrosion products and adsorption of corrosion inhibitors which alter the steel surface [17], [18]. Corresponding-ly, much of the previous research work has been undertaken in order to understand the process which lead to adsorption of compounds at the steel surfaces or precipitation of corrosion products. These studies mostly focus on the corrosion mechanisms, formation of corrosion product layers, and adsorption mechanisms for a variety of corrosion inhibitors [19], [20].

Much less attention has been paid to the fact that existence of other interfaces can directly or circumstantially affect corrosion. In oil-water concurrent flow in pipelines three interfaces are present: water-steel, water-oil and steel-oil. In a simultaneous flow of oil, water and gas, three additional interfaces are present: water-gas, oil-gas and steel-gas. As a result, any alteration of interfaces linked with those two processes can potentially affect corrosion or change the steel wetting properties.

The role of additional interfaces is mostly recognized in research related to so-called 'parasitic' adsorption of corrosion inhibitors on competitive surfaces [21]. 'Parasitic' adsorption relates the capability of some surface active corrosion inhibitors to adsorb at interfaces other than water-steel. Adsorption of considerable inhibitor quantities at those interfaces can result in loss of inhibition due to the simultaneous decrease of the amount of inhibitor at steel surfaces. Most of the available studies in the literature are related to this phenomenon, dealing with adsorption of water-sand and water-oil interfaces [22]–[24]. On the contrary, research regarding parasitic adsorption at the water-gas interface is lacking. In particular, it has been recognized that surface active corrosion inhibitors can create foams which leads to formation of large water-gas interfacial areas where significant amounts of those substances can be consumed [25], [26]. However, the effect has not been investigated in depth. Furthermore, formation oil-based foams containing similar substances has not been investigated at all.

Other aspects that received some, but not sufficient, attention are phenomena occurring at the steel-oil interface. These can be divided into two categories: wetting of precorroded surfaces and adsorption of oil soluble compounds. The first aspect related to phenomena at the steel-oil interface which received limited attention is the interaction of corrosion product on wettability of steel surfaces. Certain data is available for ironcarbonate and iron-carbide layers [27]–[30]. However, so far experiments with ironcarbide layers were performed only in the presence of surface active substances, therefore, the influence of iron-carbide remained unknown. The second aspect of was addressed in several previous studies conducted at the Institute for Corrosion and Multi-Multiphase Technology (ICMT) which investigated the influence of naturally present oil soluble compounds on corrosion inhibition and surface wettability [31]–[33]. Nevertheless, determination of the exact mechanism of their action, even after the undertaken research, remains elusive. Furthermore, interactions with the aqueous phase which can lead to ionization and change of properties of some of those compounds has not been investigated.

Corrosion engineers need to understand how the alteration of interfaces other than water-steel can affect corrosion and when they need to be accounted for. Therefore, investigations of this kind are needed in order to clarify and make future predictions of corrosion rates in pipelines more accurate. Here lies the main motivation for the present work, to extend and deepen the present knowledge related to the role of interfaces on steel wetting and corrosion.

Dissertation Outline

The dissertation is divided into eight chapters and seven appendices. In Chapter 2 a background on CO_2 corrosion, water wetting, mild steel microstructure, corrosion inhibitors and crude oil chemical composition is presented. More specific literature reviews and experimental details are presented within each of the following chapters. In Chapter 3 research objectives are stated. Chapters 4 and 5 present investigations regarding the first study aim, foam formation and its influence on corrosion inhibition. Firstly, the influence of liquid hydrocarbon on foaming and corrosion inhibition by an imidazoline-type

inhibitor is discussed in Chapter 4. The second part analyses the foaming associated with crude oil's naturally occurring surface active compounds and its influence on corrosion in Chapter 5. The next two Chapters discuss the second and third study aims - ionization of polar organic compounds and formation of iron carbide corrosion product layers and their influence on wettability and corrosion. The main focus of Chapter 6 is formation of corrosion product layer and its effect on wettability of steel surfaces. Chapter 7 examines the role of water chemistry on polarizable crude oil model compounds and how polarization affects corrosion inhibition and surface wettability. Conclusions and suggestions for future work are outlined in Chapter 8. Finally, seven appendices contain information about materials and experimental techniques employed in this research.

CHAPTER 2: BACKGROUND

Internal corrosion of pipelines depends on several processes which occur at interfaces. In particular, corrosion in pipelines can occur only if water wets the steel surface. In crude oil pipelines, this so called 'water wetting' situation is encountered due to the existence of steel-water interfaces. The second interfacial process which governs corrosion is the electrochemical reaction between chemical species in the aqueous phase and the steel surface. Finally, corrosion rate depends on the existence and adsorption of particular molecular species at the steel surface which hinder the corrosion reactions.

Physicochemical properties of phases and their spatial distribution inside pipelines will determine how those three processes occur. In view of that, chemical composition of phases and their spatial distribution as well as processes of wetting, corrosion, and corrosion inhibition are introduced in this chapter.

Composition and Spatial Distribution of Phases inside Pipelines

One of the most important aspects for understanding mechanisms of wetting and corrosion is knowledge of the characteristics and their spatial distribution of each of the three phases involved in interfacial processes in pipelines relating to:

- Composition and microstructure of the mild steel
- Chemical composition of crude oil
- Water chemistry and aqueous speciation of carbonic species
- Oil-water-gas multiphase flow

Each is reviewed in the following sub-sections, with an emphasis on CO_2 in the discussion of water chemistry and speciation.

Composition and Microstructure of Mild Steels

By definition, steels are alloys which contain iron and at least one other element [34], [35]. The most common alloying element is carbon, which can be present at concentrations of up to 2 wt.%; other common alloying elements include manganese, silicon, phosphorus, sulfur, chromium, nickel, copper, vanadium, niobium, and molybdenum. Under a microscope, steel is observed as a polycrystalline material composed of microscopic-sized crystalline phases, referred to as crystallites or grains. Size, shape and morphology of grains constitute the microscopic structure, or microstructure, of steels [36], [37].

Mild steel is a common name for steels with low carbon content and consequent good formability. Typically, pipeline steel grades which are termed "mild" contain carbon in concentrations less than 0.4 wt.% with up to several percent of other alloying elements present either as direct additives or as residual elements introduced by raw materials in the steel-making process [35], [38]. Pipeline mild steels can have a wide variety of microstructures from different steel manufacturing processes. Therefore, the term mild steel is used by pipeline fabricators to mostly reflect its good weldability and cold forming characteristics, rather than for a steel with a standardized chemical or microstructural composition and/or set of mechanical properties [39].

Single-phase microconstituents of steel include δ -ferrite, austenite (γ -Fe), α -ferrite (cubic α -Fe), cementite (iron carbide), and martensite (body centered tetragonal Fe). Common two-phase constituents of mild steel that combine iron and iron carbide are pearlite and bainite [34]. Pipeline mild steel microstructures commonly possess grains of ferrite, pearlite, and discrete cementite that can be described as being ferritic-pearlitic, martensitic, or bainitic; as well as combinations thereof [4], [37]. The ferritic-pearlitic microstructure is probably the type that is most commonly encountered [40], [41].

The aforementioned microstructural compositions result from different concentrations of alloying elements and applied heat treatments during steel production and processing. Formation of various microconstituents is commonly presented as a function of important processing parameters: carbon content, temperature and time. The iron - iron carbide (Fe-Fe₃C) phase diagram shown in Figure 2 can serve as a guide to illustrate the existence of phases as a function of temperature and carbon content. However, the Fe-Fe₃C phase diagram does not confer information relating to microstructural phases which are products associated with different cooling kinetics or heat treatments. Therefore, the transformation of austenite is commonly shown in transformation diagrams, also termed TTT (time temperature transformation) diagrams and CCT (continuous cooling transformation) diagrams. Figure 5 shows an example of a CCT diagram for one mild steel in which the formation of phases are shown as a function of constant cooling rates. It is important to note that the presences of alloying elements alter the position of the phase boundaries on the iron-iron carbide phase diagram and CCT/TTT diagrams.



Figure 2 – Iron – iron carbide (Fe-Fe₃C) phase diagram. Adapted from reference [42].

The δ -ferrite is a carbon steel phase with which exists only at high temperatures. The crystal structure of this iron allotrope is body centered cubic (BCC) with a lattice parameter of 2.93 Å, as shown in Figure 3 [43]. As can be seen in Figure 2, in pure iron-carbon alloys, δ -ferrite is the sole phase when the carbon content is less than 0.1wt.% at high temperatures, below which it transforms to austenite. This phase is normally absent at room temperature; its presence can be facilitated by addition of high concentrations of manganese, a common alloying element encountered in production of mild steels [44].



Figure 3 – Body centered cubic crystal structure. Adapted from reference [34].

Austenite is a parent phase for the formation of all the other phases encountered in mild steel. Typically, observed microstructural phases are obtained by transformation of austenite by cooling to temperatures below 910 °C [35], [45]. The crystal structure of austenite (γ -Fe or γ -iron) is face-centered cubic (FCC), with the lattice parameter of 3.65Å [43].



Figure 4 – Face centered cubic crystal structure. Adapted from reference [34].

The crystal structure of austenite can accommodate considerably higher concentrations of interstitial atoms compared to other allotropic modifications of iron. The single most important interstitial element, carbon, can be dissolved in concentrations as high as 2 wt.%, as shown on the iron – iron-carbide diagram. The other alloying elements are dissolved either interstitially or substitutionally. Ideally, carbon and alloying elements are uniformly distributed in the austenite prior to its transformation. However, steels heated into the austenite phase field may contain other phases such as undissolved inclusions, carbides, and microalloying elements [35].

The austenite phase is thermodynamically stable only at high temperatures and normally does not exist at room temperatures although some austenite can be present at room temperatures in a metastable state, in which case is termed as retained or residual austenite [46]. The temperatures at which transformations occur and structure of microconstiuents obtained after transformation are largely dependent on both the cooling rate and the presence of alloying elements. Figure 5 illustrates formation of phases resulting from transformation of austenite for various steel cooling rates [47]. The numbers on the diagram denote the percentage of austenite which transformed to the particular microconstituents; the labelled microconstituents which result from decomposition of austenite are described below.



Figure 5 – Constant cooling diagram of low-carbon, low-alloy mild steel. Adapted from reference [47].

The α -ferrite (α -Fe) phase consists of iron atoms which form the body-centered cubic (BCC) crystal structure, identical to δ -ferrite, but with the lower lattice parameter of 2.93Å [43]. At room temperature ferrite can contain up to 0.008 wt.% of carbon in interstitial lattice sites, this percentage gradually increases with temperature to 0.022 wt.%; see the phase diagram in Figure 2. There are several types of ferritic phases such as polygonal (equiaxed) ferrite, Widmanstätten ferrite, quasi-polygonal ferrite, acicular ferrite and granular ferrite which differ in their morphology [35]. Polygonal ferrite grains form as a proeutectiod phase at slow cooling rates at or inside austenite grain boundaries. Widmanstätten ferrite has an elongated structure, and forms at lower temperatures and faster cooling rates than polygonal ferrite. Quasi-polygonal ferrite forms in very low

carbon steels during rapid cooling, when the ferrite phase can accommodate all the carbon from the austenitic phase. The shape of the quasi-polygonal ferrite is similar to polygonal ferrite, but differs in the shape of grain boundaries and the existence of a subgrain structure. Acicular (bainitic) ferrite consists of fine, needle-shaped grains. Granular ferrite is equiaxed in shape.

Cementite forms when the solubility limit of carbon in iron is exceeded. It is obtained during the slow cooling process of an iron-carbon mixture which, *via* diffusion processes relating to carbon, permits formation of this phase. Cementite is an iron carbide compound with formula Fe₃C and an orthorhombic crystal structure. By weight, it contains approximately 93.3% of iron and 6.7% of carbon. The crystal structure of iron carbide is orthorhombic, with the lattice parameters of 4.51Å, 5.08Å and 6.73Å as shown in Figure 6 [43], [45]. During carbide formation some alloying elements, such as Cr, Mo, W, and V can be found in the carbide and alter the composition of this phase.



Figure 6 – Orthorhombic crystal structure of cementite. Adapted from reference [34].

At fast cooling rates austenite can partially or completely transform to a martensite phase. Martensite is a metastable phase and may be considered as a supersaturated solution of carbon in α -iron with an elongated unit cell. At fast cooling rates, the temperature at which transformation occurs is reduced and may occur at approximately 400°C or below depending on the alloying involved [44]. Transformation at these temperatures is a diffusionless process. Cementite cannot be formed and iron becomes supersaturated with carbon. The martensitic structure has a highly strained body-centered tetragonal (BCT) crystal structure with respect to the iron atoms with carbon atoms retained in interstitial positions [36].



Figure 7 – Tetragonal body centered crystal lattice of martensite. Adapted from reference [35].

The z-sites in this figure are the octahedral interstitial sites common to the FCC structure of austenite and BCC structure of ferrite and, therefore, can be occupied by carbon. Since the transformation is from FCC to BCC and is diffusionless, the interstitial carbon atoms are limited to the one common octahedral site in both the FCC and BCC structures. As a result BCC expands in the z-direction and distorts the shape of BCC of α -iron to BCT of martensite. When only substitutional solutes are present the transformed product is cubic while it is generally tetragonal if there are interstitial solutes present [44], [45].

Pearlite is a lamellar microconstituent comprised of two alternating crystalline phases, ferrite and cementite. The transformation of austenite into pearlite takes place as shown on the iron – iron carbide diagram (Figure 2). Alloying elements have a strong effect on the rate of formation and structure of pearlite. Elements such as manganese, chromium and vanadium partition to the cementite phase within pearlite lamellae, while elements such as silicon and aluminum partition to the ferrite phase [35].

Bainite is, like pearlite, composed of ferrite and cementite phases, but it forms at faster cooling rates. Due to the low solubility carbon concentrates at the ferrite grain boundaries. At sufficiently high concentrations of carbon, cementite nucleates and agglomerates. Bainite can be divided into upper bainite, which forms at higher temperatures and lower bainite, which forms at lower temperatures during transformation from austenite. The upper bainite will appear as needle-shaped ferrite, with carbides at the lath boundaries, while in the lower bainite carbide forms within the ferrite laths.

The tempered martensite microstructure results from a tempering process, when quenched steel that has yielded martensite is heated to temperatures below a critical temperature where it would be expected to transform to austenite, held isothermally, then cooled. At the elevated temperature, martensite transforms into ferrite and cementite. The cementite which forms consists of fine particles distributed within a ferrite matrix.

Most commonly, pipeline mild steels have ferritic-pearlitic microstructures, which consist of ferrite and pearlite grains [40]. Recent developments in pipeline steel technolo-

gy are aimed toward decreasing the carbon content from 0.2 wt.% to 0.05 wt.% and increasing the number of microalloying elements to yield superior mechanical properties. This compositional change confers a transition from ferrite–pearlite to ferrite–bainite or bainite–martensite microstructures in modern mild steels.

Composition of Crude Oils

Crude oils are defined as "naturally occurring mixture of hydrocarbons in a liquid state, which may also include compounds of sulfur, nitrogen, oxygen, metals, and other elements" [48]. Typically, elemental composition, with respect to mass, vary in the following ranges: 83%–87% of carbon, 10%–14% of hydrogen, 0.1%–2.0% of nitrogen, 0.05%–1.5% of oxygen, 0.05%–6.0% of sulfur and less than 1000 ppm of the metals Ni and V [48], [49]. An extremely large number of chemical species composed of the listed elements can be classified as hydrocarbon compounds, comprised only of carbon and hydrogen atoms, and non-hydrocarbon compounds, which contain additional elements (heteroatoms) and not solely carbon and hydrogen [48]. Content of hydrocarbon and nonhydrocarbon compounds greatly varies, depending on the geologic origin of the crude oil. In some light crudes, hydrocarbon content can be as high as 97 wt.%, while heavy crudes can contain as low as 50 wt.% of organic hydrocarbon constituents. Hydrocarbon compounds include alkanes (paraffins), including linear and branched chain, mono and polycyclic cycloalkanes (naphthenates), and aromatic derivatives with single or multiple benzene rings [48]. Non-hydrocarbon compounds (also termed NSO-s) exist as organic compounds with functional groups possessing sulfur, nitrogen, and oxygen as well as smaller amounts of organometallic compounds and suspended inorganic salts [49].

Sulfur-containing compounds include thiols (mercaptans), sulfides (thioalkanes and thiocycloalkanes), dithioalkanes (disulfides), thiophenols, and thiophene and thiphene derivatives. Some of the characteristic sulfur compounds are shown in Figure 8 [48], [49].



Figure 8 - Sulfur containing compounds. Adapted from reference [48].

Nitrogen containing compounds can be split into non-basic (neutral) and basic categories. As a rule of thumb, neutral nitrogen comprises about two thirds of the total nitrogen content. The non-basic nitrogen compounds are pyrrole, indole, carbazole and their homologues. Basic nitrogen compounds primarily consist of pyridine, quinolone, acridine and their alkylated derivatives. Some of the typical representatives of nitrogen containing compounds are shown in Figure 9 [48], [49].


Oxygen containing compounds mostly contain alcohol and carboxylic acid functionalities. Phenol and its derivatives are the most prevalent alcohol derivatives. Carboxylic acids are present as fatty acids, as short chain carboxylic acids and alicyclic (naphethenic) acids. Naphthenic acids are the most ubiquitous among carboxylic acids and contain single to multiple cycloalkane rings and aliphatic side chains. The presence of functionalities such as keto, ether, ester and anhydride is somewhat uncertain. An overview of some oxygen containing compounds is shown in Figure 10 [48], [49].



Figure 10 – Oxygen containing compounds. Adapted from reference [48].

Due to extreme variability of chemical compounds, crude oil composition is typically described through fractional composition. Fractions differ from one another in solubility and adsorptive character and can provide satisfactorily good compositional information for oil processing applications. Several standard methods have been developed which describe fractional information such as SARA, USBM-API, ASTM D2006 and ASTM D20007 [48], [50], [51]. SARA (or SAPA) is one of the most common standard methods for describing oil fractionation whose name is derived as an acronym of the four fractions: saturates, aromatics, resins (polars), and asphaltenes. A schematic of the fractionation process is given in Figure 10 [48].



Figure 11 – SARA separation scheme. Adapted from reference [51].

The compounds which are soluble in pentane are termed maltenes or petrolenes and are further classified based on their adsorption properties onto silica as saturates, aromatics and resins. The saturates fraction consists predominantly of saturated hydrocarbons including paraffins and cyclic paraffins. The aromatic fraction mostly includes substituted single (benzene) and multiple (naphthalene and phenantrene) fused benzene ring compounds. The composition of the resin fraction is not well known. It has been determined that compounds in this fraction contain hydroxyl groups, nitrogen functionalities, such as pyrrole(s) or indole(s), acid and ester functionalities as well as carbonyl functionalities. Ether or sulfur–oxygen compounds are also thought to be present in this fraction [48]. Asphaltenes are defined as pentane insoluble - benzene soluble fractions. The elemental composition of this fraction is different compared to petroleum, mainly in the higher carbon/hydrogen ratio and by higher content of heteroatoms. It is assumed that the molecular structure of asphaltenes may be based on large polycyclic aromatics, with molecular weights of up to several thousand atomic mass units, with alkyl side chains and incorporation of heteroatoms. However, their nature and structure remain a matter of controversy [49].

Water Chemistry and Aqueous Speciation

Water originating from petroleum reservoirs is termed as formation or connate water when inside rock formations, and produced water when brought to the surface with crude oil or natural gas [52]. Its composition is qualitatively similar between sources, but concentration of component species can vary by orders of magnitude. Typically, water co-produced with oil or gas contains cations and anions from dissolved minerals (Na⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺, Cl⁻, SO₄²⁻, CO₃²⁻, HCO₃⁻), dissolved and dispersed crude oil compounds (including polar species) with low to medium carbon number, production chemicals, solid particles, bacteria, waxes, asphaltenes, and dissolved gases [53].

For CO₂ corrosion concentration of carbonic species is especially important. Carbon dioxide is an acidic gas that is fairly soluble in water. However, only a small portion (approximately 0.2 mol%) is hydrated and forms carbonic acid, H₂CO₃. Carbonic acid is a weak, diprotic acid which dissociates in two steps into hydronium (H₃O⁺), bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions [54].

Initially, the following equilibrium is established between gaseous and dissolved CO₂:

$$CO_2(g) \rightleftharpoons CO_2(aq) \tag{1}$$

For low partial pressures of CO_2 , solubility in water is governed by Henry's law where the solubility constant, K_{sol} , is defined as:

$$K_{sol} = \frac{C_{CO_2}}{pCO_2} \tag{2}$$

 K_{sol} depends on the temperature and the ionic strength of the solution. It can be calculated using the following empirical equation [55]:

$$K_{sol} = \frac{14.5}{1.00258} \times 10^{-(2.27+5.65\times10^{-3}T_f - 8.06\times10^{-6}T_f^2 + 0.075I}$$
(3)

Where T_f is the temperature in Fahrenheit scale and I is the ionic strength of the solution:

$$I = \frac{1}{2} \sum_{i} c_{i} z_{i}^{2} = \frac{1}{2} (c_{1} z_{1}^{2} + c_{2} z_{2}^{2} + \cdots)$$
(4)

Where c_i is the concentration of each species in the solution (mol/L) and z_i is the charge of the chemical species (dimensionless). As stated above, only a small fraction of dissolved CO₂ is hydrated and forms carbonic acid:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \tag{5}$$

The corresponding equilibrium constant for hydration, K_{hy} , is defined as follows:

$$K_{hy} = \frac{C_{H_2CO_3}}{C_{CO_2}}$$
(6)

The value of the constant does not change with pressure and only insignificantly between temperatures of 20°C and 100°C [40], [56]:

$$K_{hy} = 2.58 \times 10^{-3} \tag{7}$$

Formed carbonic acid dissociates into hydrogen and bicarbonate ions:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{8}$$

The equation for the equilibrium constant K_{ca} of the reaction is given as follows:

$$K_{ca} = \frac{C_{H} + C_{HCO_3^-}}{C_{H_2CO_3}}$$
(9)

The value of this equilibrium constant depends on the temperature, pressure and ionic strength [55]:

$$K_{ca} = 387.6 \times 10^{-\left(6.41 - 1.594 \times 10^{-3} T_f + 3.52 \times 10^{-6} T_f^2 - 3.07 \times 10^{-5} p - 0.4772 I^{\frac{1}{2}} + 0.11807 I\right)}$$
(10)

The value of partial pressure (p) is in bar. Bicarbonate ions further dissociate into carbonate and hydrogen ions:

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \tag{11}$$

The equilibrium constant, K_{bi} , for this second dissociation step is defined as:

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$$K_{bi} = \frac{C_{H} + C_{CO_3^{2-}}}{C_{HCO_3^{-}}} \tag{12}$$

For a range of conditions its value can be calculated from [55]:

$$K_{bi} = 10^{-(10.61 - 4.97 \times 10^{-3}T_f + 1.331 \times 10^{-5}T_f^2 - 2.624 \times 10^{-5}p - 1.66I^{\frac{1}{2}} + 0.34661I)}$$
(13)

In aqueous systems the equilibrium associated with the dissociation of water is also considered:

$$K_{wa} = C_H + C_{OH^-} \tag{14}$$

The value of K_{wa} is temperature dependent [57]:

$$K_{wa} = 10^{-(29.3868 - 0.0737549T_k + 7.47881 \times 10^{-5}T_k^2)}$$
(15)

Where T_k is the temperature in Kelvin.

In order to obtain equilibrium concentrations of all species in the aqueous phase $(CO_2, H_2CO_3, HCO_3^-, CO_3^{-2-}, H_3O^+ \text{ and }OH^-)$ associated with the partial pressure of CO_2 in the gas phase (pCO₂), one has to solve in combination the system of equations (2), (6), (9), (12) and (14). Due to the higher number of variables (seven) than equations (five), this can be performed by reducing the number of variables and increasing the number of equations. In a practical sense a solution can be achieved either by measuring one concentration (such as pH or partial pressure of CO_2) and introducing one more equation which relates existing variables or by measuring the values of two variables, e.g., partial pressure of CO_2 and pH.

In a so-called open system, which is approximated for pipelines, partial pressure of CO_2 is considered to be constant. If the partial pressure is known, and taking into consideration the above equilibrium processes, concentrations of species can be calculated by

introducing the electroneutrality equation (16) which balances concentrations of charged species in an aqueous solution:

$$C_{H^+=}C_{OH^-} + C_{HCO_3^-} + 2C_{CO_3^{2-}}$$
(16)

The above equation is applicable only if the system does not contain any additional charged species, in which case additional equations need to be included [19].

For the same system, considering the constant and known partial pressure of CO_2 , distributions of species can be obtained by measuring a particular variable, such as pH. An example of the distribution of species for a range of pH values is shown in Figure 12 for the CO_2 partial pressure of 1 bar, at 25°C, and ionic strength 1.



Figure 12 – Concentration of carbonic species as a function of pH for an open system at a temperature of 25°C and CO_2 partial pressure of 1 bar.

This approach is convenient in situations when other ionic species in the system alter the solution pH of and accurate values can be obtained, e.g., in the laboratory. In the case when pH is unknown, distribution of species can be obtained by measuring concentration of other species, such as bicarbonates. This method is common in the field, when the water pH is not usually known [58].

Multiphase Flow and Flow Patterns

Simultaneous flow of two or more phases, such as oil, water, gas or solids is defined as multiphase flow [59], [60]. That is, multiphase flow can both refer to concurrent flow of gas and liquid, as well as concurrent flow of two mutually insoluble liquids, such as immiscible oil and water [59], [61]. In the production of oil and gas, multiphase flow is encountered during the simultaneous pipeline transport of produced hydrocarbons, water and gases from wells to separation facilities [61]. In addition, multiphase flow can be encountered in crude oil trunk lines after the separation stage due to the presence of small amounts of residual water in predominantly hydrocarbon environments.

In multiphase fluid flow, components distribute themselves differently in space and time in a way that certain distinctive types of flows are observed [61], [62]. For example, two immiscible fluids such as oil and water can simultaneously flow by forming separate continuous layers or one fluid can be completely or partially dispersed in a continuous phase of another fluid. These distinctive types of geometric distribution of components can be classified by flow pattern type, also termed flow regimes [59]. In oil-water or oil-water-gas flows, specific flow patterns result from a diverse range of flow parameters

such as fluid flow rates, volumetric fractions, and physicochemical properties of fluids and how they relate to pipe diameter, inclination or specific geometric features [61].

Two broad categorizations of flow patterns can be described based on the extent of separation of phases [59]; namely as dispersed or separated flow regimes. A disperse flow pattern is where one of the phases is broadly distributed in the form of droplets or bubbles, whilst a separated flow consists of separate streams of two or more phases [59], [63]. Dispersed flow can be further classified according to the phase which is the continuous phase in the pipe [63]. For example, dispersed flow of oil and water can be oil dominated where oil is the continuous phase containing dispersed oil, or water dominated when water is the continuous phase containing dispersed oil, as shown in Figure 13.



Figure 13 – Classification of flow regimes based on the global separation of phases: oilwater separated flow (A), oil dominated water dispersed flow (B) and water dominated oil dispersed flow (C).

It is important to note that there is no universal standard regarding the classification and naming of flow patterns. Depending on the type of fluids present and experimental conditions researchers have identified various oil-water and oil-water-gas flow patterns [63]–[67]. Flow patterns are typically displayed in the form of flow maps in which specific flow patterns are presented as a function of fluid flow rates [59]. Figure 14 and Figure 15 show the flow patterns encountered in horizontal oil-water and oil-water-gas flows based on experiments performed by Kee [61], [68].



Figure 14 – Flow map showing flow patterns in horizontal oil-water pipe flow. Adapted with permission from Kee [61].

A flow map illustrating how flow regime changes with water cut and liquid velocity is shown in Figure 14. *Stratified smooth* flow corresponds to a continuous flow of oil and water where the phases present are separated at a smooth interface. This regime occurs at oil and water flow velocity ratios close to unity, the phases are clearly separated and no mixing is evident. In the *stratified with globules* flow regime all the water present is dispersed in the form of droplets and globules which travel in clusters at the bottom of the pipe. Water does not form a continuous layer. In the *stratified with mixing layer* flow pattern the phases are partially dispersed, one into the other. Continuous layers of oil and water phases are separated with the dispersed layer which can consists of water droplets in the oil phase and oil droplets in a water phase. The *semi-dispersed* flow regime is characterized by dispersed water droplets which are inhomogeneously distributed across the pipe cross-section. Due to gravity, a majority of the larger droplets move in the lower section of the pipe. In *fully-dispersed* flow droplets are small and relatively homogenously distributed across the pipe. This flow regime is favored when the ratio of oil to water liquid velocities is high [61].



Figure 15 – Flow map showing flow patterns in horizontal oil-water-gas pipe flow. Adapted with permission from Kee [61].

Kee also constructed a flow map illustrating how mixture liquid velocity and gas velocity governs encountered flow regimes, shown in Figure 15 [61]. Stratified flow patterns of oil, water and gas are regarded as flow of fluids with nearly complete separation of phases, this corresponds to three phases flowing concurrently in a tubular and

separated by smooth interfaces; slight dispersion between oil and water and waviness between gas and oil phases may be observed. In elongated bubble (EB) type of flow oil and water move continuously while the gas travels intermittently in the form of gas plugs at the top of the tubular. Some dispersion is present between the water and oil phase, but without entrained gas bubbles [61]. Slug flow is a form of flow where top of the pipe is predominantly filled with gas and fast moving waves of liquid intermittently bridge the whole pipe cross-section. This type of flow is highly turbulent and significant mixing of fluids occurs with the passage of every liquid slug. Gas is dispersed in the form of small bubbles or foam, while water is lifted from the bottom in the form of droplets. Partial separation of fluids occurs between the transits of two consecutive slugs[61]. Wavy annular type of flow is characterized with intermittent liquid waves which do not reach the upper section of the pipe. The flow is highly dispersed due to the mixing caused by the high velocity of a gas phase. The top section of the pipe is wetted by mist and foam created by passing waves. Water is dispersed in the oil as well as the gas phase [61]. In annular-mist flow a majority of the liquid is distributed around the circumference of the pipe, while the high velocity gas and mist travel inside the pipe core. Thickness of liquid layers at the top and bottom is uneven due to gravity. This type of flow causes very high mixing of fluids between all phases. A high number of small liquid droplets is entrained in the gas core and liquid layer at the top of the pipe wall [61]. Existence of different flow patterns has a profound effect on corrosion and is utilized as a basis for modeling of surface wetting, which is presented in the following section.

Wetting of Steel Surfaces

Corrosion in pipelines can occur only if water wets the steel surface. Alongside chemical reactions in which the aqueous phase forms corrosive species from precursors such as CO₂, H₂S or acetic acid, water enables transport of chemical species to and from the surface and engages in corrosion reactions which lead to oxidative dissolution of steel. The condition in which water wets the surface is noted as the 'water wetting' state, as opposed to 'oil wetting' when oil is in the contact with the surface. It is generally accepted that factors which lead to one of those conditions can be flow related, which determine physical distribution of fluids inside the pipeline or related to local conditions at the steel surface [69]. Consequently, wetting phenomena in pipelines are analyzed and modeled within the scope of multiphase flow and surface wettability.

Flow Related Factors

Throughout their production life, crude oil and gas wells generate changing amounts of hydrocarbons and water. It is generally recognized that the probability of internal pipeline corrosion increases with increasing volume fraction of produced water *versus* extracted hydrocarbons [70]. Increased likelihood for corrosion arises from the fact that increasing the volume of produced water is one of the most important factors which enhances the probability of wetting the steel. In view of that, several simple models were developed which estimate that water wetting will occur when the water cuts are between 20% and 50% [71]–[73]. Although very important, water cut is not the only factor which determines the wetting state. Any amount of water which is positioned adjacent to the pipe wall can potentially wet the steel surface and cause corrosion [67], [69]. Conversely,

even when a larger amount of water flows close to the center of the pipe, away from a pipe wall, corrosion is prevented due to the lack of contact between water and steel. Therefore, establishing connections between multiphase flow (introduced in section 0), wetting, and corrosion can be achieved by determining the existence of different flow patterns which govern the spatial distribution of water inside a pipeline.

For flow regimes in which water forms a continuous phase or flows in a stratified layer, the likelihood for corrosion is high because the steel surface is constantly exposed to the corrosive environment [70]. However, if oil forms a continuous layer and water is dispersed, the probability for corrosion is decreased due to lack of contact, or intermittent contact, of water with the steel wall. Thus, the existence of water in the dispersed state and its entrainment in the bulk oil flow are taken as a principle criterion for assessing and modelling wetting behavior and, hence, the potential for corrosion.

In a dispersed water-in-oil turbulent flow droplets are continuously formed and destroyed by breakage and coalescence processes [61]. Multiple macroscopic parameters related to flow, piping, and fluid properties have an effect on droplet formation and breakup. *Flow velocities* of fluids influence dispersion through the level of turbulence. An increase of the flow rate increases the turbulent breaking forces which promote the droplet breakup process [61]. Also, turbulent forces are more easily sustained by the flow. Below a minimum velocity, the water droplets settle on the bottom of the pipe. Above this minimum velocity, the water droplets are entrained in the oil phase [74]. *Pipe geometry and inclination* have a profound effect on degree of dispersion. Horizontal, vertical and inclined pipe inclinations create distinct hydrodynamic properties which can create complicated wetting scenarios. *Fluid densities* play a role in that higher density differences between phases favor settling of one phase over the other, e.g., water over oil. The smaller density difference between oil and water in an oil-water dispersion system leads to harder phase separation by natural coalescence [61]. Increasing *oil viscosity* favors the entraining of water droplets in dispersions. Moreover, water droplets tend to sink more slowly in more viscous oil. Interfacial tension plays a role in opposing formation of droplets by turbulence. Therefore, a larger turbulent breaking force is required if interfacial tension between phases is higher [61].

The model of Wicks and Fraser calculates the minimum velocity at which oil can entrain the water in the form of droplets [75]. Five factors which govern the formation of droplets, namely oil and water densities, oil-water interfacial tension, oil viscosity, pipe diameter and oil velocity, were identified. A multiple step calculation based on Hinze's maximum droplet size formula and empirical data produces a minimal velocity needed for droplet formation and swiping from the pipe bottom; the model is suitable for low water cuts [70].

The most comprehensive wetting model has been developed in the Institute for Corrosion and Multiphase Technology [70]. The model was developed on the basis of previous model proposed by Brauner and Barnea for predicting the dispersed flow regimes by comparing two droplet sizes *maximum droplet size* and *critical droplet size* [76], [77]. *Maximum droplet size* - d_{max} is the maximum size of the water droplet that can resist turbulence in the oil-water flow. *Critical droplet size* - d_{crit}, is the maximum size of water droplet that can be sustained by the flow. If the diameter of maximum water droplet

size (d_{max}) is smaller than the critical water droplet size that can be sustained by the flow (d_{crit}) , water droplets are dispersed in the oil stream. Consequently, water does not form continuous phase and its contact with the steel surface is prevented [74].

Maximum droplet size diameter – d_{max} is calculated from the balance between turbulent forces and oil-water interfacial tension. Droplets having diameter larger than the maximum droplet size will be broken by the turbulence into smaller droplets. Depending on the droplet population density, two separate calculations are performed, one for dilute and for dense dispersions [70], [74].

For dilute droplet dispersions, the effect of turbulence is only on a single droplet. The maximum droplet size, d_{max} , for dilute dispersions can be calculated from a formula determined by Hinze [78]:

$$d_{max} = 0.725 \left(\frac{\rho_c}{\sigma}\right)^{-0.6} \left(\frac{2f_c U_c^3}{D}\right)^{-0.4}$$
(17)

Where ρ_c is the density of the oil phase, σ is the oil-water interfacial tension, f_c is the friction factor, U_c is velocity of the oil phase and D is the pipe diameter.

Calculation for dense droplet dispersions, takes into account the interaction of turbulence with a multiple droplets. For dense dispersions, d_{max} can be calculated from an expression derived by Brauner [76]:

$$d_{max} = 2.93 C_H^{-0.6} \left(\frac{\rho_c}{\sigma}\right)^{-0.6} \left(\frac{1-\varepsilon_d}{\varepsilon_d}\right)^{-0.4} \bar{e}^{-0.4}$$
(18)

Where C_H is a constant equal to 1, ε_d is the water cut and \overline{e} is the mean energy dissipation rate which can be calculated as follows:

$$\bar{e} = \left(\frac{dP}{dL}\right) \left(\frac{U_c}{\rho_c \varepsilon_c}\right) \tag{19}$$

Where dP/dL is the fractional pressure gradient and ε_c is the oil cut.

The critical droplet size, d_{crit} , is the maximum diameter of droplet which can be sustained by the flowing oil. Droplets having diameter larger than d_{crit} tend to concentrate close to the pipe wall, while those that are smaller are dispersed in the bulk oil phase. There are two criteria for calculating the critical droplet size, and each of them is depending on the pipe inclination [74].

The first criterion is based on gravity, which is dominant for horizontal and nearhorizontal pipe inclinations. The gravitational force acts in the downward direction and cause droplets to sink and concentrate at the bottom of the pipe. This is opposed by turbulent forces acting in the opposite direction. The key parameter associated with this is termed gravity critical droplet size, d_{CB} [77].

$$d_{CB} = \frac{3}{8} \frac{\rho_c}{\Delta \rho} \frac{f U_c^2}{g \cos \theta}$$
(20)

Where $\Delta \rho$ is the density difference between two phases, *f* is the friction factor, *g* is the acceleration due to gravity and $\cos\theta$ is the cosine of the pipe inclination angle. For droplets with diameter smaller than d_{crit}, turbulent forces are dominant, and *vice versa*, for droplets larger than d_{crit}, gravity is dominant [74].

For vertical and near-vertical flows, the effect of gravity is not dominant. However, big droplets tend to swerve from the direction of the flow. The key parameter in this case is termed the creaming critical droplet size, d_{CD} [70].

$$d_{CD} = \frac{0.4\sigma}{\Delta\rho g \cos\beta'} \tag{21}$$

Where β ' is the inclination angle of the pipeline. Droplets with diameter larger than the creaming critical droplet size tend to contact the wall surface due to the motion perpendicular to direction of flow [74].

Maximum droplet size that can exist in the pipe without further break up can be calculated as maxima of droplet sizes in dilute (17) or dense (18) solutions:

$$d_{max} = MAX(d_{max-dilute}, d_{max-dense})$$
(22)

Critical droplet size that can be sustained by the flow can be obtained as the minima of droplet sizes that can be sustained in the flow without sinking (20) or creaming (21):

$$d_{crit} = MIN(d_{CB}, d_{CD}) \tag{23}$$

The transition between dispersed and stratified flow can then be expressed as:

$$d_{max} \le d_{crit} \tag{24}$$

Therefore, when the above conditions are satisfied, the water phase will flow as dispersed droplets in the oil phase. However, if the conditions are not satisfied, some water droplets will settle down and potentially create a continuous water layer which is more likely to wet the pipe wall. In such conditions corrosion occurs at the bottom of the pipe. It is important to note that water which is in a dispersed state may also wet the pipe. Water droplets can randomly impinge the pipe wall due to flow disturbances. However, in such a case, corrosion is less likely to happen [74].

Factors Related to Wettability

Wetting ability, or wettability, is a tendency of a liquid or a solid surface to be wetted by another immiscible liquid [79]. While the term wetting relates to the action in which liquid contacts the surface and displaces the other fluid, wettability relates to surface properties or wetting preference of the surface which can, to a certain extent, affect wetting [80].

Wettability of a surface is dependent on its morphology, chemical composition, and degree of homogeneity/heterogeneity thereof [81]. Due its simplicity, the most common way to assess wettability is to measure contact angles when a liquid is contacted with a metal surface; variations of this method include "sessile drop", "vertical rod", and "capillary rise" techniques [82]. The sessile drop method is the most common technique to determine wettability of a surface. It consists of placing a droplet of liquid on a flat surface and measuring the resultant contact angle. In this way the sessile drop method utilizes wetting by a droplet of some liquid to assess wettability of that surface for that particular liquid. Figure 16 depicts five characteristic geometries, as contact angles, for liquid droplets on a solid surface.



Figure 16 – Contact angles formed by sessile liquid drops on a solid surface: A – complete wetting, B – complete non-wetting, C, D, E – partial wetting.

In the case of complete wetting, shown in Figure 16A, the droplet completely spreads on the surface and forms a thin layer; the contact angle is 0° indicating that the surface is completely wettable by liquid. In the case of complete non-wetting, Figure 16B, liquid does not contact the surface; the contact angle is 180° indicating that the surface is completely non-wettable by liquid. In the three intermediate cases depicted in Figure 16C, D and E, liquid partially wets the surface; contact angles between 0° and 180° are observed, indicating the surface is partially wettable by liquid. If a liquid has a contact angle significantly less than 90, or completely spreads, the surface has a positive affinity to be wetted by liquid. If the liquid partially or completely beads up, the surface has negative affinity to be wetted by liquid. In this case if the liquid is water, the surface is termed hydrophilic. If the contact angle is 90° the wettability of a surface is neutral, and is said to have no wetting preference [80], [83]; contact angles between 75° and 105° imply wettability is neutral [82].

In crude oil and gas pipelines wettability is a measure of the surface preference to be wetted by water or oil [84]. Therefore, wetting preference of a steel surface can be hydrophilic or hydrophobic with respect to water and, hence, oleophobic or oleophilic, with respect to oil. Steel surfaces without visible corrosion product layers, or other deposits, are naturally hydrophilic; upon exposure to air steel surfaces become covered with a thin oxide layer which confers surface hydrophilicity [84]. Measured contact angles are typically in the range of 40° to 60°. Contact angle measurements performed on iron carbonate covered surfaces are in the same range. Particular organic compounds are

able to significantly change the wetting of steel so the surface becomes hydrophobic, this will be discussed in later in Chapter 2.

Wettability is only one of the factors which affect wetting, especially on pipe surface areas which are intermittently wetted with oil and water [74]. Fluctuations in the stratified water layer or areas where water droplets can contact the steel surface play a role in wetting. If the surface is hydrophilic, droplets of water will easy attach to the surface. If the surface is hydrophobic, it will be water repellant. Water droplets touching the steel surface can be more easily swept away by the flowing oil [74].

Steel wettability has an influence of wetting when water is present in the dispersed phase. When the steel surface with adsorbed organic layer is in the contact with aqueous phase and contacts the dispersed hydrocarbon liquid, droplet will wet the surface of the steel. If the steel surface is in the contact with the oil phase and water droplet gets in the contact with the steel, water will be removed by the flowing oil [30].

Interestingly, accounting for wettability as a factor that governs wetting and corrosion in pipelines predates the concept of water entrainment [85]. However, this approach was abandoned for several decades [84]. The number of published wetting models which incorporate the effect of wettability is limited. Tang published a model based on a Water Wetting model, introduced in previous section, which incorporates the effect of surface wettability [69]. Similar to the previously discussed model above, it is based on comparison of two droplet sizes, d_{max} and d_{crit}. d_{max} is obtained from the energy balance between turbulent kinetic energy and summation of surface tension energies which can be represented as:

$$E_{ST} = \left\{ \frac{6\sigma_{ow}}{d_{max}} - \frac{L_1 \sigma_{ow}}{\varepsilon_w (\pi D^2/4)} Q_w + \frac{L_2 \sigma_{os}}{\varepsilon_w (\pi D^2/4)} Q_w + \frac{L_2 \sigma_{ws}}{\varepsilon_w (\pi D^2/4)} Q_w \right\}$$
(25)

Where E_{ST} is the sum of total rate of surface energies, Q_w is the water flow rate, σ_{ow} , σ_{os} and σ_{ws} are oil-water, oil-steel and water-steel interfacial energies. L_1 , L_2 and α are geometrical parameters of the liquid holdup and D is the pipe diameter [30].

 d_{max} can then be calculated using the formula:

$$\left[\frac{d_{max}}{D} \cdot 2U_o^3 f \frac{\rho_m}{\rho_o (1 - \varepsilon_w)}\right]^{2/3}$$

$$= \frac{\sigma_{ow}}{\rho_o} \left(\frac{\varepsilon_w}{1 - \varepsilon_w}\right) \left[C_H \left(\frac{6}{d_{max}} - \frac{4\sin\alpha}{\varepsilon_w \pi D}\right) + C_W \frac{4\alpha\cos\beta}{\varepsilon_w \pi D} \right]$$
(26)

Where C_H and C_W are proportionality constants set to 1 and 30, respectively, estimated from experimental data.

The transition criterion between dispersed and stratified flow can be expressed as:

$$d_{max} \le d_{crit} \tag{27}$$

When the condition above is satisfied, the water phase will be dispersed in the oil phase. Otherwise, droplets will settle down and wet the surface [30].

CO₂ Corrosion of Mild Steels

When mild steel is exposed to carbon dioxide containing aqueous environment, corrosion processes will occur [19]. Corrosion reactions are REDOX, heterogeneous and electrochemical in nature which, for exposure of steel to aqueous CO₂, results in oxidative dissolution of iron and evolution of hydrogen [17]:

$$Fe_{(s)} + CO_{2(aq)} + H_2O_{(l)} \to Fe_{(aq)}^{2+} + CO_{3(aq)}^{2-} + H_{2(g)}$$
 (28)

The rate at which steel corrodes is a function of water chemistry and steel chemical composition, as well as a number of physical parameters.

The reaction is composed of two half-reactions, cathodic (reduction) and anodic (oxidation) processes that simultaneously take place at the steel surface.

Cathodic Reactions

In the cathodic reaction, hydrogen ions from partially dissociated carbonic acid are reduced to molecular hydrogen at the surface of steel [17]. However, the exact mechanism of this hydrogen reduction process remains unclear. In aqueous solutions of strong, completely dissociated acids, reduction of hydrogen ions happens after dissociation of the acid, e.g., hydrogen chloride (HCl), in water to form hydronium cations and the corresponding anion; this would be chloride (Cl⁻) for the preceding example. These hydronium cations are subsequently reduced at the steel surface, and is the same reaction considered to takes place in aqueous solutions of CO₂ that have formed weak carbonic acid [19]:

$$2H_3O^+(aq) + 2e^- \to H_2(g) + 2H_2O(l)$$
⁽²⁹⁾

At pH values below 4 and CO_2 partial pressures lower than 1 bar it is assumed that reduction of hydronium ions shown in (29) is the only cathodic reaction [86]. However, in the pH range of 4 to 6, which is the most common pH in the produced waters, the corrosion rate in the presence of CO_2 is significantly higher compared to strong acids at the same values of pH [87]. This phenomenon is explained either by additional cathodic reactions or stabilizing the surface pH, *i.e.*, by a buffering effect conferred by the dissolved CO_2 in the vicinity of the surface. Additional cathodic reactions potentially include reduction of hydrogen from undissociated chemical species (H_2CO_3 , HCO_3^- and H_2O), so-called direct reduction reactions. The first reaction considered is the direct reduction of hydrogen from carbonic acid as proposed by DeWaard and Milliams [88]:

$$2H_2CO_3 + 2e^- \to 2HCO_3^- + H_2 \tag{30}$$

This reaction assumes the following mechanistic steps [88]:

$$H_2CO_3 + e^- \to H + HCO_3^- \tag{31}$$

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \tag{32}$$

$$2H \rightarrow H_2$$
 (33)

Direct reduction of carbonic acid has been accepted as the most feasible direct reduction reaction and has been adopted by other authors [87], [89].

The second suggested reaction is the reduction of hydrogen from bicarbonate ions [90], [91]:

$$2HCO_{3}^{-}(aq) + 2e^{-} \rightarrow 2CO_{3}^{2-}(aq) + H_{2}(g)$$
(34)

Concentration of bicarbonate ions gradually increases with pH, which makes it potentially important at pH values around or above pH 6. However, reaction kinetics are much slower compared with reduction of carbonic acid, which makes it less relevant in the range of common pH values for produced waters that are typically in the range of pH 4 to pH 6 [19]. Nevertheless, some authors assumed that both reactions occur at the steel surface [92], [93].

Reduction of hydrogen in water molecules is the reaction which is considered in analogy with corrosion of metals in neutral aqueous environments [94]:

$$H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq) + H_2(g) \tag{35}$$

However, on the basis of slow reaction kinetics this reaction cannot explain high corrosion rates in CO₂ containing solutions [87].

An alternative explanation to direct reduction of hydrogen is the buffering effect associated with aqueous CO₂, *i.e.*, stabilizing the surface pH by providing additional sources of hydrogen ions at the interface [95]–[98]. The direct reduction mechanism is thereby rejected on the grounds that direct reduction of carbonic acid and bicarbonate anions requires significantly higher negative over-potential compared to reduction of hydrogen ions at the same pH [40], [96].

Anodic Reactions

In the anodic reaction, iron, the main constituent of carbon steels, is being oxidized to ferrous ion which is subsequently dissolved in the aqueous phase [17].

$$Fe(s) \to Fe^{2+}(aq) + 2e^{-} \tag{36}$$

The full mechanism of anodic dissolution of iron in CO₂ containing solutions is not known. However, several mechanisms of iron dissolution have been proposed. The BDD mechanism (after Bockris, Despic and Drazic) is the mechanism of iron dissolution proposed for aqueous solutions of strong acids [99]. It has been completely or partially adopted by several authors [87]–[89]:

$$Fe(s) + OH^- \rightarrow FeOH + e^-$$
 (37)

$$FeOH \rightarrow FeOH^+ + e^-$$
 (38)

$$FeOH^+ \to Fe^{2+}(aq) + 2e^- \tag{39}$$

In this mechanism, an activated complex, FeOH is formed by reaction of iron and hydroxide ion. The rate determining step of the reaction is given in (38) and is dependent on the FeOH concentration [99]. It was found in experiments that the overall reaction order of iron dissolution with respect to OH⁻ is calculated as one, in range of pH from 1 to 4. This mechanism, however, was developed for strong acid solutions with pH lower than 4, which is lower than the pH of common produced waters. This discrepancy was experimentally confirmed by Nesic, *et al.* [87], [100].

Some authors adopted mechanisms of iron dissolution in strong acids complemented with additional reactions. Davis and Burstein proposed that bicarbonate ions play a crucial role in the dissolution of iron [101]:

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2e^-$$
 (40)

$$Fe + HCO_3^- \to FeCO_3 + H^+ + 2e^- \tag{41}$$

$$Fe(OH)_2 + HCO_3^- \rightarrow FeCO_3 + H_2O + OH^-$$

$$\tag{42}$$

$$FeCO_3 + HCO_3^- \rightleftharpoons Fe(CO_3)_2^{2-} + H^+$$
(43)

In the first two simultaneous steps, shown in (40) and (41), iron carbonate and iron hydroxide are formed at the surface. Further reaction of hydroxide with bicarbonate ions (42) also results in iron carbonate formation. A soluble complex anion $Fe(CO_3)_2^{2^-}$ is then formed (43) that leads to dissolution of iron from steel [101].

Nesic, *et al.*, proposed an anodic mechanism assuming that adsorption of dissolved CO_2 , rather than HCO_3^- , takes place [100]. The following mechanism has been proposed:

$$Fe + CO_2 \rightleftarrows Fe_L$$
 (44)

$$Fe_L + H_2 0 \rightleftharpoons Fe_L 0 H_{ad} + H^+ + e^- \tag{45}$$

$$Fe_L OH_{ad} \rightleftharpoons Fe_L OH_{ad}^+ + e^- \tag{46}$$

$$Fe_L OH_{ad}^+ + H_2 O \rightleftharpoons Fe_L (OH)_{2ad} \tag{47}$$

$$Fe_L(OH)_{2ad} \rightleftharpoons Fe_L(OH)_{2sol}$$
 (48)

$$Fe_L(OH)_{2_{sol}} + 2H^+ \rightleftharpoons Fe^{2+} + H_2CO_3$$
 (49)

Where Fe_L is iron with CO₂ adsorbed at the surface, $Fe_L = Fe(CO_2)_{ad}$.

The above mechanism assumes adsorption of OH^{-} as well as dissolved CO_{2} which acts as a ligand for iron dissolution. At pH values lower than 4, the rate determining step is the desorption reaction shown in (48) while at pH values above 5 the rate determining step is the charge transfer defined in (45). With increasing the pH the surface concentration of adsorbed hydroxyl ions also increases, until the saturation point after which hydroxyl ion concentration does not cause an increase in surface coverage [40], [100].

Notable Influential Factors

CO₂ corrosion is affected by a number of interrelated parameters. They can be physical or chemical, metallurgical or environmental, or a combination thereof [19]. Some important influential factors are listed as follows.

Formation of Iron (II) Carbonate Layers

Iron (II) carbonate (in further text: iron carbonate or $FeCO_3$) is an iron compound which is sparingly soluble in aqueous solutions. Under certain conditions iron carbonate can precipitate at the steel surface and reduce the corrosion rate by preventing diffusion of corrosive species to the steel surface [19]. In aqueous solutions of ferrous and carbonate ions the following equilibria is established [102]:

$$Fe^{2+} + CO_3^{2-} \rightleftharpoons FeCO_3(s) \tag{50}$$

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Thermodynamic condition for FeCO₃ precipitation is attained when the product of concentrations of Fe²⁺ ($C_{Fe^{2+}}$) and CO₃²⁻ ($C_{CO_3^{2-}}$) ions exceeds the solubility product *Ksp*, which is defined as follows [103]:

$$Ksp = [Fe^{2+}][CO_3^{2-}]$$
(51)

Where $[Fe^{2+}]$ and $[CO_3^{2-}]$ are the respective equilibrium concentrations of ferrous and carbonate ions and K_{sp} is the solubility constant at given conditions. The value of the solubility product (solubility limit) *Ksp* depends on the temperature and ionic strength. Its value can be determined using the empirical formula [103]:

$$logK_{SP} = -59.3498 - 0.041377T_{K} - \frac{2.1963}{T_{K}} + 24.5724log(T_{K}) + 2.518I^{0.5} - 0.657I$$
(52)

Where T_K is the temperature, in Kelvin, and *I* is the ionic strength (Equation 5).

For the solutions of ferrous and carbonate ions, saturation level *S* can be defined as follows [103]:

$$S = \frac{C_{Fe^{2+}}C_{CO_3^{2-}}}{K_{sp}}$$
(53)

Where $C_{Fe^{2+}}$ and $C_{CO_3^{2-}}$ are the respective non-equilibrium concentrations of ferrous and carbonate ions in the solution and Ksp is the solubility constant at given conditions. When S<1, the solution is undersaturated and iron carbonate formation is not feasible [102]–[104]. When S>1, the solution is supersaturated regarding iron carbonate and nucleation and crystal growth is possible. From the equation (52) and (53) it can be seen that higher temperatures and ion concentrations favor the formation of iron carbonate. In practice, much higher degrees of the supersaturation levels (denoted as SS, and equal to S when S>1) are required [54], [105]. Higher levels of supersaturation also have a major beneficial impact on precipitation kinetics [54], [106]. Scaling tendency is defined as [106]:

$$ST = \frac{PR}{CR}$$
(54)

Where ST is the scaling tendency, *PR* is the iron carbonate precipitation rate and *CR* is the steel corrosion rate. Values of *ST* higher than 1 indicate that precipitation of iron carbonate is faster than the steel corrosion rate [107], [108]. Those conditions favor the formation of protective iron carbonate layers. Values of *ST* lower than 1 indicate that metal corrodes faster than precipitation, resulting in, at best, formation of an unprotective iron carbonate layer [105], [107].

Effect of Flow

Effect of flow on corrosion is relatively complex considering the presence of multiple fluids and even solids in pipelines. Therefore, in some cases flow can accelerate or decelerate corrosion processes [19]. Under particular circumstances, increasing the fluid flow rate will help decrease corrosion rate by entraining the water in the oil above certain velocities or by removing solid materials from the metal surface that can lead to underdeposit corrosion [40], [70]. However, usually the effect of flow in the open literature is associated with two processes, enhancing the mass transfer of chemical species to and from the surface and mechanically removing corrosion product layers [17], [40].

The mass transfer of species from the bulk solution to the surface is achieved through the boundary layer. It can take place *via* molecular diffusion, convection and electromigration [54]. For a single phase turbulent flow in a pipe the mass transfer coefficient k_m can be found using the following correlation [109], [110]:

$$\frac{k_m d_p}{D} = 0.0165 Re^{0.86} Sc^{0.33} \tag{55}$$

Where k_m (m/s) is the mass transfer coefficient, d_p (m) is the pipe diameter, D (m²/s) is the diffusion coefficient, Re is the Reynolds number (dimensionless) and Sc Schmidt number (dimensionless) [40].

With an increase in velocity, turbulent eddies penetrate deeper into the mass transfer boundary layer which enhances the mass transport [54]. This influences corrosion rate when the rate of charge transfer rate is higher than the diffusion through the diffusion layer, *i.e.*, corrosion reactions are under mass transport control [109]. An increase in velocity has effect on the corrosion rate until the charge-transfer becomes the rate determining step in corrosion reaction [40].

Effect of flow on CO₂ corrosion of mild steels mostly influences mass transport of hydrogen ions to the steel surface. This is due to fact that the slowest step in the reaction of direct reduction of carbonic acid is the hydration of aqueous CO₂, not the mass transport [87]. Therefore, CO₂ corrosion is mostly sensitive to flow at pH values closer to 4 when the concentration of hydrogen ions is rather higher compared to higher pH values [17], [40], [109].

Flow was also reported to affect iron carbonate layer formation by increasing the transport of cathodic species and Fe^{2+} , which results in lower supersaturation values near the surface [108]. As a result, FeCO₃ precipitation rate is decreased and less protective films are formed. Furthermore, mechanical effect of flow has been mostly associated with

the partial removal of protective iron carbonate layers [19]. However new experimental evidence suggests that applied mechanical stresses are not sufficiently high to produce such an effect [40], [111].

Effect of pH

pH is one of the most significant parameters in CO_2 corrosion despite the fact that the pH values in pipelines are in a relatively narrow range of 4 to 6 [19]. Varying the pH of a solution can impact the corrosion rate mainly by affecting two processes. The first is the cathodic reaction in which hydrogen ions are one of the oxidative species. Increasing the concentration of hydrogen ions promotes the charge transfer current, *i.e.*, number of electrons transferred from metal to hydrogen. Consequently, this accelerates the corrosion process [87], [91], [98]. The second affected process is the formation of iron carbonate corrosion product layers. Increasing the pH increases the concentration of CO_3^{2-} in the solution, which successively promotes the precipitation of iron carbonate and reduces the corrosion rate [54]. It is important to note that in stagnant flow conditions pH in the proximity of the surface can be significantly higher than the pH in the bulk solution due to the constant consumption of hydrogen ions in the corrosion reaction, this can significantly alter the nature of corrosion products [112].

Effect of Temperature

Temperature affects a wide range of thermodynamic and kinetic parameters in CO_2 corrosion. At constant partial pressure of CO_2 , the increase of temperature will decrease the amount of dissolved carbon dioxide, which consequently leads to a relatively lower

concentration of hydrogen ions [40]. The effect of temperature is, however, more pronounced on electrochemical thermodynamics and kinetics.

The increase of temperature decreases the range of pH values at which thermodynamically stable and protective iron carbonate can be formed. Further temperature increases change the corrosion product from iron carbonate to magnetite (Fe₃O₄). As a result FeCO₃ is typically formed above 80°C and Fe₃O₄ above 200°C [113].

Temperature significantly contributes to the faster kinetics of chemical and electrochemical reactions and to a certain extent acceleration of mass transport processes [19]. When the thermodynamic conditions do not favor formation of protective corrosion product layers, which is typically encountered at pH values close to 4, temperature contributes to faster kinetics of electron charge transfer reactions and corrosion rate increases [87], [88], [91]. However, if thermodynamics favor the formation of protective layers, an increase of temperature will decrease the corrosion rate due to faster kinetics of corrosion product formation [113]. Moreover, temperature dependence of electrochemical reactions also comes via the mass transfer (km) coefficient. It was observed that an increase of temperature can lead to the change of rate determining step from chargetransfer to mass-transfer controlled at higher temperatures [87]. In practice, at pH values above 5 an increase of temperature thermodynamically favors the formation of protective layers at the surface [19]. Consequently, a peak corrosion rate is usually observed at temperatures between 60°C and 90°C due to a balance between those two factors [91].

Effect of Pressure

Increasing the pressure leads to an increase in the CO_2 corrosion rate when there is no corrosion product layer formation on the steel surface [40]. The main contribution comes from the increase of carbonic acid concentration in the aqueous phase [19]. In high CO_2 pressure conditions it is expected that corrosion rates would be higher due to higher production rate of H⁺ ions from the dissociation of H₂CO₃. However, the observed corrosion rates are higher even when the pCO₂ is increased without changing the pH [87]. It is noteworthy that at lower pCO_2 , the solubility of CO_2 in aqueous solution increases linearly with an increase of pCO₂ [40]. Consequently, corrosion rates also seem to follow a linear increase [19]. However, at a relatively high pressure of carbon dioxide, its solubility does not increase linearly. This leads to the non-linearity of corrosion rate at high CO₂ partial pressures [40], [114]. Moreover, an increase in pCO₂ could lead to the increase of $CO_3^{2^-}$ ion concentration, which can create conditions that favor formation of iron carbonate layers at higher temperatures [115]. This is especially important at supercritical levels of CO₂ partial pressure, which accelerate the formation of iron carbonate and reduce the corrosion rate [40], [116].

Effect of Organic Acids

Two classes of organic acids are commonly present in produced fluids. The first group encompasses water soluble, low molecular weight acids, such as formic, acetic or propionic acids which are corrosive to mild steel [19]. Among those, acetic is the most frequently encountered and causes severe corrosion problems [117]–[119]. Acetic acid is similar to carbonic acid and partially dissociates in the aqueous solutions. It enhances the

corrosion rate of mild steel by accelerating the reaction rate of hydrogen evolution [120]– [122]. Similar to carbonic acid, the mechanism of hydrogen evolution has been linked with the direct reduction of undissociated CH₃CO₂H moieties and the buffering effect [123]. Furthermore, it is suspected that acetic acid can promote localized corrosion by partially dissolving the iron carbonate layer [107], [124], [125]. However, some recent investigations show that this might be just a transient effect [124], [126].

The second group of acids comprises predominantly oil soluble, high molecular weight acids. When present in crude oils, they are termed naphthenic acids [48]. As opposed to low molecular acids, naphthenic acids can protect from corrosion in aqueous environments by forming a protective layers at the surface [32]. The influence of naphthenic acids on corrosion will be discussed later in this chapter.

Effect of Steel Composition

As carbon steel corrodes markedly in CO₂ containing aqueous environments, its corrosion resistance can be improved by introducing small amounts of alloying elements [127], [128]. Chromium is the most widely used alloying element which improves corrosion resistance by forming a protective, passive chromium oxide film at the steel surface [7], [10]. Other elements, such as vanadium, titanium, molybdenum or copper are also added in smaller concentrations to further improve the properties, particularly strength, of Cr-alloyed carbon steels [40], [129]. Generally, the CO₂ corrosion rate of carbon steel decreases with increasing of the chromium content. Typically, chromium is added to steel in the range of 0.5 wt.% to 3.0 wt.%, concentrations between 2 wt.% and 3

wt.% are considered to provide optimum protection and be economically justifiable [40], [129].

The secondary role of chromium is in improving the corrosion resistance of carbon steel by altering the composition and improving the protective properties of the corrosion product layers [130]. Localized corrosion attack (pitting) has not been observed with Cr-alloyed carbons steels even under high velocity flow conditions at Cr concentrations as low as 0.5 wt.%. Likewise, the presence of 0.5 wt.% Cr allowed the formation of protective iron carbonate at temperatures lower than 70° C, in conditions at which formation of sufficiently protective layers is not expected [40], [130]. It was also found that corrosion product layers contain significantly higher concentrations of Cr compared to the non-corroded steel [131]. It must also be noted that it is preferable that Cr is retained in the Fe matrix in order to enable formation of chromium oxide passive layers. Formation of chromium carbide reduces its concentration available for the formation of passive layers. To maintain a sufficient concentration of chromium in an iron solid solution, other alloying elements with higher affinity to form carbides are added. These include vanadi-um, molybdenum, and niobium [40], [128], [132].

Vanadium has been reported to have substantially beneficial effects on corrosion rate [132]. Molybdenum has been also found to improve the corrosion resistance of carbon steels, especially in the range of higher pH values [40], [129]. Copper and silicon also show beneficial effects when added to low chromium steel. Sulfur content appears to influence the CO_2 corrosion rate of carbon steels as well. Interestingly, some high-S carbon steels were more corrosion resistant than low-S carbon steels [129]. Results of

some studies show that, generally, Cr and V content can be a good indicator of corrosion properties of micro-alloyed carbon steels [40], [132].

Surface Active Properties of Surfactant-based Corrosion Inhibitors

Steel corrosion can be significantly reduced by addition of corrosion inhibitors. They are defined as materials which retard corrosion when added to an environment in small concentrations [133]. The important subclass of corrosion inhibitors are cationic surfactant compounds with amphiphilic molecular structure. The way in which alter corrosion and surface wetting is discussed in three aspects [74], [134]:

- Formation of barrier for corrosive species at the steel surfaces
- Decrease of the oil-water interfacial tension
- Changing the wettability of the steel surface from water-wet to oil-wet

In addition, their surfactant properties can cause the excessive adsorption at interfaces which can negatively impact corrosion. Each of these aspects is reviewed in the following sections.

Surfactant-based Corrosion Inhibitors

Addition of corrosion inhibitors to produced fluids is an important and commonly utilized way to mitigate corrosion in oilfield applications. In general, inhibition can be achieved by interrupting one or multiple stages in the corrosion process, either by changing the concentration of species in the environment or by formation of surface films at the steel surface which prevent contact of steel with corrosive environments. Usually, filmforming corrosion inhibitors are organic compounds which form protective films by adsorbing at steel surfaces [135], [136]. Most commonly, film-forming corrosion inhibi-
tors are amphiphilic molecules, consisting of a polar head group and non-polar hydrocarbon tail. Polar head groups are often based on nitrogen containing groups, such as amines, amides, quaternary ammonium or imidazoline-based salts as well as functional groups containing oxygen, phosphorus and/or sulfur atoms. The length of a hydrocarbon tail which is attached to a polar group varies between 12 and 18 carbon atoms [135]. Figure 17 shows some common corrosion inhibitors; thioglycolic acid is included in the figure as it is commonly added to inhibitor "packages" (formulations containing a range of compounds).



Figure 17 – Examples of common corrosion inhibitors [136]: A – Phosphate esters, B – Quaternary ammonium salts, C – Amidoethylimidazolines, D – Thioglycolic acid.

Film-forming inhibitor molecules with amphiphilic molecular structure are essentially surface active compounds (surfactants). As such, they can potentially exhibit the characteristic features of surfactant molecules such as decrease of surface tension, micelle formation, foaming, emulsification, detergency, etc. [2]. Therefore, besides corrosion inhibition properties associated with adsorption on steel surfaces, corrosion inhibitors can possibly impose significant influences on physical properties of other interfaces at which they preferentially adsorb. Adsorption of surfactants is governed by intermolecular forces in the bulk and at interfaces [137]. These include electrostatic interactions, such as between positively charged surfactant molecules and negatively charged surfaces or *vice*

versa, dipole-dipole interactions between polar head-groups and surface atoms, and dispersion interactions between hydrophobic tails of surfactants and non-polar media. These interactions are related to the molecular structures of surfactants, the nature of the head group, and the hydrocarbon tail [137].

The first and characteristic property of surfactants is their ability to reduce surface tension of liquids when present in small concentrations. The relation between concentration of chemical species at the surface and surface tension is given by the Gibbs equation:

$$d\gamma = -\sum_{i} \Gamma_{i} d\mu_{i} \tag{56}$$

Where d γ is the change in surface or interfacial tension, Γ_i is the surface excess concentration of any component in the system and d μ_i is the change in chemical potential of any system component [2]. The surface excess concentration Γ is defined as: "The excess, per unit area of interface, of the amount of any component actually present in the system over that present in a reference system of the same volume in which the bulk concentrations in the two phases remain uniform up to a hypothetical (Gibbs) dividing surface" [2]. The consequence of this relation is that if a compound preferentially adsorbs at the interface, adsorption is positive and the interfacial energy is reduced. If the concentration of a dissolved compound is lower at the interface compared to the bulk, adsorption is negative which causes an increase of surface tension. The lack of surface tension alteration with the addition of compounds indicates that its concentration is the same in an interfacial region as in the bulk [138]. Therefore, for surfactant-based corrosion inhibitors, there will be an excess concentration at the surface compared to the bulk. Corrosion inhibitor molecules, as surfactant compounds, form molecular aggregates in a bulk solution when they exceed solubility limit. The concentration at which molecules begin to aggregate is termed the critical micelle concentration (CMC), or micellar point [2], [138]. At or above the CMC, the inhibitor molecules will form ordered molecular structures as well as formation of adsorbed surfactant monolayers or bilayers on metal surfaces. At hydrophilic surfaces more than one layer of surfactant molecules can form. As a result, corrosion inhibitors are more effective at concentrations above CMC than soluble inhibitor systems below the CMC [139]. The CMC can be determined from the plot of surface tension *vs.* log of surfactant concentration, as shown in Figure 18. The critical micelle concentration is the point where surface tension does not change significantly with increasing inhibitor concentration [139].



Figure 18 – CMC from the plot of surface tension versus log of the bulk phase surfactant concentration. Adapted from [2].

Influence on Corrosion

The first and the most important property of surfactant-type corrosion inhibitors and crude oil compounds is their ability to retard corrosion by forming layers at metal surfaces which provide diffusion barriers against corrosive species [135]. Most organic corrosion inhibitors control corrosion by blocking of active corrosion sites. For corrosion inhibitors this is achieved through synergistic effects governed by the presence of polar head groups and hydrophobic tails on adjacent molecules. The function of the polar headgroups is to provide bonding between inhibitor molecules and the steel surface. This can be achieved by chemisorption where polar groups develop intramolecular bonds at and with the surface or by physisorption where they are bound to the surface by intermolecular forces [136]. Hydrophobic tails which are facing the aqueous phase provide a diffusion barrier for corrosive species due to steric repulsion of the hydrophobic tails [140]. Figure 19 shows the measured corrosion rate as a function of inhibitor concentrations for one fatty amino surfactant-based corrosion inhibitor. As can be seen from the graph, the inhibition efficiency enhances with increasing the concentration. It is widely believed that this effect is due to the higher surface area covered by inhibitor molecules, although this is a simplification of actual phenomena associated with inhibition [134].



Figure 19 – Corrosion rates obtained by LPR for different concentrations of fatty amino corrosion inhibitor. Reprinted with permission from Li [134].

Influence on Wetting

The effect of corrosion inhibitors on wetting is related to the ability of inhibitors to reduce oil-water interfacial tension and change the wettability of a steel surface. The reduction of the oil-water interfacial tension is a consequence of the amphiphilic structure of inhibitor molecules. The hydrophilic heads of inhibitor molecules are face water molecules and the hydrophobic tails are orientated towards an oil phase. This orientation is preferential due to intermolecular forces and minimization of interfacial energy between oil and water phases. Previous interfacial tension measurements showed that this reduction can be very significant even at very low concentrations. The results of Li's measurements are shown in Figure 20 [134].



Figure 20 – Oil-water interfacial tension as a function of inhibitor concentration. Reprinted with permission from Li [134].

Surfactant-based corrosion inhibitors can significantly change the wettability of the surface from preferentially water-wet to oil-wet. It is believed that when a layer of adsorbed inhibitor molecules is present on a surface, the hydrophobic tail on the inhibitor molecules face toward the bulk solution and form a hydrophobic layer. The contact angle as a way of measuring the wettability of a steel surface in oil-water two-phase systems depends on the oil-water, oil-steel and water-steel interfacial tensions.



Figure 21 – Contact angle alteration by addition of corrosion inhibitors. Reprinted with permission from Li [134].

The combined effect of reduction of interfacial tension and wettability on wetting of steel surfaces can be observed in experiments conducted in the "Doughnut Cell" experimental apparatus, performed by Li, as shown in Figure 22 [134]. The lines on the graph mark the transition between the steel wetting states as a function of oil velocity and water cut. At oil phase velocities which are lower than ones marked by the transition lines (area left from the each line) the steel is wetted by water. At oil velocities that are higher (area right from the each line) steel is wetted by oil. It can be seen from the diagram that an increase of inhibitor concentration decreases the velocities at which the transitions occur, i.e., steel is wetted with oil at lower oil velocities. Achieving an oil wetting regime in oil-water two-phase flow through the reduction of oil-water interfacial tension is a conse-

quence of enhanced entrainment of water into the oil. Lower interfacial tension promotes entrainment of water by the flowing oil and reduces the water droplet size [134].



Figure 22 – The wetting transition lines for several concentrations of "quat" corrosion inhibitor in the "Doughnut Cell". Reprinted with permission from Li [134].

Parasitic Consumption of Corrosion Inhibitors into Foams

Utilization of corrosion inhibitors in the field have shown that applied concentrations are often higher compared to those applied in laboratory experiments required to attain the same level of protection. One of the possible causes is the "adsorption loss" or "parasitic consumption" of the excessive amounts of corrosion inhibitors onto surfaces of the dispersed phases [141]. Being amphiphilic, surfactant-based corrosion inhibitors adsorb at polar-nonpolar interfaces such oil-water or water-gas. Under some circumstances corrosion inhibitors can induce formation of foams in pipelines due to fact that the main active component compounds in corrosion inhibitor formulations are usually surfactants [142]. The same driving force which makes these components adsorb at metal-water interfaces is responsible for making them adsorb at liquid-gas interface. As a result, foams can cause a "parasitic consumption" due to large areas of liquid-gas interfacial area and which result in decreased availability of corrosion inhibitor for the metal surface [25]. A dramatic increase of oil-water interface area during emulsion formation can consume appreciable amounts of inhibitor molecules [143]. The result is poorer inhibitor performance and higher than expected steel corrosion rates; this sometimes necessitates development of environment specific non-foaming inhibitor formulations [142].

Experiments performed by McMahon, *et al.*, illustrate the effect of foaming on concentration of surfactant-type alkylethoxyphosphate corrosion inhibitors in aqueous solution [25]. Foam was created by bubbling the aqueous inhibitor solution with a fritted gas sparger. In the first test, the gas flow rate was adjusted in a way that bubbling generated unstable foam, which was depleting in a foaming vessel. The portion of liquid consumed by the foam was draining back to the bulk solution, and consequently the concentration of the inhibitor remained constant at approximately 108 ppm. In the second test, gas flow rate was adjusted so that foam overflows in the second vessel. Upon foaming, concentration of inhibitor in the first solution has decreased to 86 ppm, while the concentration of inhibitor in the liquid collected in the second vessel was considerably higher, 276 ppm. Canto showed that corrosion inhibition of carbon steel by surfactant-based corrosion inhibitors can be compromised by formation of foam in aqueous CO₂ containing environments [26]. Two surfactant-type inhibiting compounds, TOFA/DETA imidazoline and benzylcocoalkylamonium chloride, and one non-surfactant inhibiting compound, sodium thiosulfate, were used. Experiments were performed in a glass vessel with a mounted gas diffuser for foam generation and carbon steel specimens for corrosion measurements. Results of the corrosion measurements, presented in Figure 23, showed that when surfactant-based corrosion inhibitors were used, higher corrosion rates (inferior inhibition) were observed when carbon steel specimens were exposed to inhibitor solutions in which gas bubbles prompted foaming. Without introducing the gas bubbles below the surface, foaming was not present and corrosion rates were lower.



Figure 23 – Effect of foam on TOFA/DETA imidazoline corrosion inhibitor performance. Blue bars denote non-foaming conditions. Orange bars denote foaming conditions. Reprinted with permission from Canto [138].

In contrast, when solutions containing non-surfactant inhibitor did not generate foam there was no difference in corrosion inhibition with and without sparging of gas, as shown in Figure 24. The results of these experiments implied that the amount of inhibitors adsorbed at the water-gas interface can be sufficiently high to cause higher corrosion rates when steel is subjected to environments in which foaming can occur [26].



Figure 24 – Effect of foam on sodium thiosulfate corrosion inhibitor performance. Blue bars denote non-foaming conditions. Orange bars denote foaming conditions. Reprinted with permission from Canto [138].

Surface Active Properties of Crude Oil Polar Compounds

Some chemical compounds native to crude oils have an ability to preferentially adsorb at steel-water, steel-oil and oil-water interfaces and alter the wetting and corrosion properties of steel surfaces. Most commonly, those compounds contain heteroatoms in their chemical structure. The way in which crude oil chemistry influence corrosion and surface wetting is with corrosion inhibitors, discussed in three aspects:

• Adsorption and formation of barrier for corrosive species at the steel surfaces

- Decrease of the oil-water interfacial tension
- Changing the wettability of the steel surface from water-wet to oil-wet

All three aspects are discussed in this Chapter.

Surface Active Compounds in Crude Oils

Crude oil chemical composition is one of the factors in a decision-making process of delaying or reducing the inhibition treatment or utilization of corrosion resistant alloys. Due to diversity of crude oil chemical composition, it is almost impossible to identify individual components which can inhibit corrosion or alter interfacial properties. Moreover, research in this field has been relatively scarce. Several approaches were taken to investigate and correlate inhibition properties of crude oils with their chemical composition [32]:

- Correlation of corrosion inhibition with composition available from crude oil assays
- Extraction of chemical compounds from crude oils
- Study of crude oil model compounds with different functional groups, such as carboxylic acids, mercaptans, etc.

The first approach is correlation of inhibition rates with parameters derived from common crude oil chemical analyses, such as content of SARA fractions (Saturates, Aromatics, Resins and Asphaltenes), TAN (total acid number) or of atomic species such as nitrogen, oxygen and sulfur. The results of these investigations are scattered in nature and, consequently, it is difficult to make definitive conclusions. In one occasion it has been reported that corrosion inhibition rate correlated with algebraic product of the organic nitrogen content and total acid number [144]. Inhibition has been also correlated with the content of resins, asphaltenes and sulfur for asphaltenic crudes and nitrogen, resins and asphaltenes for the paraffinic crudes [145]. In one occasion it was found that resin fraction was the most inhibitive. Later analysis of the same crude showed the presence of nitrogen containing compounds and carboxylic acids [146], [147]. Later use of artificial neural networks for correlating behavior of crude oils included a wide spectrum of physical and chemical parameters [148]. In general, results of those studies showed that correlations obtained by purely statistical approaches are not reliable, and that simple parameters cannot sufficiently describe inhibition properties of crude oils [32]. The second approach was to test compounds extracted from crude oils. Asphaltene fractions studied in this way from certain crudes can effectively inhibit corrosion, although at higher concentrations [33].

Ayello studied crude oil model compounds of known chemical composition with the same functional groups as native crude oil compounds [32]. The molecular structures of some of the tested compounds are shown in Figure 25. This study evaluated their influence on corrosion, interfacial tension and wettability; the effect of these compounds is further discussed below.



Figure 25 - Chemical structure of crude oil model compounds used by Ayello [74].

Influence on Corrosion

Certain crude oil compounds inhibit corrosion by adsorbing at steel surfaces. Adsorbed compounds form organic films that to some extent Polar crude oil compounds adsorb at steel surfaces through their functional group. Figure 26 shows the results of the corrosion rate measurements obtained by Ayello after steel was exposed to oil solutions containing crude oil model compounds [74].

The results of this investigation showed that aromatics were unable to have a significant effect on corrosion. Low molecular weight organic acids were increasing the corrosion rate while large molecule organic acids showed inhibitive properties. Among sulfur containing compounds, only mercaptans were able to decrease corrosion rates. Among nitrogen containing compounds, that can adsorb at the metal surface, only acridine showed a strong inhibition of corrosion, while pyrrolic compounds (neutral nitrogen) had no effect on corrosion [32].



Figure 26 – Corrosion rate measured with LPR after steel has been exposed to oils containing various crude oil model compounds. Adapted from data published by Ayello[74].

Influence on Wetting

As it can be seen from Figure 27, the effect of the crude oil model compounds on the interfacial tension was relatively insignificant. The tetrahydronaphthalene did not have effect on the interfacial tension as well majority of tested compounds. The sulfur-containing compounds had only a slight effect. The greatest effect on the interfacial tension was obtained with the carboxylic acids,



Figure 27 – Interfacial tension measured between water and oils containing various crude oil model compounds. Adapted from data published by Ayello [74].

Crude oil polar compounds can alter the wettability of steel surfaces from preferentially hydrophilic to hydrophobic. Changing the wettability of steel from hydrophilic to hydrophobic promotes the formation of a barrier by hydrophobic tails. After such surface is exposed to the oil phase, liquid hydrocarbons form an oily film which further lowers the corrosion rate. This oily film is believed to present a strong hydrophobic barrier to corrosive species and enhances the inhibitor performance. Also, formation of this film enhances hydrophobic properties of steel [74].

Compared to corrosion inhibitors which have very strong influence on steel wettability at concentrations in the ppm range, the effect of crude oil compounds strongly depended on their molecular composition. Long-chain carboxylic acids were able to significantly alter steel wettability, while the effect was much weaker with compounds with short hydrocarbon chains [74].



Figure 28 – Water-in-oil contact angle measured in oils containing various crude oil model compounds (120 min exposure). Reprinted with permission from Ayello [74].

In summary, the study of the crude oil model compounds showed that the adsorption of some oil soluble surface active compounds onto the metal surface was able to inhibit dissolution of iron. Surface wetting changes mostly due to the change of surface wettability. The change of flow pattern resulting from the change of interfacial tension due to accumulation of surface active compounds was found to be a second-order effect [74].

CHAPTER 3: RESEARCH OBJECTIVES

The main objective of this study is to expand the present knowledge related to role of interfaces on corrosion in multiphase flow by interlinking several interfacial processes which concurrently occur in pipelines. These include corrosion, emulsification of water in multiphase flow, wetting, and foaming. The following aspects of interactions between interfacial processes and chemistry are encompassed in the present investigation:

- Simultaneous occurrence of foaming and inhibition of corrosion prompted by oil-soluble naturally occurring polar compounds in crude oils.
- Foaming and corrosion inhibition by water soluble surfactant-based corrosion inhibitors with a presence of a thin oil layer covering the aqueous phase.
- Effect of formation of iron-carbide corrosion product residues on wetting properties of steel.
- Altering inhibition of corrosion and steel wetting properties by ionization of crude oil model polar compounds.

How research objectives for the current work extend prior knowledge concerning the interrelationships between interfacial processes/properties and chemical factors are presented in Table 1. The first column identifies specific processes and, in brackets, properties. The first row lists key chemical factors relating to the presence of particular species; namely inhibitors, polar molecules, and corrosion products. Previously investigated process-chemistry relationships are indicated with a single check-mark or, if no investigations have been conducted, a cross; conditions for which a relationship is not

applicable are marked N/A. The four phenomena which are investigated in the research reported herein have their chapter numbers and objectives for each listed below.

	Corrosion Inhibitors	Polar Crude Oil Compounds	Corrosion Products
Wetting (Oil-Water Interfacial Tension)	~	✓ (Chapter 7)	N/A
Wetting (Surface Wettability)	~	✓ (Chapter 7)	✓ (Chapter 6)
Corrosion	~	✓ (Chapter 7)	✓ (Chapter 6)
"Parasitic Consumption" of Inhibiting Compounds into Foams	✓ (Chapter 5)	× (Chapter 4)	N/A

Table 1 – Overview of interfacial processes (properties) and effects of chemical factors

The first phenomenon studied, presented in Chapter 4, was the accumulation of surface active compounds at the oil-gas interface. The main hypothesis was that accumulation of significant amounts of surface active compounds at the liquid-gas interface are due to formation of foam that can significantly lower the concentration of surface active compounds in the bulk solution. This concentration decrease can significantly impair corrosion inhibition.

The second part of this research, presented in Chapter 5, investigates the effect of hydrocarbon oils on the formation of aqueous-based foams stimulated by corrosion inhibitors. Hydrocarbon liquids have antifoaming properties which depend on the composition of the hydrocarbon phase. Successively, antifoaming properties of hydrocarbons can affect corrosion inhibition by reducing the amount of foam generated by aqueous inhibitor solutions.

The third investigated phenomenon, presented in Chapter 6, was the effect of Fe_3C corrosion product layer formation on wettability and corrosion. The main postulation was that corroding steel increases hydrophilicity of the surface which will have a significant effect on the persistency of water on the surface of the steel.

The fourth studied subject, presented in Chapter 7, was the effect of the aqueous phase pH on ionizable crude oil model compounds. Some crude oil compounds can be ionized in the range of pH values that are common in produced waters. The main hypothesis was that ionization consequently leads to significant changes in corrosion inhibition and steel wettability induced by the same chemical compounds. This is due to the fact that ionization results in significantly different chemical properties compared to those observed for non-ionized molecules of the same compound.

Therefore, the current study is aimed to cover several possible effects of interfacial chemistry on corrosion inhibition. There is a paucity of research in this field and, due to its potentially significant effects on corrosion. Those aspects are addressed in this dissertation.

CHAPTER 4: EFFECT OF POLAR CRUDE OIL COMPOUNDS ON FORMATION OF FOAMS AND SUBSEQUENT CORROSION INHIBITION

Foams are omnipresent in the petroleum industry. Foaming occurs in pipelines causing pressure drop, shearing and mixing of fluids, particular at pressure reducing valves and pipe elbows [149]. If present, foams produced by an aqueous phase can negatively impact corrosion *via* parasitic consumption of corrosion inhibitor compounds at watergas interfaces [26]. In addition, chemical compounds which simultaneously cause foaming and corrosion inhibition of carbon steels can be present in crude oil. Therefore, the connection between foaming and corrosion inhibition prompted by compounds native to crude oils was investigated.

Research Hypothesis

Previous investigations with aqueous-based corrosion inhibitors, presented in Chapter 2, have shown that processes of foaming and corrosion inhibition can become interrelated. When corrosion inhibition and foaming are induced by the same surfactant-type compound, which adsorb at the water-steel and water-gas interfaces, foaming processes can compromise corrosion inhibition [26]. Adsorption of excessive amounts of inhibitors at large water-gas interfacial areas, such as those created by foams, causes a decrease of inhibitor concentration in bulk aqueous solutions which degrades inhibitor performance [25].

However, it is unknown if equivalent, or similar, processes can occur with inhibiting compounds present in a crude oil phase. Crude oils contain polar organic compounds which are preferentially soluble in the oil phase and which, by adsorption on steel, can inhibit corrosion and even make the surface hydrophobic. Therefore, steel surface areas which are intermittently wetted with oil and water can become partially protected by adsorption of organic molecules which occurs while the surface is wetted by the oil phase. The results of investigation of the model compounds with those properties were presented in Chapter 2. Therefore, for the oil solutions which contain polar organic compounds which have corrosion inhibition properties the following can be hypothesized:

If oil contains chemical compounds which can inhibit corrosion by adsorbing at oilsteel interfaces and simultaneously cause foaming of oils by adsorbing at the oil-gas interface, then foaming of such oil solutions reduces their ability to inhibit corrosion due to the substantial decrease of compound concentration in the bulk oil solution.

Testing this hypothesis requires an insight into foaming processes and, more specifically, foaming of crude oils in order to identify compounds which were previously found to be associated with foaming and inhibition of corrosion.

Mechanism of Foam Formation

Liquid foams are dispersions of gas in a liquid continuous phase. They are organized as agglomerates of spherical or polyhedral bubbles separated by films of liquid [150]. In high velocity liquid flows, large quantities of gas bubbles can be entrained in the liquid phase. Turbulent flow in a breaking wave, which occurs in the slug flow regime, is one type of strong agitation suitable for foam formation [151].

When ascending bubbles reach the surface of a liquid they immediately burst, unless the liquid contains a foaming agent which stabilizes the liquid film which separates them from the bulk gas phase and from other gas bubbles [150]. Therefore, significant amounts of foam cannot be formed from pure liquids unless some foaming agent is present [2], [150], [151]. Foaming agents are generally surface active materials which include solid particles, polymers, amphiphilic organic molecules, or specific adsorbed cations or anions from inorganic salts [152].

The process of foam formation goes through several stages, shown in Figure 29. The ascending gas bubbles at first form the spherical foam, also termed "kugelschaum", which consists of spherical gas bubbles separated by liquid at a thickness of the same order of magnitude as the diameter of the bubbles. Due to the drainage of liquid, spherical bubbles gradually acquire the polyhedral shape, and collectively form "polyederschaum" where entrapped gas is separated by thin films of liquid, much thinner than a size of a bubble. A thin liquid film is termed a foam lamella, and the spots where lamellae meet plateau borders (Figure 29) [2], [150].



Figure 29 – Evolution of foam from spherical to polyhedral type.

Foams are thermodynamically unstable; still, their lifetime can be considerably long. The process of foam degradation is induced by drainage followed by coalescence and by bubble disproportionation. Drainage is a process which causes thinning of foam liquid films. It occurs due to gravity pull and capillary suction from foam lamellae into plateau borders due to differences in capillary pressure. Upon reaching a certain thickness, bubble coalescence can occur due rupture of thin liquid films [150], [153]. The process of rupture is a probability event and not well understood, but it is driven by thermal and mechanical disturbances at the liquid gas interface. In a process of disproportionation, degradation occurs due to coarsening of gas bubbles. The larger gas bubbles grow at the expense of smaller ones due to differences in capillary pressure [150], [152].

Drainage and coalescence from foam lamellae are hindered or promoted following liquid and thin film properties governed by viscosity of the bulk liquid phase, elasticity of a liquid film, surface film viscosity, and repulsion associated with the electrical double layer [150]. Surfactant monolayers influence the aforementioned drainage and coalescence processes, it is often stated that liquid foams produced without surfactants quickly deplete [2], [152]. However, depending on the nature of the surface active compounds, foaming properties can vary significantly.

Foam Film Elasticity occurs due to the Marangoni effect. If some part of a thin liquid film gets locally elongated and thinned due to mechanical disturbance, concentration of surfactant at a surface decreases and a higher surface tension results compared to adjacent areas. Due to the Marangoni effect, the liquid with the lower surface tension will tend to flow in the direction of the liquid with higher surface tension therefore the thinned film will tend to "self-heal", as shown in Figure 30.



Figure 30 – Simplified schematic representation of thin film stabilization by the Marangoni effect. Adapted from reference [2].

Surface viscosity is the resistance to shear in the plane of an interface [154]. Adsorbed layers of some surfactants cause a significant increase of viscosity at the water-gas interface which retards drainage and surface deformations. Therefore, influence of bulk and surface viscosity on overall foam stability usually acts to resist drainage from the foam lamellae that are thinning, but do not contribute directly to stabilization of foam lamellae [2].

Existence of the double layer stabilizes foams of aqueous surfactant solutions, due to adsorption of ionic surface active compounds on both sides of the thin water film. When the water layer becomes thin enough (200nm or less) it is stabilized by electrostatic repulsion between surfaces of the lamella and by hindering the thinning of the water layer due to high osmotic pressure in the overlapping layers of counterions [2].

Decreased *gas diffusion due to packing of alkyl (hydrocarbon) tails* is an additional effect of surfactant layers which affects disproportionation processes. Densely packed surfactant layers at the surface of the liquid decrease gas diffusion from smaller to larger bubbles and water evaporation, which slows down the process of disproportionation [2].

Bulk liquid *viscosity* is a factor which is not necessarily associated with surface active compounds. In liquids with high viscosity motion is greatly retarded, which decelerates drainage as well as lateral wavy motion prior to coalescence [150].

It is important to note that the role of surface active compounds in stabilization of aqueous foams is much more significant compared to non-aqueous foams. The mechanism of foam stabilization, such as the Marangoni effect, is associated with the decrease of surface tension induced by surfactants. However, in non-aqueous solutions, the surface tension changes are relatively small and, therefore, in such cases it is considered that stability of foams is mostly related to their drainage rate [155].

Identification of Crude Oil Foaming Agents

Formation and stability of crude oil foams is determined by several physicochemical characteristics including bulk properties of liquids, the shear and dilatational (rheological) viscoelastic properties of the gas-oil interface, nature of the filler gas, and chemical composition of the liquid phase [156]. Oil viscosity is considered by many researchers to be the most important property of the bulk oil phase that influences foaming. More viscous oils tend to produce more stable foams due to lower liquid drainage rates from foam lamellae [156]. Correlations between bulk oil viscosity and foam stability have been determined on several occasions [157], [158]. However, in some cases very high viscosity can impair bubble formation and thus negatively impact foaming ability of crude oils [158]. Foam stability was also found to correlate with an increase of oil density [158]. This correlation was, however, applicable only for crudes from the same geographic origin. Surface tension and surface rheological properties are also considered to have a very significant role in formation and stabilization of crude oil foams [159], [160]. Poindexter, *et al.*, found a correlation between an increase of foamability and foam stability and an increase of surface tension [158]. However, it was assumed that foaming properties were not directly linked with surface tension, but with the presence of chemical compounds which simultaneously cause alteration of surface tension and viscoelastic film properties. Links between film viscoelastic properties and foaming were postulated by Callaghan, *et al.*, who found a profound effect on dilatational and shear viscoelasticity for several crude oils with different geographic origins [157], [159], [161]. The influence of the filler gas on foaming properties is mainly related to their ability to diffuse through foam lamellae [156]. In general, gases that are less soluble in the liquid phases tend to form more stable foams due to slower diffusion between gas bubbles. However, some exceptions to this rule have been found [156].

On several occasions foaming of crude oils were investigated regarding chemical composition of the liquid phase [161], [162]. Due to the high variety and complex structures of chemical compounds found in crudes, researchers typically identify chemical classes rather than particular chemical species, when they conduct analyses. The asphaltene compound group has been linked with foaming of crude oils by several researchers [160]. Their mechanism of foam stabilization is supposed to be primarily related to adsorption at the oil-gas interface with concomitant alteration of surface viscoelastic properties [162]–[164]. Poindexter, *et al.*, correlated foam stability with the percentage of asphaltenes present for several crudes [158]. For crudes with a low percentage of an asphaltene fraction, foaming was correlated with the content of resins and,

in one case, wax. Zaki, et al., investigated foaming of several mixtures composed of mineral oil and toluene with addition of asphaltenic and resinous compounds [164]. They concluded that adsorption of asphaltenic and resinous compounds at the oil-gas interface can both contribute to petroleum foaming. The effect of asphaltenes was more prominent. They presumed that asphaltene aggregates accumulate at the oil-gas interface and generate elastic and rigid molecular structures which stabilize the foam by altering the viscoelastic properties. Other researchers also associated the asphaltene fraction with foaming of crude oils. Claridge and Prats proposed that the stability of foams is related to the adsorption of the asphaltenic molecules at the liquid-gas interface [162]. Adil and Maini suggested that asphaltene aggregates prevent gas bubble coalescence [163]. Alternatively, Bauget proposed that the role of asphaltenes was more related to their ability to increase viscosity of oils instead of creating specific molecular structures at the oil-gas interface [165]. Carboxylic acids and phenols are the second group of compounds identified in several crude oils [161]. Their ability to stabilize foams is also related to alteration of viscoelastic film properties. Callaghan and coworkers identified organic acid compounds in isolated fractions from 16 crude oils [161]. Detailed analysis of one crude oil extract, which was only 0.02% in weight, showed the presence of linear, branched, monocycloalkanoic and phenylalkanoic acids with predominantly 7-11 carbon atoms as well as phenols with molecular weight less than 400 g/mol. However, these researchers left open the possibility that higher molecular weight acids were not extracted. It has been shown that this acidic fraction has a major effect on viscoelastic properties of oil-gas

surfaces [161]. However, molecular interaction mechanisms which caused alteration of the observed foaming properties remain unknown.

Corrosion inhibition and foaming of crude oils can be facilitated by the same classes of chemical compounds naturally present in crude oils. That is, the same groups of compounds can perform as foaming agents and as corrosion inhibitors. The first to be considered is the asphaltenic compound class, which is believed by many researchers to play a major role in stabilization of crude oil foams [160]; recall that it has been demonstrated that compounds within this class can effectively inhibit corrosion of mild steel [33]. The second compound group are carboxylic acids, which on a case-by-case basis have been identified to stabilize foams of several crude oils as well as to inhibit corrosion [32], [161].

Experimental Strategy

The study to determine how carboxylic acids and asphaltenes influence foaming and corrosion inhibition properties of oils was achieved using a two pronged experimental approach. The first approach was to study the hydrocarbon liquid with dissolved model acid compounds representative of those found in real crudes. Although somewhat simplified, this approach was already successfully used in previous studies [31]–[33]. Myristic acid and a naphthenic acid mixture dissolved in LVT200 model oil were used to simulate the crude oils containing organic acids. The second approach, employed in the study of asphaltenes, was to test the whole crude with a significant weight percent of this class of compound. Crude oil containing approximately 4 wt.% of asphaltenes was used as received, without any further alteration of its chemical composition. A test matrix show-

ing oil types used is shown in Table 2. The gaseous phase was CO₂, while the aqueous phase used for corrosion measurements was a 1 wt.% NaCl solution buffered at pH 5 with CO₂/NaHCO₃. Experiments were performed at ambient conditions with respect to temperature and pressure. Detailed information about physicochemical properties of the used materials is given in the Appendix A.

			Test Type			
No Oil Type	Polar compound	Interfacial Tension	Foaming	Corrosion Inhibition		
1		None	X	X	-	
2	LVT 200	Myristic acid (0.1wt%)	X	Х	Х	
3		Naphthenic acid mixture (1wt%)	Х	Х	Х	
4	Crude oil	Asphaltenes* (≈4wt%)	Х	Х	Х	
Test conditions: pH 5 aqueous solution 1wt% NaCl adjusted with CO ₂ /NaHCO ₃ , 1bar CO ₂ ambient temperature ($\approx 25^{\circ}$ C)						

Table 2 – Test matrix for testing the foaming and corrosion inhibition properties of crude oil polar compounds

* Value obtained from crude oil assay [166].

Experimental Setup and Procedure

Three types of experiments were employed in this investigation: oil-gas interfacial

tension, foaming characterization and corrosion inhibition.

Interfacial Tension Measurements

Oil-gas surface tension measurements were performed to evaluate the surface activity

of acidic compounds. Despite the diversity of encountered chemical compositions, oil-gas

interfacial tension of crude oils and refined petroleum products are generally in a relatively narrow range which can impair use of such measurements for analytical purposes [78], [144]. However, when detectable, even the smallest alterations caused by addition of chemical compounds can signify positive or negative adsorption effects at interfaces. Experiments were performed using the Du-Nouy ring method described in the Appendix B. LVT200 and chemicals that were added were weighed then thoroughly mixed for at least 90 minutes using a magnetic stirrer, while being continuously sparged with CO₂. Measurements were performed with 30-40ml of the oil phase. Each measurement was repeated at least three times.

Foaming Characterization

Foaming characteristics were assessed by measuring two parameters, foaminess and foam stability. In this work foaminess is defined as the maximum foam volume which can be created during the foam generation process. Foaminess confers information on the propensity of liquid to create foam, e.g., on spots in pipelines where foam can be continuously created, such as at pipe bends. Foaminess was tested by bubbling CO₂ into the oil. Alternative methods which involve mixing or shaking exist, but the bubbling method is preferred due to the ability to easily control the amount of gas introduced by bubbling into a liquid [152]. Foam stability is the second parameter which is defined as time needed for complete foam depletion after gas sparging stops. This parameter should quantify the rate of foam decline after conditions responsible for its creation ceased to exist. Experiments were performed in a 250 ml graduated cylinder in 100 ml of the oil phase poured therein. A fritted glass sparger (pore size 25-50 µm) was then placed to the

bottom of the cylinder which was then partially closed at the top with a rubber bung. The sparger was connected to an Omega FL-3539ST rotameter *via* a plastic tube with a valve. Gas flow rate for all measurements was set constant to 1062 ml/min. The maximum foam volume (foamability) for all experiments was measured and recorded when the foam reached the maximum level during the bubbling. After recording the maximum volume, sparging with gas was stopped. Decreasing foam volume was measured every 10 seconds until there was complete foam depletion.

Corrosion Experiments

Corrosion measurements were performed to test the relationship between foam formation and corrosion inhibition. An experimental procedure was established which compares the steel corrosion rate by exposing the electrode to foamed and non-foamed oils that contain polar compounds. Experiments were performed using the procedure shown schematically in Figure 31. The experimental setup included the following equipment and materials:

- Vertical transparent PVC tube for foam formation (2" diameter)
- Fritted gas sparger placed inside the PVC tube (25-50 µm pore size)
- Rotameter for CO2 flow rate measurements
- 2L glass cell for corrosion measurements using rotating cylinder electrode (described in the Appendix C)
- Oil solution containing polar compounds
- Aqueous solution containing 1 wt.% NaCl buffered to pH 5 with CO2/NaHCO3

Approximately 1 liter of the oil solution was prepared in a flask. Components were weighed, mixed and sparged with CO₂ for at least 1 hour. The brine solution in the glass cell was prepared by adding NaCl and solid NaHCO₃ for approximate pH adjustment, this was purged with CO₂ for 1-1.5 hours using a fritted glass tube. pH was then precisely adjusted to 5.0. Throughout experiments, the fritted glass spargers were lifted from the solutions and placed approximately 5 millimeters above the liquid surface to preserve CO₂ blanketing. Steel rotating cylinder specimens were polished using 600 grit silicon carbide sandpaper using deionized water and isopropanol as coolant. The specimens were then cleaned in an ultrasonic bath for at least two minutes and briefly dried with a heat gun.



Figure 31 – Experimental procedure for testing the influence of foam formation on corrosion inhibition.

The experimental procedure for corrosion measurements can be divided into four consecutive stages: precorrosion, oil addition, direct inhibition and persistency. In the precorrosion stage, polished specimens were immersed in the aqueous solution and corrosion rate was recorded. Linear polarization measurements were performed every 5 minutes over the first 20 minutes of each test. In the *oil addition* stage 0.3 liters of oil was poured inside the glass cell, so it formed a layer of oil on top of the aqueous solution. This was performed slightly differently for experiments with and without foam formation. In the experiment without foam formation (denoted 1 in Figure 31) oil was directly poured from the Erlenmeyer flask. In the experiment with foam formation (indicated by 2' and 2'' in Figure 31) 0.4 liters of the same solution of inhibiting compound was poured into the 2" diameter vertical PVC tube in the presence of CO₂. The sparger was then immersed into the oil phase and CO₂ bubbling was started in order to generate foam. When the foam in the tube reached the maximum level, 0.3 liters of oil was drained from the bottom of the tube (during the bubbling) and poured into the glass cell. This operation was performed promptly in order to minimize contact of oil with air. After pouring the oil in the glass cell the steel specimen was lifted up from the water phase into the oil layer and rotated for 20 minutes during the *direct inhibition* stage. Rotation speed in the oil phase was set to 2000 rpm when LVT200 was used. The specimen immersed in the crude oil had to be rotated at 1000 rpm in order to reduce agitation and avoid emulsification. No corrosion rate measurements were taken during this stage since the specimen was immersed in model oil, which is a non-conductive liquid. During this stage it is expected that polar components from the oil phase get adsorbed at the steel

surface. In the *persistency* stage, after immersion in oil, the specimen was lowered back into the water phase and rotated at 2000 rpm. Open circuit potential was monitored until it became sufficiently stable for LPR measurements to be conducted, the time for this to occur ranged from 20 to 40 minutes. Corrosion rate was then measured every 5 minutes for at least 1 hour. Corrosion rate measured in this stage quantify the inhibitive effect of polar compounds and persistency of an adsorbed layer.

Results and Discussion

In a limited context, the connection between foaming and corrosion inhibition has been investigated in the past. However, the link between foaming of an oil phase and corrosion inhibition has not been investigated. Changes of liquid interfacial tension upon introducing a solute is an indication of changes of chemical composition at an interface. The anticipated surface tension changes for solutions of carboxylic in hydrocarbons are minute. Previous surface tension measurements have shown that dissolving as much as 1.4 wt.% of myristic acid decreases the surface tension of a mixture of liquid cycloalkanes (naphthenes) by less than 1 dyne/cm, which was interpreted as an indication that in hydrocarbon solutions the molecules of solute and solvent were comparatively similar so that solvent molecules were not completely displaced from the surface [167].

The results of surface tension measurements are presented in Figure 32. The average surface tension of LVT200 model oil was 25.8 dyne/cm. The slightly higher average surface tension of 26.0 dyne/cm was measured for a 0.1 wt% solution of myristic acid and the equal average value was obtained with the 1 wt.% naphthenic acid solution.



The results of current surface tension measurements show relatively small variability considering the absolute values of measured surface tensions. However, there was still a significant overlap between measured values of different oils. Therefore, it can be concluded that surface tension measurements were not found to be significantly different for tested solutions, it can only be concluded that the test method does not provide sufficient-ly good accuracy with this number of repeated measurements.

The results of foaminess and foam stability measurements are presented in Figure 33. Foaminess of the pure LVT200 model oil was minute. During continuous bubbling the maximum foam volume slightly fluctuated around the mean value of 20 ml. Foam depleted approximately 7 seconds after gas injection stopped. Little or no alterations of foaming properties were observed with addition of acids. Foamability and foam stability of myristic acid solution was identical to solute-free LVT200. The maximum foam
volume obtained with the naphthenic acid solution was slightly higher, 25 ml, while foam depletion time was 8 seconds. The foaminess of crude oil was substantially higher. The maximum recorded foam volume obtained with crude oil was 160 ml. After bubbling stopped the initial very sharp rate of foam decay decreased with time, until foam completely depleted after 46 seconds. Visual observations revealed that foams created in the experiments were mostly spherical type and only small amounts of polyhedral foam was observed with crude oil.



Figure 33 – Foam stability of model oil with carboxylic acids and the crude oil.

The results of foaminess and foam stability measurements showed that all solutions were only able to produce short-lived, transient foams. Furthermore, myristic acid and naphtehenic acids did not alter the foaming characteristics of LVT 200. Substantially higher foaminess which is observed with crude oil can be potentially explained by either higher bulk viscosity of crude oil (9.1 cp) compared to LVT 200 (2.7 cp), or by the differences in chemical composition. According to the available literature, the time for foam collapse of different examined crude oils varies from 2 to 8 minutes [158]. The experimental procedure is not completely comparable with other studies that were investigating this issue. Nevertheless, it should be mentioned that in this study, with the crude oil that was tested, the collapse time was significantly shorter.

The results of corrosion measurements are presented in Figure 34, Figure 35 and Figure 36. Figure 34 show results of corrosion rate measurements performed with addition of myristic acid oil solution. Initial corrosion rate obtained in the first experiment, before adding non-foamed oil solution, was 1.9 mm/y which dropped to 0.2 mm/y after exposing the specimen to oil and remained constant until the end of the experiment. In the second test, the initial measured corrosion rate was approximately 1.6 mm/y. The corrosion rate was reduced to approximately 0.2 mm/y after exposure to oil.



Figure 34 – Comparison of corrosion rates with 0.1 wt.% myristic acid in LVT200 with and without foaming.

Results presented in Figure 35 show comparison of corrosion rates obtained before and after exposing the steel specimens to a solution of the naphthenic acid mixture dissolved in LVT 200. In the first experiment, where non-foamed oil solution was used, the initial measured corrosion rate was 1.6 mm/y. During addition of oil, rotation in the oil phase and open circuit potential stabilization period, LPR data were not recorded (which is shown as the blank area on the graph). Corrosion rate measured at the onset of stabilization, which presents 62% inhibition. In the second experiment, initial measured corrosion rate was 1.7 mm/y, whereas the final value reached 0.8 mm/y. Relative to measured initial corrosion rate, this is a decrease of 52%. It is interesting to note that corrosion rate continued to decrease with time after the specimen was was reimmersed in the aqueous phase.



Figure 35 – Comparison of corrosion inhibition with 1 wt.% naphthenic acid solution in LVT200 with and without foaming.

Corrosion measurement results shown in Figure 36 are recorded with addition of Crude 3. In the experiment with non-foamed oil initial measured corrosion rate was 1.6 mm/y before the oil was added. After immersion and open circuit potential stabilization, corrosion rate dropped to 0.6 mm/y. The initial measured corrosion rate in the second experiment was 1.4 mm/y which is then lowered to 0.4 mm/y after the specimen was in contact with oil. It should be noted that in this case a rotation speed of 1000 rpm was used instead of 2000 rpm in order to avoid emulsification of oil in the glass cell.



Figure 36 – Comparison of corrosion inhibition for Crude oil with and without oil foaming.

Corrosion inhibition efficiency is a measure of the reduction of the corrosion rate, expressed in percentages, which is attained by addition of a corrosion inhibitor. Inhibition efficiency is calculated according to the formula:

$$IE = \frac{CR_{uninhibited} - CR_{inhibited}}{CR_{uninhibited}} \times 100$$
(57)

Where IE is the inhibition efficiency (%), CR_{uninhibited} (mm/y) and CR_{inhibited} (mm/y) are the corrosion rates measured in the aqueous phase before and after treating the solution with corrosion inhibitor, respectively. Inhibition efficiency is a function of concentration of the inhibiting compound [139]. If other system parameters, such as pH, temperature or flow rate, do not change, higher concentrations of inhibitors increase inhibition efficiency. The opposite can be applied to compare two inhibited solutions.

Inhibition efficiency can indicate which solution has a higher concentration of the inhibitor by taking into account that all other test conditions are the same.

For current measurements inhibition efficiencies were calculated to assess the effect of foaming on corrosion inhibition. Corrosion rates used for calculations were computed from the last datapoints obtained from LPR measurements before exposing steel to the oil solution ($CR_{uninhibited}$) and the last datapoints obtained in each experiment ($CR_{inhibited}$). The results are presented in Table 3.

Oil phase	Foaming	CR _{uninhibited} (mm/y)	CR _{inhibited} (mm/y)	IE (%)
1 wt.% naphthenic acid in LVT 200	No	1.62	0.61	62
	Yes	1.74	0.84	52
0.1 wt.% nyristic acid solution in LVT 200	No	1.66	0.2	88
	Yes	1.86	0.2	89
Crude oil (≈4 wt. % asphaltenes)	No	1.63	0.62	62
	Yes	1.38	0.38	72

Table 3 – Inhibition efficiencies obtained after exposing the specimen to oils containing different polar organic compounds.

Inhibition efficiency of the foamed naphethenic acid solution was 10% lower than for the non-foamed solution of the same compound. However, foaming solutions of myristic acid and naphtehenic acid solution showed the opposite tendency to alter corrosion rate. Obtained inhibition efficiencies were, respectively, 1% and 10% higher for the solutions which were foamed. Previous results obtained by Canto with the surfactant-based corrosion inhibitors TOFA/DETA imidazoline and a quaternary ammonium compound in aqueous solutions showed that inhibition was always at least 50% lower when the test solution was foamed. The same set of experiments also showed that the effect of foaming was not observable due to the lack of surface activity of thiosulfate, a common component compound in inhibitor formulations, at the water-gas interface [138]. The current corrosion measurements did not show strong effect of foaming on inhibition properties as it was in the measurements performed by Canto. Furthermore, crude oil, which showed the best foaming characteristics, was also more inhibitive in foaming condition. Therefore, it is more likely that obtained differences in corrosion rates can be attributed to other factors rather than the effect of foaming.

Significant changes in corrosion rates can be observed only if there is a significant difference in a concentration of solutes between foamed and non-foamed bulk oil solutions. Those differences can be only obtained if the concentration of solutes (organic acid or asphaltenes) is significantly higher in the portion of liquid foam. Furthermore, this change should be only observable if a concentration of solute is significantly higher at the oil-gas interface compared to the bulk, *i.e.*, if there is a surface excess concentration of solutes. This presence of solutes where there is excessive adsorption would be most probably observed in a change of surface tension and foaming properties, reflecting the corrosion inhibition by foaming solutions. However, none of the performed experiments indicated with the investigated compound classes indicated that the excess concentrations at the oil-gas interface would have an impact on corrosion. This implies that concentra-

tion of acids in the bulk oil solution remained unchanged or not significantly different during foaming. The reason for this is probably the absence of preferential adsorption of tested compounds at the oil-gas interface, which is driven by solute-solvent-surface intermolecular interactions. However, based on current results, the true reason is unknown.

Summary

Experiments were performed to test the hypothesis that corrosion inhibition by naturally present polar compounds in crude oils can be compromised by 'parasitic adsorption' of excessive amounts of those compounds into foam. Compound classes which were chosen to test the hypothesis, namely asphaltenes and carboxylic acids, were previously reported to have corrosion inhibition and foam-forming characteristics. However, the results on the representative compounds used in this research did not show dual foaming and corrosion inhibition properties. Therefore, the results of this study indicated that there is no general principle which would connect the sole presence of those compound classes with 'parasitic consumption' and consequent loss of inhibition.

CHAPTER 5: EFFECT OF LIQUID HYDROCARBON ON FOAMING OF AN IMIDAZOLINE-TYPE CORROSION INHIBITOR AND SUBSEQUENT CORROSION INHIBITION

Some types of surfactant-based corrosion inhibitors can adsorb at water-gas interfaces and cause foaming. Such occurrences in gas pipelines can potentially compromise corrosion inhibition of steel due to adsorption of excessive amounts of inhibitor at the water-gas interface which causes a decrease of inhibitor concentration in the bulk aqueous solution. To some extent foaming can be suppressed by small amounts of a hydrocarbon liquid phase which is almost always present in pipelines. Furthermore, antifoaming properties vary with chemical composition of hydrocarbon. Therefore, even small amounts of hydrocarbons can circumstantially impact corrosion by reducing the amount of generated foam. This chapter presents the results of an investigation into the influence of hydrocarbon oils on formation of foam by corrosion inhibitor and inhibition of corrosion.

Research Hypothesis

Results of the previous corrosion measurements, introduced in Chapter 2, indicated that adsorption of excessive amounts of surfactant-based inhibitors at water-gas interfaces due to foaming causes decreased inhibitor concentration in bulk solutions. Corrosion rates of mild steels exposed to such solutions are higher compared to non-foaming solutions [26]. However, all previous investigations were performed without taking into account that liquid hydrocarbons are almost always present in pipelines. The role of liquid hydrocarbons on foaming of corrosion inhibitors in gas pipelines was also documented in one field case. It has been reported that: "The absence of hydrocarbon liquids production in each wells gas production (40 to 70 mmscfd) increased operational risks that foam would develop in the production system once the injected corrosion inhibitor partitioned into the produced brine phase." [142]. Previous research on aqueous foam-oil interactions in crude reservoirs suggest that different liquid hydrocarbon oils can, to various degrees, destabilize foams [168]–[170]. However, other investigations indicate that some foams may, in fact, be stabilized by certain types of oils [171], [172]. It is still unknown how hydrocarbon liquids, which are almost always present in pipelines, can affect inhibition of corrosion by influencing formation of foam by surfactant-based corrosion inhibitors. Furthermore, it is even less known if different oils can have destabilizing or stabilizing effects on foaming of solutions of different inhibiting compounds. Therefore, it can be hypothesized that:

Presence of hydrocarbon oil on top of an aqueous inhibitor solution can partially or completely suppress the foaming and consequent loss of inhibition. Furthermore, the impact of light hydrocarbon liquid will be such that they most likely have stronger antifoaming properties.

This aspect can be particularly important in gas pipelines which most commonly carry phases other than water and gas, but also hydrocarbon liquid condensate. This condensate is a mixture of liquid hydrocarbon compounds which, due to decreases of temperature and changing pressure, pass below their dew points and condense inside the pipeline. The composition of condensate can significantly vary with pressure and temperature even along the same pipeline. Because of such influences, it is necessary to extend the previous knowledge related to loss of inhibition due to foaming by incorporating the effect of a hydrocarbon oil layer on foam formation and corrosion inhibition.

Mechanisms of Oil - Foam Interaction

There are several proposed mechanisms which explain stability of foams in the presence of oils. Here, will be present theories which describe the interaction of small oil globules which are dispersed (emulsified) in a foam structure and their ability to subsequently emerge (enter) to the surface of the of the foam lamellae [152]. The process of oil globule entering a foam structure depends on the stability of the thin film which separates the oil globule from the surface of the lamella. This film-within-the-film, shown in Figure 37, is termed a pseudoemulsion film and is bounded by water-oil and water-gas interfaces. If the pseudoemulsion film is stable, oil droplets are unable to enter the surface of the lamella in which case droplets can migrate into the Plateau borders and retard the drainage of water and to some extent stabilize the foam [173]. Successively, entrance of oil globules can occur in plateau borders due to compression after a sufficient amount of water has been drained. On the other hand, unstable pseudoemulsion films can rupture and oil droplets can enter the gas-water interface. Subsequently, droplets can spread at the surface or pseudoemulsion film emerges on the opposite side of the lamella and form the oil "bridge". The thermodynamic aspect of this process is qualified by the "entry coefficient", while the kinetic aspect of this process is discussed in terms of stability of the pseudoemulsion film; this is a thin aqueous film separating the oil drop and gas-water interface [174].



Figure 37 – Oil drop entering the surface of aqueous foam lamella.

The entry (or entering) coefficient is a value obtained from three interfacial tensions:

$$E = \sigma_{w/g} + \sigma_{o/w} - \sigma_{o/g} \tag{58}$$

Where $\sigma_{w/g}$ is the water-gas interfacial tension, $\sigma_{o/w}$ is the oil-water interfacial tension, and $\sigma_{o/g}$ is the oil-gas interfacial tension. For negative values of entering coefficient (*E*<0), the oil droplet cannot enter the water-gas interface and stays entrapped within foam lamella. If the value is positive (*E*>0) the oil droplet can enter the surface. The kinetics of the entry process, however, does not depend on the magnitude of the entry coefficient. The magnitude of this can be quantified by measuring the "entry barrier" which is the experimentally determined value of pressure needed to cause coalescence [175]. Therefore, if the entry coefficient *E* is positive and the entry barrier is relatively low, oil droplet can enter the water-gas surface. However, if *E* is positive but the entry barrier is high, the process of entering is kinetically slow which can *de facto* prevent the entry of an oil droplet to the lamella surface [174].

Lamella may burst by one of the mechanisms related to oil spreading or bridging [173]. Several rupture mechanisms have been proposed or identified namely as "bridging-stretching", "bridging-dewetting", "spreading-fluid entrainment" and "spreadingwave generation" [174]. The bridging-steretching mechanism (Figure 38A) occurs due to the stretching of a bridge in a direction parallel to the surface, as a result of capillary pressures at the oil-water and oil-air interfaces, which leads to thinning of an oil film and its rupture. Bridging-dewetting mechanism (Figure 38B) supposes that the oil bridge is dewetted, by the aqueous phase due to the hydrophobic surface of the oily globule. Typically, this is only possible if the oil phase is viscous so the time needed for dewetting is faster than the time needed for rupture by the bridging-stretching mechanism [173].



Figure 38 – "Bridging-stretching" (A) and "Bridging-dewetting" (B) mechanisms.

In relation to the mechanism of foam destruction by the bridging mechanism, this has been related to the "bridging coefficient" *B*, derived from the interfacial energies of the three phases:

$$B = \sigma_{w/g}^{2} + \sigma_{o/w}^{2} - \sigma_{o/g}^{2}$$
(59)

This coefficient is derived from the balance of interfacial tensions at the three phase oil-water-gas contact line and capillary pressures across the oil-water and water-gas interfaces. Detailed derivation of the coefficient can be found in the literature [176]. A positive value of the bridging coefficient (B>0) implies an unstable oil bridge, leading to lamellae being more prone to rupture by the bridging-stretching or bridging-dewetting

mechanisms. In such a case, the unstable oil bridge is more vulnerable to mechanical perturbations of foam lamellae which are able to displace the bridge from mechanical equilibrium and eventually destroy the oil bridge. When the value of the entering coefficient is negative (B<0), the bridge is stable and the film does not rupture. The stable bridges would tend to restore their shape when they are exposed to small mechanical perturbations [173].

In the "spreading-fluid entrainment" mechanism spreading oil from the antifoam globule is assumed to cause a Marangoni flow of liquid in the foam film, which results in local film thinning and rupture [173]. The "spreading-wave generation" mechanism states that spreading oil induces large amplitude capillary waves on the surface of the foam films. The waves lead to foam film rupture within a short time period, of no more than a few seconds, even at relatively large average film thicknesses. It is believed that a "spreading oil probably 'sweeps' some of the surfactant adsorbed on the foam film surface, which results in film destabilization" [173].



Figure 39 – "Spreading-fluid entrainment" and "Spreading-wave generation" mechanisms.

Oil droplets will spread depending on the value of their spreading coefficient:

$$S = \sigma_{w/g} - \sigma_{o/w} - \sigma_{o/g} \tag{60}$$

If the spreading coefficient is positive, oil will spread at the surface. If the coefficient is negative, however, oil will reside as a lens at the surface of the water until. It has been noticed that oils which spontaneously spread at the surface of the water have a general tendency to be more detrimental for foams compared to ones which don't spread [174].

Experimental Strategy

The experiments were designed to evaluate the influence of two different hydrocarbon liquids on foaming and corrosion inhibition by one surfactant-based corrosion inhibitor. TOFA/DETA imidazoline-based corrosion inhibitor was chosen because it is surfactant-type and ubiquitous in standard corrosion inhibitor formulations. Two hydrocarbon liquids were selected, heptane (C-7 paraffinic hydrocarbon) and LVT200 model oil (mixture of paraffinic hydrocarbons with carbon number C13-C15). They are chosen to represent the lightest and heaviest hydrocarbon liquid fractions.

Two types of measurements were performed. The first set of measurements included measurements to quantify foaming properties of the oil solutions. Foamability, which is the ability of a solution to produce foam and foam stability, defined as the lifetime of foam, are common parameters for foam characterization [177]. They depend on many physical factors including surface tension, critical micelle concentration (CMC), bulk and surface viscosities, Marangoni effect, disjoining pressure, and hydrophobic interactions [178]. The second set of measurements was designed to test direct connections between foam formation and corrosion. That was achieved by comparing the steel corrosion rates

in 3 aqueous inhibitor solutions namely "non-foamed", "foamed" and "foamed with the presence of hydrocarbon liquid layer". The test matrix is given in Table 4.

Inhibitor Con- centration	0.14	Test Type		
	Oli type	Foaming	Corrosion Inhibition	
25ppm	No oil	Х	Х	
	LVT200	Х	Х	
	heptane	Х	-	
100ppm	No oil	Х	-	
	LVT200	Х	-	
	heptane	Х	-	
Test conditions: pH 5 aqueous solution 1 wt.% NaCl adjusted with CO ₂ /NaHCO ₃ , 1 bar CO ₂ , ambient temperature (\approx 25°C)				

Table 4 – Test matrix for antifoaming properties of hydrocarbon oils

Experimental Setup and Procedure

Two types of experiments were employed in this investigation: foaming characterization and corrosion inhibition.

Foaming Characterization

Foaming experiments were performed using 100 ml of inhibited water solution poured in a 250 ml graduated cylinder. A fritted glass sparger (pore size 25-50 μ m) was then placed to the bottom of the cylinder. In the experiments with model oils, a desired

amount was then slowly poured on the top of the aqueous phase. The test vessel was subsequently closed from the top with a punctured rubber bung. The sparger was then connected to a rotameter with a three-way valve between them, which served as a switch that allowed the gas to be quickly directed into the sparger or to the atmosphere. Gas flow rate for all measurements was set constant to 1062 ml/min using the Omega FL-3539ST rotameter. The maximum foam volume (foaminess) for all experiments was measured and recorded when foam reached a maximum level during the bubbling process. After recording the maximum volume, bubbling was stopped. Time needed for complete foam depletion was then recorded.

Corrosion Experiments

Corrosion inhibition experiments were performed using the procedure schematically shown in Figure 40. The experimental setup included the following equipment and materials:

- Vertical transparent PVC tube for foam formation (2" diameter)
- Fritted gas sparger placed inside the PVC tube (25-50 µm pore size)
- Rotameter for CO2 flow rate measurements
- 2L glass cell for corrosion measurements using rotating cylinder electrode (described in the Appendix C)
- Aqueous solution containing 1 wt.% NaCl buffered to pH 5 with CO2/NaHCO3

Two brine solutions were prepared in a flask and in a glass cell using the same procedure. Required amounts of NaCl and solid NaHCO₃ were measured and added into the vessels. Deionized water was added and the resultant solution sparged with CO_2 for 1-1.5 hours using a fritted glass tube. pH was then precisely adjusted to 5.00. The brine solution was then inhibited and the sparger was lifted above the surface to prevent unwanted foaming. The brine solution in the glass cell was sparged until the start of the experiment. Throughout experiments glass spargers were lifted from the solutions and placed a few millimeters above the liquid surface to preserve its CO₂ blanket. Rotating cylinder specimens were polished using 600 grit silicon carbide sandpaper using deionized water and isopropanol as a coolant. Specimens were then cleaned in an ultrasonic bath for at least two minutes and briefly dried with a heat gun.



Figure 40 – Experimental setup for testing the influence aqueous foam formation on corrosion inhibition; 1-no foam formation; 2-foam formation without oil layer; 3-foam formation with oil layer.

The procedure for corrosion inhibition experiments can be divided into three stages:

precorrosion, addition of inhibited solution and inhibition stage.

Precorrosion stage: Steel specimen immersed in the glass cell filled with 1.7 liters of uninhibited aqueous solution and the RCE rotation speed was set to 2000 rpm. Corrosion rate was recorded using the LPR technique every 5 minutes for 1.5-2 hours to determine the corrosion rate baseline.

Addition of inhibited solution: After measuring the baseline corrosion rates 0.3 liters of inhibited brine solution was poured into the glass cell so the total volume reached 2.0 liters. The solution was then stirred with a magnetic stirrer for a few seconds to homogenize the solution. Inhibited brine solutions that were added into the glass cell were prepared in a distinct way for each of the three experiments (schematically represented as 1, 2 and 3 in Figure 40).

In the experiment without foam formation (marked 1 in Figure 40) 25ppm of imidazoline inhibitor (K1) was dissolved in the flask which contained 0.3 liters of inhibited solution and was then poured into the glass cell.

In the experiment with foam formation without presence of oil (marked 2 in Figure 40) 0.4 liters of the same inhibited solution (25ppm K1 concentration) was poured into the 2" diameter vertical PVC tube that was previously purged with CO_2 . The sparger was then immersed into the water phase and CO_2 bubbling was started in order to generate foam. When the foam level in the tube reached the maximum, 0.3 liters of inhibited liquid solution was drained from the bottom of the tube (during the bubbling) and poured into the glass cell.

In the experiment with foam formation with addition of oil (marked 3 in Figure 40) 0.4 liters of inhibited solution was poured into the vertical PVC tube followed by 20 ml of LVT 200 model oil. Bubbling with CO_2 was started and when the foam in the tube reached the maximum level, 0.3 liters of inhibited liquid solution was drained from the bottom of the tube (during the bubbling) and slowly poured into the glass cell.

Inhibition: After addition of the inhibited water solution, corrosion rate measurements in the glass cell were continued for the next 9-10 hours.

Results and Discussion

Although the influence of inhibitor foaming on corrosion inhibition has previously been investigated, incorporating the effect of various liquid hydrocarbons on foaming of corrosion inhibitors is a novelty. The results of foaminess measurements are presented in Figure 41 and Figure 42. In the baseline foaminess tests, aqueous solutions of TOFA/DETA imidazoline added at 25ppm and 100ppm concentrations formed 120 ml and 250 ml of foam, respectively. Addition of hydrocarbon oil on top of the aqueous phase significantly decreased the maximum volume of generated foam. For the solution containing 25 ppm of inhibitor, both hydrocarbon oils were able to reduce foaminess approximately tenfold. The foaminess with LVT 200 was 10-15 ml with 5 ml and 10 ml of LVT 200 and 8-10 ml with 20 ml and 40 ml of LVT 200. Foaminess obtained with heptane was uniform, in the range from 8 to 10 ml for all oil volumes. For 100 ppm inhibitor solution the decrease of foam volume was gradual with increasing the volume of added oil. Foaminess values obtained with LVT 200 were 90-110 ml for 5 ml, 100-130 ml for 10 ml, 80-100 ml for 20 and 70-90 ml for 40 ml of oil.



Figure 41 – Foaminess of 25 ppm aqueous inhibitor solutions when two types of model oils (LVT 200 and heptane) were added on top of the water phase.



Figure 42 – Foaminess of 100 ppm aqueous inhibitor solutions when two types of model oils (LVT 200 and heptane) were added on top of the water phase.

Foam stability was assessed as the time needed for complete foam depletion. The depletion time as a function of the added volume of oil is shown in Figure 43 and Figure 44. For 25 ppm inhibitor concentration solution depletion time was 3 minutes when no oil was added. Addition of hydrocarbon significantly shortened the time needed for depletion. Both hydrocarbon liquids showed similar performance and shortened the depletion time to 4-8 seconds. The depletion time of foam obtained with 100 ppm inhibitor solution was 9 minutes, which is an threefold increase compared to 25 ppm inhibitor solution. Foams which were formed with addition of hydrocarbons had shorter depletion times. Foam which was created with LVT 200 had depletion times which were approximately 2-3 minutes. The slightly lower time was observed with the foam formed with 40ml of LVT 200 compared to the others. For heptane, there was a trend of decrease in depletion time with an increase in fluid volume. The most stable foam, which depleted 4 minutes after sparging was stopped, was observed with the lowest amount of added hydrocarbon. The measured depletion time gradually decreased to less than 10 seconds for the highest amount of oil.

The high variability foam stability results are related the effect of partial attaching of foam to wall of graduated cylinder. Secondly, during the foaming a small amount of oil was brought up with the foam to the cylinder wall leaving the oil residue, which prevented the foam from sticking to the cylinder wall. Those to factors (sticking to the cylinder wall and oil residue) led to variation in foam stability results.



Figure 43 – Foam stability of 25 ppm aqueous inhibitor solutions when two types of model oils (LVT 200 and heptane) were added on top of the water phase.



Figure 44 – Foam stability of 100 ppm aqueous inhibitor solutions when two types of model oils (LVT 200 and heptane) were added on top of the water phase.

Cationic surfactants generally have lower foaming properties compared to anionic surfactants. However, foaming properties of fatty acid imidazoline derivatives are considered to be relatively good [179]. Foamability results show an increase in foam volume of more than twofold with increasing concentration from 25 ppm to 100 ppm. In general, foamability of aqueous solutions increases with surfactant concentration and reaches the maximum for concentrations slightly higher than the CMC [2]. Reported CMC value for this TOFA/DETA imidazoline inhibitor is in the range of 36ppm. However, in this particular case an increase of maximum foam volume can originate from one additional factor. Since foamability was assessed by measuring the maximum foam volume during the bubbling process, surfactant concentration in the bulk solution gradually decreases until it reaches the level which is too low to produce persistent foam bubbles. This process, known as foam fractionation, is sometimes exploited by design to separate surfactants from aqueous bulk solutions [180]. At that concentration the balance between foam generation and decay equalizes and the foam level slightly fluctuates. Since the higher concentration of surfactant implies a higher amount of surfactant in the foaming vessel, more foam can be created before the concentration reaches that value.

The second effect which had a substantial effect of oil on foamability of the aqueous solution was the presence of oil. In this case it was shown that, like for the most of the other surfactants, oil had a detrimental effect on foams. The nature of oil, however, seems to play a significant effect only with higher concentration (100 ppm) of TOFA/DETA imidazoline-based inhibitor. At lower concentration of inhibitor (25 ppm) both oils performed the same. A majority of previous studies reported lower foaminess and foam

stabilities in the presence of alkanes with shorter chain length. The results of current measurements, however, cannot explain the mechanism by which the lower molecular weight hydrocarbons are more detrimental to foams. It has been suggested that mechanisms can be different for entering and spreading at the surface. The lower molecular weight hydrocarbons have a higher tendency to enter and spread at the surface. In contrast, higher molecular weight hydrocarbons either form lenses which are possibly covered with thin pseudoemulsion films [181].

Results of corrosion inhibition experiments are presented in Figure 45. The initial measured corrosion rate ranged from 1.7 mm/y to 2.0 mm/y for all three specimens. Sharp drops in the measured corrosion rates correspond to time points when the inhibited solutions were added into the glass cell, which was approximately 90 minutes after the start of the experiment. In the corrosion experiment with addition of non-foamed inhibited solution a gradual and initially very steep decrease of corrosion rate was observed. The final corrosion rate observed 12 hours after starting the experiment was 0.1 mm/y. In the second experiment (2), the inhibited solution was foamed and added to the glass cell. Corrosion rate slowly decreased by approximately 23%, to 1.3 mm/y, which is 71%lower inhibition compared to the first experiment. The rate of corrosion rate decline was correspondingly lower. In the third experiment (3), inhibitor solution was foamed in the presence of oil on top of the aqueous phase. The observed corrosion rate was lowered to 0.6 mm/y, which is a 72% decrease compared to initial corrosion rate. That is an intermediate value compared to the previous two experiments. The rate of corrosion rate decline was also correspondingly intermediate. As can be seen, significant difference were

observed for inhibition without foam formation (1), with foam formation (2), and when the foaming was induced with LVT200 model oil on top of the water (3).



Figure 45 – Comparison of corrosion rates in tests with foamed and non-foamed TOFA/DETA imidazoline-based inhibitor solutions.

Corrosion inhibition results coincide with previous results for the same inhibitor obtained by C. Canto [26]. Formation of foam significantly reduced the corrosion inhibition, which is due to the "parasitic" consumption of inhibitor on water-air interfaces. The current results showed that the presence of oil on top of the aqueous inhibitor solution can significantly alter not only the foaming properties, but also the inhibition properties. Table 5 shows a comparison of inhibition efficiencies calculated according to Equation (58).

Oil phase	CR _{uninhibited} (mm/y)	CR _{inhibited} (mm/y)	IE (%)
Nonfoamed solution	1.7	0.1	94
Foamed solution	1.9	1.3	32
Foamed solution with LVT200 added oil	2.0	0.6	70

Table 5 – Inhibition efficiencies of TOFA/DETA imidazoline inhibited water solutions

In this study only one experiment was performed in the presence of one type of oil and with low inhibitor concentration, so no conclusions can be made related to the potential influence of oil type on corrosion inhibition. It can be assumed that those differences can be found with the solution containing 100ppm of inhibitor, for which different hydrocarbons exhibited different antifoaming characteristics.

Summary

Foaming and corrosion inhibition experiments were performed to test the hypothesis that liquid hydrocarbons can suppress formation of foams generated by corrosion inhibitors. Furthermore, it was hypothesized that the lighter hydrocarbon liquid will have more detrimental effects on foaming. The components which were chosen for the research were TOFA/DETA imidazoline-based corrosion inhibitor and two hydrocarbon liquids, heptane (C7) and a mixture of C13-C15 hydrocarbons. The results of foaming measurements showed that maximum foam volume and foam stability of inhibitor were reduced in the presence of oil. The lighter hydrocarbon (heptane) had a more deleterious effect on foaminess and stability. Corrosion experiments showed that loss of inhibition due to foaming was reduced when oil was added to foaming solution of inhibitor.

Therefore, the results of this study indicated that presence of oils can reduce 'parasitic consumption' of surfactant-type inhibitors and partially preserve their efficiency in foaming conditions.

CHAPTER 6: EFFECT OF PRE-CORRODED SURFACES ON THE PERSISTENCY OF WATER LAYER ON MILD STEEL

Internal pipe steel surfaces are seldom pristine. Even in an as-delivered condition, pipes are likely to have a mill scale on their surfaces originating from manufacturing processes [182]. Furthermore, during oil and gas production, various types of deposits can be developed at pipeline steel surfaces. Precipitation of carbonate compounds such as iron, calcium and magnesium carbonates or surface deposition of organics such as paraffins or asphaltenes are common occurrences and can have significant implications for corrosion [31], [33], [183]. However, even in the absence of all environmental factors which lead to precipitation, dissolution of iron from steel leaves behind corrosion product residues that accumulate at the surface. This product of selective dissolution is a layer which consists mostly of uncorroded iron-carbide (Fe₃C) in combination with small amounts of alloying elements [129]. The structure of this layer is strongly connected with the microstructure of steel which is developed during the pipe manufacturing process [184]. Similarly to other deposits, the corrosion process is strongly dependent on the presence of this layer. This section covers the basics of iron-carbide film formation and its influence on corrosion and surface wetting.

Research Hypothesis

Studies on mild steel wettability in surfactant-free environments are relatively scarce. Usually, steel wettability is investigated in the presence of corrosion inhibitors or other surface active compounds [27], [185], [186]. Their role on altering steel wettability is usually given greatest prominence while other factors are expected to have secondary roles. However, on some occasions observations of steel wettability in fluids free of surfactant compounds raise questions that require for further investigation.

One such observation originates from the experimental procedure for testing the inhibitive properties of oils, such as one that was employed as described in Chapter 4. Testing is performed in multiple stages in which specimens are periodically exposed to water and hydrocarbon phases. A simplified schematic of the experimental sequence is shown in the Figure 46. In the first stage of the experiment the rotating cylinder specimen is the aqueous phase and corrosion rate is monitored. Subsequently, the specimen is immersed and rotated in the hydrocarbon oil layer, to allow adsorption of oil soluble inhibiting compounds. The specimen is then immersed in the aqueous phase for a second time, and the corrosion rate measured.



Figure 46 – Simplified schematic of procedure for testing inhibitive properties of oils in the glass cell: A – specimen is submerged to the aqueous phase, B – specimen is exposed to the hydrocarbon phase, C – specimen is reimmersed in the aqueous phase.

Visual observations of specimens during this experimental sequence indicated that specimen surfaces do not always completely contact the oil phase when fluids did not contain surfactant additives. Some specimens would retain the thin layer of water even after being rotated in the oil phase for prolonged periods of time. It was suggested that the observed differences were due to longer times during which specimens were corroded in the aqueous phase before being exposed to the hydrocarbon oil. Figure 46A shows a rotating cylinder specimen which was corroded for 9 hours prior to immersion in oil. A thin layer of water is noticeable on the steel surface after rotation ceased. In contrast, water was almost completely displaced from the specimen which was corroded for 20 min, as shown in Figure 46B.

 \mathbf{R}



Figure 47 - Images showing two rotating cylinder specimens in the oil phase after being corroded for different amount of time: A – corroded for 9h; B – corroded for 20min. Thin water layer can be observed on the specimen corroded for 9h.

It can be seen from Figure 47 that the two specimen surfaces differ in their visual appearance. The specimen which is corroded for 9h has a black, thicker corrosion product layer covering the surface, which is almost completely absent from the surface corroded for the short amount of time. The corrosion product which forms at this set of experimental conditions (1 wt.% NaCl aqueous solution, 1 bar CO₂, adjusted to pH 5 with NaHCO₃ at 25°C) consists of residual metallic carbides, originating from steel manufacturing processes, which were not dissolved in the corrosion process [129]. This was an indication that the buildup of corrosion product layers which consists mainly of iron

carbide can alter the wettability of steel surfaces. Therefore, the following hypothesis was developed:

The metallic carbide-based corrosion product layer which develops during the corrosion process is rendering the steel surface more hydrophilic compared to non-corroded steel. This can enhance the affinity of the surface to become wetted with water and promote further corrosion.

Accordingly, the main objective of this part of the research was to investigate the influence of corrosion and subsequent formation of an iron carbide corrosion product layers on steel wettability and corrosion.

Effect of Corrosion Product Layers on Wettability of Steel Surfaces

The influence of metallic carbide corrosion product layers on corrosion processes has received substantial attention and was discussed in Chapter 2. However, the influence of carbides as well as other corrosion product layers on steel wettability has received very little attention. Tang, *et al.*, investigated the effect of iron carbonate on steel wettability by means of contact angle measurements. He found that corroded surfaces with iron carbonate deposits were moderately more hydrophilic than uncorroded steels in environments free of any surface active compounds. The measured water-in-oil contact angles were *ca.* 40°, approximately 10° lower compared to non-corroded surfaces [30], [187]. Foss, *et al.*, performed contact angle measurements on surfaces containing several types of corrosion-related deposits [27]–[29]. Contact angles were measured on a low carbon ferritic-pearlitic steel corroded for 24 hours at pH 3.9 in the presence of 1 bar partial pressure of CO₂, however, they were reported without specific mention of the nature of

the corrosion product that formed on the steel surface [27]. The water-in-oil and oil-inwater contact angles were 100° and 25°, respectively. The same authors performed contact angle measurements on surfaces covered with iron carbonate (FeCO₃) corrosion product deposits [28]. Water-in-oil contact angles obtained on iron-carbonate surfaces in the same conditions and fluids as the preceding research were approximately 40°, which suggests that the surface was hydrophilic at the given conditions. Oil-in-water contact angles in the same conditions were approximately 20° [28]. In the third study performed by the same authors, the surface was covered with ferrous and ferric corrosion products containing FeCO₃ and FeO(OH) [29]. Oil-in-water contact angles were performed yielding values of approximately 10°, which was indicative of development of a very hydrophilic surface [29].

Experimental Strategy

Two sets of experiments were performed. The first set was to characterize the influence of metallic carbide corrosion product layers on steel wettability. The second set examined the effect which surface wettability will impose on corrosion and wetting. The steel which was chosen for this research was a low-carbon steel with a quenched and tempered microstructure, as employed in previous investigations. The micrography and detailed information about steel chemical composition are given in the Appendix A. The evaluation of steel wettability was performed by means of water-in-oil contact angle measurements on surfaces precorroded for predesignated amounts of time. The second set of measurements comprised of corrosion rate determinations in the glass cell using rotating cylinder electrodes. This method was chosen as the most compact method which can encompass visual observations of steel surface wetting in dynamic conditions being conducted with corrosion rate measurements by the LPR technique. Where it was applicable after finishing experiments, surface characterization was performed with surface profilometry and scanning electron microscopy (SEM), which are described in Appendix F and Appendix G, respectively. The test matrix is given in Table 6.

Corrosion Time	Test Type			
	Water-in-Oil Contact Angle	Corrosion Inhibition		
0 min	Х	X		
20 min	-	X		
2h	X	-		
8h	Х	-		
16h	Х	-		
72h	-	X		
Test conditions: pH 5 aqueous solution 1wt% NaCl adjusted with CO ₂ /NaHCO ₃ , 1bar CO ₂ , ambient temperature ($\approx 25^{\circ}$ C)				

Table 6 – Test matrix for wettability and corrosion rate of corroded surfaces

Experimental Setup and Procedure

Contact Angle Measurements

Corroding the specimen for wettability measurements and determining water-in-oil contact angles of a sessile drop were performed in the goniometer cell (Appendix D). The test solution was prepared in an Erlenmeyer flask with 1L of deionized water with 10.1 g of NaCl and 0.15 g of NaHCO₃, weighted with ± 1 mg precision, dissolved therein. The solution was purged with CO₂ for at least 1.5 hours and mixed with a magnetic stirrer. pH was then measured and adjusted to 5.00 with solid NaHCO₃. After pH adjustments, the

salt solution was poured into the goniometer cell and purged for at least 30 minutes inside the cell. A single disk-shaped goniometer steel specimen was completely coated with a chemically resistant fluoropolymer coating before the first polishing. Specimens were polished on one side using a rotating plate with 600 grit silicon-carbide sandpaper. Tap water was used as a coolant during initial polishing, followed by DI water and isopropanol as cooling fluids. The specimen was then submerged in ultrasonic bath and cleaned for at least 2 minutes, dried with an air gun and promptly placed in the filled goniometer cell to minimize the time at which the specimen was in contact with air. After placing the specimen in the goniometer, the CO₂ sparger tube was raised above the water surface and the specimen was corroded for the designated time. After finishing the corrosion test, the solution was removed from the cell and the specimen was quickly rinsed twice with 400ml of deionized water to remove the NaCl from the surface which can potentially retain humidity and affect the results. After rinsing, each specimen was dried with CO_2 for 15 minutes inside the goniometer cell until it visually appeared to be completely dry. Following the drying step, the cell was carefully filled with LVT 200 model oil which was deoxygenated with CO₂ for at least 1 hour prior to the beginning of the next experimental step. During the process of solution draining, rinsing and addition of oil, the flow rate of CO₂ into the cell was significantly increased in order to prevent oxygen ingress. After pouring the oil into the cell, purging was continued for 1 hour before starting the contact angle measurements.

All measurements that were performed were water-in-oil type contact angle measurements, in which each specimen is immersed in the oil phase and the water droplets are deposited on the upper surface of the specimen. For water-in-oil contact angle measurements, 4-6 droplets were deposited with the micro-syringe from a height of approximateapproximately 5mm above the steel surface within the time period of 10 min. The volume of each droplet was in the range of 5μ L to 7μ L, due to variability in size at the point of the detachment from the micro-syringe needle. After droplet deposition, the appearance of the specimen surface was recorded with the camera for 2 hours. After each experiment, the steel specimen was taken out from the goniometer cell, rinsed with isopropanol, dried and characterized by scanning electron microscopy and profilometry. Contact angles were determined from images processed by Rincon imaging software.

Corrosion Experiments

Corrosion experiments were carried out in the standard three electrode (working, counter and reference) 2 liter glass cell (Appendix E). Electrolyte (1 wt.% NaCl, pH 5) was prepared by adding 1.6 liters of deionized water, 16.16 g of NaCl and 0.3 g of solid NaHCO₃ (added for approximate pH adjustment). The solution was then purged with CO₂ for at least 1.5 hours at 25°C. After purging, solution pH was precisely adjusted to 5.00 with solid NaHCO₃. Rotating cylinder electrode (RCE) specimens were prepared by degreasing with isopropanol, polished with 600 grit sandpaper with water and isopropanol, ultrasonicated in isopropanol bath for at least two minutes and dried with a heat gun. After polishing, a specimen was quickly mounted on the shaft and placed inside the glass cell. The RCE rotation speed was set to 2000 RPM. The specimen was corroded at 25°C for the designated amount of time (Table 6). Corrosion rates during this stage were recorded using the LPR electrochemical technique. After pre-corroding the specimen,
rotation was stopped and 0.4 liters of oil (deoxygenated for at least 1 hour) was poured into the glass cell, so it formed a layer of oil on top of the aqueous solution. The specimen was then lifted up from the water phase into the oil layer and rotation was continued for 1 hour at 2000 rpm. During this stage no corrosion rate measurements were taken since the specimen was immersed in the model oil. After the immersion period, the specimen was returned back in the water phase and rotated at 2000 rpm, while the OCP was monitored until it reached a value stable enough to perform LPR measurements. Measurements of linear polarization resistance were then taken every 5 minutes for at least 2 hours. Processes of immersion in oil, rotation in oil and re-immersion in the water phase were recorded with a camera for later visual analysis. After completion of experiments, surface characterization of the specimens was performed with scanning electron microscopy (SEM) and surface profilometry.

Results and Discussion

Contact Angle Measurements

Water-in-oil contact angles were measured with respect to the water phase, where an angle of 90° or less indicates that the steel surface is hydrophilic and higher than 90° hydrophobic. Examples of obtained images of sessile drops as they appear on the screen during the measurements are shown in Figure 48.



Figure 48 – Contact angles of water droplets deposited on the steel surfaces corroded for different time periods: A – initial, B – 2 hours, C – 8 hours, D – 16 hours.

The results of the contact angle measurements shown as a function of time are presented in Figure 49. The moment at which the droplet contacts the surface is set as time zero on the graph. For the non-corroded surfaces, the only data which is available is after 60 minutes and 120 minutes. For corroded surfaces, contact angles measured 1 minute after droplet deposition were in the range of 89° for the surface which was precorroded for 16h to 108° for the surface precorroded for 2 hours; 30 minutes after droplet deposition all contact angles of droplets deposited on the surface gradually decreased. For the surface which was corroded for 2 hours the angle was 70°, while contact angles of 80-85° were measured for surfaces precorroded for 8 hours and 16 hours; 60 minutes after droplet deposition, contact angles for the 16 hour corroded surface did not change, while the contact angles for 2h and 8h corroded surface decreased by approximately 10° to 15°. By the time the experiment finished, 2 hours after droplet addition, no change in contact angle was noticed for 8 hour and 16 hour corroded surfaces. However, contact angles of the non-corroded surface and the surface corroded for 2 hours displayed a very slow decline of approximately 5° during the last hour.



Figure 49 – Water-in-oil contact angles at surfaces corroded for different amount of time.

An increase of contact angles is an indication that the surface is becoming more hydrophobic as corrosion proceeds, which indicates that the residual metallic carbide layer makes the surface more hydrophobic. Water-in-oil contact angles obtained by Foss at surfaces which favored formation of carbides were higher (100°) compared to contact angles obtained at the same conditions on the surfaces covered with iron-carbonate (40°) [27], [28]. These measurements also show that the surface was more hydrophobic compared to the 40° contact angles obtained by Tang on iron carbonate [187]. Therefore, by comparing previous results with the current finings, it can be deduced that iron carbide steel surfaces are more hydrophobic compared to surfaces covered by other corrosion product deposits.

Corrosion Rate Measurements

The results of the corrosion rate measurements with the rotating cylinder electrode are presented in Figure 50 through Figure 53. Corrosion rate measurements were performed after a time delay, denoted as "OCP stabilization" on the diagrams. Open circuit potentials (OCP) measured during that time indicated a rise after the specimen has been reimmersed in the aqueous phase. This would make LPR measurements unreliable and linear polarization measurements were resumed after the OCP stabilized.

Figure 50 shows the results of corrosion rate measurements obtained for the noncorroded specimen after immersion in the oil phase. The initial measured corrosion rate was 1.7 mm/y and gradually increased to 1.8 mm/y after two hours of exposure.



Figure 50 – Corrosion rate measured by LPR of noncorroded specimen after exposure to the oil phase.

Figure 51 shows corrosion rates measured by LPR of the specimen which was initially corroded for 20 minutes before it was exposed to the oil phase. During the short period of time before immersing in the oil phase measured corrosion rates were in the range of 1.5 mm/year to 1.6 mm/year. After the specimen was immersed in the oil phase the corrosion rate was measured as 1.65 mm/year in the aqueous phase and gradually increased to approximately 1.75 mm/year.



Figure 51 – Corrosion rates measured by LPR of the specimen which was corroded for 20 minutes before it was exposed to the oil phase.

Figure 52 shows the results of corrosion rate measurements of the specimen precorroded for 12 hours. The initial corrosion rate was 1.45 mm/y. The corrosion rate continued to increase to a stable rate to 1.85 mm/y during the 12 hour period before the specimen was immersed in the oil phase. The measured corrosion rate was subsequently 1.9 mm/y and increased to 1.95 mm/y by the time the experiment was stopped.



Figure 52 – Corrosion rates measured by LPR of the specimen which was corroded for 12h before it was exposed to the oil phase.

Figure 53 shows corrosion rates measured by LPR of the specimen which was initially corroded for 3 days before it was exposed to the oil phase. During this prolonged period of time measured corrosion rates were constantly increasing. The initial corrosion rate measured during that period was 1.6 mm/y and gradually increased to 3.2 mm/y after 3 days. After immersing the specimen in the oil phase, the measured corrosion rate was 3.3 mm/y and after two hours in the aqueous phase it gradually increased to approximately 3.5 mm/y.



Figure 53 – Corrosion rates measured by LPR of the specimen which was corroded for 3days before it was exposed to the oil phase.

For all experiments with the rotating cylinder electrode, the measured initial corrosion rate at pH 5, 2000 rpm and 25°C was approximately the same at 1.5-1.6 mm/y and was steadily increasing with time. During the corrosion process in the CO₂ containing environment at pH 5, the metallic carbide layer is the only corrosion product which is formed at the steel surface and no precipitation of iron carbonate is expected at higher pH values [188]. In terms of chemical composition, this layer is mostly composed of iron carbide and residual alloying elements [129]. The observed increases of the corrosion rate are due to the electroconductive nature of this layer, which produces a galvanic effect when it is coupled with uncorroded steel. The constantly increasing surface area of this layer facilitates hydrogen ion reduction which accelerates anodic dissolution of iron [189].

Figure 54 shows a comparison of the corrosion rates obtained before and after immersing in the oil phase. It can be seen that for every experiment there was no change in the corrosion rates before and after immersion in the oil phase. Therefore, it can be concluded that exposing the steel to the hydrocarbon did not affect corrosion properties of steel. However, it has to be noted that the current findings are related only to surfactant-free environments.



Figure 54 – Comparison of corrosion rates obtained before and after immersing of specimens in the oil phase. Time has been adjusted to show comparison between experiments with different corrosion times.

Wetting of the Rotating Cylinder Electrode during Corrosion Measurements

With the exception of the specimen which was not corroded prior to immersion in the oil phase, all rotating cylinder specimens which were corroded in the aqueous phase were slowly lifted up in the oil phase. In all cases thin, a uniform layer of water stayed remained on the specimen surface. After starting the rotation at 2000 rpm in the oil phase, the water layer is not immediately removed and remains adherent to the steel surface for

an extended period of time. After 1 hour of rotation in the oil phase there was little (with 20 minute and 8 hour precorrosion) or no visible water (with 72 hour precorrosion) that remained on the specimen surface, as can be seen in Figure 55.



Figure 55 – Images of the rotating cylinder electrode after completing one hour of rotation in the oil phase; A – non-corroded specimen, B – 20 minute corroded specimen, C – 12 hour corroded specimen, D – 70 hour corroded specimen

Gravitational effects and specimen vibrations cause local thinning of the water layer at the upper part and local thickening of the water layer at the lower part of the specimen surface, as shown in Figure 56. With time, small droplets are cast off from the thick part of the water layer at the bottom of the specimen into the oil phase. For a specimen which is 12 mm in diameter, rotation at 2000 rpm produces a linear velocity v of 1.26 m/s at the specimen surface and centrifugal acceleration a_c of 264.6 m/s², approximately 27 G.



Figure 56 -Sketch of the rotating cylinder electrode partially covered with water layer. Centrifugal acceleration a_c acts to remove the layer of water.

After reimmersing the specimens in the water phase, it can be noticed that there was a small amount of model oil adsorbed at the upper part of the steel specimen that was precorroded for 20 minutes, but not for the specimens that were precorroded for 12 hours and 70 hours, as shown in Figure 57. Specimens that were not precorroded had a thin layer adsorbed on the whole specimen surface (not visible in Figure 57).



Figure 57 – Images of the rotating cylinder electrode after completing one hour rotation in the oil phase into the aqueous phase; A – non-corroded specimen, B – 20 minute corroded specimen, C – 12 hour corroded specimen, D – 70 hour corroded specimen

After starting the rotation in the water phase the oil layer which was adsorbed at the non-corroded specimen and specimen corroded for 20 minutes was removed after a few seconds. Table 7 contains a short summary of the visual observations of the wetting experiments.

	<i>After 1 hour of rotation in oil</i>	After reimmersion in water before rotation started	After reimmersion in water after rotation started
No precorro- sion	-	Thin oil layer ad- sorbed	Oil layer easily removed
20 minutes precorrosion	Water stayed ad- sorbed on lower part of the specimen	A little bit of oil adsorbed on the upper part of the specimen	Oil layer easily removed
12 hour precorrosion	Water stayed ad- sorbed on lower part of the specimen	No visible oil ad- sorbed on the specimen	-
72 hour precorrosion	No visible water stayed adsorbed on the specimen after immersion in oil	No visible oil ad- sorbed on the specimen	-

Table 7 – Summary of visual observations of rotating cylinder specimen surfaces

Development of Carbide Layer and its Influence on Wetting

The development of a carbide layer causes only a gradual change not only of chemical composition of the surface, but also in surface morphology. Figure 58 shows surface topography of specimens obtained by scanning electron microscope (SEM) after completing contact angle measurements.



Figure 58 – SEM images of the steel surfaces before and after corrosion: (A) before (B) 2 hours of corrosion, (C) 8 hours of corrosion, (D) 16 hours of corrosion.

The SEM image of non-corroded specimen shown in Figure 58A reveals a steel surface which is intersected by micrometer sized polishing marks. However, the steel surface between them is relatively smooth. On the sample which was corroded for 2 hours, shown in Figure 58B, polishing marks are still noticeable. However, as a result of corrosion, changes in surface topology on the submicrometer scale start to occur, which are observed as white features on the image. As the corrosion time reaches 8 hours (Figure 58C) polishing marks start to disappear and are almost unnoticeable on the specimen which was corroded for 16 hours (Figure 49D). However, coarsening due to corrosion increases. Optical surface profilometry can to an extent capture the tridimensional profile of the surface and roughness parameters can numerically describe and quantify the surface topography. The working principle of optical profilometry and calculation of mean surface roughness are described in Appendix F. Figure 59 shows roughness measurements of specimens observed under scanning electron microscopy. The measurement was performed in a way to minimize any artifacts originating from steel polishing. However, they could not be completely avoided. Nevertheless, Figure 59 shows a trend of growing roughness (Ra) with increasing the corrosion time. These measurements coincide with the observations of steel surfaces made with scanning electron microscopy.



Figure 59 – Steel surface roughness for as a function of corrosion time.

Figure 60 shows a side-to-side comparison of the Nital etched X65 steel surface and surface corroded for 16 hours. It can be seen that coarsening patterns approximately

resemble the size and the shape of the grains. This suggests that the origin of the coarsening is in the residual metallic carbide from the grain boundaries. Selective dissolution of the iron inside the grains exposes undissolved intergranular carbide to the surface.



Figure 60 - SEM images of nital etched steel surface (A) and steel surface corroded for 16h (h). Similar patterns can be observed.

Figure 61 and Figure 62 show simplified schematics of the proposed mechanism on the influence of carbide corrosion product on wetting of steel surfaces. Due to corrosion, steel surfaces leave a residual iron carbide layer. When oil is introduced, the visible water layer gets slowly removed from the surface due to the effect of flow. The removal process of the visible water layer generally does not depend on corrosion time. However, if the corrosion time was short, the iron carbide layer is thin and the surface remains relatively smooth. In that case water can be removed from the surface completely, and model oil adsorbed (Figure 61). When the specimens were corroded for longer amounts of time, water resides in the cavities at the surface in between the carbide structures and cannot be displaced by oil, as shown in Figure 62. Latter contact of steel with water easily removes oil from the surface.



Figure 61 – Wetting transitions for short-corroded surface: A – water corrodes the surface, B – oil completely displaces the water from the surface, C – thin layer of oil stays adsorbed at the surface, D – water easily displaces the oil from the surface.



Figure 62 - Wetting transition for long-corroded surface: A - water corrodes the surface, B - oil is able to displace the water just from the top of the cementite layer (water stays adsorbed between the cementite), C - water easily displaces the oil from the surface.

Summary

The main objective of this research was to test the hypothesis that the metallic carbide

based corrosion product layer which is creating the surface which is more hydrophilic

than non-corroded steel. The steel which was used in this research was low-carbon, low-

alloy steel with a quenched and tempered martensite microstructure. The results of

contact angle measurements disproved the initial hypothesis and steel was more hydrophobic as the corrosion product developed at the surface. However, corrosion and wetting experiments in the glass cell showed that the porous cementite layer can retain water inside the cavities which flowing oil was unable to displace.

CHAPTER 7: EFFECT OF pH ON CORROSION INHIBITION AND WETTABILITY BY CRUDE OIL MODEL POLAR COMPOUNDS

Crude oils and produced waters can contain naturally occurring surface active compounds. Previous studies have shown that the presence of those chemical species can significantly influence wetting and corrosion [32], [33]. However, physicochemical properties of some of those compounds, including those related to their surface activity, can be altered by molecular ionization which results from changes of the aqueous phase pH; specifically protonation or deprotonation. Consequently, these modifications in surface properties can have significant effect on corrosion and wetting. This chapter describes the research undertaken to investigate how change of pH of the aqueous phase alters wettability and corrosion through ionization of polar model organic compounds.

Research Hypothesis

Previous studies have shown that naturally occurring polar organic compounds can have a significant effect on surface wetting and corrosion. Adsorbed organic molecules form films which partially prevent contact of steel with corrosive species in the water phase and change the steel wettability [32], [33]. Studies were performed with model compounds that were selected to represent the naturally occurring chemical components in the crude oil, such as fatty and naphthenic acids, basic and neutral nitrogen compounds, mercaptans, and disulfides. Alternatively, surface active compounds, such as asphaltenes, were extracted from the crude oil and used in the studies. However, all corrosion and wettability tests were performed at constant composition of the aqueous phase [74], [190], [191]. Previous investigations on crude oil wetting properties in petroleum reservoir rock formations have shown that varying pH of the aqueous phase can significantly affect the interfacial properties of crude oils, such as oil-water interfacial tension or wettability which result from the existence of ionized and non-ionized (protonated and deprotonated) forms of crude oil polar organic compounds [192], [193]. The process of protonation and deprotonation is determined by the pH and the logarithm of the ionization constant (pKa) of the polar organic compounds. Furthermore, the process of ionization has its most marked effects when the pH is varied close to the pKa values of the organic compounds in question. Therefore, it can be hypothesized that:

Surface active properties of naturally present polar organic compounds in crude oils can be significantly altered with changing the pH if their pKa values are within the range of common pH values found in pipelines (pH 4 - pH 7). This will result in significantly changes to their corrosion inhibition and wetting which significantly impact corrosion and wetting processes in pipelines.

The main goal of this part of the research is to investigate the effect of pH on corrosion inhibition and wettability of carbon steel in the presence of polar organic compounds native to crude oils which can be ionized in the range of pH values commonly found in pipelines.

Background on the Ionization of Organic Compounds

Monoprotic organic acids of formula R-COOH dissociate in aqueous solution to form hydrogen ions and their conjugate base anions:

$$RCOOH(aq) + H_2O(l) \rightleftharpoons RCOO^{-}(aq) + H_3O^{+}(aq)$$
(61)

A quantitative measure of the acid strength in the aqueous solutions can be expressed as the acid dissociation constant K_a . This dissociation constant is given as a quotient of equilibrium concentrations of dissolved species:

$$K_a = \frac{[RC00^-][H_30^+]}{[RC00H]}$$
(62)

Since the value of K_a can vary over several orders of magnitude, pKa was introduced as a more convenient way of expressing the acid dissociation constant.

$$pK_a = -\log K_a \tag{63}$$

At a given pH, stronger acids dissociate more and their Ka value is higher and pKa value lower compared to weaker acids. In this example it will be assumed that Ka of the acid is 10⁻⁵ so the pKa value is 5. The logarithm of equation (62) relates pKa, pH and concentrations of ionized and non-ionized species in the solution. The equation is known as the Henderson-Hasselbalch equation [194]:

$$pH = pK_a + \log \frac{[RCOO^-]}{[RCOOH]}$$
(64)

In the case when pH of the aqueous solution can be adjusted by addition of some other strong acid, it is possible to alter the concentrations of the non-ionized acid (RCOOH) and conjugate base anion (RCOO⁻) in the solution by changing the pH. Figure 63 shows the relation between percent of the ionized and non-ionized species as a function of pH.



Figure 63 – Ionization of organic acidic species as a function of pH.

As can be seen from Figure 63, ionization of the acid is not linear, but lies within a relatively narrow pH range. It can also be noticed that the pKa value of the acid (pKa=5, in the given example) is not only the quantitative measure of the acid strength, but also determine the percentage of an acid that will be ionized at a certain pH value. At pH 5, which is equal to its pKa value in the above example, the concentration of ionized and non-ionized species will be equal; 50% each will be present. If the pH value of the solution is raised for one pH unit above pKa, the percentage of the ionized species will rise to 91%, and the percent of non-ionized and only 1% of the molecules in the non-ionized form. Lowering the value of pH for one and two units below the pKa will produce 91% non-ionized and 9% ionized species, and 99% non-ionized and 1% ionized species, respectively.

Strength of bases is characterized by the dissociation constant K_b . The following example is for an organic amine (R-NH₂) in aqueous solution, note that in addition to hydroxide an ammonium ion forms as a conjugate acid:

$$RNH_2(aq) + H_2O(l) \rightleftharpoons RNH_3^+(aq) + OH^-(aq)$$
(65)

The dissociation constant K_b is given as a quotient of equilibrium concentrations of dissolved species:

$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$
(66)

 pK_b is defined as the negative logarithm of the constant K_b .

$$pK_b = -\log K_b \tag{67}$$

The constants K_b and pK_b can be converted to K_a and pK_a for their conjugate acids, correspondingly, by using the following relationships:

$$K_a = \frac{K_w}{K_b} \tag{68}$$

and

$$pK_a = 14 - pK_b \tag{69}$$

where K_w is the dissociation constant of water (1x10⁻¹⁴ at 25°C). As stated above, the K_a and pK_a values in this case refer to a dissociation constants and it's logarithm of the compound's conjugate acid, *i.e.*, protonated amine (R-NH₃⁺). After substituting the constant K_b with K_a , the Henderson-Hasselbalch attains the following form for primary amines:

$$pH = pK_a + \log \frac{[RNH_2]}{[RNH_3^+]}$$
(70)

Plotting the percentage of ionized/non-ionized amine species as a function of pH for the primary amine, pKa=10 in the given example, is shown in Figure 64.



Figure 64 – Ionization of primary amine species as a function of pH.

As can be seen from Figure 64, at a pH value of 10 that is equal to the pK_a value of the amine (pK_a=10), the concentration of ionized and non-ionized species will be equal. However, if the pH value of the solution is raised one pH unit above pKa, the amine will be less ionized and the percentage of the non-ionized species will rise to 91%, and the percent of ionized will drop to 9%. Further increase in pH by one more pH unit will lead to 99% non-ionized and only 1% of the molecules in the ionized form. Lowering the value of pH to one and two units below the pKa will produce 91% ionized and 9% non-ionized species, and 99% ionized and 1% non-ionized species, respectively. Using the previous examples of an organic acid with pK_a value of 5 and primary amine with pK_a value of 10, it can be seen that the percentage of the ionized species will vary significantly if the pH value is varied close to the pK_a value of the compound. If the pH value of the aqueous phase is determined by the presence other chemical species and varied, e.g., between pH 4 and pH 7, than the pH will have a different effect on ionization of the polar compounds within that pH range (Figure 65). At pH=4, 91% of the species will be non-ionized (9% ionized), while at the same pH the proportion of ionized amine species will be close to 100%. At Ph 7 approximately 98% of the acidic species will be ionized (2% non-ionized), while the amine will have almost the same proportion of ionized species which is close to 100%. Therefore, it is clear that varying the pH between 4 and 7 will have a much stronger influence on ionization of organic acids, since the percent of ionized species will rise from 9% to 98%, while the percent of ionized amine will remain practically the same.



Figure 65 – Comparison of the ionization of organic species with different pK_a values. Increasing the pH from 4 to 7 will much more affect the ionization of organic acid compared to amine due to different pK_a values of the compounds ($pK_a=5$ for acid vs. $pK_a=10$ for amine).

Selection of Crude Oil Model Compounds Based on pK_a Values

The starting point for the selection of compounds for testing was the list of model compounds used by F. Ayello, which was presented in Chapter 2 [74]. The central criterion for the selection of potentially the most active compounds was that their pK_a values are between 4 and 7, based on the pH which is commonly found in produced waters [87]. The most significant influence of pH on oil-water-steel interfacial properties can be expected if the pK_a of the crude oil polar compounds is in the pH range commonly seen in the produced waters collected in pipelines (pH 4 - pH7). This criterion is based on the fact that influence of pH on ioniziation or deionization of those compounds will be the most substantial contributing factor which can produce the most significant changes on corrosion and wetting. According to that criterion, two model compounds were selected for further research: myristic acid and acridine. The other compounds from the list were either non-ionizable (dibenzothiophene, dioctyl sulfide) or had a pK_a value outside of the specified range (teradecanethiol, carbazole). Interestingly, myristic acid and acridine were the ones which were the most inhibitive to corrosion (acridine) and had the highest influence on steel wettability (myristic acid).

Myristic acid (Figure 66) is a C-14 saturated fatty acid, heavy and soluble in water. In aqueous solutions myristic acid dissociates to hydrogen ions and myristrate anions; its acid dissociation constant pK_a is 4.9 at normal conditions [195].



Figure 66 – Dissociation of myristic acid.

Acridine (Figure 67) is a heterocyclic nitrogen compound. In aqueous solutions, acridine reacts with water and produces acridinium cation and hydroxide ions. The pKa of acridinium is 5.6 at normal conditions [196].



Figure 67 – Dissociation of acridinium.

Experimental Strategy

With the aim of investigating the influence of pH on ionization of polar organic compounds four types of measurements were performed. The first included interfacial tension measurements in order to characterize changes that occur at oil-water interfaces. The second set of measurements included water-in-oil and oil-in-water contact angle measurements in order to characterize the steel surface wettability alteration. The effect of pH was then evaluated in the third set of measurements performed in the doughnut cell in order to evaluate the link between wettability and wetting. The fourth set of experiments were corrosion rate measurements in the glass cell using a rotating cylinder electrode. The test matrix is given in Table 8.

Model Compound	рН	Test Type				
		Interfacial tension	W-in-O Contact Angle	O-in-W Contact Angle	Corrosion	Doughnut Cell
Myristic acid	4	Х	Х	Х	Х	Х
	5	Х	Х			
	6	Х	Х			
	7	Х	Х	Х	Х	Х
Acridine	4	Х	Х	Х	Х	
	7	Х	Х	Х	Х	
Test conditions: 1 wt.% NaCl, 1 bar CO ₂ , ambient temperature (≈25°C)						

Table 8 – Test matrix for testing the influence of pH on wetting and corrosion properties of polar model organic compounds

Experimental Setup and Procedure

Material Preparation

Materials used in the experiments were prepared using the same procedures as described above. For oil solutions components were weighed, mixed and purged with CO₂ using a fritted glass sparger for at least 1hour. Myristic acid was dissolved in LVT 200; acridine in a 60:40 weight ratio of LVT 200 and Aromatic 200. The test solution was prepared by adding NaCl, to 1 wt.% concentration, and solid NaHCO₃ for approximate pH adjustment. Solutions were purged with CO₂ for 1-1.5 hours using a fritted glass tube. pH was then precisely adjusted to the desired value. When required, oil and water solutions were then mixed and agitated overnight to allow partitioning of model compounds. Steel specimens were polished using 600 grit silicon carbide abrasive paper using deionized water then isopropanol as a coolant. Specimens were then cleaned in an ultrasonic bath for at least two minutes and briefly dried with a heat gun.

Interfacial Tension Measurements

Oil-water interfacial tension measurements were performed using the Du Nouy ring tensiometer, described in Appendix B. Prior to every measurement, the platinum ring was immersed in acetone and deonized water then exposed to a flame in order to remove all organic contaminants. The ring was then put in a clean and dry 50 ml beaker and placed in the closed vessel that was continuously purged with CO₂. A 20 ml volume of water was then pipetted from the 1 litre Erlenmeyer flask which contained the oil-water mixture and slowly poured into the beaker. This operation was performed through the opening in the vessel in order to avoid contact with air. Subsequently, 10 ml of oil was pipetted and

slowly poured on top of the water phase. The beaker was then left in the closed vessel in the CO_2 atmosphere for 5 minutes prior to every measurement. After that, the beaker was taken out from the vessel and immediately taken for oil-water interfacial tension measurement. The whole measurement procedure was repeated three to four times.

Contact Angle Measurements

Contact angle measurements were performed in the goniometer cell, shown in Appendix D. Two steel specimens were used for the experiments. The first one for water-inoil, and the second one for oil-in-water contact angle measurements. Each specimen was first completely coated with a chemically resistant fluoropolymer coating and then polished on one side. Specimens were polished according to the procedure and promptly placed in the goniometer cell to minimize the contact time with air.

In *water-in-oil type contact angle* measurements, the specimen is immersed in the oil phase and the water droplet is deposited on top of the steel specimen surface. Before each experiment oil and aqueous solutions were mixed in 8:2 oil-water volume ratio and slowly agitated overnight. At the beginning of every experiment, 0.8 liters of oil was poured from the Erlenmeyer flask into the goniometer. The cell was then sealed and purged with carbon dioxide gas for at least 30 minutes. A clean, polished specimen was then placed in the holder that was then completely immersed in the oil phase with continued purging for another 30 minutes. The remaining water was then poured in the 250 ml Erlenmeyer flask and CO_2 sparging continued throughout the experiment. For these measurements, 3-5 droplets were deposited from a height of approximately 5 mm above the steel surface within the 10 minute period. The volume of each droplet was 5-7 μ L and

they were injected using the 10 μ L syringe. Droplets were then recorded with a camera for at least 1 hour in order to make sure that contact angles reached the equilibrium value. Contact angles of droplets were then measured using the Rincon imaging software.

For *oil-in-water type contact angle* measurements, the specimen is immersed in the water phase and the oil droplet is deposited on below the steel specimen surface. Before each experiment oil and aqueous solutions were mixed in 8:2 oil-water ratio and slowly agitated overnight. Initially, 0.8 liters of water was poured from the Erlenmeyer flask into the goniometer, taking precaution that oil does not enter the goniometer. The remaining oil was then poured in the 250 ml Erlenmayer flask and purging continued. The cell was then sealed and purged with carbon dioxide gas for at least 30 minutes. The specimen was then placed at the bottom of the goniometer with the polished side facing up and continued sparging for another 30 minutes. This step was performed in order to avoid accumulation of CO_2 bubbles at the polished side of the specimen, when the specimen is placed on the holder with polished side facing downwards. After that, the specimen was placed on the holder and 1-2 oil droplets were deposited below the steel surface. The volume of each droplet was 8-10 μ L. Droplets were then recorded with a camera for several minutes before the surface got covered with CO₂ bubbles. Recorded images were then processed with imaging software in order to measure the contact angles.

Corrosion Measurements

All corrosion measurements were carried out using the rotating cylinder electrode (RCE) specimen in the standard three electrode (working, counter and reference) 2 liter glass cell setup, shown in Appendix C. Two types of corrosion measurements were

performed, partitioning tests and direct inhibition tests. Fluids and specimens were prepared according to the procedure for other experiments with polar organic compounds.

Partitioning experiments were performed in two stages. In the first stage (precorrosion), polished specimen was immersed in the water solution, and specimen rotation was set to 2000 rpm. Corrosion rates were then measured using the LPR every 5 minutes for 20 minutes. After the 20 minute period elapsed, the second stage (partitioning) was started by pouring the 0.4 liters of model oil with dissolved compounds (myristic acid or acridine) inside the glass cell. After addition, oil formed a layer on top of the salt solution. Special care was taken in order to minimize the contact of oil with air during the transfer of oil from the Erlenmeyer flask. Specimen rotation was again set to 2000 rpm and LPR corrosion measurements were taken every 5 minutes for 4 hours.

For direct inhibition tests 0.4 liters of oil was poured inside the glass cell, so it formed a layer of oil on top of the aqueous solution. The solution was then left to equilibrate overnight. The polished specimen was immersed into the oil layer and rotated for 1 hour at 2000 rpm. No corrosion rate measurements were taken during this stage, since the model oil is a nonconductive liquid. After immersion in crude oil, the specimen was put back into the water phase and rotation was continued at 2000 rpm. Corrosion rate was measured every 5 minutes for 4 hours.

Doughnut Cell Experiments

The doughnut cell is the apparatus constructed in order to simulate multiphase flow conditions found in pipelines. The parts which comprise the doughnut cell are explained in the Appendix E. Water and oil solutions were prepared using the same procedure, but in total volume of 4 liters. The mixture was then gently stirred and purged with CO₂ from 12 to 24 hours to allow partitioning of the compounds between the oil and water phases. Before each experiment, the doughnut cell was thoroughly cleaned using isopropanol and deionized water in order to ensure that the inner surface is free of any contaminants. After cleaning, the doughnut cell was closed and purged with carbon dioxide prior to addition of test fluids. After purging with CO_2 , a small amount of oil was added to the doughnut cell in order to oil prewet the steel bottom of the cell. Purging was then continued and the oil was left for 30 minutes. After that, the whole amount of oil and water was poured into the cell. The cell was then completely closed in order to avoid oxygen contamination and connected to CO_2 during the entire time of the experiment. Experiments were then started by increasing the speed from the lowest to the highest rotating velocity. After setting the rotation was stopped for a few minutes to allow water to settle down before starting the measurement at higher velocity.

Results and Discussion

The influence of pH on interfacial tension for three oil solutions containing different concentrations of myristic acid is shown in Figure 68. As can be seen, for all tested concentrations there was a tendency of decrease in interfacial tension with increasing the pH from pH 4 and pH 7. For the lowest measured concentration of 0.01 wt%, the decrease was the most significant, from around 40 dyne/cm at pH 4 – pH 6 to 25.5 dyne/cm at pH 7. For 0.05 wt% myristic acid the decrease in interfacial tension seems to be more gradual, decreasing from 40 dyne/cm to 34 dyne/cm between pH 4 and pH 6,

and then dropping to 30 dyne/cm at pH 7. 0.1 wt% myristic acid showed a steady decrease from 37 dyne/cm to 35 dyne/cm between pH 4 and pH 6, and then a sudden drop to 25 dyne/cm at pH 7.



Figure 68 – Oil-water interfacial tension measured for different concentrations of myristic acid at different pH values.

The results of interfacial tension measurements of acridine solutions are presented in Figure 69. At pH 4 surface tension of 0.1 wt.% solution of acridine was 32.4 dyne/cm. At the same pH, 1 wt.% acridine had a surface tension of 25.3 dyne/cm. At pH 7 surface tension for both concentrations of acridine decreased. For 0.1 wt.% measured interfacial tension was 29.2, which 3.2 dyne/cm lower compared to the surface tension of the same solution at pH 7. Measured oil-water interfacial tension of a 1 wt.% solution of acridine was 21.1 dyne/cm, 4.1 dyne/cm lower than compared to interfacial tension of the same solution at pH 4.



Figure 69 – Oil-water interfacial tension measured for different concentrations of acridine at different pH values.

Alteration of interfacial tension between hydrocarbon oils and water in the presence of organic acids has been extensively studied in the past by several researchers, who identified major factors that influence the oil-water interfacial tension [193], [197]. It is well known that presence of fatty acids causes the decrease of the oil-water interfacial tension due to their amphiphilic (polar-nonpolar) molecular structure which gives them surfactant properties [198]. After addition of fatty acids in hydrocarbon oil and mixing with water, part of it will diffuse to the water solution and part of it will stay adsorbed at the oil-water interface. The portion of the acid that diffused to the water solution will dissociate and form fatty acid anions, and the remaining acid will stay undissociated. The concentrations of both species in the water solution will depend on the pKa of the acid at a given conditions and a pH of the solution. For every value of pH, equilibrium will be established between the concentration of fatty acid dissolved in oil, fatty acid dissolved in water, and fatty acid anion also dissolved in water. It is a widely accepted principle that acid anion species are more surface active than non-ionized ones and will cause more significant decrease of interfacial tension [195]. It was noticed, however, that interfacial tension will continue to decrease at pH values higher than those needed for complete ionization of the fatty acids in the aqueous solution [198]. The effect was interpreted by Danielli, who employed the concept of interfacial pH in order to explain observed behavior [199]. He suggested that the surface pH was lower than the bulk pH, so the acids at the oil-water interface did not become completely ionized. In a more recent study, Rudin and Wasan suggested that the interfacial tension is a function of simultaneous adsorption and desorption of ionized and non-ionized acids to the interface [193], [197].

Current measurements show that for all concentrations there was a significant decrease in interfacial tension at pH 7, compared to the decrease between pH 4 and pH 6. This decrease is associated with ionization of the acid groups at the water-oil interface. The significant decrease, however, occurs at pH values of 7 which is in line with results of other researchers and higher than would be expected according to pK_a values of the fatty acids. Since the reported pK_a value of the myristic acid is 4.9, it would be expected that at pH 5 approximately 50% of the acid groups to be ionized, and around 98% at pH 7. If that was the case, then the interfacial tension would start to decrease significantly at pH values lower than 7. However, compounds which are adsorbed at the interface have "interfacial *pKa*" whose value is higher compared to *pKa* in the bulk solution. Beside the pH, ionic strength is an important factor which influences the interfacial tension. The increase in the ionic strength of the solution will lead to a "salting out" effect which changes concentrations of compounds in the oil and aqueous phases [200], [201]. Table 9 shows the calculated values of ionic strength in a system where the pH is adjusted in a CO₂/NaHCO₃ system.

	c(H ₃ O ⁺), mol/dm ³	c(OH ⁻), mol/dm ³	c(HCO ₃ ⁻), mol/dm ³	$c(CO_3^{2-}),$ mol/dm ³
pH 4	1.00×10 ⁻⁴	9.02×10 ⁻¹¹	2.14×10 ⁻⁴	2.80×10 ⁻¹⁰
рН 5	1.00×10 ⁻⁵	9.02×10 ⁻¹⁰	2.14×10 ⁻³	2.82×10 ⁻⁸
рН 6	1.00×10 ⁻⁶	9.02×10 ⁻⁹	2.18×10 ⁻²	3.00×10 ⁻⁶
pH 7	1.00×10 ⁻⁷	9.02×10 ⁻⁸	2.48×10 ⁻¹	4.99×10 ⁻⁴

Table 9 – Calculated ionic strengths for different pH solutions

Table 9 (cont.) – Calculated ionic strengths for different pH solutions

C(NaCl), mol/dm ³	c(Na ⁺), mol/dm ³	c(Cl ⁻), mol/dm ³	Ionic strength
0.1709	0.1711	0.1709	0.1712
0.1709	0.1731	0.1709	0.1731
0.1709	0.1927	0.1709	0.1927
0.1709	0.4196	0.1709	0.4201
As can be seen ionic strength of the aqueous solution increases together with increasing the pH. The relative increase in ionic strengths for pH 5 and pH 6 are relatively small, at 1% and 13%, respectively, compared to solution adjusted to pH 4. At pH 7, however, the increase is in the ionic strength is 113%, which suggests that increase in ionic strength can be considered to have a secondary effect on the decrease of the interfacial tension. Experiments at constant ionic strength are needed in order to clarify this effect.

Surface tension of acridine decreases with increasing the pH. This implies that acridine becomes more interfacially active as a percentage of ionized molecules decreases. The similar result was obtained by Standal, *et al.*, where the unprotonated form of quinoline was more interfacially active [201]. This result is opposite to the effect which ionization had on the interfacial tension of myristic acid. Further tests with intermediate pH values are needed to clarify if the change in interfacial tension is gradual or a rapid change occurs within the narrow pH range.

Water-in-Oil Contact Angle Measurements

Contact angle measurements of myristic acid are shown in Figure 70. For the lowest concentration of 0.01wt%, there was no significant change of contact angles measured between pH 4 and pH 6, which were in range from 110 to 115 degrees. However, at pH 7 contact angle increased to 130 degrees. For 0.05 wt% the increase in contact angle seems to more gradual, from 145 degrees to 155 degrees between pH 4 and pH 6 then a value of 160 degrees at pH 7. For the highest concentration used, contact angles seem to be quite uniform throughout the pH 5 – pH 6 range of approximately 155-160 degrees. At pH 7, however, two different results were obtained. In the first case droplets would form a

contact angle which was around 160 degrees, like for the lower pH values. However, the rest of the droplets did not wet the surface. After the deposition, they rolled out from the specimen. Figure 71 shows an example of images taken by the camera of the goniometer system.



Figure 70 – Water-in-oil contact angles measured for different concentrations of myristic acid and different pH-s.



Figure 71 – Water-in-oil contact angles of 0.1 wt.% myristic acid at pH 4 (A) and pH 7 (B); 0.1 wt.% of acridine at pH 4 (C) and pH pH 7 (D).

Water-in-oil contact angles measured with acridine are given in the Figure 72. For the 0.1 wt.% concentration measured contact angles were 81° at pH 4 and 61° at pH 7. Contact angles when the concentration of acridine was increased to 1 wt.% were measured at 128° for pH 4 and 113° for pH 7.



Figure 72 – Water-in-oil contact angle measurements for different concentrations of acridine and different pH values.

Strong influence of myristic acid on wetting properties was already shown in the study by F. Ayello, which was performed at pH 5 and 1 wt.% NaCl solution [32]. For all concentrations and pH values, it appears that the increase in contact angle at pH 7 is associated with the decrease in interfacial tension. The effect of producing the non-wettable surface was in this case clearly associated with adsorption at the steel surface and changing the pH of the aqueous solution. After the immersion of specimens in oil, myristic acid adsorbs at the steel surface. Since the concentration of the myristic acid is constant throughout the whole pH range, concentration of the myristic acid at the steel surface must be constant for every pH. The observation of absolutely non-wettable surface must be attributed to the changes at the oil-water interface. During the formation of water droplets in the oil phase, a layer of myristic acid and myristate anions are adsorbed at the oil-water interface. After releasing the droplet from the syringe, it reaches

the surface of the steel. Figure 73A illustrates the possible mechanism which takes place after droplet deposition at the steel specimen at the pH values from 4 to 6. As the water droplet approaches the steel interface hydrocarbon chains that are adjacent to the oilwater interface interact with molecules that are adsorbed at the steel interface. Since density of the molecules at the oil-water interface is not high, water penetrates the layer of fatty acid hydrocarbon chains at the steel surface and establishes contact with the steel surface. After depositing the water some of the molecules can stay adsorbed at the surface.

At pH 7, however, the density of the molecules at the water-oil interface is higher due to the higher concentration of ionized species at the oil-water interface (Figure 73B). In this case the density of the hydrocarbon chains at the oil-water interface increases which lateral interaction. This causes the repulsion between the interfaces and prevents the contact of water with the steel surface. Fatty acids are widely used as lubrication agents due to those properties [202]. The macroscopic effect has been observed as rolling a droplet on a steel specimen surface.

Water A	В
}}}}}}}}}	***************************************
Oil	
Steel	

Figure 73 – Simplified schematic of proposed mechanism of droplet-steel interaction of myristic acid at low (A) and high (B) pH values

For acridine, contact angles decreased from with increasing the pH and the concentration. This result is opposed to one obtained with the myristic acid where higher degree of ionization led to decrease in contact angles. The effect of rolling droplet that was described for myristic acid was not observed. This is probably due to the fact that acridine is not a amphiphilic compound and the interaction between hydrocarbon chains is lacking.

Oil-in-Water Contact Angle Measurements

For oil-in-water contact angles the steel specimen is immersed in the aqueous phase, and the oil droplet is deposited below the steel surface. Since there is a significant accumulation of CO_2 bubbles below the surface of the specimen, only measurements were possible within the short time, which was around a few minutes.

As can be seen in Figure 74 for 0.1 wt.% myristic acid in the oil phase there was no significant difference in contact angles between pH 4 and pH 7; the oil droplet resided at the bottom side of the specimen. From the shown pictures it is not clear whether the droplets are in the contact with the steel surface or if they reside below a thin layer of water which separates them from the steel surface.



Figure 74 – Oil-in-water contact angles of 0.1 wt.% myristic acid at pH4 (A), and pH pH7 (B).

For acridine, the difference between contact angles obtained at two pH values can be clearly seen from Figure 75. At pH 4 the oil droplet readily wetted the steel surface, which was not the case at pH 7. The higher concentration of acridine made the surface more hydrophobic.



Figure 75 – Oil-in-water contact angles of 0.1 wt.% acridine at pH 4 (A) and pH 7 (B); 1 wt.% of acridine at pH 4 (C) and pH 7 (D).

The difference in contact angles between myristic acid and acridine is associated with significant partitioning of the later compound in the water phase. Figure 76 shows the predicted values of the distribution coefficients of myristic acid and acridine for the octanol-water system as a function of pH.



Figure 76 - Octanol-water distribution coefficient for myristic acid and acridine

From the figure it can be clearly seen that the amount of the acridine that partitioned in the water phase is two orders of magnitude higher than for the myristic acid at pH4. From the given results is not clear, however, whether the ionized or non-ionized species are responsible for the adsorption at the surface.

Corrosion Measurements - Partitioning

The results from partitioning tests with myristic acid at pH 4 and pH 7 are shown in Figure 77 and Figure 78. At pH 4 the initial corrosion rate measured for the first 20 minutes was around 3.8mm/y, which was slightly higher compared to the result obtained during the baseline test at pH 4 (3.3 mm/y). Corrosion rate started to gradually decrease and after two hours reached the stable value of approximately 2.8 mm/y. It remained constant until the end of the test. At pH 7 the initial corrosion rate quickly stabilized after the addition of oil at 1.1 mm/y, which is the same value obtained during the corrosion

baseline test. The corrosion rate remained stable at 1.1 mm/y throughout the whole test duration. The results at pH 4 and pH 7 indicate that myristic acid in the partitioning test was unable to inhibit corrosion.



Figure 77 – Corrosion rate measured in partitioning test at pH4 for 0.1 wt. % myristic acid solution.



Figure 78 – Corrosion rate measured in partitioning test at pH7 for 0.1 wt. % myristic acid solution.

The results from partitioning tests with acridine at pH 4 and pH 7 are shown in Figure 79 and Figure 80, respectively. At pH 4 the initial corrosion rate in the water phase was 3.6 mm/y and started to decline at the same rate as in the baseline test. When the oil was added on top of the water phase, the corrosion rate sharply declined during the first 2 hours of the test, after which it stabilized at 0.03 mm/y and remained constant by the end of the test period. At pH 7 initial corrosion rate declined from 2.0 mm/y to 1.0 mm/y in the first hour and remained at the value which was obtained in the baseline test. The partitioning tests performed at pH 4 and pH 7 indicate that acridine can inhibit corrosion at low aqueous pH values.



Figure 79 – Corrosion rate measured in partitioning test at pH 4 for 0.1 wt.% acridine solution.



Figure 80 - Corrosion rate measured in partitioning test at pH 7 for 0.1 wt.% acridine solution.

Corrosion Measurements – Direct Inhibition

The results from partitioning tests with myristic acid at pH 4 and pH 7 are shown in Figure 81 and Figure 82. At pH 4 initial corrosion rate measured for the first 20 minutes was around 1.5 mm/y, which was significantly lower compared to the result obtained during the baseline test at pH 4 (3.3 mm/y). After the initial high value, corrosion rate started to increase and continued at the same trend until the end of the test. At pH 7 the initial corrosion rate was very low, less than 0.1mm/y. Approximately half an hour after the test started, corrosion rate increased sharply to 0.3 mm/y and continued to gradually increase until it reached 0.8 mm/y at the end of the test. The direct inhibition tests at pH 4 and pH 7 indicate that myristic acid at the given concentration was able to inhibit corrosion, but the effect was gradually diminishing.



Figure 81 – Corrosion rate measured in direct inhibition test at pH 4 for 0.1 wt.% myristic acid solution in model oil.



Figure 82 – Corrosion rate measured in direct inhibition test at pH 7 for 0.1 wt.% myristic acid solution in model oil.

Corrosion rates measured with acridine in the direct inhibition tests are shown in Figure 83 and Figure 84. Corrosion rate remained very low, less than 0.008 mm/y and continued to gradually decrease throughout the experiment until it reached the final value of 0.004 mm/y. At pH 7 initial corrosion rate was slightly lower compared to the baseline test. However, one hour into the experiment it equalized with the baseline value and continued to slowly decrease during the experiment until it reached 1.0 mm/y at the end of the test. The results of direct inhibition tests with acridine showed that inhibition was equal with the tests obtained in the partitioning tests and unaffected by the presence of oil.



Figure 83 – Corrosion rate measured in direct inhibition test at pH4 for 0.1 wt. % acridine solution in model oil.



Figure 84 - Corrosion rate measured in direct inhibition test at pH7 for 0.1 wt. % acridine solution in model oil.

Doughnut Cell Experiments

Doughnut cell experiments were performed in order to characterize the influence of 0.1 wt.% myristic acid in the oil phase on phase wetting in flow conditions. Figure 85 shows the percentage of water wetted pins as a function of rpm. A higher percentage of water wetted pins indicates that the surface is more wetted with water. For all velocities it can be seen that there is a decrease in the number of pins wetted with water as the flow becomes more dispersed. It can also be seen that for all velocities the percentage of water wetted pins decreases with increasing the velocity as the flow becomes more dispersed. The highest number of water wetted pins was obtained at pH 4 without the presence of any surfactant. The highest percentage of water wetted pins was with pure LVT200 model oil without any surfactant present. With the addition of myristic acid at pH 4 the percentage of water wetted pins drops significantly and drops more with an increase of the pH. A further increase of pH was achieved with boric acid buffer which lead to an almost completely oil wetted surface for all velocities.



Figure 85 – Water wetting degree as obtained in Doughnut Cell experiments.

Summary

Interfacial tension, contact angle, corrosion inhibition and doughnut cell wetting experiments were performed to test the hypothesis that changing the pH of the aqueous solutions can alter the wetting and corrosion inhibition properties of oils by ionization of polar crude oil model compounds. Chemical components which were selected for this research (myristic acid and acridine) have pK_a values which is the range of common pH values of produced waters (pH4 to pH7), and therefore, their ionization is the most affected by change of in the selected range.

The experimental results showed that the most significant change in surface tension and contact angle occurred in the solution containing myristic acid at pH7. This change of surface tension properties was most likely due to ionization of myristic acid at the interface which normally occurs at pH values higher than in the bulk aqueous solutions. The results of corrosion measurements showed that the most significant change of corrosion inhibition properties was obtained with acridine, due to the partitioning in the aqueous phase.

Therefore, the results of this part of the study confirmed the initial hypothesis that the corrosion inhibition and wettability properties of polar organic compound were significantly altered by changing the pH of aqueous phase.

CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The aim of this study was to expand and deepen the present knowledge related to the role of interfacial chemistry on wetting and corrosion in multiphase flow pipelines. This was achieved by investigating four aspects which interlink interfacial processes that concurrently occur in pipelines with chemical composition, conclusions for each are described below.

1. Simultaneous foaming and inhibition of corrosion prompted by oil-soluble naturally occurring polar compounds in crude oils.

The main hypothesis of this part of the study was that accumulation of significant amounts of preferentially oil soluble surface active compounds at the liquid-gas interface due to formation of foam can significantly lower their concentration in the bulk oil solution. Consequently, it was hypothesized that 'parasitic consumption' can cause concentration decreases of inhibiting compounds and impair corrosion inhibition. Compound classes which were tested, namely asphaltenes and carboxylic acids, were previously reported to have dual corrosion inhibition/foam-forming characteristics. It was found that there is no universal rule which would connect the presence of these compound classes in crude oils with 'parasitic consumption' and consequent loss of inhibition. The characteristic properties of molecules which drive adsorption to the oilgas interfaces differ from those that govern adsorption at steel-oil interfaces and, therefore, a simple association cannot be established. However, formation of molecular agglomerates, such as inverse micellar structures, can produce species which can be potentially surface active and adsorb at the oil-gas interface [203]. Therefore, it can be postulated that compounds with such characteristics can be found in the asphaltene or acid fractions of crude oils; further research is needed which would test this hypothesis.

2. Foaming and corrosion inhibition by water soluble surfactant-based corrosion inhibitors with the presence of an oil layer covering the aqueous phase.

For this part of the research it was hypothesized that hydrocarbon liquids have antifoaming properties which depend on the composition of the hydrocarbon phase. Successively, antifoaming properties of hydrocarbons can affect corrosion inhibition by reducing the amount of foam generated by aqueous inhibitor solutions. The components which were chosen for the research were a TOFA/DETA imidazoline-based corrosion inhibitor and two hydrocarbon liquids, heptane and a mixture of saturated linear hydrocarbons with predominantly 13-15 carbon atoms. It was found that hydrocarbon liquids can suppress foaming and decrease its undesirable effect on corrosion inhibition. However, it still remained unknown how composition of liquid hydrocarbon can influence corrosion behavior. Therefore, future research in this direction should be aimed towards examining the effects of hydrocarbon liquids with chemical compositions which are closer to ones found in real gas pipelines and with other types of surfactant-based inhibitors, such as quaternary ammonium chlorides, phosphate esters, etc. It is important to note that composition of liquid hydrocarbons can significantly change along the gas line. Due to cooling, water and the heaviest hydrocarbons with highest boiling points condense first, followed by lighter hydrocarbons as the temperature in the line gradually decreases. Therefore, antifoaming properties of hydrocarbon liquids may significantly vary from the beginning to the end of the pipeline, which in turn can impact corrosion.

3. Effect of formation of iron-carbide corrosion product residues on wetting properties of steel.

The main hypothesis of this part of the research was that corroding steel increases hydrophilicity of the surface which will have a significant effect on the persistency of water on the surface of the steel. The steel which was used in this research was low-carbon, low-alloy steel with a quenched and tempered martensite microstructure. It was found that the corrosion product layer is a metallic carbide that does not increase hydrophilicity of the steel surfaces on which it forms, but the opposite. However, it was also found that water was retained in the cavities of this porous residual iron carbide that cannot be displaced by the flowing oil. Corrosion rates which are observed in such voids are significantly lower due to fast saturation of the aqueous phase with generated ferrous ions, and a concomitant strong tendency to form protective iron carbonate layers [200], [201]. Further research is needed to clarify a long-term effect of retained water on corrosion processes in the areas which are intermittently wetted by water and oil, such as steel areas in the proximity of the oil-water interface in stratified flow regimes. That can lead to alternating formation and dissolution of iron carbonate depending on the level of water and cause localized attack. Furthermore, it is worth investigating if and under which conditions oil can displace water from the cavities. It can be assumed that in porous cementite structures wetting phenomena play a significant role.

4. Altering inhibition of corrosion and steel wetting properties by ionization of crude oil model polar compounds.

The main hypothesis of the fourth part of this research was that altering the pH of the aqueous phase causes ionization of polar organic compounds innate to crude oils and produced waters. Ionization consequently leads to significant changes in their surface active properties, such as oil-water interfacial tension and adsorption properties, which in turn influences corrosion inhibition and steel wettability. The chemical compounds which were selected for this research, myristic acid and acridine, have pKa values which are in the range of common pH values of produced waters, *i.e.*, pH 4 to pH 7. It was found that ionization causes significantly different surface active properties compared to those observed for non-ionized molecules. Furthermore, properties were also determined by the ability of compounds to partition between hydrocarbon and aqueous phases. For compounds which partition in the aqueous phase, bulk pKa was determining their surface active properties; while for compounds that preferentially partition in the oil phase, surface properties were determined by their surface pKa. It was previously shown that pKa of ionization of long chain organic acids at the interface can change properties of water-gas interfaces by changing the distance between the molecules, as described elsewhere [204].



Figure 86 – Intermolecular distance of fatty acids at the interface as a function of pH and pKa at the surface. Adapted from reference [204].

Therefore, it can be hypothesized that there is a 'sweet point' of pH at which polar organic compounds have 'optimum' degree of ionization at the oil-water interface and exhibit especially strong influence on corrosion inhibition and wetting properties. Research in this direction can be relevant for real systems which contain mixtures of acidic and basic nitrogen compounds that produce opposite charges at the oil-water interfaces. Lastly, it would be interesting to examine how corrosion inhibition and wettability properties of strong inhibiting compounds, such as mercaptans, but with pKa values outside of the pH 4-pH 7 are affected by changes in pH.

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APPENDIX A: PROPERTIES OF STEEL, FLUIDS, AND CHEMICALS USED IN THIS PROJECT

X65 Mild Steel

The carbon steel used in this research is an API 5L X65 mild steel, produced by a quenching and tempering process. For this mild steel grade, the American Petroleum Institute (API) specifies minimum yield strength of 65300 psi [205]. Chemical composition of the X65 steel is given in Table 10 [206].

Table 10 – Chemical composition of API 5L X65 carbon steel [206]

Element	Cr	Mo	S	V	Si	C	Fe	Ni	Mn	Р
Content, wt%	0.14	0.16	0.009	0.047	0.26	0.13	Balance	0.36	1.16	0.009

The micrograph shown in Figure 87 shows a grain structure typical of a tempered martensite with small spheroidal cementite particles. The spheroidal cementite originates from the tempering process and is concentrated predominantly at grain boundaries.



Figure 87 – Micrograph of X65 mild steel: A – tempered martensite grains, B – spheroidized martensite (courtesy of Fernando Farelas)
Fluids

Deionized Water

Deionized water used in the experiments was obtained by purification of tap water through an active carbon filter in combination with one cationic, one anionic and two mixed bed ion-exchange resin columns. The degree of water purification was measured with a conductivity meter at the exit from the last column. The conductivity of water at the exit of the deionizer was less than 1μ S/cm.

LVT 200 Paraffinic Oil

LVT 200 (CAS number 64742-47-8) is a brand name for a hydrotreated light distillate petroleum fraction. LVT200 is a light paraffinic liquid of API gravity of 39.5. The typical distribution of paraffinic hydrocarbons, according to the manufacturer, is given in Table 11 and physical properties in Table 12 [207], [208].

Table 11 – Hydrocarbon distribution of LVT200 [207]:

Element	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C ₁₇
Content, vol%	1.8	20.1	39.7	33.1	4.6	0.7

Table 12 – Physical properties of LVT 200 [208]

Property	Value
Density @15°C (g/cm3)	0.827
Viscosity @40°C (mPas)	1.94
Distillation, Initial Boiling Point (°C)	229
Distillation, Final Boiling Point (°C)	266

Aromatic200 Oil

Aromatic 200 (CAS number: 1338-24-5) is a brand name of oil which contains a complex mixture of aromatic hydrocarbons that are predominantly derivatives of benzene and naphthalene [209]. The approximate range of carbon number is $C_{10} - C_{13}$. Physical properties of Aromatic 200 are given in Table 13.

Table 13 – Physical properties of Aromatic 200 [210]

Property	Value
Density @ 15°C	0.985 g/cm^3
Viscosity@25°C	3.03 mPas
Distillation, Initial Boiling Point	227 °C
Distillation, Final Boiling Point	287 °C

Crude oil

The physical characteristics of crude oil, given in Table 14, were determined in the Institute for Corrosion and Multiphase Technology. The chemical properties are from the crude oil assay [166].

Table 14 – Physical properties of Crude oil

Property	Value
Density @ 25°C	0.853 g/cm^3
API gravity	32.0
Viscosity@25°C	9.1 mPas

Chemicals

Myristic Acid

Myristic (tetradecanoic) acid (CAS number: 544-63-8) is a C-14 saturated fatty acid (Figure 88). At normal temperature and pressure, myristic acid is a white crystalline substance. 99% pure Myristic acid is obtained from Sigma and used without any further purification; its physicochemical properties are given in Table 15.

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Figure 88 – Molecular structure of myristic acid

Property	Value
Formula	$C_{14}H_{28}O_2$
Molecular Weight	228.37 g/mol
Melting Point	52-54 °C
Boiling Point	250 °C

Table 15 – Physicochemical properties of myristic acid [211]

Acridine

Acridine (CAS number: 260-94-6) is a heterocyclic nitrogen compound (Figure 89). At normal conditions of temperature and pressure acridine is a yellow crystalline substance. Acridine (97% pure) was obtained from Sigma and used without further purification; the physical properties of acridine are given in Table 16.



Figure 89 – Molecular structure of acridine

Property	Value
Formula	C ₁₃ H ₉ N
Molecular Weight	179.22g/mol
Melting Point	107 - 110 °C
Boiling Point	346 °C

Table 16 – Physicochemical properties of acridine [212]

Naphthenic acid mixture

Naphthenic acids (CAS number: 1338-24-5) is a mixture with a chemical composition that can vary, but typically naphthenic acids consist of 1-4 fused cycloaliphatic rings with bonded aliphatic side chains and carboxylic groups (Figure 90) [213]. At standard conditions of temperature and pressure a naphthenic acid mixture is a yellow, viscous liquid; its physicochemical properties are given in Table 17.



Figure 90 – Molecular structures of common naphthenic acids [213]

Droporty	Value
Property	value
Formula	Variable
Molecular Weight	Variable
Melting Point	223 °C
Boiling Point	31 °C
Total Acid Number	216 mg(KOH)/g

Table 17 – Physicochemical properties of Naphthenic acid mixture [214]

TOFA/DETA Imidazoline-type Corrosion Inhibitor (K1)

Compounds synthesized from tall oil fatty acids (TOFA) and diethylenetriamine (DETA) are very common surfactant-based corrosion inhibitors. The TOFA/DETA imidazoline-based corrosion inhibitor used in this work is also termed K1. In aqueous acidic solutions the inhibitor exists predominantly as a cation with a delocalized positive charge on the head group (imidazolinium) [179]. The molecular structure of a prevalent form is shown in Figure 91.



Figure 91 – Molecular structure of TOFA/DETA imidazoline-type corrosion inhibitor.

APPENDIX B: DU NOUY RING TENSIOMETER METHOD INTERFACIAL TENSION MEASUREMENTS

Oil-water interfacial tension measurements were performed using the CRC Scientific 70545 Du Nouy ring tensiometer shown in Figure 92. The main parts of the tensiometer include a platinum ring, torsion wire, dial, beaker holder and set of knobs and lever arms mounted on a steel frame. The Du Nouy method is based on measurement of force needed to slowly lift a platinum ring through the interface between a liquid and gas or two immiscible liquids. From the applied force, surface tension of liquid can be calculated.



Figure 92 – Du Nouy ring tensiometer.

The method is sensitive to contaminants so before each measurement the platinum ring has to be thoroughly cleaned with toluene, acetone and deionized water and briefly exposed to flame. The platinum ring is mounted on a vertical rod with two lever arms which are connected to a torsion wire. One end of the torsion wire is fastened to a gear which rotates the hand on the instrument dial. The dial displays the tension in mN/m (dyne/cm).

The platinum ring is fully immersed in liquid in a beaker so that the fluid completely wets the ring surface. It is important to note that the ring can be pulled up as well as pushed down through the interface, depending on the type of measurement (e.g., water-oil *vs.* oil-water interfacial tension). In this work only an upward pull is used, from liquid to gas or from higher to lower density liquid. As the ring is slowly pulled up and contacts the interface, it drags the thin layer of liquid into another phase (oil or gas), as shown in Figure 93.



Figure 93 – Extending of surface during interfacial tension measurements.

The force which is opposing the upward motion is mainly from the surface tension of liquid that acts to contract the surface. As the ring is pulled from one phase into the other, the interface is approaching a vertical position. That causes an increase of the vertical component of surface tension and force exerted on the ring increases. The maximum force is reached when the film is in vertical position [215]. Further upward movement

causes a slight reduction of pulling force, followed by the film rupture and end of the measurement.

Vertical motion of the ring is synchronized with the set of lever arms and torsion wire with the rotation of the hand on the instrument's dial. At film breaking point, the value shown on a dial is defined as apparent surface tension P (dyne/cm). The theoretical accuracy provided by the instrument is ± 0.1 dyne/cm, although in practice an accuracy of ± 1 dyne/cm is considered to be satisfactory. The apparent surface tension *P* equals force divided by twice the circumference of a ring:

$$P = \frac{F}{4R\pi} \tag{71}$$

Where *F* is the force exerted on a ring and *R* is the mean radius of a ring. In order to obtain the true value of surface tension the apparent surface tension *P* has to be corrected to account for the effect of factors which in some cases can alter the result up to 30% [216], [217]. These factors include gravity, buoyancy and complex geometry of a liquid at point of rupture. Correction is achieved by multiplying apparent surface tension with the correction factor β in order to obtain the correct value of surface tension σ :

$$\sigma = \beta P \tag{72}$$

The most common ways to obtain the values of correction factor β are given by Harkins & Jordan, Zuidema & Waters, or Huh & Mason [216], [218], [219]. In this work and according to recommendations from the tensiometer manufacturer, Zuidema-Waters, the correlation factor used which can be expressed as [218]:

$$\beta = 0.725 + \sqrt{\frac{0.00363P}{\pi^2 R^2 \Delta \rho} + 0.04534 - 1.679\frac{r}{R}}$$
(73)

Where *P* is an apparent surface tension in dyne/cm (mN/m), *R* is the radius of a ring in cm, $\Delta \rho$ is the density difference between two phases in kg/m³ and *r* is the radius of a platinum wire in cm.

APPENDIX C: CORROSION MEASUREMENTS IN A GLASS CELL – LINEAR POLARIZATION RESISTANCE METHOD

Corrosion experiments were performed using the three electrode glass cell apparatus coupled with a GamryTM potentiostat. The apparatus is suitable for small scale corrosion experiments at atmospheric pressures. The main parts of the glass cell setup are listed in Figure 94. Liquid is contained in a 2 liter vessel sealed with a lid made from Teflon[®] with adaptable openings for electrodes, sensors and gas inlet and outlet. The temperature of liquid in a glass cell is continuously measured with a thermocouple connected to a hot plate. Heaters in a hot plate are switched on and off automatically based on the temperature ture readings in order to maintain the constant solution temperature. A fritted glass tube is used to purge the test liquid with CO₂ or other gases. Solution pH is monitored with a pH electrode connected to the Omega pH meter.



Figure 94 – Three electrode glass cell set-up for corrosion inhibition measurements: 1reference electrode, 2-gas outlet, 3-temperature probe, 4-platinum counter electrode, 5rotator, 6-gas inlet, 7-pH-electrode, 8-Luggin capillary, 9-working electrode (rotating cylinder), 10-hot plate

The system for electrochemical corrosion measurements consists of three electrodes. The working electrode is a rotating cylindrical steel specimen mounted on the shaft with a variable rotational speed. The carbon steel specimen has 12 mm O.D., 6 mm I.D. and height of 14 mm. The surface area of the specimen exposed to test solution is 5.3 cm². A silver-silver chloride (Ag/AgCl) reference electrode saturated with KCl is connected *via* a salt bridge (1M KCl solution) to a Luggin capillary placed inside the test solution. A platinum mesh is used as an auxiliary (counter) electrode.

Carbon steel corrosion rate measurements were performed using the linear polarization resistance technique (LPR). LPR is a fast, non-destructive and extensively used electrochemical method for corrosion rate measurements. During measurements of corroding specimens, reference and auxiliary electrodes are connected to a potentiostat (three electrode setup). During measurements a corroding specimen (working electrode) is polarized in the narrow range of potentials (±5-10 mV) relative to open circuit potential (OCP). Open circuit potential is potential of a corroding specimen, measured relative to the Ag/AgCl reference electrode. Polarization induces flow of current between the corroding specimen and the auxiliary electrode, which is measured by potentiostat. If potential of a corroding electrode is slightly removed from the open circuit potential, current is a linear function of applied overpotential (Figure 95).



Figure 95 – Overpotential-current curve of corroding electrode.

The proportionality constant which relates potential and current in that narrow region is defined as polarization resistance, Rp [12]:

$$R_p = \frac{\Delta E}{\Delta I_{\Delta E \to 0}} \tag{74}$$

Therefore, polarizing resistance Rp can be experimentally obtained from the potential-current density curve by measuring the slope of potential *vs*. current. The corrosion current density i_{corr} (A/m²) can be derived from the polarizing resistance using the approximation derived by Stern and Geary [220]:

$$i_{corr} = B \frac{1}{R_p} \frac{1}{A} \tag{75}$$

Where *A* is the surface area of the specimen exposed to the corrosive environment and *B* is a constant. *B* value can be determined experimentally or derived from polarization curves:

$$B = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \tag{76}$$

where β_a and β_c are the respectively anodic and cathodic Tafel slopes., which are calculated as follows:

$$\beta_a = \frac{2.303RT}{\alpha_a F} \tag{77}$$

$$\beta_c = \frac{2.303RT}{\alpha_c F} \tag{78}$$

Where *T* is the temperature in the Kelvin scale, *R* is the universal gas constant, α_a and α_c are the symmetry factors for anodic and cathodic reactions and *F* is the Faraday constant (96485 C/mol). Typical values of α_a and α_c are 1.5 and 0.5, respectively.

Corrosion rate (CR) in mm/y can be calculated using equation (79):

$$CR = \frac{m}{At\rho} = \frac{i_{corr}M_w}{\rho nF} = 1.16 \, i_{corr} \tag{79}$$

Where *m* is the metal loss (kg), *t* is the time in seconds, ρ is the density of the material in kg/m³, M_w is the "molecular weight" of the material (X65 carbon steel) in kg/mol, *n* is the number of electrons exchanged in the electrochemical reaction.

In every corrosion experiment open circuit potential was first measured until it became stable enough to start the LPR. Stable values were usually achieved a few minutes after immersing the corroding specimen in the aqueous phase. Specimens were then polarized 5 mV lower than OCP and potential was gradually increased to 5 mV above the value of OCP. The signal generated by potentiostat approximates the linear sweep with a staircase potential sweep with small potential steps [221]. The current is then measured at the end of each step, before the next increase of potential Figure 96.



Figure 96 – Approximation of linear potential sweep with staircase potential sweep.

The typical potential-current diagram which was obtained in measurements is shown in Figure 97. The Rp value can be found by measuring the slope in middle range of \pm 5mV region. Typically, *Rp* was measured in the range of \pm 3 to \pm 4 mV vs. OCP in order to avoid non-linear parts of the plot, which commonly occur at lowest range of overpotentials.



Figure 97 – Typical overpotential-current curve obtained with LPR measurements.

Once open circuit potential became stable, fast EIS measurement was conducted to measure the solution resistance. EIS was carried out in the frequency range of 10 kHz to 1 Hz with an applied AC potential of \pm 10 mV. Correction of *Rp* values is needed in order to apply in LPR measurements. Subtraction of IR drop which originates from solution resistance and instrument circuitry. Corrosion rate was then calculated using corrected *Rp* values using equations (76) and (79). *B* value used was 0.026 based on the previous experimental results in similar experimental conditions [222].

APPENDIX D: SURFACE WETTABILITY: CONTACT ANGLES – SESSILE DROP METHOD

Contact angle measurements of a sessile drop were performed in the goniometer system shown in Figure 98 which was developed by Tang [30]. The goniometer system consists of a goniometer cell, digital camera, light source and PC with software for image processing. The central part of the system is the goniometer cell which accommodates a steel specimen for contact angle measurements. The sessile drop method is the most simple and common way for measuring contact angles [79], [82]. the method includes deposition of a liquid droplet on a surface which is in contact with another immiscible fluid. Measuring the angle of contact where three phases meet is used to evaluate the wettability of a surface regarding the deposited liquid [223].



Figure 98 – Goniometer system for contact angle measurements.

The goniometer cell is a 4.5" O.D., 4" I.D. and 6" high stainless steel vessel [30]. Two circular transparent glass windows are mounted on the opposite sides to provide an optical view of the specimen inside the goniometer. The cell is hermetically closed from the top with a transparent acrylic lid. The cell has several adaptable ports on the sides for oil drainage and liquid droplet injection, and several ports on the lid which accommodate gas inlet and outlet, thermometer and a pH probe. Inside the cell, a steel specimen is placed on two Teflon® holders which are mounted on a stainless steel disk (Figure 99). Carbon steel specimens are coated with a resilient fluoropolymer coating except on the surface used for measurements. Prior to each measurement the goniometer cell has to be thoroughly cleaned using organic solvents, DI water, and dried. The cell can be filled with gas, oil or water. A steel specimen is then inserted in the cell and placed horizontally on specimen holders. The image capture system is composed of a camera, a backlight, and software for image processing. The specimen surface is illuminated with a backlight through one of the circular windows in the goniometer cell. During the measurement a camera placed on the opposite side continuously records the process. The camera used is an IMAGING PLANET® model 221-XS monochrome CCD camera with 768 x 494 pixel array, and resolution 570 horizontal lines [30]. The camera is connected to a PC card installed in the computer. Contact angles were calculated from the captured images using RINCON® and ImageJ image analysis software.



Figure 99 – Holder with a mounted steel specimen for water-in-oil (left) and oil-in-water (right) contact angle measurements.

Droplets can be deposited above or below the specimen depending on droplet buoyancy (Figure 99). If the continuous phase is oil or gas, a water droplet is deposited above the steel surface. On the other hand, deposition of oil droplets in a continuous aqueous phase is performed underneath. Correspondingly, contact angles which are measured are termed as water-in-oil and oil-in-water.

The experimental process of droplet deposition, spreading, and formation is shown in Figure 100. Deposition of a droplet on a specimen surface is performed by microliter syringe with a long needle coated with a fluoropolymer coating to ease droplet detachment. The needle is inserted into the goniometer either from the top through one of the ports on the acrylic lid or through a port on the side, depending on the type of the contact angle which is being measured.



Figure 100 – Spreading of droplet in water-in-oil and oil-in-water type contact angle measurements.

The preferable maximum volume of liquid that is injected to form a droplet is determined by the diameter of a droplet which liquid forms. Smaller liquid droplets are able to retain a spherical shape upon contacting the surface. At larger droplet diameters, the effect of gravity disrupts the shape of a droplet into a puddle which can affect the accuracy of measurement. Commonly, capillary length is taken as the upper limit for maximum droplet diameter [224]:

$$L_{\lambda} = \sqrt{\frac{\sigma_{12}}{\rho_1 g}} \tag{80}$$

Where L_{λ} is the capillary length (m), σ_{12} is the interfacial tension between liquid in droplet and surrounding fluid (N/m), ρ_1 is the density of liquid (kg/m³) and g is gravitational acceleration (m/s²). Therefore, the maximum volume of liquid used to form is:

$$V = \frac{1}{6}L_{\lambda}^3 \tag{81}$$

In current experiments the commonly used volume was in the range of 5-7 μ l. After forming the droplet at the tip of a needle, the syringe is slowly tapped in order to release

the droplet approximately 5mm from the surface. The liquid droplet is then driven to the steel surface by gravity or buoyancy, depending on the type of performed measurements. After contacting the steel surface the droplet starts to spread as already explained in Chapter 2. The dynamics of spreading can vary and therefore experimental time has to be adjusted accordingly. Experiments were stopped when no change of spreading over time could be observed. Therefore, the final contact angles correspond to a state of equilibrium or stage when spreading kinetics became negligibly small. From extracted video images contact angles are measured optically between the steel-water and oil-water contact lines. As shown in Figure 100, this refers to angles formed either by the droplet or by the continuous phase.

APPENDIX E: DOUGHNUT CELL – APPARATUS FOR SURFACE WETTING MEASUREMENTS IN OIL-WATER FLOW

The Doughnut cell is a small scale apparatus designed by Li to simulate oil-water multiphase flow conditions in pipelines [134]. The Doughnut cell system shown in Figure 101 consists of the flow cell, electric motor, and electronic boards for data acquisition mounted on a steel cart. The flow cell has a shape of a hollow cylinder and thus bears a resemblance with a doughnut. The device simulates oil-water flow in pipelines by driving the oil and water in a circular motion inside the annular space. The main advantages of using the Doughnut cell over large scale equipment such as a multiphase flow loop are low cost, ease of operation, and relatively small amount of fluids needed for each experiment.



Figure 101 – Doughnut cell.

The cross-sectional schematic of the flow vessel is given in Figure 102. The bottom plate is made from 316 stainless steel (4), inner (3) and outer (2) acrylic cylinders and the

acrylic rotating wheel (5) form the annular flow channel. The diameter of the outer cylinder is 18", the inner one 13.7", and the width of the annular space is 1.81". The height of the rotating wheel can be adjusted and for this study is set to be 2.75" relative to the upper steel plate surface. The total volume of liquid in the annular flow channel is 4.2 liters. The electric motor placed in the middle of the cylinder is connected to the rotating wheel. The other three acrylic flanges and acrylic lid are used to seal the cell. Additional technical details about the construction of the Doughnut cell are provided by Li [134].



Figure 102 – Cross-sectional schematic of the Doughnut cell: 1-top flange, 2-outer cylinder, 3-inner cylinder, 4-bottom flange, 5-rotating ring, 6-flow channel, 7- conductivity pins.

The cell has to be thoroughly cleaned with organic solvents and deionized water before starting an experiment. The amount of oil and water used varies depending on the experiment but the total volume is always 4.2 liters. Upon charging the fluids in the flow channel the rotating lid is set so its lower surface is in contact with the oil phase. A rotational speed set by an electric motor controller is used to adjust circumferential velocity of the rotating wheel. The shear stress that is applied on oil by rotational motion of the wheel causes movement of a liquid in the flow channel. At low circumferential velocities, oil and water flow in stratified layers. With the increase of velocity of the rotating lid, oil velocity increases and formation of water droplets occurs which get entrained in the oil phase. Further increase of velocity causes more water from the bottom to be entrained by the flowing oil phase. Depending on the parameters used, water can be partially or fully entrained in the oil. When the rotational velocity of the rotating wheel is reduced, the reverse process of water dropout occurs.

The surface of the stainless steel plate at the bottom simulates the bottom area of the pipe inner wall in the phase wetting study. This process is monitored visually by observing the flow through the transparent acrylic cylinder and by collecting the data from the conductivity sensor probes. The sensors used to determine wetting in the Doughnut cell consist of an array of electrical conductance probes flush mounted in the stainless steel plate at the bottom of the annular flow channel. Stainless steel pins are embedded in epoxy resin and isolated from the plate. From the bottom side of a steel plate pins are connected to circuit boards.

Each conductivity pin is part of an electrical circuit based on a voltage divider and voltage comparator. The basic circuit schematic is shown in Figure 103. The conductivity pin and the resistor of $1M\Omega$ fixed resistance (R1) are connected to the source of electric potential V_E, while the steel plate is connected to the circuit's ground. The conductive path between the potential source and the ground can be established through the fluid which bridges the top of the pin and the steel plate. The electrical resistance through that path is marked as R_{PIN}. Non-inverting input (+) of the operational amplifier (op-amp) is

connected to the node located between the resistor R_1 and the pin. V_{REF} is the manually set voltage supplied to the inverting input of the amplifier (-).



Figure 103 – Simplified schematic of conductivity pin circuitry.

The potential source generates a 5V signal with time interval of 5ms. If a nonconductive fluid such as oil or gas wets the top of the pin and plate, resistance of the pin (R_{PIN}) is theoretically infinitely high and current does not flow through the circuit. There is no potential drop across the resistor R_I and therefore V_{IN} equals V_E . If a conductive fluid such as brine bridges the pin and the surrounding plate, resistance R_{PIN} is finite and direct current I flows through the circuit. V_{IN} than equals to:

$$V_{IN} = IR_{PIN} \tag{82}$$

$$V_{IN} = \frac{R_{PIN}}{R_1 + R_{PIN}} V_E \tag{83}$$

Therefore, V_{IN} can be equal to V_E or lower depending on the fluid which wets the surface. When used as voltage comparator op-amp compares the potential V_{IN} with respect to V_{REF} and produces output voltage V_{OUT} . For $V_{IN} < V_{REF}$, V_{OUT} is positive with respect to the

potential of circuit ground, while for $V_{IN} > V_{REF}$, V_{OUT} is negative. Therefore, V_{REF} is preset to be in a range between V_E and a value which was determined empirically by measuring the resistance of a pin in brine solution with a potentiostat. Output voltage from each individual pin is measured and processed by the microprocessor on the board and sent to the computer. A graphical presented on the screen is shown in Figure 104.



Figure 104 – Doughnut cell conductivity pin array as seen on a computer screen.

Figure 104 illustrates the bottom of the doughnut cell. The array of conductivity pins is presented in the form of circles. Empty, open, circles represent conductivity pins wetted by oil. The solid circles signify pins wetted by water. The number and position of the pins indicate wetted bottom areas of the doughnut cell.

APPENDIX F: SURFACE PROFILOMETRY - FOCUS-VARIATION METHOD

Surface profilometry measurements were performed using an Alicona® InfiniteFocus® microscope (IFM) shown in Figure 105. The main components of the system include sensor head, stage movable in two horizontal directions and vibration adsorption system [225]. The sensor head contains an optics system with multiple objectives, light source, z-stage and nosepiece. The instrument is connected to PC for control and data processing.



Figure 105 – Alicona® InfiniteFocus® microscope.

The microscope and associated software build an optical 3D image replica of a surface created by the focus-variation method. The core principle of the focus-variation method is in combining multiple snapshots in a direction normal to the surface utilizing the small depth of focus and vertical movement of an optical system [226]. The method is schematically presented in Figure 106.





The light source illuminates the specimen with a white conical light. After hitting a specimen reflected light is collected by an objective and directed onto a color digital optical sensor. Very small depth of field of the optics ensures that only areas of surface which are approximately of the same distance from the sensor are in focus and sharply imaged [226]. To perform a complete 3D image of the surface in vertical direction, the lens is moved along the vertical axis while continuously capturing pictures. For each vertical position sharpness is calculated by the software and only sharp areas of images are used for surface topography reconstruction. Vertical movement of optics is used to gain information about the distance of surface elements. Software algorithms convert the acquired data into 3D image of a surface, as shown in Figure 107.



Figure 107 – 3D image of 145 x 110 μm steel surface obtained by focus-variation method.

In this work 3D optical replica of a surface created by IFM was used to determine surface roughness parameters. Surface roughness is alongside lay (form) and waviness of the elements of surface topography, which are schematically presented in Figure 108 [227], [228]. Lay is a direction of the predominant surface shape which is determined by the manufacturing process. Waviness and roughness are forms of deviations from desired shape, which differ in the wavelength of spaced components. Roughness consists of fine irregularities with shorter wavelengths and lower amplitudes compared to waviness [228].



Figure 108 – Basic elements of surface texture.

To an extent surface roughness can be characterized by numerical roughness parameters which quantify the number, amplitude and spacing of ridges and troughs which occur at the surface [229]. Parameters can be calculated on a line (profile parameters) or on the whole specimen surface area (areal parameters). Profile parameters are more commonly used and easier to measure.

There is no profile single parameter which can completely describe the surface shape and, therefore, several types of parameters are usually employed. They can be grouped into amplitude, spatial and mixed [230]. In this work, average roughness *Ra* is the most commonly used amplitude roughness parameter. *Ra* is defined as: "the area between the roughness profile and the mean line, or the average absolute deviation of roughness irregularities from the mean line over the evaluation length" (Figure 109) [30].

Ra

Figure 109 – Average roughness.

Average roughness can be calculated as follows:

$$R_{a} = \frac{1}{L} \int_{0}^{L} |z(x)| \, dx \tag{84}$$

Where *L* is the length of profile being assessed and z(x) is the height deviation of the profile from the mean line. Other roughness parameters, such as Root mean square roughness R_q , maximum height of peaks, R_p , maximum depth of valleys, R_v , or mean of maximum peak to valley height, R_{tm} , exist but are not employed in the current study. IFM calculates profile roughness parameters with the IF-MeasureSuite processing software. The sampling line is drawn on a top view image of the surface. A commonly used zig-zag sampling pattern and the obtained profile are shown in Figure 110. Based on these measurements, built-in algorithms then calculate a series of parameters which are presented in tabular form.



Figure 110 – Zig-zag sampling pattern and obtained roughness profile.

APPENDIX G: SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) is very common technique for high resolution imaging of the steel surfaces. Topographic and composition information are obtained by detecting electrons and electromagnetic waves which are emitted or reflected from the surface after surface is being illuminated by a beam of electrons. In this work microscopic images were obtained using the JEOL JSM-6390LV electron microscope, shown in Figure 111. The main parts of the system include an electron optical system, specimen stage, electron and X-ray detectors, image display unit and an operation system [231].The electron optical system consists of an electron gun, condenser lens, objective lens, and scanning coil.



Figure 111 – JEOL JSM-6390LV scanning electron microscope.

Figure 112 shows the basic construction of a scanning electron microscope [231]. The electron gun generates a beam of electrons, called primary electrons. Electrons are

emitted from a filament made of thin tungsten wire heated at high temperature (cathode) and stream towards the positively charged hollow plate (anode). A fraction of the emitted electrons passes through the hole in the anode and forms a beam. A negatively charged Wehnelt electrode positioned between the filament and plate regulates the current of electrons.



Figure 112 – Basic construction of a SEM: 1-electron gun, 2-electron beam, 3-scanning coil, 4-X-ray detector, 5-specimen, 6-filament, 7-Wehnelt electrode, 8-anode, 9-electromagnetic lens, 10-backscttered electron detector, 11-secondary electron detector

The beam is focused on small portion of the surface and imagery is obtained by scanning a wider area of a specimen. Flowing electrons pass through the condenser lens which regulates the width of a beam. The scanning coil guides the beam into a rectangular scanning pattern on a specimen surface. The objective lens is used for focusing and determines the diameter of the electron beam which scans a surface. Interaction of primary electrons causes emission of secondary electrons, backscattered electrons, Auger electrons, X-rays and cathodoluminescence from various depths below a specimen surface [231]. The simplified schematic of incident beam interaction is shown in Figure 113.



Figure 113 – Schematic of primary electron beam interaction.

SEM used in this research has incorporated detectors for secondary electrons, backscattered electrons and X-rays. Secondary electrons (SE) are emitted due to collision of the primary electrons with the valence electrons of a specimen. This kind of emission is restricted to relatively shallow specimen depths and the emission depends on the angle of at which the beam enters the specimen surface. Thus, the secondary electrons are used to observe the topography of a specimen.

Backscattered electrons (BS) are electrons which are reflected back from the surface. The yield of backscattered electrons correlates to the atomic number of the constituent atoms in the specimen. Therefore, images obtained by backscattered electrons provide a good contrast based on chemical composition of the near surface. X-rays are emitted from the atoms when electrons from the outer-electron shells fill the orbits of the secondary electrons ejected from inner-shells. The energy of emitted Xrays corresponds to the energy difference between the outer-shell and the inner-shell energy levels. An energy dispersive X-ray spectrometer (EDS) is then used to analyze characteristic X-ray spectra by measuring the energies of the X-rays. An X-ray spectrum is a function of chemical composition and therefore EDS can provide approximate atomic composition of the surface.



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