The Rheology of Crude Oil and Carbon Dioxide Mixtures

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DECLARATION

I declare that this thesis is entirely my own work under the supervision of Dr. John Crawshaw, Professor Martin Trusler and Dr. Edo Boek. All the material which is not my own work has been properly referenced and acknowledged. This work has not been previously, in a whole or in part, to any other academic institution for a degree or any other qualification.

Ruien Hu

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The rheology of crude oil mixtures at equilibrium with carbon dioxide (CO$_2$) was studied at elevated pressures and temperatures, similar to those found for oil reservoir conditions. The focus of the work presented in this thesis concerns the measurement of the rheological properties of CO$_2$ saturated mixtures of crude oil. The rheology measurements were made using a high-pressure rheometer coupled to a fluid flow system designed and built in this project. The flow system comprised a mixing vessel and fluid flow loop that allowed the test fluid to be brought into equilibrium with CO$_2$ by stirring and circulating through the rheometer measurement geometry under the pressure and temperature required. Measurements were made for three different fluids saturated with CO$_2$: a light crude oil from the Gulf of Mexico (GoM), Zuata heavy crude oil, and an emulsion of Zuata crude oil with deionized water.

The rheological measurements for the GoM crude oil were performed at temperatures of 23 °C and 50 °C and pressures from ambient to 220 bar. The CO$_2$ addition did not change the Newtonian behaviour of the light crude oil, but reduced its viscosity until the phase equilibrium points of CO$_2$. Beyond the CO$_2$ phase equilibrium points, the CO$_2$ mixture viscosity increased with increasing CO$_2$ pressure, which was expected when the fluid density increased without change in composition.

The experiments using the Zuata heavy crude oil and its dilutions with toluene were done at temperatures from 23 °C to 50 °C and pressures from ambient to 220 bar. The Zuata crude oil was changed from a non-Newtonian fluid to Newtonian by CO$_2$ dissolution. All of its toluene dilutions behaved as a Newtonian fluid, as well as their CO$_2$ saturated mixtures, except for one sample. The exception was a diluted crude oil with 30 wt% toluene, which was found to be shear-thinning when CO$_2$ dissolved into it in a certain pressure range. It is believed that the non-Newtonian behaviour in this diluted crude oil was not caused by asphaltene precipitation but instead by the formation of asphaltene micelles or by the multiphase behaviour with liquid CO$_2$. The viscosity of the heavy crude oil and its dilutions was exponentially reduced by CO$_2$ addition until the CO$_2$ phase equilibrium points, above which the viscosity was increased with CO$_2$ pressure.

Furthermore, a view cell system was built to study the phase behaviour of the CO$_2$ saturated mixtures with the GoM crude oil, Zuata crude oil and the toluene dilutions of Zuata crude. When brought to equilibrium with CO$_2$, it was found that the CO$_2$ solubility and the oil rich phase volume were inversely correlated to the mixture viscosity.

The Zuata crude oil emulsion was prepared by mixing 50 wt% Zuata heavy crude oil and 50 wt% deionized water using a high-shear mixer. The rheology measurement of the emulsion saturated with...
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CO₂ was made at 50 °C and pressures up to 120 bar. The emulsion without dissolved CO₂ was found to be slightly shear thinning below a critical shear rate, above which the viscosity jumped to a much lower value. After the viscosity jump the shear thinning effect was still observed. The CO₂ dissolution not only reduced the emulsion viscosity at low shear while preserving the shear thinning behaviour, but also increased the critical shear rate at which the viscosity jump occurred. The dissolved CO₂ eliminated the shear thinning effect after the viscosity jump. The emulsion viscosity jumped to a lower level than that of the original continuous phase (oil), indicating that the viscosity jump occurred due to phase inversion. However, direct evidence of phase inversion was very difficult to provide.

In addition, a new correlation to evaluate Newtonian viscosity of hydrocarbons is proposed. In this correlation the hydrocarbon viscosity can be calculated based on its density. This correlation requires less experimental data to work out the parameters compared to the methods given in the literature. The proposed correlation was tested with pure alkanes, alkane mixtures and gas-saturated hydrocarbons, and the prediction gave a reasonable accuracy.
I would like to express my sincerest gratitude to my supervisors Dr. John Crawshaw, Professor Martin Trusler and Dr. Edo Boek for their invaluable support, guidance and contribution for my PhD. As a PhD student, I believe I have the best combination of the supervisors. John has thought me an extensive knowledge of experimental research and offered wide range of practical experience in operations. Without John’s support the experiments conducted in this work would hardly be possible. From Professor Martin Trusler I learned how to be rigorous in analysing measurement data and theoretical developments. During my PhD, Dr. Edo Boek gave me great freedom to explore the research topics I was interested in, and constantly encouraged me to do original research. The skills and spirit of research I learned from them are extremely beneficial in my lifetime.

It is enjoyable to work in the Complex Fluids Group. A special mention goes to my colleagues: Dr. Christine Seifried, Dr. Emily Chapman, Dr. Farrel Gray, Dr. Daniel Ross and Dr. Nathan Welch. It is a wonderful working experience with you in the laboratory, and your support and the tea break sessions definitely relieve the frustration caused in the experiment.

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CHAPTER 1  INTRODUCTION

1.1 Climate Change and Carbon Dioxide

Carbon dioxide (CO\textsubscript{2}) released by the massive consumption of fossil fuels makes a significant contribution to global warming and extreme weather. Its stability and considerable concentration in the Earth’s atmosphere makes CO\textsubscript{2} one of most important greenhouse gases. The surplus of CO\textsubscript{2} is caused by our extensive use of fossil fuels, which emits a huge amount of CO\textsubscript{2} into the atmosphere, and deforestation, which reduces the absorption of CO\textsubscript{2} during photosynthesis [1].

Like any other thermodynamic phenomena, the temperature on the Earth’s surface can be described by the first law of thermodynamics. When the energy from the sun, transferred in the form of visible light, is absorbed by Earth, the temperature rises. When energy is released back into space, the Earth’s temperature decreases. The amount of CO\textsubscript{2} in the atmosphere alters the Earth’s temperature through the greenhouse effect [1].

The earth’s surface can either absorb sunlight or reflect it back into space. When sunlight is absorbed, some of the energy is released back into the atmosphere in the form of infrared radiation. Greenhouse gases such as water vapour, methane and carbon dioxide absorb this infrared radiation, preventing or slowing down the energy transfer back to space. In other words, the greenhouse gases are like a jacket on Earth, making it warmer by blocking the energy release. This process is called the greenhouse effect [1, 2]. Since the Earth’s temperature is rising due to the greenhouse effect, extreme weather occurs more and more frequently. Immediate actions are required to control CO\textsubscript{2} emission, in order to prevent us from losing our security and prosperity by the extreme weather.

1.2 Carbon Capture, Utilisation and Storage

As the primary greenhouse gas, the global emission of CO\textsubscript{2} from fossil fuel shows a 2.7% annual increase over the past 10 years and is now 60% beyond the level in the 1990s when the Kyoto Protocol was adopted [3]. To reduce the CO\textsubscript{2} emission, a range of solutions based on different principles has been proposed, one of which is carbon capture and storage (CCS). CCS is a set of technologies and process operations that aim at capturing CO\textsubscript{2} from fuel combustion or industrial plants, transporting CO\textsubscript{2} through ships and pipelines, and storing CO\textsubscript{2} underground, such as in depleted oil fields [4]. However, CCS faces a number of technical and economic challenges that must be overcome before it can be applied on a large scale [5]. The biggest economic obstacle for CCS is the fact that it is a process which requires huge amount of capital investment but does not generate any profit [6]. The economic feasibility consideration leads to an alternative to CCS: carbon capture, utilisation and storage (CCUS).
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CCUS is a process that generates valuable chemical products and fuels through the consumption of waste CO$_2$, while at the same time contributing to climate change mitigation [5]. The obvious advantage of CCUS over CCS is that the utilisation of CO$_2$ is able to generate profit for the operator through the valuable products. One of the direct utilisations of CO$_2$ is enhanced oil recovery (EOR), where CO$_2$ is used to extract crude oil from an oil field. This method has been widely practiced for over 40 years in several oil producing countries, such as Norway, Canada and the USA [7].

1.3 Enhanced Oil Recovery

Enhanced oil recovery (EOR), also called tertiary production, is usually considered as the last phase of the oil production with economic feasibility. The first, or primary, phase of oil production begins with the production from an oilfield using the pressure difference between the oil reservoir and the surface, to push the oil to the production wells and subsequently to the surface. When this pressure difference is reduced and thus production declines, a secondary phase of production is implemented to increase the reservoir pressure by injecting water. When the water to oil produced ratio reaches the economic production limit, the profit of the production shrinks, since the cost of water treatment and injection progressively rises to the same level of the income from the produced oil. Then the tertiary period of EOR production begins. During this stage of production, chemicals and/or thermal energy are injected into the reservoir to enhance the oil production. Actually, EOR may be initiated at any time during the history of an oil reservoir when it becomes evident that chemical or thermal energy injection are required to stimulate the oil production [8].

The performance of an EOR process is determined by the overall displacement efficiency, $E$, which is defined by the following equation:

\[ E = E_D E_V \]  

(1.1)

where $E_D$ is the microscopic displacement efficiency and $E_V$ the macroscopic displacement efficiency. The microscopic displacement is the oil displacement or mobilization at the pore scale. Thus, $E_D$ represents the efficiency of the displacing fluid in mobilizing the oil inside the rock where the displacing fluid is contact with the oil. On the other hand, the macroscopic displacement efficiency is the effectiveness of the displacing fluids in contact with the oil in a volumetric sense [9]. In other words, $E_V$ is a measure of how effectively the displacing fluid sweeps out the volume of a reservoir in terms of area or depth, as well as how effectively the displacing fluid moves the oil toward production wells.

There are numbers of techniques applied in EOR processes. These techniques can be classified into three categories: chemical, miscible and thermal processes. In chemical processes, certain chemicals, such as surfactants or alkaline agents, are injected with displacing fluids altering phase behaviour and interfacial properties [8]. Some of these chemicals are able to generate foams with the displacing fluid
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in order to control its mobility. In miscible processes, the fluids injected are directly miscible with the oil or generate miscibility in the reservoir through the changes in composition. Phase behaviour is a major factor in the application of such processes. Finally, thermal processes are designed to inject thermal energy (such as steam) or generate heat in the oil reservoir (combustion with air or oxygen) to improve oil recovery [10].

1.4 CO₂ Flooding

Among all the EOR processes, CO₂ flooding is attracting the most market interest and has been piloted and demonstrated by many industrial players. Since 1950, systematic research has been conducted by the oil industry into the use of CO₂ to increase oil recovery. Recently, because of the growing awareness and concern regarding the ecological and economic threats posed by global warming, an increasing interest has been demonstrated by governments and industries in the sequestration of CO₂ into depleted oil reservoir to produce oil at the same time.

The CO₂ injected into oil reservoirs could improve oil displacement by a number of mechanisms. Although not usually miscible with crude oil on initial contact, the miscibility of CO₂ with crude oil is progressively increased by means of the extraction of light fractions in oil (C₅ to C₃₀) into the CO₂ phase. Consequentially CO₂ may create a miscible front where CO₂ and crude oil mix in a single phase. Furthermore, in CO₂ flooding a number of other fluids would be injected with CO₂, either sequentially or in an alternating matter. Generally, in reservoirs where the displacement is horizontal, the CO₂ flooding process would involve alternating injection of CO₂ and water to attempt to control the mobility of the fluids, as illustrated in Figure 1-1, whereas in vertical floods the various fluids would be in injected sequentially [11].
Regardless of how CO₂ is injected into the oil field, the following factors may contribute to increase the oil recovery by CO₂ injection [12]:

- **Significant reduction in crude oil viscosity.** As CO₂ is dissolved in crude oil, a large reduction in the viscosity of that oil occurs. This dissolution, which has a similar effect as temperature on crude oil viscosity, can reduce the oil viscosity to one-tenth or one one-hundredth of the original value.

- **Swelling of crude oil.** The swelling effect has two contributions in improving the oil recovery. First, the amount of oil that is left in the reservoir after flooding is inversely proportional to the swelling factor. That is, the higher the swelling factor, the less oil abandoned in the reservoir. Second, swollen oil droplets will force water out of pore spaces, creating a drainage rather than imbibition process for water-wet reservoirs. The relative permeability for drainage is higher than for imbibition, generating a more favourable oil flow environment. CO₂ is highly soluble in hydrocarbon oils, and the dissolved CO₂ could yield a significant increase in the mixture volume, compared with the oils without CO₂ saturation.

- **Solution gas driving.** CO₂ needs to be injected into the reservoir at a pressure higher than reservoir pressure. Thus, some of the CO₂ is dissolved in the oil at a higher pressure during the injection. After the injection, when the reservoir pressure returns to its original level, the additional CO₂ dissolved at higher pressure will come out from the oil and continue to drive it into the wellbore. This
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mechanism of blowdown recovery is similar to solution gas drive during normal production depletion of an oil field.

1.5 Phase Behaviour of Crude Oil Mixtures

1.5.1 Classification of Phase Behaviour for Binary Mixtures
The phase behaviour of a binary mixture can be classified into six types according to the theoretical study by Van Konynenburg and Scott [13], in which the van der Waals equation of state and quadratic mixing rule were used to determine the phase diagram. With significant improvement in computational power and better understanding of molecular interactions, the limitations inherent in the van der Waals equation of state and quadratic mixing rule have been overcome by newly developed phase behaviour models based on statistical thermodynamics [14]. These six types of phase behaviour provide a very useful framework to classify the phase diagrams obtained from different binary mixtures. A brief description of each type of phase behaviour is provided here.

1.5.1.1 Type I Phase Behaviour
For a Type I mixture, as shown in Figure 1-2, the pressure-temperature ($P$-$T$) phase diagram is constructed by the vapour-liquid saturation curve of pure component 1 (line 1) and that of pure component 2 (line 2), as well as the critical locus (dashed line) which connects the critical point of pure component 1 ($C_1$) and that of pure component 2 ($C_2$). Each point in the critical locus represents the critical point of the mixture at a given composition. Also, line 1 represents the more volatile component in the mixture while line 2 is for the less volatile one. Liquid-liquid immiscibility is not observed in Type I mixture. A typical example of a Type I mixture is CO$_2$/n-butane, as shown in [15].

![Figure 1-2](image_url)

*Figure 1-2. A sketch of the $P$-$T$ phase diagram for a Type I binary mixture. C = critical point.*
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1.5.1.2 Type II Phase Behaviour
The difference between a Type I and Type II mixture is that, in a Type II mixture, component 1 is immiscible with component 2 in the liquid state at low temperature. Therefore, as shown in Figure 1-3, there is an additional saturation curve in the $P$-$T$ phase diagram, representing the boundary of the two immiscible liquids coexisting. For most non-fluorinated hydrocarbons, this curve is located below the vapour-liquid saturation curve of component 1 [14], and the mixture under the conditions within these two curves shows a liquid-liquid-vapour equilibrium. Thus, this curve is usually called the liquid-liquid-vapour (LLV) saturation curve. Above the LLV curve the mixture shows two separated liquid phases, whereas below it the two liquid phases merge into a single liquid phase. The LLV line is terminated at the upper critical end point (UCEP), at which the two liquids become miscible regardless of pressure and temperature. The UCEP is a function of temperature, and the dashed line in Figure 1-3 extending from the UCEP illustrates the locus of UCEP at different temperature. Note that the slope of this dashed line can be negative or positive, depending on the nature of the molecular interactions between the mixture components. A typical example of Type II mixture is CO$_2$/n-octane, as shown in [16].

![Figure 1-3. A sketch of the P-T phase diagram for a Type II binary mixture. C = critical point; UCEP= upper critical end point; LLV = liquid-liquid-vapour saturation curve.](image)

1.5.1.3 Type III Phase Behaviour
In a Type III mixture, the immiscibility of the two liquid components is so large that the LLV curve extends to higher temperature, and disrupts the vapour-liquid critical locus. It results in the fact that the vapour-liquid critical locus is broken down into two branches, as shown in Figure 1-4. One connects the critical point of the more volatile component to the UCEP, while the other one extends from the critical point of less volatile component to higher pressure. If a mixture is at the UCEP, then one of its liquid phases will merge with the vapour phase to generate a larger vapour phase, which is at equilibrium with the remaining liquid phase. A typical example of Type III mixture is water/propane, as shown in [17].
1.5.1.4 Type IV Phase Behaviour

In a Type IV mixture, the LLV curve has two parts, as shown in Figure 1-5. The first part is in the low temperature region, and terminated at an UCEP from which a critical locus extends to higher pressure. The second part is from the lower critical end point (LCEP) to another UCEP which is at higher temperature. Between the two parts of the LLV curve, there is a temperature-pressure range in which the two liquids are miscible with each other. The vapour-liquid critical locus is separated into two branches. One is connecting the critical point of the more volatile component to the UCEP at higher temperature, while the other one is connecting the critical point of the less volatile component to the LCEP. A typical example of Type IV mixture is CO₂/nitrobenzene, as shown in [18].

Figure 1-5. A sketch of the P-T phase diagram for a Type IV binary mixture. C = critical point; UCEP= upper critical end point; LCEP = lower critical end point; LLV = liquid-liquid-vapour saturation curve.
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1.5.1.5 Type V Phase Behaviour

The difference between Type IV and Type V is that the part of the LLV curve found at lower temperature in Type IV disappears in Type V, as shown in Figure 1-6. It means that the two liquids become completely miscible below the LCEP. Furthermore, one branch of the vapour-liquid curve is connecting the critical point of the less volatile component to the LCEP. Type V phase behaviour can be found in n-alkane mixtures with large molecular size difference [14]. An example of these mixtures is methane/n-hexane, as shown in [19].

Figure 1-6. A sketch of the P-T phase diagram for a Type V binary mixture. C = critical point; UCEP= upper critical end point; LCEP = lower critical end point; LLV = liquid-liquid-vapour saturation curve.

1.5.1.6 Type VI Phase Behaviour

As shown in Figure 1-7, Type VI mixture is similar to Type II, given that a LLV curve can be observed in the phase diagram and the vapour critical locus is connecting the two critical points of pure component. However, in a Type VI mixture, the LLV curve is terminated at the LCEP, below which the two liquids are miscible with each other. Furthermore, there is a critical locus connecting the UCEP and LCEP, leading to a closed dome of immiscibility [14]. Hydrogen bonds usually occur in one or both components that comprise the mixture showing Type VI phase behaviour. An example of such a mixture is water/2-butanol, as shown in [20].
1.5.2 Multiphase Behaviour in Crude Oil

Given its complex nature, crude oil presents significant challenges in understanding its phase behaviour from both experimental and modelling points of view. Crude oil can be considered as a mixture that contains innumerable hydrocarbon components and shows a wide range of physical and chemical characteristics. However, unlike simple hydrocarbon mixtures, in which a single homogeneous phase can be observed, crude oil usually exhibits multiphase behaviour in itself or when contacted with other fluids [21]. For example, as demonstrated by Shelton et al. [22], at 41 °C, when a recombined crude oil with API of 27.3 was mixed with a driving gas comprising mostly light alkanes and a small amount of nitrogen and CO$_2$, the resulting mixture showed four phases at a specific pressure: a vapour phase, a driving gas rich liquid phase, an oil rich phase, and an asphaltene precipitate phase. For a constant driving gas composition around 80%, only a narrow pressure range resulted in the four-phase equilibrium. At pressures lower than this range one of the liquid phase disappeared, whereas at higher pressure the vapour phase was not observed. This multiphase phase behaviour can be also found in the study by Robinson [23] and Turek et al. [24].

1.5.3 CO$_2$ and Crude oil Mixtures

Numerous papers report the phase behaviour of CO$_2$ and crude oil mixtures. Similar to the mixture of CO$_2$ with alkanes, CO$_2$ and crude oil mixtures show liquid-liquid or liquid-liquid-vapour equilibria at temperatures and pressures lower than the CO$_2$-crude oil minimum miscibility point. The upper limit of this low temperature is determined by the crude oil composition, since CO$_2$ extracts the light and intermediate components in the crude oil to generate a CO$_2$-rich liquid phase [25]. If the temperature is high enough, the CO$_2$ can be either in supercritical or vapour phase according to the pressure and temperature [26].
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As reported by many papers, CO\textsubscript{2} solubility in crude oil normally increases with increasing pressure but decreases with increasing temperature \[27-31\]. The pressure sensitivity of the CO\textsubscript{2} solubility at high pressures depends on the phase of CO\textsubscript{2}: when CO\textsubscript{2} is in the liquid phase, the solubility is least sensitive to pressure \[28, 32\]. On the other hand, there are two determining factors on crude oil density: the compression effect by pressure and the swelling effect by dissolved CO\textsubscript{2} \[27-29, 32\]. Therefore, how the crude oil density changes with CO\textsubscript{2} pressure depends on the nature of the crude oil and the operational conditions.

1.6 Crude Oil Emulsions

Crude oil is often not produced alone. In the later stages of production it is normally mixed with water from the formation, which occurs either as free water that separates quickly from the oil, or in the form of an emulsion stabilised by the surface-active agents occurring naturally in the crude oil \[33\]. The determining factors in the stability of a water/oil emulsion are the presence of surface-active agents and the extent of mixing. In oil production, especially of heavy crude oil, both factors can be in place, making water/oil emulsions a problem in subsequent processing. The surface-active agents can be waxy components, asphaltenes, or clay particles in crude oil. On the other hand, the constrictions in the production tubing provide the required mixing to form an emulsion. When water and crude oil are squeezed through the constrictions together, the water or oil can be broken up into droplets and stabilised by the surface-active agents, which gives rise to the formation of emulsions.

Water/crude oil emulsions can cause several operational challenges. Usually, the water is separated from the oil for disposal before the oil is transported for processing. However, the formation of a persistent emulsion prevents easy separation and increases the cost of the surface facilities. On the other hand, emulsion formation may be beneficial in the transport of very viscous heavy-crude oils. The pressure drop in the oil pipeline can be lower for an oil-in-water emulsion than that of the heavy crude oil alone, or that of a water-in-oil emulsion \[34\]. Another challenge worth mentioning is that water/crude oil emulsions may damage catalysts used in downstream processes. The water content can corrode the transition metals in a solid catalyst, which reduces the effective surface area in the catalyst and eventually completely deactivates it \[33\]. Therefore, dewatering is usually a necessary operation for the upstream oil producers.

1.7 Project Motivation and Objectives

Physical properties such as viscosity, density, swelling factor and CO\textsubscript{2} solubility, of crude oil and CO\textsubscript{2} mixtures are required to design and simulate the CO\textsubscript{2} flooding process. The effects of CO\textsubscript{2} on the physical properties of crude oils must be determined to design an effective oil displacement process. Based on the experimental data, a predictive model for the properties of crude oil and CO\textsubscript{2} mixtures
Introduction

will be established, and the model will be useful in process design and screening. This research project focuses on measuring and understanding the viscosity of crude oil and its CO₂ mixtures.

The traditional approach to study the viscosity of a crude oil and CO₂ mixture is to measure the effect of temperature, pressure and composition. In this project the viscosity of a crude oil and CO₂ mixture is revisited from a rheology point of view, considering shear rate as another variable in the equation. By doing so, the relationship between viscosity and shear rate can be revealed, answering the question whether the crude oil and CO₂ mixture behaves as a Newtonian fluid or non-Newtonian fluid. Also the system built for the rheological measurement allows high pressure rheology study of gas and liquid mixtures, which has useful applications in many other fields.

Phase behaviour measurements are also needed to interpret viscosity measurements. Apart from showing phase behaviour changes under different conditions, phase behaviour measurements could shed some light on the cause of any viscosity changes.

1.8 Thesis Outline

Chapter 2 introduces basic rheology principles focusing on a non-Newtonian fluid. It illustrates the physical properties used to describe non-Newtonian fluids, and the possible causes of non-Newtonian behaviour.

Chapter 3 reviews the viscosity models for crude oil in the literature. The reviewed viscosity models were classified into two groups: one describing a Newtonian fluid, and the others non-Newtonian fluids. The models within each group were further classified according to the theory underneath.

Chapter 4 describes a new model developed in this work, which calculates the hydrocarbon viscosity based on its density. The model links the hydrocarbon density and viscosity in an effective way, such that few parameters are required for fitting. The model was tested with literature data of alkanes and hydrocarbons.

Chapter 5 describes in detail the rheology and phase behaviour measurement systems built in this work, as well as the experimental procedures. It also provides test results to show the measurement accuracy.

Chapter 6, Chapter 7, and Chapter 8 present, respectively, the rheology and phase behaviour measurement results of the CO₂ saturated mixtures of Zuata crude oil and its dilutions, of a light crude oil from the Gulf of Mexico, and that of Zuata crude oil/water emulsions.

Chapter 9 presents the conclusions drawn from this work and discusses potential future work.
2.1 The Definition of Viscosity

The deformation produced by a force acting on a body depends on the magnitude of the force per unit area, rather than the magnitude of the force itself. The force acting on a continuous volume of a solid or liquid can be classified into two categories: surface forces, which are acting on the surface of the material, or body forces, such as gravity, which act throughout the material. Surface forces could be divided into a component normal to the surface and one parallel to it. The normal component per unit area is called the normal stress, while the parallel component is called the shear stress, \( \sigma \) [35].

![Figure 2-1. Deformation of a rectangular element by shear stress at the top plate](image)

The shear stress applied to a material causes deformation. The relationship between the shear stress and deformation can be derived as follows. Suppose a shear stress is acting on the top surface of a rectangular element of material with height \( l \), as shown in Figure 2-1. The shear stress causes the successive layers of material to move, in their own planes, relative to the bottom layer in such a way that the displacement \( \delta l \) of a layer is proportional to their distances from the bottom. The relative displacement of two layers divided by their separation, \( \delta l/l \), is called the shear strain. Lines originally perpendicular to the bottom layer rotate through an angle \( \theta \). Therefore for small \( \theta \), \( \theta \) equals the shear strain since [35]:

\[
\tan(\theta) = \frac{\delta l}{l} \approx \theta
\] (2.1)

The instantaneous rate of strain, or shear rate, \( \gamma \), is defined by

\[
\gamma = \frac{d\theta}{dt}
\] (2.2)

Then the viscosity, \( \eta \), is defined by the equation
Principles of non-Newtonian Rheology

\[ \eta = \frac{\sigma}{\gamma} \]  

(2.3)

In industry the kinematic viscosity \( \nu \) of a fluid is also used:

\[ \nu = \frac{\eta}{\rho} \]  

(2.4)

where \( \rho \) is the density of the fluid.

2.2 Non-Newtonian Fluids

Fluids can be classified as Newtonian or non-Newtonian, according to how their shear stress responds to shear rate. Most fluids with low molecular mass, such as water, organic solution or gas, exhibit the characteristic that the shear stress is directly proportional to the shear rate at given temperature and pressure, leading to a constant viscosity in Equation (2.3). As an example, Figure 2-2 shows the typical flow curve (\( \sigma \) versus \( \gamma \)) for a hydrocarbon fluid, which is linear and passes through the origin. It also illustrates that the viscosity is independent to the shear rate. Such fluids are classified as Newtonian, named after Isaac Newton who first derived the relation between shear stress and shear rate [36]. The viscosity of most liquids decreases with temperature and increases with pressure, while the viscosity of gases increases both with temperature and pressure.

![Figure 2-2. Typical flow curve for a Newtonian fluid. The sample used here is a viscosity standard oil N35 from Paragon Scientific Ltd.](image)

\( \sigma \), shear stress at 25 °C; \( \gamma \), viscosity at 25 °C; \( \sigma \), shear stress at 40 °C; \( \gamma \), viscosity at 40 °C;

The most obvious deviation from the Newtonian fluid behaviour is that the flow curve does not pass through the origin and/or is no longer linear. Therefore, for non-Newtonian fluids, the viscosity, the slope of the flow curve, is not constant but a function of shear rate or shear stress. Studies have also shown that the viscosity of a non-Newtonian fluid can depend on the kinematic history of the fluid [37].
**Principles of non-Newtonian Rheology**

Such fluids are conveniently grouped into three general classes. The first one includes the fluids whose shear rate, at any position of the fluid, is related only to the value of the shear stress at that position at any given time. These fluids are usually called “time-independent” fluid. The second class is for those more complex fluids for which the relationship between shear stress and shear rate is also a function of time. They are called “time-dependent” fluids. Finally, the third class is for those fluids that behave as a fluid under shear but as an elastic solid at rest (viscosity is infinite). They are categorised as “visco-plastic” fluids. Most real materials illustrate a combination of these features under certain conditions.

### 2.2.1 Time Independent Fluid

Since time-independent fluids are the most common non-Newtonian fluids, a more detailed description of their characteristics is provided here. As described above, the shear stress of a time-independent fluid is related only to the instantaneous value of the shear rate:

\[ \sigma = f(\gamma) \]  

(2.5)

Given the definition of viscosity in Equation (2.3) we have

\[ \eta = g(\gamma) \]  

(2.6)

A comparison of the three main classes of time-independent fluids is shown in Figure 2-3, where the upper part of the figure shows the shear stress and shear rate relationships for different fluids while the lower part shows the viscosity and shear rate relationships. The Bingham plastic material is a solid in that it behaves as an elastic solid for stresses less than a critical value called the yield stress \( \sigma_Y \) and, for greater stress it flows as a fluid. Unlike Bingham plastics, the pseudoplastic fluid does not have a yield stress, but its viscosity decreases with increasing shear rate, also known as shear-thinning. If the fluid viscosity increases with increase of shear rate then it is called a dilatant or shear-thickening fluid.
Shear thinning is perhaps the most frequently observed non-Newtonian behaviour in engineering applications, especially in polymers. The viscosity of a shear thinning fluid is inversely proportional to the shear rate:

$$\eta = f\left(\frac{1}{\gamma}\right)$$ \hspace{1cm} (2.7)

The viscosity might approach a Newtonian plateau at low or high shear rates,

$$\eta_0 = \lim_{\gamma \to 0} \sigma = C_1$$ \hspace{1cm} (2.8)

$$\eta_\infty = \lim_{\gamma \to \infty} \sigma = C_2$$ \hspace{1cm} (2.9)

where \(C_1\) and \(C_2\) are constant. With increasing shear rate, the fluid viscosity decreases from the zero shear viscosity, \(\eta_0\), to the infinite shear viscosity, \(\eta_\infty\) [37]. In polymer solutions the value of infinite shear viscosity \(\eta_\infty\) can be approximated by the solvent viscosity with acceptable error. However, this infinite shear viscosity is not observed in the flow curve of polymer melts and blends, or foams, emulsions or suspensions. The values of shear rates at which the viscosity is approaching to \(\eta_0\) or \(\eta_\infty\) are determined by polymer properties, such as the polymer concentration, the molar mass distribution and the nature of solvent. It is difficult to propose a generalised equation for the onset shear rate for each \(\eta_0\).
or $\eta_\infty$, but many materials exhibit their limiting viscosities at shear rates below $10^{-3} \text{ s}^{-1}$ and above $10^5 \text{ s}^{-1}$, respectively [37].

2.2.2 Mathematical Models for shear thinning fluid behaviour

Many mathematical expressions have been proposed in the literature to model how viscosity responds to the shear rate for a shear thinning fluid. Some of them are straightforward curve fitting, giving empirical expressions for viscosity-shear rate curves, while others have some theoretical basis in statistical mechanics, extending the application of kinetic theory to non-Newtonian liquid or the theory of molecular dynamics.

These equations need at least four parameters to describe the viscosity as a function of shear rate in the complete spectrum of shear thinning behaviour. One of those equations is the Cross equation [35]:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (K\gamma)^m}$$

(2.10)

or

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = (K\gamma)^m$$

(2.11)

If $\eta >> \eta_\infty$ and $\eta_0 >> \eta_\infty$, the Cross equation reduces to

$$\eta = \frac{\eta_0}{(K\gamma)^m}$$

(2.12)

which, with a simple redefinition of parameters can be written

$$\eta = K_2\gamma^{n-1}$$

(2.13)

This is the well-known power-law model and $n$ is called the power-law index. $K_2$ is called the “consistency”. For $n < 1$, the fluid exhibits shear thinning behaviour; for $n = 1$, the fluid is Newtonian, while for $n < 1$, the fluid is shear-thickening.

Sisko developed the following equation for viscoplastic behaviour [35]:

$$\eta = a + b\gamma^{c-1}$$

(2.14)

where $a$, $b$, and $c$ are parameters for curve fitting.

Saeed [39] developed a generalised rheological model for shear thinning fluids with or without yield stress, deriving and expanding from the coordination equation of ellipse:
Principles of non-Newtonian Rheology

\[
\left( \frac{\gamma + \delta A}{A} \right)^n - \delta \left( \frac{\tau}{B} \right)^n = 1
\]  

(2.15)

where \(A, B,\) and \(n\) are constants, and \(\delta\) is either +1 or -1.

2.2.3 The Causes of non-Newtonian Behaviour

Non-Newtonian behaviour is mostly observed in a structured fluid, a material which contains a continuous phase and a dispersed phase [40]. By contrast, when a material has one homogenous phase, such as a solution or pure substance is referred to as a simple fluid. Another important difference between structured fluids and simple fluids is in their response to shear stress (or shear rate). Most structured fluid systems contain the so-called flow units, which are normally formed by the dispersed phase in the fluid. Examples of flow units include drops in emulsions, long entangled molecules surrounded by solvent, or particle clusters loosely formed in suspensions. The associating network in a structured fluid, generated by the attraction forces between the flow units, can easily be perturbed by applying relatively low stress. For example, while the molecular network of an alkane remains unperturbed by stress up to \(1 \times 10^6\) Pa, a network of macromolecules in a polymer solution would be perturbed under stress of 100 Pa. It is this degree of ease with which the structure can be perturbed that gives rise to non-Newtonian flow behaviour in a system [37, 41].

Figure 2–4 shows schematically four types of fluid structure perturbation under shear in non-Newtonian fluids. At rest, the micro-structured flow units rearrange to reach the minimum chemical potential. When the stress is low, the interaction between the fluid units is strong enough to resist any deformation by shear, leading to a high viscosity or a yield stress. As the value of the stress is progressively increased, the flow units respond by

a) Aligning themselves with the flow direction (Figure 2-4.a),
b) Straighten out along the flow direction (Figure 2-4.b),
c) Deforming to obey the flow (Figure 2-4.c), or
d) Breaking down into smaller flow units by stress (Figure 2-4.d).

All these changes in micro-structures reduce the resistance to flow, resulting in a lower viscosity under shear, which is the shear thinning effect [41, 42].
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![Figure 2-4. Schematics of structures in non-Newtonian fluid at rest and under shear](image)

The response of the fluid structure to external stress determines the type of non-Newtonian behaviour exhibited by the fluid. Before the fluid is subjected to flow, the fluid structure can be altered by system parameters such as temperature, pressure or concentration. These parameters determine the interaction within the flow units, and provide a methodology to engineer the non-Newtonian response. For example, given a tubular particle geometry, a kaolin suspension with 45% solid content behaves as a Newtonian fluid, but for solid content > 60%, the suspension becomes pseudoplastic [43]. Therefore, by adjusting the solid content, one can control the appearance of the non-Newtonian behaviour. More detailed discussions about the relationship between the fluid physical properties and its non-Newtonian behaviour can be found in literature [44-47].

### 2.3 The Effect of Asphaltene on Heavy Crude Oil Rheology

Asphaltene is the heaviest component in crude oils. Because of its complex chemical structure, the definition of asphaltene is still based on its solubility: the portion of a crude oil that precipitates out in n-alkanes and is soluble in an aromatic solvent [48]. Asphaltene is considered as one of the key components leading to the high viscosity in a heavy crude oil. Argillier *et al.* [49, 50] showed that the viscosity of a Venezuelan heavy crude oil was increased with increasing asphaltene weight fraction. Their measurements showed that the crude oil viscosity was first increased linearly with asphaltene concentration, then above a critical concentration the viscosity was increased with a steep gradient.
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Using Small Angle X-ray Scattering measurement, it was revealed that at low concentration the asphaltene particles were independent from each other, but at high concentration the particles overlapped with each other and gave rise to a nonlinear increase in the crude oil viscosity. It should be pointed out that the rheology measurements by Argillier et al. were performed at shear rate up to 30 s⁻¹ and no shear thinning effect was observed in this shear rate range. In addition, Lilian et al. [51] measured the viscosity and microstructure of five Brazilian heavy crude oils, and confirmed the asphaltene aggregates as the cause of the high viscosity of heavy crude oil.

Asphaltene also plays a role in determining the yield stress of heavy crude oil. The definition of yield stress can be found in Section 2.2.1. Evdokimov et al. [52] showed that the yield stress of a synthetic oil, containing toluene and vacuum residue from a heavy crude oil, was increased exponentially with increasing asphaltene concentration. Their measurements demonstrate that at low asphaltene concentration the yield stress is negligible and the oil can be considered a Newtonian fluid. However, at high asphaltene concentration, the yield stress is significant and the oil can be described as a Bingham plastic (see Section 2.2.1 for details), one type of non-Newtonian fluid. In other words, increasing the asphaltene concentration in the oil causes the transition from Newtonian to non-Newtonian behaviour.

2.4 Phase Inversion in Water/Oil Emulsion

An emulsion consists of multiple immiscible liquids. In its simplest form, a two-phase emulsion usually contains an aqueous phase (water) and an organic phase (oil). Both water and oil phases can be the continuous phase. If it is a water-in-oil emulsion, the continuous phase is oil and the dispersed phase is water. If it is an oil-in-water emulsion then oil forms the dispersed phase in a water continuous phase.

Phase inversion is the phenomenon whereby a phase interchange occurs in a liquid-liquid emulsion: the dispersed phase inverts to become the continuous phase and the continuous phase to become the dispersed phase under operational conditions [53]. Phase inversion can be achieved by a change in the various operational parameters and emulsion physical properties, such as temperature, liquid volume fraction, shear strain and type of oil. Yeo et al. provided a good review of the effect of the various parameters on the phase inversion behaviour [53]. The phase inversion achieved by changing the water/oil ratio is normally referred to as a catastrophic inversion, and the water/oil ratio corresponding to the inversion is called phase inversion composition. The term “catastrophic” came from the idea that the catastrophe theory might be useful to describe the dynamics of the phenomenon. However, catastrophe theory still requires further development to provide a predictive model for phase inversion [54, 55]. In addition, phase inversion caused by altering the properties of the interface agent at a constant water/oil ratio is called the transitional phase inversion. Examples of the properties related to the interface agent include the composition of the hydrophilic head in a surfactant molecule [56], and the wettability of the particle surface for particle stabilised emulsions [55].
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Anisa et al. [57] examined the transitional and catastrophic phase inversion of water-in-oil emulsions with different types of crude oil. Among the three crude oils they studied, transitional phase inversion was observed only in the emulsion with the thinnest crude oil with temperature increasing. On the other hand, although catastrophic phase inversion was obtained in all emulsions, the critical volume fraction of phase inversion is proportional to the crude oil viscosity.

Phase inversion is an important phenomenon in chemical process operations. It can result in a more effective technology in liquid-liquid separation, but can also be undesirable, for example, in mixer-settlers. In spite of the widespread application and the extensive literature study on phase inversion, its governing mechanisms are still a matter for debate. Although recently flow visualisation technologies have been applied to facilitate the study of phase inversion, no theoretical model is available to satisfactorily predict phase inversion [58].
CHAPTER 3 REVIEW OF VISCOSITY MODELS FOR CRUDE OIL

The methods for viscosity estimation can be categorized as theoretical, semi-theoretical or empirical, and further distinguished as predictive or correlative [59]. The theoretical description of liquids is difficult due to the complex intermolecular forces network, which consists of short-range forces such as repulsion and hydrogen bonding, long-range electrostatic forces, and long-range attraction forces [60]. There is no widely-accepted simple theoretical model for liquid viscosity. Therefore, most of the viscosity models applied in engineering are semi-theoretical or empirical.

The models for estimating the viscosities of crude oils and their mixtures with different solvents or gases are more complicated than those models designed for pure components or well-defined mixtures, because of the complex nature of crude oils and their mixtures. The inherent uncertainty in the makeup of the oil for carbon numbers greater that seven sets a limit to the generality of any proposed viscosity calculation procedure for crude oils and their mixtures [59]. Unless a universal characterization scheme is found, a given crude oil viscosity model will be dependent on its own calculation procedure to determine the empirical fitting parameters. Furthermore, since most of the viscosity models were originally based on the understanding of pure substances, mixing rules need to be introduced in the model to allow viscosity estimation for a mixture. Parameters are also introduced to link the results of well-understood substances/mixtures to the experimental measurements of investigated crude oils and mixtures.

3.1 Viscosity Models for Crude Oil as a Single Phase Fluid

3.1.1 Semi-theoretical Methods
Semi-theoretical models are based on the principle of corresponding states or kinetic theory. These methods give viscosity as a function of temperature and density, which necessitates the coupling of a density prediction method with the viscosity model.

3.1.1.1 Corresponding States
According to the principle of corresponding states, a dimensionless property of one substance is equal to that of another substance when both are evaluated at the same reduced conditions [61]. The reduced temperature $T^*$, pressure $P^*$, and molar volume $V_m^*$ are defined as
Review of Viscosity Models for Crude Oil

\[ T^* = \frac{T}{T^c} \]
\[ P^* = \frac{P}{P^c} \]
\[ V_m^* = \frac{V}{V_m^c} \]  

(3.1)

where \( T, P, V \) are temperature, pressure, and volume respectively, and \( T^c, P^c, V_m^c \) are critical temperature, pressure and molar volume respectively.

Ely and Hanley [62] developed a procedure based on corresponding states and conformal solution theories to predict the transport properties of hydrocarbons and their mixtures. The only input data required are the critical parameters, molar mass, and Pitzer’s acentric factor. Baltatu [63] applied Ely and Hanley’s method to estimate the viscosity of crude oil fractions by considering petroleum fraction as a hypothetical pure substance, with estimation of the required input parameters from specific gravity and average boiling point of the crude oil fractions. It should be pointed out that Baltatu’s work did not provide an estimation of the overall crude oil viscosity or that of the crude oil/CO\(_2\) mixture, but only that of the petroleum fractions.

In Baltatu’s work, the viscosity \( \eta \) of the fraction at density \( \rho \) and temperature \( T \) is given in terms of the viscosity of a reference fluid evaluated at the corresponding density and temperature. The equation is given by [62]

\[ \eta_x = \eta_0 F_\eta \]  

(3.2)

where the subscripts \( x \) and \( 0 \) designate the fraction and the reference fluid respectively, and \( F_\eta \) is given by

\[ F_\eta = \left( \frac{M_x}{M_0} \right)^\frac{1}{2} f_{x,0}^{\frac{1}{2}} h_{x,0}^{\frac{3}{2}} \]  

(3.3)

where \( M \) the molar mass. The scaling ratios \( f \) and \( h \) in Equation (3.3) are defined as

\[ f_{x,0} = \left( \frac{T_x^c}{T_0^c} \right) \theta_{x,0} \left( T^*_x, V^*_x, \omega_x \right) \]  

(3.4)

\[ h_{x,0} = \left( \frac{V_x^c}{V_0^c} \right) \phi_{x,0} \left( T^*_x, V^*_x, \omega_x \right) \]  

(3.5)

where the superscripts \( c \) and \( * \) denote the critical value and reduction of the variable by the critical value respectively; \( V \) is the specific volume (=1/\( \rho \)). The functions \( \theta \) and \( \phi \) are the shape factors expressed in terms of the Pitzer acentric factor, \( \omega \), as follows [64]
Review of Viscosity Models for Crude Oil

\[ \theta_{s,0}(T^*_s, V^*_s, \omega_s) = 1 + (\omega_s - \omega_0) \left[ \frac{0.0892 - 0.0493\ln T^*_s + \left(0.3063 - \frac{0.4506}{T^*_s}\right)(V^*_s - 0.5)}{0.8493 - 0.5} \right] \]  

(3.6)

\[ \phi_{s,0}(T^*_s, V^*_s, \omega_s) = 1 + (\omega_s - \omega_0) \left[ 0.3903 \left(V^*_s - 1.0177\right) - 0.9462 \left(V^*_s - 0.7663\right) \ln T^*_s \right] \]  

(3.7)

Baltatu introduced from literature the equation of state, \( P_c = P(\rho_0, T_0) \), and the viscosity, \( \eta_0 = \eta(\rho_0, T_0) \), of the selected reference fluid to incorporate with Ely and Hanley’s procedure. The critical properties and molar mass of the crude oil fraction is estimated through the method proposed by Riazi and Daubert [65]. The results showed an overall average absolute deviation (AAD) of 6.14% for all different boiling point fractions studied.

With the viscosity of the corresponding fractions, it would be possible to work out the whole crude oil viscosity via mixing rules proposed by Mehrotra [66, 67]. Mehrotra also showed that the mixing rules can be applied in crude oil/CO\(_2\) or crude oil fraction/CO\(_2\) mixtures [68]. Given that the fraction cut \( i \) (or CO\(_2\)) with mole fraction, \( x_i \), and mass fraction, \( w_i \), in the whole crude oil mixture has viscosity \( \eta_i \), the whole crude oil mixture viscosity \( \eta_{\text{whole}} \), is given by

\[ \log \left( \frac{\eta_{\text{whole}}}{\eta_{\text{ref}}} + 0.8 \right) = \sum_i v_i \log \left( \frac{\eta_i}{\eta_{\text{ref}}} + 0.8 \right) \]  

(3.8)

where \( \eta_{\text{ref}} = 1 \) mPa\( \cdot \)s and \( v_i = \sqrt{x_i w_i} \). Another mixing rule is given by

\[ \log \left( \frac{\eta_{\text{whole}}}{\eta_{\text{ref}}} + 0.8 \right) = \sum_i v_i \log \left( \frac{\eta_i}{\eta_{\text{ref}}} + 0.8 \right) + \sum_{ij} v_i v_j B_{ij} \]  

(3.9)

where \( B_{ij} \) (with \( B_{ii}=B_{jj}=0 \) and \( B_{ij}=B_{ji} \)) is a viscous interaction term that is determined empirically from binary mixture viscosity data.

### 3.1.1.2 Modified Chapman-Enskog Method

Chung and co-workers [69] extended their earlier viscosity model based on the Chapman-Enskog theory for dilute gases to dense fluids and mixtures by introducing empirical correlation as a function of density and temperature into the Enskog sphere theory. In this model, the viscosity of a dense fluid is computed as

\[ \eta = \eta_k + \eta_p \]  

(3.10)

where \( \eta \) is in Pa\( \cdot \)s. \( \eta_k \) and \( \eta_p \) are defined as
Review of Viscosity Models for Crude Oil

\[ \eta_c = \eta_0 \left( \frac{1}{G_2} + A_5 Y \right) \]  \hspace{1cm} (3.11)

\[ \eta_p = \left[ 36.344 \times 10^{-6} \times \left( \frac{MT}{V^2} \right)^{1/2} \right] \cdot A_4 Y^2 G_2 \exp \left( \frac{A_8}{T^*} + \frac{A_{10}}{T^{*2}} \right) \]  \hspace{1cm} (3.12)

where \( M \) is the molar mass, \( T^* \) the critical temperature in K, and \( V^* \) the critical volume in cm\(^3\)/mol. The dimensionless temperature \( T^* \) is related to the potential energy parameter \( \varepsilon \) and Boltzmann’s constant \( k \) by

\[ T^* = \frac{kT}{\varepsilon} \]  \hspace{1cm} (3.13)

\( \eta_0 \) is the viscosity of low pressure gas proposed by Chung et al. [69], and \( Y = \rho V_c/6 \) where \( \rho \) is density in g/cm\(^3\). The parameters \( G_1 \) and \( G_2 \) are defined in terms of \( Y \):

\[ G_1 = \frac{1 - 0.5Y}{(1 - Y)} \]  \hspace{1cm} (3.14)

\[ G_2 = \frac{A_1 [1 - \exp(-A_4 Y)] / y + A_2 G_1 \exp(A_3 Y) + A_5 G_1}{A_4 + A_5 + A_6} \]  \hspace{1cm} (3.15)

where the constants \( A_i \) are linear functions of the acentric factor \( \omega \), the reduced dipole moment \( \mu_r \), and the association factor \( \kappa \):

\[ A_i = a_{0i} + a_{1i} \omega + a_{2i} \mu_r^4 + a_{3i} \kappa \quad i = 1 \ldots 10 \]  \hspace{1cm} (3.16)

The constants \( a_0 \) and \( a_1 \) were determined by regression of the viscosity data for nonpolar fluids, and \( a_2 \) and \( a_3 \) determined similarly from the data of polar and associating fluids. The values of \( a_0, a_1, a_2 \) and \( a_3 \) are given in Table 3-1 [69].
The model has been tested with 25 hydrocarbons. Most viscosity values are predicted within about 3% deviation for paraffins and olefins, whereas the deviations are slightly higher for ring compounds with an AAD of 4%.

The model was then modified to predict the viscosity of petroleum fractions. Instead of the acentric factor, a characterization parameter was used which was determined by regression to match the boiling point and specific gravity of petroleum fractions with an equation of state [59]. The modified model was tested by two crude oil samples resulting in an AAD ranging from 3.7% to 8.3%. However, no literature was found to show any results in applying the modified Chapman-Enskog method to predict the viscosity of crude oil and CO₂ mixtures.

### 3.1.2 Empirical Methods

#### 3.1.2.1 Viscosity Correlations Considering Temperature and Pressure Only

The following empirical equation for the variation of liquid viscosity with temperature has been widely used and is known as the Andrade equation [70]:

\[
\ln(\eta) = A + \frac{B}{T} 
\]  

(3.17)

For many liquids, the above equation has successfully correlated the viscosity response to temperature from the freezing to boiling points. Amin and Maddox [71] collected the viscosity data for four crude oils from American fields and four other crude oil fractions, and applied the Andrade equation to correlate the viscosity as a function of temperature by fitting the two parameters empirically. With generalized parameters, the overall AAD for the estimation was about 10%.

A third parameter, C, was added to Equation (3.17) to obtain the Vogel equation [72]:

\[
\ln(\eta) = A + \frac{B}{T + C} 
\]  

(3.18)

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**Table 3-1. Constants used in Equation (3.16)**

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<tr>
<td>9</td>
<td>-0.23816</td>
<td>0.067695</td>
<td>-0.8163</td>
<td>4.02528</td>
</tr>
<tr>
<td>10</td>
<td>0.068629</td>
<td>0.34793</td>
<td>0.59256</td>
<td>-0.72663</td>
</tr>
</tbody>
</table>
Review of Viscosity Models for Crude Oil

Another two-parameter viscosity equation is the Walther equation [73].

\[
\log\left( \log\left( \frac{\nu}{\nu_{\text{ref}}} + 0.7 \right) \right) = b_1 + b_2 \log(T)
\]  (3.19)

where \( \nu \) is kinematic viscosity and \( \nu_{\text{ref}}=1 \text{ mm}^2/\text{s} \). On the other hand, the viscosity of liquids increases exponentially with isotropic pressure. Barus [74] established an empirical equation to describe the isothermal viscosity-pressure relationship for a given liquid:

\[
\ln \left( \frac{\eta}{\eta_0} \right) = \alpha P
\]  (3.20)

where \( \eta_0 \) is the atmospheric viscosity.

Mehrotra [75] proposed a three-parameter model based on the Walther equation and modified it to include the effect of pressure on crude oil viscosity:

\[
\log\left( \frac{\nu}{\nu_{\text{ref}}} + 0.7 \right) = 10^{b_1} T^{-3.5} + b_3 P^x
\]  (3.21)

where \( \nu \) is kinematic viscosity, \( \nu_{\text{ref}}=1 \text{ mm}^2/\text{s} \) and \( P^x \) dimensionless gauge pressure \((=P/P_0 - 1)\). \( P \) is in psi and \( T \) is in K. Values of \( b_1 \) and \( b_3 \) were regressed for 20 sets of viscosity-temperature-pressure data for middle-east crude oils from Al-Besharah et al. [76]. The following correlations are proposed for predicting the parameters \( b_1 \) and \( b_3 \) for the middle-east crude oil mixtures in terms of its density at an arbitrarily chosen temperature of 25 °C:

\[
b_1 = -3.3648 + 23.569 \rho_{25^\circ C} - 11.019 \rho_{25^\circ C}^2
\]  (3.22)

\[
b_3 = 57.818 \times 10^{-4} - 155.75 \times 10^{-4} \rho_{25^\circ C} + 111.19 \times 10^{-4} \rho_{25^\circ C}^2
\]  (3.23)

The mixture density \( \rho_{25^\circ C} \) (in g/cm\(^3\)) should be calculated as \( \rho_{25^\circ C} = (\sum x_i/\rho_i)^{-1} \), where \( x_i \) denotes the mass fraction. The model has an AAD of less than 5%.

3.1.2.2 Viscosity Correlations Considering Dissolved Gas

3.1.2.2.1 The LBC Correlation

It has been demonstrated that the viscosity of crude oil is changed with the quantity of CO\(_2\) dissolved in the oil. Correlations have been developed to predict the viscosity of CO\(_2\)/crude oil mixtures based on the concentration of CO\(_2\) in the oil and both the viscosities of CO\(_2\) and crude oil. In the oil industry, the correlation developed by Lohrenz, Bray, and Clark (LBC) is widely accepted as a standard for estimating the viscosity of crude oil and nature gas/crude oil mixtures, and then applied to the CO\(_2\)/crude oil system. The method was developed by adapting a pure-component viscosity correlation for mixtures
Review of Viscosity Models for Crude Oil

via combinatorial rules to obtain the correlation parameters for a multicomponent system [77]. In the LBC method the viscosity of crude oil and CO$_2$ mixture $\eta_m$ is correlated with the reduced density of the mixture $\rho_r$:

$$\left[ (\eta_m - \eta^*) \tilde{\xi} + 10^{-4} \right]^{\frac{1}{4}} = 0.1023 + 0.023364 \rho_r + 0.058533 \rho_r^2 - 0.040758 \rho_r^3 + 0.0093324 \rho_r^4$$

(3.24)

where $\tilde{\xi}$ is the inverse viscosity parameter defined by

$$\tilde{\xi} = \frac{T_i^{\frac{1}{6}}}{M_i^{\frac{1}{2}} P_i^{\frac{c}{3}}}$$

(3.25)

where $M_i$, $T_i$, and $P_i^c$ is the molar mass, critical temperature and critical pressure of component $i$. Given that the molar fraction of component $i$ is $x_i$, $\eta^*$ in Equation (3.24) is given by a mixing rule:

$$\eta^* = \frac{\sum_i x_i \eta_i M_i^\frac{1}{2}}{\sum_i x_i M_i^\frac{1}{2}}$$

(3.26)

Similarly,

$$T^c = \sum_i x_i T_i^c$$

(3.27)

$$P^c = \sum_i x_i P_i^c$$

(3.28)

$$M = \sum_i x_i M_i$$

(3.29)

and the critical molar volume of the mixture $V_{mix}^c$ is given by

$$V_{mix}^c = \sum_{i=C_7} x_i V_i^c + x_{C_7} V_{C_7}^c$$

(3.30)

The $C_7$ critical molar volume was correlated in terms of its mole fraction-averaged molecular weight and specific gravity.

Lansangan et al. [78] compared the calculation results of the LBC method with 393 data points. It is shown that the deviation from experimental measurements generally increases with the viscosity, with an AAD of 40.5%.
Review of Viscosity Models for Crude Oil

To improve the accuracy Lansangan et al. modified the LBC viscosity prediction through a deviation function $\Gamma(\rho_i)$, i.e. [79],

$$\eta_m = \eta^{\text{LBC}} + \Gamma(\rho_i) \quad (3.31)$$

where $\Gamma(\rho_i)$ is given by

$$\Gamma(\rho_i) = \alpha \rho_i^\beta \quad (3.32)$$

The constants $\alpha$ and $\beta$ were determined by fitting with experimental data. Also, the mixing rule applied in the work of Lansangan et al. is given by [79]:

$$\frac{T_i}{P_i} = \sum_i \sum_j X_i X_j \left( \frac{T_i}{P_i} \right)^{\frac{1}{3}} \quad (3.33)$$

$$T_{ij} = \zeta_{ij} \left( \frac{T_i}{P_i} \right)^{\frac{1}{3}} \quad (3.34)$$

$$P_{ij} = \frac{8T_{ij}^{\frac{1}{3}}}{\left[ \left( \frac{T_i}{P_i} \right)^{\frac{1}{3}} + \left( \frac{T_j}{P_j} \right)^{\frac{1}{3}} \right]^3} \quad (3.35)$$

where $\zeta_{ij}$ is the binary interaction parameter and set to unity for unlike components. The resulting AAD based on 393 data points is 12.5%.

3.1.2.2.2 The Ladeter Equation

Shu [80] pointed out that the Lederer equation is excellent in representing the CO$_2$/heavy crude oil mixture. The Lederer equation is given by:

$$\ln \eta_m = X_0 \ln \eta_0 + X_s \ln \eta_s \quad (3.36)$$

with

$$X_s = \frac{V_s}{\alpha V_o + V_s}, \text{ and } X_0 = 1 - X_s \quad (3.37)$$

where $V$ is volume fraction and the subscripts o, s, and m stand for heavy oil, CO$_2$ and CO$_2$/heavy-oil mixture respectively. In Equation (3.37), $\alpha$ is an empirical parameter that has to be determined by fitting.
Review of Viscosity Models for Crude Oil

data. Chung et al. [81] proposed the following correlation for $\alpha$ to relate it with temperature, pressure and specific gravity, $SG$, [80]:

$$
\alpha = 0.255 (SG)^{-4.16} T_r^{-1.85} \left[ \frac{e^{7.36} - e^{7.36(1-P_r)}}{e^{7.36} - 1} \right] 
$$

(3.38)

where $T_r = T/547.47$ K and $P_r = P/7.38$ MPa are reduced temperature and pressure, respectively. The volume fraction of CO$_2$ in the mixture can be obtained from the CO$_2$ solubility or swelling factor according to their definitions. To examine the proposed correlation, Chung et al. compared the correlated viscosity with the measured viscosity of the CO$_2$/crude oil mixtures for four heavy oils measured by Miller and Jones [82]. The AAD between calculated and measured viscosity is 3.5% for 429 data points.

Apart from the correlations mentioned above, Table 3-2 surmises some other viscosity correlations widely used in petroleum industry.
## Table 3-2. Summary of other methods widely used in the petroleum industry

<table>
<thead>
<tr>
<th>No</th>
<th>Authors</th>
<th>Underline Principle</th>
<th>Description</th>
<th>Independent Variables</th>
<th>Applied in Gas and Liquid Mixture</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Assael et al.</td>
<td>The hard-sphere theories of transport</td>
<td>The viscosity is expressed by reduced coefficient of viscosity, which is</td>
<td>Temperature,</td>
<td>No</td>
<td>[83]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>properties</td>
<td>correlated with molar volume by experimental data.</td>
<td>Molar volume</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Motahhari et al.</td>
<td>The Expanded Fluid Viscosity Model</td>
<td>The expanded fluid model is based on the empirical observation that, as the</td>
<td>Temperature,</td>
<td>No</td>
<td>[84]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>fluid expands, its viscosity decreases.</td>
<td>Density,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pressure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Macias-Salinas et al.</td>
<td>The Eyring Theory</td>
<td>Modifying the Eyring theory for mixtures, the activation energy of flow</td>
<td>Fugacity,</td>
<td>Yes</td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>is expressed in terms of fugacity coefficients and molar volume, which</td>
<td>Molar Volume,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>are evaluated from the known equation of state.</td>
<td>Molar Fraction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Soltani et al.</td>
<td>The Eyring Theory</td>
<td>The model is based on the Eyring theory to predict the temperature</td>
<td>Temperature</td>
<td>No</td>
<td>[86]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dependence of kinematic viscosity by using two reference fluids. The</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>reference fluids are selected based on the molar mass of the studied liquid.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Cao et al.</td>
<td>The Eyring Theory</td>
<td>This viscosity model for pure liquids and liquid mixture is developed based</td>
<td>Temperature</td>
<td>No</td>
<td>[87]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>on statistical thermodynamics, local compositions, and Eyring's absolute</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>rate theory.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Xuan et al.</td>
<td>The Eyring Theory</td>
<td>The model is based on the modified Eyring equation for viscosity, where</td>
<td>Temperature,</td>
<td>No</td>
<td>[88]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>the activation energy of flow is expressed in terms of activation volume.</td>
<td>Pressure</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>The activation volume is then given by a modified Tait equation.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2 Viscosity Models for Crude Oil as a Multiphase Fluid

The non-Newtonian behaviour of a multiphase crude oil mixture can be found in subsea pipelines where the temperature is usually lower than 25 °C [89]. Reliable rheological models are thus essential for a large number of oil technology applications, introducing shear rate dependence of viscosity for crude oils showing multiphase behaviour over the wide ranges of conditions.

3.2.1 Viscosity Correlations for Waxy Crude Oil

The presence of precipitated wax or water droplets may induce non-Newtonian rheological behaviour in crude oils. To understand the non-Newtonian viscosity of such multiphase system from a more theoretical point of view, the mixtures of crude oil with precipitated wax and water can be quantitatively analysed as a dispersed system. Then the non-Newtonian effect of the crude oil mixture could be studied from the theory of emulsions, relating the shear rate dependent viscosity to the concentrations of dispersed wax or water droplets.

Above the wax appearance temperature (WAT), a waxy crude although chemically very complex is a simple Newtonian fluid. If a waxy crude is allowed to cool to temperatures below the WAT, wax will precipitate and the crude will become a two-phase dispersion with wax solid particles dispersed in liquid hydrocarbon. After wax crystals appear, wax agglomerates may form due to the attractive forces between the particles. These agglomerates immobilize significant amount of the continuous phase within themselves [90]. Upon increasing the shear rate, the size of the agglomerates decreases and this process releases some of the continuous phase originally immobilized within the agglomerates. As a result, the effective dispersed phase concentration decreases, and leads to a decrease of viscosity. The viscosity decreases with increasing shear rate until the agglomerates are completely broken down into the basic particles. So the waxy crude system shows non-Newtonian behaviour.

Al-Zahrani and Al-Fariss [91] developed the following correlation to predict non-Newtonian viscosity of waxy crude oils in terms of shear rate, temperature, and wax concentration:

\[
\eta = \frac{B}{\gamma} \left[ \left( \frac{\gamma + A}{A} \right)^n - 1 \right] - \frac{1}{n} \exp \left( \frac{C}{T} + DW \right)
\]  (3.39)

where \( W \) is the percentage of precipitated wax and \( A, B, C, \) and \( n \) are the model parameters. The model parameters were determined by least-squares nonlinear regression analysis on rheology data of four Saudi crude oils from different fields. The viscosity model showed a good fit with an AAD of 2.5% in the range of shear rates investigated.
Pedersen and Ronningsen [92] also proposed a shear-rate-dependent viscosity model. The model is based on the correspondence between viscosity and volume fraction of precipitated wax, and is developed from the Casson rheological fluid model [93]. The model is given by

$$\eta = \eta_{\text{liq}} \left[ \exp(AW) + \frac{BW}{\sqrt{\gamma}} + \frac{CW^4}{\gamma} \right]$$

(3.40)

where $\eta_{\text{liq}}$ is the viscosity of the liquid phase which is treated as Newtonian and carries the temperature effect of viscosity. $A$, $B$, and $C$ are fitting parameters. Using 713 measured viscosity data points for 15 North Sea crude oils, the parameters were determined to be $A = 37.82$, $B = 83.96$, $C = 8.558 \times 10^6$. The model was tested on three oils, which were not included in the fitting data basis. The non-Newtonian viscosities of these oils were calculated with an average ADD of 47%.

Pal and Rhodes developed an empirical equation based on 16 sets of emulsion viscosity data [94]:

$$\eta_e = (1 - K_0 K_F (\gamma) \phi)^{-2.5}$$

(3.41)

where $\phi$ is the volume fraction of the dispersed phase, $K_0$ is the hydration factor, $K_F(\gamma)$ is the flocculation factor which depends on the shear rate. For a Newtonian system, $K_F(\gamma)$ will be unity.

Given that $c$ is the weight of precipitated wax particles relative to the total oil weight in %, the relation between the volume fraction $\phi$ and the mass fraction $c$ is

$$\phi = \left( \frac{\rho_0}{\rho_w} \right) c$$

(3.42)

where $\rho_0$ is the overall density of the crude oil, and $\rho_w$ is the density of the dispersed phase.

### 3.2.2 Frictional Theory of non-Newtonian Crude Oil

The frictional theory has been applied to predict crude oil viscosity, given a fully detailed characterization of the crude oil and a corresponding equation of state. In the frictional theory of viscosity, the viscosity of crude oil is given by the following equation [95]:

$$\eta = \eta_{0,\text{mix}} + \eta_p + K_c \eta_{\text{II}}$$

(3.43)

where $\eta_{0,\text{mix}}$ is the gas limit term viscosity contribution, and $\eta_p$ the friction viscosity contribution from all components in the crude oil mixture, except the pseudo-fraction. $\eta_{\text{II}}$ is an adjustable friction term viscosity contribution. The gas limit viscosity $\eta_{0,i}$ for a component $i$ can be calculated by the modified Chapman-Enskog theory proposed by Chuang et al. [69]. Then $\eta_{0,\text{mix}}$ can be calculated through the mixing rule:
Review of Viscosity Models for Crude Oil

\[
\ln(\eta_{0,\text{mix}}) = \sum_{i} x_i \ln(\eta_{0,i}) \quad (3.44)
\]

where \(x_i\) is the mole fraction of component \(i\). Furthermore, \(\eta_p\) is defined as,

\[
\eta_p = \kappa_{a,i} p_a + \kappa_{r,i} p_r + \kappa_{n,i} p_t^2 \quad (3.45)
\]

where the parameters \(\kappa_{a,i}\), \(\kappa_{r,i}\) and \(\kappa_{n,i}\) are given by

\[
\kappa_{a,i} = \sum_{i=1}^{m} Z_i \frac{\eta_{c,i} \kappa_{r,i}}{p_{c,i}} \quad (3.46)
\]

\[
\kappa_{a,i} = \sum_{i=1}^{m} Z_i \frac{\eta_{c,i} \kappa_{r,i}}{p_{c,i}} \quad (3.47)
\]

\[
\kappa_{n,i} = \sum_{i=1}^{m} Z_i \frac{\eta_{c,i} \kappa_{r,i}}{p_{c,i}} \quad (3.48)
\]

where \(\kappa_{a,i}\), \(\kappa_{r,i}\) and \(\kappa_{n,i}\) are functions of critical properties of component \(i\), and their expression can be found in the paper from Kumar et al. [95].

Similarly \(\eta_{II}\), which accounts for the heavier pseudo-fraction in the crude oil, is given by [96]

\[
\eta_{II} = \kappa_{a,II} p_a + \kappa_{r,II} p_r + \kappa_{n,II} p_t^2 \quad (3.49)
\]

where the parameters are written as follows:

\[
\kappa_{a,II} = \sum_{i=m+1}^{n} Z_i \left( \frac{M_{w,i}^{0.5} P_{c}^{2/3}}{T_{c,i}^{1/6}} \right) \frac{\kappa_{a,i}}{p_{c,i}} \quad (3.50)
\]

\[
\kappa_{r,II} = \sum_{i=m+1}^{n} Z_i \left( \frac{M_{w,i}^{0.5} P_{c}^{2/3}}{T_{c,i}^{1/6}} \right) \frac{\kappa_{r,i}}{p_{c,i}} \quad (3.51)
\]

\[
\kappa_{n,II} = \sum_{i=m+1}^{n} Z_i \left( \frac{M_{w,i}^{0.5} P_{c}^{2/3}}{T_{c,i}^{1/6}} \right) \frac{\kappa_{n,i}}{p_{c,i}} \quad (3.52)
\]

In Equation (3.43) the parameter \(K_c\) is the tuning parameter and is a constant for Newtonian fluid. For a non-Newtonian fluid, \(K_c\) is modified to be a function of shear rate and temperature to account for the effect of shear rate on viscosity [97]:

33
Review of Viscosity Models for Crude Oil

\[ K_c = K_0 \left( 1 + \frac{1}{1 + \gamma_0 \gamma^{0.7}} \right) \exp \left[ \left( 1 + \left( s_0 \left( T_r - T_s \right) \right)^6 \right) \left( s_1 \left( T_r - T_s \right) \right)^3 + \frac{s_2}{\left( T_r - T_s \right)^{0.5}} \right] \] (3.53)

where \( \gamma \) is the shear rate, \( \gamma_0 \) a shear rate parameter. \( T_s \) is an adjustable reduced temperature, and \( T_r \) is the reduced temperature defined as

\[ T_r = \frac{T}{T_{C+}} \] (3.54)

The reducing the temperature \( T_{C+} \) is calculated with the same empirical equation used in the estimation of the critical temperature of the heavy crude oil fraction:

\[ T_{C+} = -423.587 + 210.152 \ln \left( M_{w+} \right) \] (3.55)

where \( M_{w+} \) is the total molar mass of the heavy fraction. The three dimensionless parameters, \( s_0 \), \( s_1 \) and \( s_2 \), are given by the following correlations [97]:

\[ s_0 = -26.219 \left( \frac{K_0}{K_{ref}} \right) + 46.718 \] (3.56)

\[ s_1 = -1.1684 \left( \frac{K_0}{K_{ref}} \right) + 0.28159 \] (3.57)

\[ s_2 = 4.03395 \gamma_0 + 1.29209 \] (3.58)

where \( K_{ref} \) is 0.79483.

3.3 Viscosity and Volume Fraction Relationships for Emulsions

The volume fraction dependence of the viscosity of an emulsion is usually developed from the rheology of solid-in-liquid suspensions. A solid-in-liquid dispersion can be considered to be an extreme case of an emulsion, where the dispersed phase viscosity is infinitely high. For a very dilute emulsion, where the volume phase of the dispersed phase \( \phi \) is less than 0.01, the emulsion viscosity can be related to \( \phi \) by the Einstein equation for suspensions [98]:

\[ \eta_r = 1 + 2.5\phi \] (3.59)

where the relative viscosity, \( \eta_r \), is defined as the ratio of the emulsion viscosity to the continuous phase viscosity. When the volume fraction of an emulsion is increased, the relative viscosity no longer follows
the linear relationship with $\phi$ as Equation (3.59). Instead, the following polynomial has been used to describe the viscosity of concentrated emulsions:

$$\eta_r = 1 + k_1\phi + k_2\phi^2 + k_3\phi^3 + \cdots$$  \hspace{1cm} (3.60)

where $k_1=2.5$ as in the Einstein equation, $k_2=6.2$ accounting for hydrodynamic interactions between the dispersed droplets. For an emulsion with $\phi \leq 0.2$, the first three terms in Equation (3.60) are sufficient to describe the viscosity [98]. For a higher volume fraction it is usually necessary to introduce higher terms in Equation (3.60), and the coefficient $k_i (i \geq 3)$ is used as a curve fitting parameter.

Another suspension viscosity equation widely applied in the emulsion literature is the Mooney equation:

$$\eta_r = \exp \left( \frac{2.5\phi}{1-\phi/\phi_m} \right)$$  \hspace{1cm} (3.61)

where $\phi_m$ is the maximum packing volume fraction and determined empirically. Furthermore, the Krieger and Dougherty equation [100], also developed for dense suspensions, is frequently used in the study of dense emulsions:

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-2.5\phi_m}$$  \hspace{1cm} (3.62)

In Equation (3.61) and (3.62), when $\phi = \phi_m$ the viscosity of the emulsion becomes infinite.

Pal [101] generalised Equation (3.61) and (3.62) for emulsions by introducing the viscosity ratio to these two equations. The viscosity ratio, $\lambda$, is defined as the ratio of the disperse phase viscosity to the continuous viscosity. The emulsion viscosity equations by Pal are given by:

$$\eta_r \left( \frac{2\eta_r + 5\lambda}{2 + 5\lambda} \right)^{3/2} = \exp \left( \frac{2.5\phi}{1-\phi/\phi_m} \right)$$  \hspace{1cm} (3.63)

$$\eta_r \left( \frac{2\eta_r + 5\lambda}{2 + 5\lambda} \right)^{3/2} = \left(1 - \frac{\phi}{\phi_m}\right)^{-2.5\phi_m}$$  \hspace{1cm} (3.64)

Pal [101] compared the viscosities evaluated by Equation (3.63) and (3.64) with a large amount of experimental data for various emulsions, and the results were satisfactory.
3.4 The Critical Capillary Number for Concentrated Emulsions

For a single liquid droplet immersed in another immiscible liquid (continuous phase), the droplet breakup under a simple shear flow is determined by the capillary number and the viscosity ratio between the droplet ($\eta_d$) and the continuous phase ($\eta_c$). The capillary number, $Ca$, is the ratio between the shear stress $\sigma_c$ of the continuous phase, and the Laplace pressure $\sigma_{IFT}/a$:

$$Ca = \frac{\sigma_c a}{\sigma_{IFT}}$$

(3.65)

where $\sigma_{IFT}$ is the interfacial tension and $a$ denotes the un-deformed drop radius. Substituting $\sigma_c = \eta_c \gamma$, where $\gamma$ is the shear rate, one obtains:

$$Ca = \frac{\eta_c \gamma a}{\sigma_{IFT}}$$

(3.66)

There is a maximum value for the capillary number corresponding to each viscosity ratio beyond which the droplet will break up. This maximum value is called the critical capillary number, and its relationship with viscosity ratio can be described by the Grace curve [102].

The critical capillary number given by the Grace curve is valid only for dilute emulsions where the interaction between droplets is negligible. However, for a concentrated emulsion, where the droplets interact with each other frequently, the droplet breakup depends not only on the interplay between the droplet and continuous phase, but also on the interactions among droplets. Jansen and Golemanov [103, 104] demonstrated that, in order to make the results from the single droplet studies applicable in concentrated emulsions, the capillary number $Ca_{em}$ and viscosity ratio $\lambda_{em}$ for a concentrated emulsion need to be modified by replacing the continuous phase viscosity by the emulsion viscosity:

$$Ca_{em} = \frac{\eta_{em} \gamma a}{\sigma_{IFT}}$$

(3.67)

$$\lambda_{em} = \frac{\eta_d}{\eta_{em}}$$

(3.68)

3.5 Conclusion

A large number of viscosity models for crude oil can be found in the literature. Most of these models are not truly predictive, but require knowledge of the crude oil viscosity or other physical properties under certain conditions as model inputs. Therefore, tuning parameters cannot be avoided in these viscosity models. Although it was claimed that the frictional theory of viscosity contains only one parameter in the model, the detailed knowledge that it recalls from the equation of state has already resulted in a considerable number of parameters. Also, it is difficult to judge the accuracy and reliability...
of the viscosity models reviewed because different methods have been tested with different crude oil databases. The challenge in crude oil viscosity modelling remains in reducing the number of tuning parameters and increasing the model reliability for wider arrays of crude oils.
CHAPTER 4  THE VISCOSITY CORRELATION DEVELOPED IN THIS WORK

A new method is proposed to calculate the hydrocarbon viscosity given the knowledge of density. Based on the Eyring theory of viscosity, the method links the liquid viscosity with its density in an effective way, requiring only one parameter for pure liquid and two for mixtures. The performance of the proposed method is examined using published viscosity data for pure alkanes, binary alkane mixtures and saturated vapour-liquid hydrocarbon mixtures. The method can provide reasonable accuracy for viscosity predictions, demonstrated by the good match between the calculated and experimental values.

4.1 Model Development

The Eyring theory of viscosity is a solution of the cell model of a liquid to explain viscosity. The Eyring theory of viscosity $\eta$ is given by,

$$
\eta = \frac{hN_A}{V_m} \exp \left( \frac{\Delta G^+}{RT} \right)
$$

(4.1)

where $h$ is the Planck constant, $N_A = \text{Avogadro constant}$, $V_m = \text{molar volume of the liquid}$, $\Delta G^+ = \text{the standard free Gibbs energy change of flow}$, $R = \text{the gas constant}$ and $T$ the temperature.
The Viscosity Correlation Developed in This Work

Figure 4-1. The relationship between $\Delta G^+$ and $A_{RH}$ for three selected alkanes at ambient pressure and different temperatures. ◆, dodecane; △, tridecane; □, octadecane. —, the line for Equation (4.3) for $k_{RH}$ evaluated at the lowest temperature (corresponding to the lowest $\Delta G^+$).

A comparison between the value of $\Delta G^+$ obtained from Equation (4.1) with the molar volume of an alkane, in Figure 4-1, suggested the following correlation

$$k_{RH} \Delta G^+ = PV_m - PV_m \ln \left( \frac{V_m}{V_0} \right)$$

(4.2)

where $P$ is pressure, and $V_0$ was assigned to be 1 m$^3$/mol. If we define $A_{RH} = PV_m - PV_m \ln V_m$ then the Gibbs free energy of flow is given by

$$\Delta G^+ = \frac{A_{RH}}{k_{RH}}$$

(4.3)

It turns out that the parameter $k_{RH}$ is only a weak function of temperature and can be assumed constant at a specific pressure. Therefore, from one data point the fluid viscosity $k_{RH}$ can be evaluated, and then used to predict the viscosity at other temperatures with the knowledge of molar volume.

4.2 Model Validation with Pure Alkanes

The proposed model was first examined with the experimental data from NIST Webbook [105] of viscosity and density for nine n-alkanes at atmospheric pressure. The calculations were performed according to the following procedure: the free energy of flow at the minimum temperature was first evaluated to calculate the value of $k_{RH}$ knowing the molar volume; using the value of $k_{RH}$ and molar volume, the free energy of flow at other temperatures was worked out by Equation (4.2); the predicted viscosity was computed by Equation (4.1). The performance of the prediction was measured by the absolute average derivation (AAD) defined as
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\[ AAD = \frac{1}{n} \left( \sum_{n} \left| \frac{\eta_e - \eta_p}{\eta_e} \right| \right) \]  

(4.4)

where \( n \) is the number of experimental values, \( \eta_e \) and \( \eta_p \) the experimental and predicted viscosity values, respectively. The results of the calculation applying Equation (4.1) and (4.2) for the normal hydrocarbons are summarized in Table 4-1. The AADs for the nine samples are all less than 2.56%. The maximum deviation and overall AAD values with Equation (4.1) are 4.46% and 1.53%. It demonstrates that the proposed model is able to predict viscosity with good accuracy through one viscosity point.

<table>
<thead>
<tr>
<th>No</th>
<th>Comp.</th>
<th>( M_w ) / g/mol</th>
<th>( T ) / K</th>
<th>( k_{RH} )</th>
<th>AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hexane</td>
<td>86.2</td>
<td>303.15</td>
<td>323.15</td>
<td>0.0200</td>
</tr>
<tr>
<td>2</td>
<td>Heptane</td>
<td>100.2</td>
<td>303.15</td>
<td>323.15</td>
<td>0.0205</td>
</tr>
<tr>
<td>3</td>
<td>Octane</td>
<td>114.2</td>
<td>298.15</td>
<td>373.15</td>
<td>0.0210</td>
</tr>
<tr>
<td>4</td>
<td>Nonane</td>
<td>128.3</td>
<td>303.15</td>
<td>323.15</td>
<td>0.0215</td>
</tr>
<tr>
<td>5</td>
<td>Decane</td>
<td>142.3</td>
<td>298.15</td>
<td>373.15</td>
<td>0.0221</td>
</tr>
<tr>
<td>6</td>
<td>Undecane</td>
<td>156.3</td>
<td>303.15</td>
<td>323.15</td>
<td>0.0226</td>
</tr>
<tr>
<td>7</td>
<td>Dodecane</td>
<td>170.3</td>
<td>298.15</td>
<td>473.15</td>
<td>0.0232</td>
</tr>
<tr>
<td>8</td>
<td>Tridecane</td>
<td>184.4</td>
<td>293.15</td>
<td>353.15</td>
<td>0.0238</td>
</tr>
<tr>
<td>9</td>
<td>Octadecane</td>
<td>254.5</td>
<td>323.15</td>
<td>473.15</td>
<td>0.0266</td>
</tr>
</tbody>
</table>

In Figure 4-2, the viscosity measured for three normal hydrocarbons is compared with the viscosity evaluated from Equation (4.1). The predicted viscosities values are in excellent agreement with the data for all three samples at all temperatures. Similar results were obtained for all other samples in Table 4-1.
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Figure 4-2. Comparison between the experimental data [105] and calculated results for octane, dodecane and octadecane. ◊, experimental data for octane; Δ, experimental data for dodecane; ‡, experimental octadecane; –-, - - -, and –, calculated results.

The value of \( k_{RH} \) from Equation (4.2) was plotted against the molar mass \( M_w \) of the alkanes, as illustrated by Figure 4-3. Figure 4-3 shows a clear linear trend between \( M_w \) and the parameter \( k_{RH} \) for all nine hydrocarbons. The regression line in Figure 4-3 represents the following linear relationship between \( k_{RH} \) and \( M_w \) with \( r^2 \) greater than 0.999:

\[
k_{RH} = 3.9205 \times 10^{-5} M_w + 0.01653
\]  
(4.5)

Figure 4-3. Variation of the parameter \( k_{RH} \) in Equation (4.2) with the molar mass for the 9 alkanes. ◊, the \( k \) value calculated by Equation (4.2) for each alkane; –, regression line.

4.3 Further Model Development for Hydrocarbons Mixtures

In an extension from pure hydrocarbons, the proposed model was examined with binary alkane mixtures to test its ability to predict the mixture viscosity from the knowledge of pure components. The aim of
The Viscosity Correlation Developed in This Work

the model is to use the viscosities of pure components and the density of the mixture to predict its viscosity.

Considering that most density data for mixtures is given in terms of mass instead of molar volume and that molar mass measurement for crude oil requires a large effort, it would be beneficial if Equation (4.1) is given in terms of mass density \( \rho \). Since \( V_m = M_w/\rho \), Equation (4.1) becomes

\[
\eta = \frac{\rho h N_A}{M_w} \exp\left(\frac{\Delta G^+}{RT}\right)
\]

Introducing a dimensionless parameter \( C \) and \( M_{w,0} = 1 \text{ g/mol} \), the molar mass can be given by

\[
\frac{1}{M_w} = \frac{1}{M_{w,0}} \exp\left(\frac{C RT}{RT}\right)
\]

Subsuming Equation (4.7) into (4.6), one obtains:

\[
\eta = \frac{\rho h N_A}{M_{w,0}} \exp\left(\frac{CRT}{RT}\right) \exp\left(\frac{\Delta G^+}{RT}\right)
\]

\[
\eta = \frac{\rho h N_A}{M_{w,0}} \exp\left(\frac{CRT + \Delta G^+}{RT}\right)
\]

Let \( \Delta G^+_C = CRT + \Delta G^+ \), then the above equation becomes:

\[
\eta = \frac{\rho h N_A}{M_{w,0}} e^{\Delta G^+_C/RT}
\]

Using Equation (4.2), a comparison between the values of \( \Delta G^+_C \) calculated from Equation (4.9) and the mass density of a binary mixture \( \rho_{\text{mix}} \) as shown in Figure 4-4, suggests the following correlation:

\[
\frac{P - P\ln\left(\frac{\rho_0}{\rho_{\text{mix}}}\right)}{\rho_{\text{mix}} \Delta G^+_C} = a_{\text{RH}} \rho_{\text{mix}} + b_{\text{RH}}
\]

where \( \rho_0 = 1 \text{ kg/m}^3 \), and \( a_{\text{RH}} \) and \( b_{\text{RH}} \) are constant.
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Figure 4.4. The relationship between \(P - P\ln(\rho_0/\rho_{\text{mix}}))/(\rho_{\text{mix}}\Delta G_c^\circ)\) and \(\rho_{\text{mix}}\) for three selected mixtures at 298.15 K. \(\bigtriangleup\), \(n\)-heptane and \(n\)-hexane mixture; \(\bigtriangledown\), \(n\)-nonane and \(n\)-dodecane mixture; \(\times\), \(n\)-hexadecane and \(n\)-tetradecane mixture. \(--\) is a linear regression line. Data was taken from [106].

For binary liquid-liquid mixtures, \(a_{RH}\) and \(b_{RH}\) can be evaluated from the density and viscosity of the two pure liquids. For example, at a given temperature, there are two liquids named 1 and 2 with the density and viscosity of \(\rho_1\) and \(\eta_1\), and \(\rho_2\) and \(\eta_2\), respectively. The mixture of these two liquids has two extreme cases where one is 100% liquid 1 and the other liquid 2. Therefore, \(a_{RH}\) and \(b_{RH}\) can be calculated from these two extremes by solving the following system of equations:

\[
\begin{align*}
\frac{P - P\ln(\rho_0/\rho_1)}{\rho_1\Delta G_{C,1}^\circ} &= a_{RH}\rho_1 + b_{RH} \\
\frac{P - P\ln(\rho_0/\rho_2)}{\rho_2\Delta G_{C,2}^\circ} &= a_{RH}\rho_2 + b_{RH}
\end{align*}
\] (4.11)

where \(\Delta G_{C,1}^\circ\) and \(\Delta G_{C,2}^\circ\) can be worked out by Equation (4.9) knowing \(\eta_1\) and \(\eta_2\).

Using Equations (4.9) and (4.10) with the values of \(a_{RH}\) and \(b_{RH}\), the viscosity of the mixture can be evaluated from the information of the mixture density at a specific temperature. The viscosity data of 35 binary alkane pairs at 298.15 K from the literature [106] were used to test the performance of the model, and the results are shown in Table 4-2. Table 4-2 shows that the model can give an excellent viscosity prediction for binary alkane mixtures with an AAD of 0.72%.
The Viscosity Correlation Developed in This Work

Table 4-2. Summary of the viscosity calculation by Equation (4.6) for liquid-liquid mixtures

<table>
<thead>
<tr>
<th>No</th>
<th>Mixture</th>
<th>$a_{RH}\times10^4$</th>
<th>$b_{RH}$</th>
<th>AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-hexane + n-heptane</td>
<td>-1.72275</td>
<td>0.178527</td>
<td>0.36%</td>
</tr>
<tr>
<td>2</td>
<td>n-hexane + n-octane</td>
<td>-1.74444</td>
<td>0.179948</td>
<td>0.51%</td>
</tr>
<tr>
<td>3</td>
<td>n-hexane + n-nontane</td>
<td>-1.77097</td>
<td>0.181686</td>
<td>0.52%</td>
</tr>
<tr>
<td>4</td>
<td>n-hexane + n-decane</td>
<td>-1.80174</td>
<td>0.183702</td>
<td>0.56%</td>
</tr>
<tr>
<td>5</td>
<td>n-hexane + n-dodecane</td>
<td>-1.84972</td>
<td>0.186845</td>
<td>1.22%</td>
</tr>
<tr>
<td>6</td>
<td>n-hexane + n-tetradecane</td>
<td>-1.89407</td>
<td>0.189750</td>
<td>0.71%</td>
</tr>
<tr>
<td>7</td>
<td>n-heptane + n-octane</td>
<td>-1.77221</td>
<td>0.181888</td>
<td>0.63%</td>
</tr>
<tr>
<td>8</td>
<td>n-heptane + n-nontane</td>
<td>-1.80508</td>
<td>0.184122</td>
<td>0.05%</td>
</tr>
<tr>
<td>9</td>
<td>n-heptane + n-decane</td>
<td>-1.84295</td>
<td>0.186695</td>
<td>0.04%</td>
</tr>
<tr>
<td>10</td>
<td>n-heptane + n-dodecane</td>
<td>-1.89670</td>
<td>0.190347</td>
<td>0.12%</td>
</tr>
<tr>
<td>11</td>
<td>n-heptane + n-hexadecane</td>
<td>-1.98144</td>
<td>0.196105</td>
<td>0.66%</td>
</tr>
<tr>
<td>12</td>
<td>n-octane + n-nontane</td>
<td>-1.84571</td>
<td>0.187022</td>
<td>0.50%</td>
</tr>
<tr>
<td>13</td>
<td>n-octane + n-decane</td>
<td>-1.89162</td>
<td>0.190230</td>
<td>0.04%</td>
</tr>
<tr>
<td>14</td>
<td>n-octane + n-dodecane</td>
<td>-1.94734</td>
<td>0.194122</td>
<td>0.08%</td>
</tr>
<tr>
<td>15</td>
<td>n-octane + n-tetradecane</td>
<td>-2.00136</td>
<td>0.197895</td>
<td>0.40%</td>
</tr>
<tr>
<td>16</td>
<td>n-octane + n-hexadecane</td>
<td>-2.03730</td>
<td>0.200406</td>
<td>0.54%</td>
</tr>
<tr>
<td>17</td>
<td>n-nontane + n-decane</td>
<td>-1.99426</td>
<td>0.194416</td>
<td>0.26%</td>
</tr>
<tr>
<td>18</td>
<td>n-nontane + n-dodecane</td>
<td>-1.99718</td>
<td>0.197837</td>
<td>0.17%</td>
</tr>
<tr>
<td>19</td>
<td>n-nontane + n-tetradecane</td>
<td>-2.05448</td>
<td>0.201928</td>
<td>0.44%</td>
</tr>
<tr>
<td>20</td>
<td>n-nontane + n-hexadecane</td>
<td>-2.09008</td>
<td>0.204470</td>
<td>0.33%</td>
</tr>
<tr>
<td>21</td>
<td>n-decane + n-dodecane</td>
<td>-2.02790</td>
<td>0.200127</td>
<td>0.22%</td>
</tr>
<tr>
<td>22</td>
<td>n-decane + n-tetradecane</td>
<td>-2.09376</td>
<td>0.204911</td>
<td>0.33%</td>
</tr>
<tr>
<td>23</td>
<td>n-decane + n-hexadecane</td>
<td>-2.12966</td>
<td>0.207518</td>
<td>0.33%</td>
</tr>
<tr>
<td>24</td>
<td>n-dodecane + n-tetradecane</td>
<td>-2.18558</td>
<td>0.211882</td>
<td>0.19%</td>
</tr>
<tr>
<td>25</td>
<td>n-dodecane + n-hexadecane</td>
<td>-2.20912</td>
<td>0.213636</td>
<td>0.05%</td>
</tr>
<tr>
<td>26</td>
<td>n-tetradecane + n-hexadecane</td>
<td>-2.23909</td>
<td>0.215944</td>
<td>0.14%</td>
</tr>
<tr>
<td>27</td>
<td>3-methylpentane + n-decane</td>
<td>-1.91965</td>
<td>0.192265</td>
<td>0.66%</td>
</tr>
<tr>
<td>28</td>
<td>3-methylpentane + n-hexadecane</td>
<td>-2.00294</td>
<td>0.197761</td>
<td>2.29%</td>
</tr>
<tr>
<td>29</td>
<td>2-methylpentane + n-hexadecane</td>
<td>-1.92518</td>
<td>0.191773</td>
<td>2.11%</td>
</tr>
<tr>
<td>30</td>
<td>2-methylpentane + n-tetradecane</td>
<td>-1.95411</td>
<td>0.194308</td>
<td>1.00%</td>
</tr>
<tr>
<td>31</td>
<td>2,3-methylpentane + n-tetradecane</td>
<td>-2.17086</td>
<td>0.210764</td>
<td>1.82%</td>
</tr>
<tr>
<td>32</td>
<td>2,2-dimethylpentane + n-decane</td>
<td>-1.73571</td>
<td>0.178906</td>
<td>1.18%</td>
</tr>
<tr>
<td>33</td>
<td>Isooctane + n-hexane</td>
<td>-1.93324</td>
<td>0.192316</td>
<td>1.21%</td>
</tr>
<tr>
<td>34</td>
<td>Isooctane + n-decane</td>
<td>-1.68987</td>
<td>0.175577</td>
<td>0.26%</td>
</tr>
<tr>
<td>35</td>
<td>Isooctane + n-tetradecane</td>
<td>-1.87454</td>
<td>0.188267</td>
<td>2.12%</td>
</tr>
</tbody>
</table>

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The Viscosity Correlation Developed in This Work

Figure 4-5. Comparison between the experimental data [106] and calculated results for n-decane mixtures. ◆, experimental data for n-decane and n-dodecane mixture; ▲, experimental data for n-decane and n-tetradecane; ■, experimental data for n-decane and n-hexadecane; ---, calculated results.

Figure 4-5 illustrates the comparison between the calculated results from Equation (4.6). This includes the experimental data for three binary mixtures: n-decane/n-dodecane, n-decane/n-tetradecane, and n-decane/n-hexadecane.

The above method is also able to predict the viscosity of saturated gas-liquid mixtures. For a given temperature, the parameters $a$ and $b$ can be evaluated from the density and viscosity of the pure liquid at atmospheric pressure, and that of the gas saturated mixture at a specific pressure, $P_{\text{exp}}$. The method then is able to calculate the viscosity of the saturated vapour-liquid mixture between $P_0$ and $P_{\text{exp}}$ given the mixture density. Figure 4-6 illustrates the data requirements to evaluate the parameters $a_{\text{RH}}$ and $b_{\text{RH}}$ for saturated vapour-liquid mixtures.

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>Ambient</th>
<th>$P_1$</th>
<th>$P_2$</th>
<th>...</th>
<th>$P_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⋮</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_{n-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_n$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Required Data</th>
<th>Predicted</th>
</tr>
</thead>
</table>

Figure 4-6. Data requirement matrix for saturated vapour-liquid mixtures
The Viscosity Correlation Developed in This Work

The method is tested for methane/ethane + hydrocarbons systems. The results are summarized in Table 4.3. The average AAD is 2%. Figure 4-7 illustrates the results predicted by the method with the experimental data for a heavy crude oil.

Table 4-3. Summary of the viscosity calculation by Equation (4.6) for saturated vapour-liquid mixtures

<table>
<thead>
<tr>
<th>System</th>
<th>$T$ / K</th>
<th>$x_{gas}$</th>
<th>$P$ / MPa</th>
<th>AAD</th>
<th>Data Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$ + Tetradecane</td>
<td>294.8</td>
<td>0.364</td>
<td>0.1</td>
<td>9.49</td>
<td>1.70%</td>
</tr>
<tr>
<td></td>
<td>324.1</td>
<td>0.342</td>
<td>0.1</td>
<td>9.54</td>
<td>0.39%</td>
</tr>
<tr>
<td></td>
<td>373.5</td>
<td>0.317</td>
<td>0.1</td>
<td>9.5</td>
<td>1.64%</td>
</tr>
<tr>
<td></td>
<td>447.6</td>
<td>0.303</td>
<td>0.1</td>
<td>9.47</td>
<td>1.19%</td>
</tr>
<tr>
<td>CH$_4$ + Octadecane</td>
<td>323.1</td>
<td>0.358</td>
<td>0.1</td>
<td>5.89</td>
<td>1.33%</td>
</tr>
<tr>
<td></td>
<td>347.9</td>
<td>0.341</td>
<td>0.1</td>
<td>9.47</td>
<td>1.11%</td>
</tr>
<tr>
<td></td>
<td>398.2</td>
<td>0.33</td>
<td>0.1</td>
<td>9.59</td>
<td>0.84%</td>
</tr>
<tr>
<td></td>
<td>447.6</td>
<td>0.33</td>
<td>0.1</td>
<td>9.51</td>
<td>1.26%</td>
</tr>
<tr>
<td>CH$<em>4$ + Decane + Tetradecane ($x</em>{decane}/x_{tetradecane} = 3$)</td>
<td>294.6</td>
<td>0.329</td>
<td>0.1</td>
<td>8.02</td>
<td>2.92%</td>
</tr>
<tr>
<td>CH$<em>4$ + Decane + Tetradecane ($x</em>{decane}/x_{tetradecane} = 1$)</td>
<td>294.6</td>
<td>0.338</td>
<td>0.1</td>
<td>7.99</td>
<td>2.73%</td>
</tr>
<tr>
<td>CH$<em>4$ + Decane + Tetradecane ($x</em>{decane}/x_{tetradecane} = 1/3$)</td>
<td>294.6</td>
<td>0.327</td>
<td>0.1</td>
<td>8.02</td>
<td>0.73%</td>
</tr>
<tr>
<td>CH$<em>4$ + Decane + Hexadecane ($x</em>{decane}/x_{hexadecane} = 3$)</td>
<td>294.5</td>
<td>0.32</td>
<td>0.1</td>
<td>7.92</td>
<td>2.03%</td>
</tr>
<tr>
<td>C$_2$H$_6$ + Octadecane</td>
<td>422.6</td>
<td>0.477</td>
<td>0.1</td>
<td>5.94</td>
<td>1.02%</td>
</tr>
<tr>
<td></td>
<td>372.8</td>
<td>0.474</td>
<td>0.1</td>
<td>4.08</td>
<td>1.15%</td>
</tr>
<tr>
<td>C$_2$H$_6$ + Tetradecane</td>
<td>373.5</td>
<td>0.279</td>
<td>0.1</td>
<td>5.01</td>
<td>0.89%</td>
</tr>
<tr>
<td></td>
<td>422.5</td>
<td>0.47</td>
<td>0.1</td>
<td>6.05</td>
<td>1.98%</td>
</tr>
<tr>
<td>CH$_4$ + Heavy Crude Oil</td>
<td>288.6</td>
<td>N/A</td>
<td>N/A</td>
<td>8.51</td>
<td>7.25%</td>
</tr>
</tbody>
</table>
The Viscosity Correlation Developed in This Work

Figure 4-7. Comparison of the experimental measurements [113] and calculated results for a methane saturated heavy crude oil. ◇, experimental data; —, calculated results.
CHAPTER 5 EXPERIMENTAL SETUP AND PROCEDURE

This chapter describes in detail the circulation system built for rheology measurements and the view cell system for phase behaviour measurement. Furthermore, the tests with reference fluids are also described to show the performance of the systems.

5.1 The Circulation System for Rheology Measurements

5.1.1 System Description
The system designed and built to allow for the rheology measurement of gas-saturated crude oils is a circulation system, which contains four off-the-shelf pieces: a syringe pump, mixer, gear pump, and rheometer, as shown in Figure 5-1 and Figure 5-2.
Figure 5-1. The scheme of the circulation system with CC29/Pr pressure cell. Valve B, C, and F are release valve.
Experimental Setup and Procedure

**Syringe Pump**
- **Description**: Syringe Pump
- **Manufacturer**: Teledyne ISCO
- **Model**: 65D
- **Capacity**: 67 ml
- **Pressure Range**: 0.7 to 1390 bar
- **Operating Temperature**: 5 - 40°C

**Gear Pump**
- **Description**: Gear Pump
- **Manufacturer**: Teledyne ISCO
- **Model**: CIP-32/1.5
- **Main Body Material**: Stainless Steel
- **Material**: Alloy Steel
- **Pressure Cell**: GD35.12/PR
- **Geometry**: Double Gap

**Mixer**
- **Description**: Mixer
- **Manufacturer**: Parr Instruments
- **Material**: Stainless Steel
- **Vessel Volume**: 250 ml
- **Max. P**: 410 bar
- **Max. T**: 350°C

**Rheometer**
- **Description**: Rheometer
- **Manufacturer**: Anton Paar
- **Main Body Model**: MCR 301
- **Pressure Cell**: GD35.12/PR
- **Material**: Titanium
- **Geometry**: Double Gap
- **Max. P**: 400 bar
- **Max. T**: 300°C

**Figure 5-2.** The scheme of the circulation system with DG35.12/Pr pressure cell. Valve B, C, and F are release valves.
Experimental Setup and Procedure

5.1.2 Mixer

As shown in Figure 5-3, the mixer is a Parr Instruments 4651 reactor with a vessel volume of 250 ml, mounted on a series 4923EE bench-top heater with a series 4838 temperature controller. The mixer, manufactured in 316 stainless steel, is sealed with a polytetrafluoroethylene (PTFE) flat gasket and split ring arrangement, operated at a maximum working pressure of 410 bar and up to 350 °C.

The head of the reactor contains three ports as illustrated in Figure 5-4. Port A is connected to a gas inlet valve (1/4” NPTF process connection) through a pressure gauge. Port B is connected to a liquid outlet valve (1/4” NPTF process connection). The liquid loaded in the mixer will flow through a dip-tube inside the mixer and then to the liquid outlet valve. The end of the dip-tube is 27.65 mm above the bottom of the cell. Finally Port C is connected to the liquid return loop via a Tee connection, which provides another port for the rupture disc assembly.

Stirring of the mixture is performed by a stirring bar placed at the bottom of the vessel, which is driven by a rotating magnet set. The benchtop heater is modified to include a magnet set rotated via an electric motor. Figure 5-5 shows the scheme of the modification. The gear of the electric motor is mounted on the standing platform of the heater, while the motor main body is corrected to the gear. The motor provides stirring speeds adjustable from 0 to 1700 rpm. The gear is connected to one end of a stainless steel bar, which passes through the bottom of the heater. At the other end of the bar a magnet set is mounted. The magnet set contains two SmCo magnetic metal blocks assembled on a mild steel yoke. The magnet set is fixed at the stainless steel bar via a screw. The Figure 5-6 shows the magnet set installed inside the heater.
In order to mount the mixer into the heater properly, a frame with two lifting columns was designed and built, as illustrated in Figure 5-7. The dimension of the frame is 120 cm × 45 cm × 45 cm. Two lifting columns are located at two sides of the frame and mirror each other. Each lifting column is driven by a low voltage motor and provides a maximum tensile force of 1000 N. The lifting columns are used to adjust the location of a plate between them. Standing on the plate, the heater can be mounted around or removed from the mixer by the lifting columns.

5.1.3 Rheometer

The viscosity measurement is performed in a high-pressure cell mounted on the Anton Paar MCR301 rheometer. There are two types of pressure cells that have been applied in this work. One is with coaxial
Experimental Setup and Procedure

cylinder geometry (model number CC29/Pr) and the other with double gap geometry (model number DG35.12/Pr).

As illustrated in Figure 5-9, CC29/Pr is a pressure cell for highly viscous fluid measurement. It has a concentric cylinder geometry with a 0.5 mm gap; it can be pressurized up to 400 bar and operated in a temperature range from 25 to 300 °C. The sample volume is 18 ml. The measuring cylinder is magnetically coupled with an outer magnet cup, which is attached to the rheometer spindle. This system has a maximum rotation speed of 1200 rpm, and its minimum torque depends on the lubrication properties of the sample.

![Image of CC29/Pr pressure cell](image)

Figure 5-9. The rheometer mounted with CC29/Pr pressure cell.

The design of the pressure cell allows for high shear rates to be applied to viscoelastic samples without encountering problems, such as the Weissenberg effect or the sample escaping from the gap [114]. Also because the pressure cell is completely sealed and entirely flushed with sample, there is no room for loading errors and the sample loading is repeatable. The accuracy of the viscosity measurement was examined by the UKAS certified viscosity standards N35 and S600 (100% hydrocarbons, from Paragon Scientific Ltd). Figure 5-10 and Figure 5-11 show the measurement error, $\Delta$,

$$\Delta = \frac{|\eta - \eta_{\text{ref}}|}{\eta_{\text{ref}}}$$  \hspace{1cm} (5.1)
Experimental Setup and Procedure

where $\eta_m$ is the measurement value and $\eta_{ref}$ the reference value of the viscosity standard. The agreement with the standards in temperature range $25 - 80 ^\circ C$ was better than 3.5%. The repeatability of the rheological measurements was better than 1%.

![Graph showing viscosity measurement error of CC29/Pr pressure cell for N35 viscosity standard.](image1)

Figure 5-10. Viscosity measurement error of CC29/Pr pressure cell for N35 viscosity standard. ◆, $25 ^\circ C$; ■, $40 ^\circ C$; ▲, $50 ^\circ C$; ●, $60 ^\circ C$; ✗, $80 ^\circ C$.

![Graph showing viscosity measurement error of CC29/Pr pressure cell for S600 viscosity standard.](image2)

Figure 5-11. Viscosity measurement error of CC29/Pr pressure cell for S600 viscosity standard. ◆, $25 ^\circ C$; ■, $30 ^\circ C$; ▲, $35 ^\circ C$; ●, $40 ^\circ C$; ✗, $45 ^\circ C$.

On the other hand, the DG35.12/Pr pressure cell is designed for low viscosity fluid. It has a double gap geometry with a working temperature up to $200 ^\circ C$ and pressure up to 400 bar. The sample volume is 5.8 ml. As illustrated in Figure 5-12, the magnetic coupling mounted on the rheometer motor conveys the torque of the measuring drive to the pressure head and to the measuring cylinder mounted in the
Experimental Setup and Procedure

pressure head. This system has a maximum rotation speed of 1200 rpm, and its torque range is from 100 μNm to 150 mNm.

Figure 5-12. The rheometer mounted with DG35.12/Pr pressure cell.

When using the DG35.12/Pr pressure cell, a good measurement results from a careful loading of sample – the sample fluid only immerses the measuring system, which includes the measuring cylinder and the inner part of a double gap system. If the sample fluid reaches a higher level than the measuring system, the measurement might be too large since the extra fluid could cause additional friction. As seen in Figure 5-2, the flow rate of the fluid entering the pressure cell is controlled by the gear pump, whereas the outlet flow rate is determined by gravity alone. To prevent overflowing, the rotational speed of the gear pump needs to be adjusted to a suitable value such that the inlet flow rate is less than or equal to the outlet flow rate. It is achieved by constantly monitoring the fluid level at the outlet of the pressure cell. If the fluid immerses the inner part while the fluid level at the outlet is decreased or kept constant, then the current rotational speed of the gear pump is acceptable. In addition, since the inlet and outlet flows are driven differently, there is a maximum limit on the fluid viscosity measured by the
Experimental Setup and Procedure

DG35.12/Pr pressure cell. If the fluid viscosity is too high, then the outlet flow, driven by gravity, will always be slower than the inlet even if the gear pump is operated at the lowest rotational speed. In that case, overflowing cannot be prevented. Thus the DG35.12/Pr pressure cell is not suitable for very viscous fluids. Also, as noted by the manufacturer, the shear rate applied in DG35.12/Pr should not be higher than 300 l/s because the resulting turbulence will cause significant noise in the measurement. The viscosity measurement accuracy of the pressure cell was tested with the UKAS certified viscosity standards N100 (100% hydrocarbons, from Paragon Scientific Ltd). As seen in Figure 5-13, the agreement with the standards in the certified temperature range 20 – 60 °C at shear rates above 30 s⁻¹ was better than 1.44%.

![Figure 5-13. Viscosity measurement error of DG35.12/Pr pressure cell for N100 viscosity standard. ◆, 25 °C; ■, 30 °C; ▲, 40 °C; ●, 50 °C; X, 60 °C.](image)

5.1.4 Gear Pump

5.1.4.1 The Carbon Gear Pump

The carbon gear pump circulating the fluid is a GAH X21 suction shoe gear pump from Micropump, as illustrated in Figure 5-14. The pump is a rotating positive displacement pump, which can be operated at up to 345 bar and 120 °C. The main body of the gear pump is fabricated of stainless steel, while the gears and suction shoes are made of carbon. The pump is magnetically coupled to a drive motor. The driven magnet inside the pump is fixed to the driving gear. Rotation of the magnet cup by the motor causes the driven magnet and driving gear to rotate synchronously around a non-rotating shaft. The magnet cup thus provides a pressure boundary between the pumped fluid and the surrounding environment. Fluid enters the inlet port and is swept by the gears around the cavity to the outlet port. Pressure is developed in the pump by the restrictions on the outlet, which loads the gears against the
Experimental Setup and Procedure

suction shoe and shafts. Initial start-up of the pump is facilitated by a spring that holds the suction shoe in place until differential pressure across the shoe dominates the load on the shoe.

To order to protect the gears, a bypass loop is installed around the gear pump as shown in Figure 5-15. The bypass loop contains a check valve with a cracking pressure of 1.8 bar. Thus when the pressure of the gear pump outlet is 1.8 bar higher than that of the inlet, the check valve will be activated to reduce the pressure difference by releasing fluid from the pump outlet to inlet. It can prevent the gears inside the pump from overloading. This also leads to the fact that the maximum differential pressure produced by the gear pump is 1.8 bar.

![Figure 5-14. GAH X21 gear pump mounted on the motor](image1)

![Figure 5-15. The bypass loop designed to protect the gear pump](image2)

5.1.4.2 The Hardened Steel Gear Pump

The hardened steel gear pump used to circulate highly viscous fluid is a Polymer Systems Inc. (PSI) chemical industrial pump, with a model number of CIP-12/1.5 (Figure 5-16). The gear pump can be operated up to at 345 bar and 454 °C, and provides a maximum differential pressure ($\Delta P$) of 69 bar. The foundation of the pump head is a solid forging of precision-machined alloy steel. Each side of the pump head has a pair of bearings held in place by two side-plates bolted to the pump head. The drive gear shaft extends through the side-plate and is sealed with an anti-galling visco seal. Inside the pump head, a figure-eight shaped cavity houses the bearings that support the gears. Both side-plates have integral ports for pressure transducers.
5.1.5 Experimental Procedure

The rheological measurement procedure is as follows. First, the mixer was disconnected and removed from the system to load the crude oil sample. Once fully loaded, the mixer was connected back to the system, and then the whole system was primed (see below for detail). Then the remaining volume in the system was evacuated for 30 min to remove the air, using an EDWARDS A48015960 vacuum pump. The system was then brought to the set point temperature. CO₂ was introduced into the mixer via the syringe pump that controlled the system pressure. Inside the mixer, a stirrer coupled with a rotating magnet was used to enhance the mixing between the crude oil and CO₂. The mixture was circulated into the pressure cell of the rheometer by the gear pump. Once the pressure cell was completely full, the mixture was recycled back to the mixer and the circulation continued for more than 24 h to ensure equilibrium. The circulation was then stopped and the viscosity measurement is performed at the rheometer. During the circulation, the stir was kept rotating to ensure that the liquid had a uniform composition. The suction tube in the mixer removed fluid from close to the bottom of the mixer, sampling the liquid and not the vapour phase. After reaching equilibrium, the circulation was stopped and the viscosity was measured in the rheometer. The CO₂ and crude oil equilibrium was confirmed at each pressure by repeating the cycle of circulation for several hours followed by rheology measurements until no further changes in viscosity were observed.
Experimental Setup and Procedure

To prime the system with the CC29/Pr pressure cell, valves A, D, F and G in Figure 5-1 were closed and valve C opened. Then by opening valves H and E, compressed nitrogen gas (provided by BOC with cylinder number of 270090-V, 100% purity) was introduced into the mixer through the syringe pump. The pressure of the nitrogen was up to 20 bar, and directly proportional to the viscosity of the crude oil. By opening valve A, the crude oil pressurised by nitrogen flowed through the suction tube in the mixer, entering the circulation loop, and flowed out from the system through value C. When the crude oil constantly dripped down from valve C, indicating the gear pump and rheometer were full of oil, the system was confirmed to be primed. Valve F was then opened to release the nitrogen gas. The remaining nitrogen gas was removed by evacuation.

To prime the system with the DG35.12/Pr pressure cell, valves A, D, F, I, and G in Figure 5-2 were closed and valve C opened. Then by opening valves H and E, the compressed nitrogen gas was introduced into the mixer. The pressurised oil flowed into the circulation loop through the suction tube, and entered the DG35.12/Pr pressure cell through the inlet hole at the bottom of the inner cylinder (see Figure 5-2). After the oil immersed the inner part of the double gap and started to flow down through the pressure cell outlet, valve F was opened to release the pressure. Then the gear pump was turned on, and its rotational speed was carefully adjusted to ensure that the inlet flow rate was less than the outlet flow rate, to prevent the oil from overflowing. After a suitable rotational speed was found and the oil constantly dripped down from valve C, the system was confirmed to be primed. The remaining nitrogen gas was removed by evacuation.

5.1.6 Testing the Circulation System

The complete circulation system was tested with a reference fluid to investigate its performance. The circulation system with CC29/Pr pressure cell was tested with squalane and its saturated mixture with CO$_2$ at 25 °C, while the circulation system with DG35.12/Pr was tested with squalane at temperatures from 22 °C to 40 °C. A comparison between the viscosity measurements in this work and literature values gives a clear indication of the system performance.

The squalane sample used in the test was sourced from Sigma-Aldrich with a purity of 99%, and the CO$_2$ (mole fraction $x \geq 0.99995$) was obtained from BOC. Both were used without further purification.

In the case of the complete system with CC29/Pr, the viscosity measurement of pure squalane was performed at 25 °C and 1 bar. As shown in Figure 5-17, the viscosity of pure squalane is independent of shear rate, behaving as a Newtonian fluid. When CO$_2$ was mixed with squalane at 25 °C and 4.3 bar, the saturated mixture had a lower viscosity than pure squalane, but also behaved as a Newtonian fluid. Compared to the literature values, the measurement errors for pure squalane and CO$_2$-squalane mixture are 2.4% and 3.8%, respectively. The literature value of pure squalane viscosity was obtained from Ciotta et al. [115] while that of the CO$_2$ + squalane mixture was extrapolated from Tomida et al. [116]
Experimental Setup and Procedure

and Chai et al. [117]. In addition, the pressure cell gives a good measurement at a shear rate of 500 1/s. It indicates that shear rates up to 500 1/s do not cause any flow instabilities in the pressure cell, and the measurement is reliable.

In the case of the complete system with DG35.12/Pr, the viscosity measurement was performed at atmospheric pressure, and temperatures from 22 °C to 40 °C. As illustrated in Figure 5-18 the measurement shows that squalane behaves as a Newtonian fluid at all temperatures. Compared with the literature [115], the average measurement error is 3.2%.

Figure 5-17. Viscosity measurement error of the complete circulation system with CC29/Pr pressure cell for squalane. ◆, 1 bar, pure squalane; ■, 4.3 bar, squalane saturated with CO₂.

Figure 5-18. Viscosity measurement error of the complete circulation system with DG35.12/Pr pressure cell for squalane at atmospheric pressure. ◆, 22 °C; ■, 25 °C; ▲, 40 °C.
Experimental Setup and Procedure

5.2 View Cell System for Phase Behaviour Measurement

5.2.1 Apparatus Description

The phase behaviour experiments are carried out in a view cell (CORE LAB’s VC-series) placed in an oven, as shown in Figure 5-19. The view cell was kindly provided by A. Wilson (Schlumberger Gould Research). The oven is a Binder’s ED 115 with a temperature range up to 300 °C and temperature fluctuations of ± 0.4 °C. The view cell contains two opposed glass windows, between which there is a 4.5×2.5×8.8 cm chamber where the tested fluid could be observed optically. To rapidly reach equilibrium, the cell is equipped with a magnetic stirrer coupled to a rotating magnet driven by an electric motor. By mounting a light source to one side and a SRL camera with a borescope to the other side of the cell, the fluid can be observed and photographed and the phase behaviour information can be recorded. The borescope is an Olympus Series 5 rigid borescope with a diameter of 10 mm and length of 38 cm. It has a field of view of 50° and is connected to an optical zoom adaptor. The optical zoom adaptor was adjusted to its highest magnification to record the details of fluid phase behaviour. Because of the magnification, the images taken only cover the central section of the view cell, which is about 50% of the window height. In a typical experiment the crude oil will be first loaded into the view cell and then CO₂ is introduced from the syringe pump. The system pressure is controlled by the CO₂ syringe pump, while the temperature is controlled by the oven. The equilibrium saturation of the crude oil with CO₂ is confirmed by continuous measurements of the pump volume after a step in pressure until no further changes are observed.
Experimental Setup and Procedure

Figure 5-19. Schematic of the view cell system.

Figure 5-20. View cell system.
Experimental Setup and Procedure

5.2.2 Solubility Measurement Using The View Cell System

5.2.2.1 Measurement Principle

The view cell setup can be used to measure the amount of CO$_2$ dissolved into the crude oil under certain assumptions, and consequentially the CO$_2$ solubility. The accuracy might not be as good as standard PVT measurements, but the advantage is that such a setup is capable to handle all kinds of crude oils including very heavy crudes. There are two operation protocols that have been used to measure the CO$_2$ solubility, each corresponding to different assumptions. In this section, a detailed description is given for each protocol and the assumptions underlined.

5.2.2.1.1 Protocol 1 (RH)

The scheme of the view cell setup is illustrated by Figure 5-21. A ball valve is installed at the middle of the pipeline and used to isolate the view cell and syringe pump, namely section ① and ②, respectively.

![Figure 5-21. The scheme of the equipment setup used to measure the gas solubility in liquid by protocol 1. Valve closed, no stirring.](image)

In a typical experiment, a specific mass of crude oil, $m_{oil}$, is loaded into the view cell first. The remaining volume of the system is then evacuated for 15 minutes to remove the air. Then the valve in the middle is closed and CO$_2$ is introduced to fill up the syringe pump. Because of the additional gas, the pressure in section ② will be higher than that in section ①, $P_2 > P_1$. Furthermore, the temperature of the syringe pump is kept constant at $T_2$ by a chiller, while the view cell temperature, $T_1$, is controlled by the oven. $T_1$ and $T_2$ can be different from each other.
Experimental Setup and Procedure

Figure 5-22. The scheme of the equipment setup used to measure the gas solubility in liquid by protocol 1. Valve open, no stirring.

After the temperature stabilised, the valve is opened to introduce the gas from the syringe pump to the mixer and equalise the pressures, as shown in Figure 5-22. Although the gas now contacts the liquid, if the gas diffusion rate into the liquid is small, the pressure drop due to the gas diffusion is negligible given that there is no stirring and the mixing mechanism at this stage is diffusion only. The pump is then set to operate in constant pressure mode with the desired pressure value, $P$. If the pressure is different from the desired value, the syringe pump moves its piston to adjust the system pressure to the desired value.

Figure 5-23. The scheme of the equipment setup used to measure the gas solubility in liquid by protocol 1. Valve open, stirring on.

After the system pressure stabilises, the stirrer is turned on to start the mixing, as shown in Figure 5-23. The mixing causes CO$_2$ to dissolve into the oil and the pump compensates to keep pressure constant, resulting in a volume change in the syringe pump. After equilibrium is reached (24+ hour operation), the volume change in the syringe pump, $\Delta V = V_{2,1} - V_{2,2}$, is recorded. Given that the temperature and
Experimental Setup and Procedure

Pressure inside the syringe pump were kept constant, the density of the \( \text{CO}_2, \rho_{\text{CO}_2}, \) inside the pump was found from the NIST WebBook [105] and hence the mass of \( \text{CO}_2 \) injected into the vessel could be determined as \( m_{\text{CO}_2} = \rho_{\text{CO}_2} \Delta V \). Thus the solubility can be calculated as \( x_{\text{CO}_2} = m_{\text{CO}_2}/(m_{\text{CO}_2} + m_{\text{oil}}) \).

5.2.2.1.2 Protocol 2 (MT)

Similar to above, a known mass of oil, \( m_{\text{oil}} \) is first loaded into the view cell, but now the height of the oil level at the cell window is measured by a ruler. Knowing the dimension of the internal chamber of the view cell, it is easy to work out the volume of the loaded oil, and the space above the oil, \( V_{\text{space}} \). The remaining volume of the system is then vacuumed for 15 minutes to remove the air. With the middle valve closed, \( \text{CO}_2 \) is introduced into the syringe pump where the temperature is controlled by the chiller at \( T_2 \). The volume of the \( \text{CO}_2 \) inside the syringe pump is recorded, \( V_{2,1} \).

![Figure 5-24. The scheme of the equipment setup used to measure the gas solubility in liquid by protocol 2. Before stirring](image)

Setting the pump to operate at constant pressure \( P \), the middle valve is opened. The \( \text{CO}_2 \) will flow into the view cell and the pump piston will move up to keep the pressure at the desired value. After the piston settles down to a constant position the stirrer is turned on.
Experimental Setup and Procedure

Figure 5-25. The scheme of the equipment setup used to measure the gas solubility in liquid by protocol 2. After 24 hour stirring

After 24 hour of stirring the oil is saturated by CO₂, the remaining volume of CO₂ in the syringe pump is recorded, $V_{2,2}$. Assuming that the space above the oil in the view cell is filled with pure CO₂, the mass of the CO₂ injected into the view cell before the stirring can be worked out by $m_{CO₂,space} = V_{space} \rho_{CO₂}(T_1)$, where $\rho_{CO₂}(T_1)$ is the density of CO₂ at $T_1$, the temperature of the view cell. Then the total amount of the CO₂ injected into the view cell, including the CO₂ dissolved into the oil, can be calculated by $m_{CO₂,total} = (V_{2,1} - V_{2,2}) \rho_{CO₂}(T_2)$, where $T_2$ is the temperature of the syringe pump. The density data was again obtained from the NIST WebBook [105]. The amount of the CO₂ dissolved into the oil is $m_{CO₂,diss} = m_{CO₂,total} - m_{CO₂,space}$, and thus $x_{CO₂} = \frac{m_{CO₂,diss}}{m_{CO₂,total} + m_{oil}}$.

5.2.2.2 Testing the Solubility Measurement

The solubility of CO₂ in decane at 38 °C and various pressures was measured by protocol 1 (RH) to test the accuracy of the solubility measurement by the view cell system. The following table shows the difference between the CO₂ solubility in decane measured by this method and the values from literature. Compared to Forte et al. [118], the average error is 3.53%. It should be pointed out that the measurement by the view cell system is always higher than the reference value. It is caused by the fact that the reading from the thermocouple of the syringe pump is slightly lower than the actual temperature value. It leads to a higher CO₂ density chosen in the calculation, which gives rise to the overestimation of the amount of CO₂ dissolved. The results show that the setup is able to measure the solubility with reasonable accuracy.
Experimental Setup and Procedure

Table 5-1. Comparison between solubility measurement of CO\(_2\) in decane by this work and the value from literature. The temperature is at 38 °C. The solubility is in g/g.

<table>
<thead>
<tr>
<th>P / bar</th>
<th>This Work</th>
<th>Ref. [119]</th>
<th>Difference</th>
<th>Ref. [118]</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.1029</td>
<td>0.1021</td>
<td>0.83%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>0.2175</td>
<td>0.2058</td>
<td>5.69%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>0.3062</td>
<td>0.3095</td>
<td>1.09%</td>
<td>0.3111</td>
<td>1.60%</td>
</tr>
<tr>
<td>40</td>
<td>0.4218</td>
<td>0.4132</td>
<td>2.07%</td>
<td>0.3966</td>
<td>6.36%</td>
</tr>
<tr>
<td>50</td>
<td>0.5371</td>
<td>0.5170</td>
<td>3.89%</td>
<td>0.5064</td>
<td>6.06%</td>
</tr>
<tr>
<td>60</td>
<td>0.6413</td>
<td>0.6207</td>
<td>3.31%</td>
<td>0.6407</td>
<td>0.09%</td>
</tr>
<tr>
<td>Average</td>
<td>3.21%</td>
<td>Average</td>
<td>3.53%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.2.3 Discussion of Density Measurement Using The View Cell System

Theoretically, the mixture density can also be measured using the view cell. A certain amount (\(m_{\text{oil,1}}\)) of the crude oil sample is loaded into the view cell. From a scale placed in front of the view cell window, the height of the oil phase can be measured. Knowing the internal dimensions of the sample chamber of the view cell (from its data sheet), the volume of the oil phase, \(V_{\text{oil,1}}\), and the volume above the oil phase, which is occupied by CO\(_2\), \(V_{\text{CO2,1}}\), can be worked out. The total mass of CO\(_2\) injected in the view cell, \(m_{\text{CO2,1}}\), including both the CO\(_2\) dissolved into the oil and that occupying the volume above the oil phase, can be measured through the volume change in the syringe pump. The total mass balance in the view cell is

\[
m_{\text{oil,1}} + m_{\text{CO2,1}} = \rho_{\text{oil}}V_{\text{oil,1}} + \rho_{\text{CO2}}V_{\text{CO2,1}}
\]

(5.2)

where \(\rho_{\text{oil}}\) and \(\rho_{\text{CO2}}\) are the density of oil rich phase and CO\(_2\) rich phase, respectively. The mass balance of CO\(_2\) is given by

\[
m_{\text{CO2,1}} = w_{\text{CO2}}^{\text{oil}}\rho_{\text{oil}}V_{\text{oil,1}} + w_{\text{CO2}}^{\text{CO2}}\rho_{\text{CO2}}V_{\text{CO2,1}}
\]

(5.3)

where \(w_{\text{CO2}}^{\text{oil}}\) and \(w_{\text{CO2}}^{\text{CO2}}\) are the mass compositions of CO\(_2\) in the oil rich phase and CO\(_2\) rich phase respectively. If the experiment is then repeated with a different loading of crude oil, \(m_{\text{oil,2}}\) then we have

\[
m_{\text{oil,2}} + m_{\text{CO2,2}} = \rho_{\text{oil}}V_{\text{oil,2}} + \rho_{\text{CO2}}V_{\text{CO2,2}}
\]

(5.4)

\[
m_{\text{CO2,2}} = w_{\text{CO2}}^{\text{oil}}\rho_{\text{oil}}V_{\text{oil,2}} + w_{\text{CO2}}^{\text{CO2}}\rho_{\text{CO2}}V_{\text{CO2,2}}
\]

(5.5)

As long as the temperature and pressure are the same for both experiments, for a given crude oil sample the densities in Equation (5.2) and (5.4), and mass compositions in Equation (5.3) and (5.5) are the same. Therefore, solving these two systems of equations can provide the values of the density and the CO\(_2\) composition of each phase.
However, the accuracy of the above method is very sensitive to the accuracy of the volume measurement. To illustrate this, given that the total mass in the view cell is \( m_{T,1} = m_{oil,1} + m_{CO2,1} \) and \( m_{T,2} = m_{oil,2} + m_{CO2,2} \), solving Equation (5.2) and (5.4) leads to

\[
\rho_{CO2} = \frac{m_{T,2}V_{oil,1} - m_{T,1}V_{oil,2}}{V_{oil,1}V_{CO2,2} - V_{CO2,1}V_{oil,2}} \tag{5.6}
\]

Knowing that the total volume of the view cell is a constant \( V_T \), and \( V_T = V_{oil,1} + V_{CO2,1} = V_{oil,2} + V_{CO2,2} \), Equation (5.6) can be reduced to

\[
\rho_{CO2} = \frac{m_{T,2}V_{oil,1} - m_{T,1}V_{oil,2}}{V_T(V_{oil,1} - V_{oil,2})} \tag{5.7}
\]

Given that mass measurement is reasonably accurate and the focus here is the effect of the volume measurement, the mass is treated as a constant. Then the standard deviation of \( \rho_{CO2} \), \( \sigma_{\rho} \), can be approximated by the propagation of errors formula [120]:

\[
\sigma_{\rho}^2 \approx \left( \frac{\partial \rho_{CO2}}{\partial V_{oil,1}} \right)^2 \sigma_{V_{oil,1}}^2 + \left( \frac{\partial \rho_{CO2}}{\partial V_{oil,2}} \right)^2 \sigma_{V_{oil,2}}^2 + 2 \left( \frac{\partial \rho_{CO2}}{\partial V_{oil,1}} \right) \left( \frac{\partial \rho_{CO2}}{\partial V_{oil,2}} \right) \sigma_{V_{oil,1}V_{oil,2}} \tag{5.8}
\]

where \( \sigma_{V_{oil,1}} \) is the standard deviation of \( V_{oil,1} \), and \( \sigma_{V_{oil,1}V_{oil,2}} \) the covariance between \( V_{oil,1} \) and \( V_{oil,2} \). Given that the errors in measurement of \( V_{oil,1} \) and \( V_{oil,2} \) are independent, \( \sigma_{V_{oil,1}V_{oil,2}} = 0 \), Equation (5.8) is simplified to

\[
\sigma_{\rho}^2 \approx \left( \frac{\partial \rho_{CO2}}{\partial V_{oil,1}} \right)^2 \sigma_{V_{oil,1}}^2 + \left( \frac{\partial \rho_{CO2}}{\partial V_{oil,2}} \right)^2 \sigma_{V_{oil,2}}^2 \tag{5.9}
\]

The measurement of the oil volume is done by reading the height of the oil phase, \( h_i \), and then by multiplying with the dimension of the view cell chamber. So \( V_{oil,i} = W \times L \times h_i \) where \( W \) and \( L \) are the constant width and length of the view cell chamber, respectively, and the subscript \( i \) is for different oil loading. The standard deviation of \( V_{oil,i} \) is given by:

\[
\sigma_{V_{oil,i}}^2 = WL \sigma_{h_i}^2 \tag{5.10}
\]

where \( \sigma_{h_i} \) is the standard deviation of \( h_i \). In our experiments we estimate \( \sigma_{h_i} = \pm 1 \text{ mm} \).

The error propagation of Equation (5.7) was examined using the literature data. Assigning two different liquid loadings, one can calculate the total mass for two loadings using Equation (5.2) and (5.4) given the density measurements provided in the literature. Then the partial differential terms in Equation (5.9) can be evaluated, and also the standard deviation of density in Equation (5.9). By comparing the
Experimental Setup and Procedure

calculated standard deviation \( \sigma_\rho \) and the measurement value given in the literature \( \rho_{\text{literature}} \), one can judge the measurement error of Equation (5.7) using the relative deviation, \( \sigma_\rho/\rho_{\text{literature}} \).

Day et al. have measured both the vapour and liquid phase densities of a CO\(_2\) and ethanol mixture at equilibrium [121], and their data was used to evaluate Equation (5.7). At pressures below 30 bar, the average relative deviation of vapour phase density for \( \sigma_{\text{h}} = \pm 1 \) mm is 116\%, but if \( \sigma_{\text{h}} = \pm 0.01 \) mm it is 1.2\%. This means that a normal ruler cannot provide the accuracy required by Equation (5.7) to give an acceptable density value, but a travelling microscope would be required. As this was not available, the view cell was not used to measure the mixture density.
CHAPTER 6  EXPERIMENTAL RESULTS FOR HEAVY CRUDE OIL

6.1 Materials

Five samples were used in the measurement, as shown in Table 6-2. The diluted crude oils were mixtures of different amounts of toluene and Zuata heavy crude oil provided by Shell, Netherlands, with an \( n \)-heptane asphaltene content of 18.8 w%. The key properties of the heavy crude oil are listed in Table 6-1. The toluene used was sourced from Sigma-Aldrich with a purity of 99.8%. The crude oil and toluene were used without further treatment. The compositions of the diluted crude oil samples and the range of experimental conditions are shown in Table 6-2.

Table 6-1. The characteristics of the Zuata crude oil used in this study. The data is provided by Shell.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
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<tbody>
<tr>
<td>API Gravity</td>
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</tr>
<tr>
<td>Barrel Factor (bbl/t)</td>
<td>6.27</td>
</tr>
<tr>
<td>Total Sulphur (% wt)</td>
<td>3.35</td>
</tr>
<tr>
<td>Reid Vapour Pressure (kPa)</td>
<td>1</td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>24</td>
</tr>
<tr>
<td>Existing H(_2)S Content (ppm)</td>
<td>-</td>
</tr>
<tr>
<td>Potential H(_2)S Content (ppm)</td>
<td>115</td>
</tr>
<tr>
<td>Potential HCl Content (ppm)</td>
<td>-</td>
</tr>
<tr>
<td>Calc. Gross Cal. Value (kJ/kg)</td>
<td>41855</td>
</tr>
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</table>

Table 6-2. The list of samples for viscosity measurement and their measurement conditions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Composition</th>
<th>Measurement Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Crude Oil</td>
<td>100 w% Zuata Crude Oil</td>
<td>( T / ^{\circ} \text{C} ) = 50, ( P / \text{bar} ) = 1 ~ 220, ( \gamma / \text{s}^1 ) = 10 ~ 500</td>
</tr>
<tr>
<td>Diluted Crude Oil 1</td>
<td>80 w% Zuata Crude Oil + 20 w% Toluene</td>
<td>( T / ^{\circ} \text{C} ) = 25, ( P / \text{bar} ) = 1 ~ 220, ( \gamma / \text{s}^1 ) = 40 ~ 500</td>
</tr>
<tr>
<td>Diluted Crude Oil 2</td>
<td>85 w% Zuata Crude Oil + 15 w% Toluene</td>
<td>( T / ^{\circ} \text{C} ) = 25, ( P / \text{bar} ) = 1 ~ 220, ( \gamma / \text{s}^1 ) = 40 ~ 500</td>
</tr>
<tr>
<td>Diluted Crude Oil 3</td>
<td>90 w% Zuata Crude Oil + 10 w% Toluene</td>
<td>( T / ^{\circ} \text{C} ) = 40 ~ 50, ( P / \text{bar} ) = 1 ~ 220, ( \gamma / \text{s}^1 ) = 40 ~ 500</td>
</tr>
<tr>
<td>Diluted Crude Oil 4</td>
<td>70 w% Zuata Crude Oil + 30 w% Toluene</td>
<td>( T / ^{\circ} \text{C} ) = 50, ( P / \text{bar} ) = 1 ~ 220, ( \gamma / \text{s}^1 ) = 35 ~ 250</td>
</tr>
</tbody>
</table>
6.2 Measurement Results

6.2.1 Rheology Measurement

The original crude oil, diluted crude oil 1, 2, and 3 were studied with the CC29/Pr pressure cell. The rheological measurement started with a 0.5 min pre-shearing at 10 \text{s}^{-1} followed by 1 min resting time. Different pre-shearing rate (20 \text{s}^{-1}) and resting time (2 min) were tested but showed no effect on the results. In each measurement the shear rates were varied from 500 \text{s}^{-1} to 10 \text{s}^{-1} with a shear rate adjusting time of 0.2 min. From high to low shear rate, the measurement duration at each shear rate step was logarithmically increased from 0.5 min to 1 min, excluding the shear rate adjusting time. The entire measurement lasted for around 9 min. Only measurements decreasing in shear rate were performed.

The viscosity measurement of the original crude oil and its mixture with CO\textsubscript{2} is shown in Figure 6-1 and Table 6-3. The red dashed line in Figure 6-1 shows the minimum shear rate at a given viscosity recommended by the manufacturer. Viscosity data below this limit showed significant measurement noise. Figure 6-2 illustrates the relative viscosity, which is the ratio of a given viscosity value, $\eta$, to the viscosity at the lowest shear rate, $\eta_{\text{min}}$. The dashed lines in Figure 6-2 represent the measurement fluctuation (about ±3%) within the data, which is caused by the bearing friction of the measuring system.

![Figure 6-1](image)

Figure 6-1. Viscosity measurement for the original heavy crude oil with CO\textsubscript{2} at 50 °C and various shear rates. ---, lower shear rate limit; ○, 1 bar; ■, 20 bar; ●, 40 bar; □, 60 bar; ●, 80 bar; □, 100 bar; x, 120 bar; ■, 140 bar; ●, 160 bar; □, 180 bar; x, 220 bar.
Table 6-3. The rheology experiment data of the original crude oil saturated with CO$_2$ at temperature of 50 °C.

<table>
<thead>
<tr>
<th>$P$ / bar</th>
<th>Ambient</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>120</th>
<th>140</th>
<th>160</th>
<th>180</th>
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<td></td>
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</tr>
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<td>118.2</td>
<td>79.2</td>
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<td>118.5</td>
<td>79.5</td>
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<td>74.5</td>
<td>77.5</td>
<td>79.2</td>
<td>83.5</td>
</tr>
</tbody>
</table>

At atmospheric pressure, the heavy crude oil behaved as a non-Newtonian fluid, becoming slightly shear thinning, as can be seen in Figure 6-2, at shear rates above 30 s$^{-1}$. At 20 bar, when significant CO$_2$ has dissolved into the crude oil, the Newtonian region is extended to a shear rate of 85 s$^{-1}$. At higher shear rates the shear thinning effect can still be observed, but with a smaller gradient than at atmospheric pressure. At 40 bar, with more CO$_2$ dissolved, the shear thinning effect is further weakened and the viscosity change is within the measurement fluctuation range. At higher pressure, the shear thinning effect completely disappeared, and the viscosity became independent of shear rate. Furthermore, as illustrated in Figure 6-3, up to 120 bar the low shear rate viscosity decreased exponentially with increasing pressure, while beyond 120 bar the logarithm of viscosity increased with pressure at a gentle gradient.
Experimental Results for Heavy Crude Oil

Figure 6-2. The relative viscosity for the original crude oil with CO\(_2\) at 50 °C and various shear rates. ———, measurement fluctuation range; ●, ambient pressure; ●, 20 bar; ○, 40 bar; Δ, 60 bar; ●, 80 bar; ●, 100 bar; ×, 120 bar; ×, 140 bar; ×, 160 bar; ×, 180 bar; ×, 220 bar.

Figure 6-3. Low shear viscosity of Zuata heavy crude oil and its mixture with CO\(_2\) at various pressures.

Figure 6-4 to Figure 6-8 illustrate the viscosity measurements of the diluted crude oil 1, 2, and 3 at pressures up to 220 bar. In Figure 6-4 and Figure 6-5 the measurements at atmospheric pressure represent the viscosities of the diluted crude oils without CO\(_2\) dissolved at 25 °C, and the value was 157.8 mPa·s for the diluted crude oil 1 and 354.0 mPa·s for the diluted crude oil 2 (the values can be found in Table 6-4 and Table 6-5). The increase of toluene by 5 w% reduced the crude oil viscosity by around 55%. Additionally, Figure 6-6 to Figure 6-8 show the measurements of diluted crude oil 3 performed at temperatures from 40 to 50 °C, which was above the critical temperature of CO\(_2\). At atmospheric pressure, the viscosity of diluted crude oil 3 was 523.6 mPa·s, 331.0 mPa·s and 289.7
mPa·s at temperature of 40 °C, 45 °C and 50 °C respectively, an exponential decrease in viscosity with increasing temperature.

The data in Figure 6-4 to Figure 6-8 all fall on horizontal lines showing that the viscosities of all the diluted crude oils were Newtonian, i.e. independent of shear rate. When the pressure increased, more and more CO₂ dissolved into the crude oil and reduced the mixture viscosity significantly. However, from 90 bar the crude oil viscosity started to increase with CO₂ pressure. As a possible explanation, while toluene does not cause asphaltene precipitation, CO₂ can (ref needed). Also, suspended solid asphaltene particles could be present [122]. However our measurement shows that the asphaltene particles precipitated in these three diluted crude oils by CO₂ dissolution did not cause non-Newtonian effects. Therefore, although the dissolved CO₂ could cause the precipitation of asphaltene, the dispersed particles did not appear to form an interacting network for these crude oils.
Experimental Results for Heavy Crude Oil

Table 6-4. The rheology experiment data of diluted crude oil 1 saturated with CO₂ at temperature of 25 °C.

<table>
<thead>
<tr>
<th>$P$ / bar</th>
<th>Ambient</th>
<th>10</th>
<th>40</th>
<th>60</th>
<th>100</th>
<th>140</th>
<th>220</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ / 1/s</td>
<td>$\eta$ / mPa·s</td>
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</table>

Figure 6-5. Viscosity measurement for diluted crude oil 2 with CO₂ at 25 °C and various shear rates. ---, lower shear rate limit; ▲, 1 bar; ▲, 15 bar; ▲, 30 bar; ▲, 45 bar; ×, 60 bar; ×, 100 bar; ×, 140 bar; ×, 180 bar; ×, 220 bar.
Experimental Results for Heavy Crude Oil

Table 6-5. The rheology experimental data of diluted crude oil 2 saturated with CO₂ at temperature of 25 °C.

<table>
<thead>
<tr>
<th>$P$ / bar</th>
<th>Ambient</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
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<tbody>
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<td>$\gamma$ / 1/s</td>
<td>$\eta$ / mPa·s</td>
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Figure 6-6. Viscosity measurement for diluted crude oil 3 with CO₂ at 40 °C and various shear rates. – – –, lower shear rate limit; ■, 1 bar; ■, 20 bar; ■, 40 bar; ■, 60 bar; ■, 80 bar; X, 100 bar; X, 120 bar; X, 140 bar; X, 160 bar; X, 180 bar; X, 220 bar
### Experimental Results for Heavy Crude Oil

Table 6-6. The rheology experiment data of diluted crude oil 3 saturated with CO\(_2\) at temperature of 40 °C.

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Figure 6-7. Viscosity measurement for diluted crude oil 3 with CO\(_2\) at 45 °C and various shear rates. – – –, lower shear rate limit; ■, 1 bar; ■, 20 bar; ■, 40 bar; ■, 60 bar; ■, 80 bar; ■, 90 bar; ■, 100 bar; ■, 120 bar; ■, 140 bar; ■, 160 bar; ■, 180 bar; ■, 220 bar.
### Table 6-7. The rheology experiment data of diluted crude oil 3 saturated with CO$_2$ at temperature of 45 °C.

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**Figure 6-8.** Viscosity measurement for diluted crude oil 3 with CO$_2$ at 50 °C and various shear rates. ––, lower shear rate limit; ■, 1 bar; □, 20 bar; □, 40 bar; □, 60 bar; □, 80 bar; □, 90 bar; ×, 100 bar; ×, 120 bar; ×, 140 bar; ×, 160 bar; ×, 180 bar; ×, 220 bar.
Experimental Results for Heavy Crude Oil

Table 6.8. The rheology experiment data of diluted crude oil 3 saturated with CO$_2$ at temperature of 50 °C.

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Figure 6-9 summarizes the viscosity measurements of the diluted crude oils and their CO$_2$ saturated mixtures. For the CO$_2$ saturated mixtures, the change in the pressure dependence of viscosity can be separated into two main regions. Firstly, as the CO$_2$ pressure was increased from zero, a region of exponential decrease in viscosity was observed. Secondly, a region where the viscosity increased with pressure was seen at higher pressures. Between these two regions is a transition point where the viscosity reached a minimum. In addition, the transition point appeared at around 50 bar at 25 °C for diluted crude oil 1 and 2. However for diluted crude oil 3, the transition point appeared at higher pressure when the temperature is higher.
Further interesting results were obtained from the viscosity measurement of diluted crude oil 4 at 50 °C. Diluted crude oil 4 was studied with the DG35.12/Pr pressure cell. Before the measurement, there was a 0.5 min pre-shearing at 10 s⁻¹ followed by 1 min resting time. Different pre-shearing rate (20 s⁻¹) and resting time (2 min) were tested but showed no effect on the results. In each measurement the shear rates were decreased from 250 s⁻¹ and 10 s⁻¹ with a shear rate adjusting time of 0.2 min. From high to low shear rate, the measurement duration at each shear rate step was logarithmically increased from 0.3 min to 1 min, excluding the shear rate adjusting time. The entire measurement lasted for around 8 min. Only descending measurements were performed.

The viscosity measurements were done with two samples of the diluted crude oil 4, both using the crude oil from the same barrel. After the preparation, both Sample (a) and (b) were kept in a glass container. However, Sample (a) has been stored for more than one year before the experiment, and Sample (b) for one month. These two samples showed different rheological results. As seen in Figure 6-10, at ambient pressure, Sample (a) of diluted crude oil 4 behaved as a Newtonian fluid because the viscosity was independent of shear rate. However, for pressure from 30 to 60 bar, the fluid became slightly shear thinning with a Newtonian plateau at high shear rate. This shear thinning effect is more clearly illustrated in Figure 6-11, which shows the relative viscosities at different pressures. For pressures above 60 bar, the fluid behaved as a Newtonian fluid again. Seifried et al. found that the onset point of asphaltene precipitation for Sample (a) of diluted crude oil 4 was between 80 to 100 bar [123]. Therefore, the cause of the non-Newtonian effect was not the asphaltene components precipitating out.
Experimental Results for Heavy Crude Oil

Figure 6-10. Viscosity measurement for Sample (a) of diluted crude oil 4 with CO$_2$ at 50 ºC and various shear rates. — lower shear rate limit; ◇, 1 bar; ◇, 10 bar; ◇, 20 bar; ◇, 30 bar; ◇, 40 bar; ◇, 50 bar; ◇, 60 bar; ◇, 70 bar.

Figure 6-11. The relative viscosity for Sample (a) of diluted crude oil 4 with CO$_2$ at 50 ºC and various shear rates. — measurement fluctuation range; ◇, 1 bar; ◇, 10 bar; ◇, 20 bar; ◇, 30 bar; ◇, 40 bar; ◇, 50 bar; ◇, 60 bar; ◇, 70 bar.
Experimental Results for Heavy Crude Oil

Figure 6-12. Viscosity measurement for Sample (a) of diluted crude oil 4 with CO₂ at 50 °C and various shear rates. – – –, lower shear rate limit; ×, 80 bar; ×, 100 bar; ×, 120 bar; ×, 140 bar; ×, 160 bar; ×, 180 bar; ×, 200 bar; ×, 220 bar.

Table 6-9. The rheology experiment data of Sample (a) of diluted crude oil 4 with CO₂ at temperature of 50 °C.

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Experimental Results for Heavy Crude Oil

Table 6-10. The rheology experiment data of Sample (a) of diluted crude oil 4 with \( \text{CO}_2 \) at temperature of 50 °C.

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<td>8.602</td>
<td>9.439</td>
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<tr>
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<td>137.4</td>
<td>3.089</td>
<td>4.881</td>
<td>5.744</td>
<td>6.468</td>
<td>7.3</td>
<td>8.103</td>
<td>8.612</td>
</tr>
<tr>
<td></td>
<td>177.6</td>
<td>3.073</td>
<td>4.858</td>
<td>5.693</td>
<td>6.43</td>
<td>7.241</td>
<td>8.034</td>
<td>8.64</td>
</tr>
<tr>
<td></td>
<td>210.7</td>
<td>3.055</td>
<td>4.856</td>
<td>5.66</td>
<td>6.47</td>
<td>7.34</td>
<td>8.078</td>
<td>8.706</td>
</tr>
<tr>
<td></td>
<td>229.5</td>
<td>3.071</td>
<td>4.865</td>
<td>5.725</td>
<td>6.477</td>
<td>7.246</td>
<td>8.037</td>
<td>8.717</td>
</tr>
<tr>
<td></td>
<td>249.9</td>
<td>3.075</td>
<td>4.871</td>
<td>5.672</td>
<td>6.459</td>
<td>7.234</td>
<td>8.089</td>
<td>8.691</td>
</tr>
</tbody>
</table>

We speculate that the non-Newtonian behaviour was caused by micelles formed by the asphaltene molecules under \( \text{CO}_2 \) dissolution. A micelle is an aggregate of molecules such as surfactants and asphaltene which self-associate into a geometric shape in a solution [124]. This molecular assembly or aggregation occurs only when the amount of molecules in the solution exceeds the critical micelle concentration (CMC), which can be affected by temperature and the solvent composition [125]. The effect of \( \text{CO}_2 \) dissolution on the CMC of the micelles formed by a surfactant was studied by Zhao et al. [126]. Their CMC measurements of lecithin micelles in cyclohexane at different \( \text{CO}_2 \) pressures revealed that, in a low-pressure range, the dissolved \( \text{CO}_2 \) enhanced the micelle formation by reducing the CMC, but the \( \text{CO}_2 \) destabilised the micelles in the high pressure range by increasing the CMC. They suggested that \( \text{CO}_2 \) affected the CMC through two competing factors [125]. One is that \( \text{CO}_2 \) inserted into the interfacial area of the micelles, providing additional stability for the micelles and thus enhancing their formation. On the other hand, the \( \text{CO}_2 \) in the solvent decreased the hydrophobicity of the solvent, which was in favour of a higher CMC.

Since some literature has shown that petroleum asphaltenes can form micelles in aromatic solvents such as toluene [124], the asphaltene molecules in sample (a) may also form micelles, which were affected
Experimental Results for Heavy Crude Oil

by the dissolved CO\textsubscript{2} in a way similar to the lecithin/cyclohexane system studied by Zhao et al. [126]. In that case, the non-Newtonian behaviour observed in Figure 6-10 can be explained as follows. The addition of CO\textsubscript{2} reduced the CMC of asphaltene micelles by interacting with asphaltene molecules, and consequently more and more micelles were formed. At pressures from 30 to 60 bar, the number of asphaltene micelles was so high that the distance between micelles were within the effective range of the van der Waals attraction force. Thus, an associating network was formed among the micelles and caused the shear thinning effect. However, when the pressure was above 60 bar, CO\textsubscript{2} started to increase the CMC by its effect on the solvent or the non-asphaltene molecules. Thus, the asphaltene micelles were destabilised, which led to the disappearance of the associating network. It must be pointed out that further investigations need to be done to reveal the true reason of the non-Newtonian behaviour and the details of the CO\textsubscript{2} effect. However, given time and equipment limitations, these studied were not carried out.

Another speculation about the cause of the non-Newtonian behaviour is provided here. When the CO\textsubscript{2} pressure was between 30 and 60 bar, there was a CO\textsubscript{2} rich liquid phase generated, which led to the mixture forming a liquid-liquid-vapour (LLV) system. The mixing mechanism, stirring and circulation, of the measurement system gave rise to an emulsion of these two liquids, and the CO\textsubscript{2} liquid phase might be stabilised by the asphaltene in the crude oil. This emulsion illustrated non-Newtonian behaviour because the dispersed phase, the CO\textsubscript{2} rich liquid, formed an associated network: the CO\textsubscript{2} droplets coalesced and/or broke down under shear. However, with more CO\textsubscript{2} added into the mixture at pressure above 60 bar, the two liquid phases became miscible again, and led to a liquid-vapour (LV) mixture composed of a crude oil rich liquid in equilibrium with a CO\textsubscript{2} rich vapour. The crude oil rich liquid behaved as a Newtonian fluid. Such LLV mixtures between CO\textsubscript{2} and crude oil, and the transition from LLV to LV were reported in literature [22, 24].

Figure 6-13 summarizes the viscosity of Sample (a) of diluted crude oil 4 at the high shear rate of the CO\textsubscript{2} saturated mixtures. For pressure from 1 to 80 bar, the dissolved CO\textsubscript{2} caused the diluted crude oil mixtures to have an exponential decrease in viscosity with increased CO\textsubscript{2} pressure, whereas above 100 bar the viscosities was increased with pressure.
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Figure 6-13. Viscosity at high shear rate for diluted crude oil 4 with CO₂ at 50 °C and various pressures. ●, Sample (a); ●, Sample (b).

However, when the viscosity measurement was repeated for a newly prepared diluted crude oil 4, (Sample (b)), the non-Newtonian behaviour disappeared, as shown in Figure 6-14 and Figure 6-15. In the pressure range from 30 to 60 bar where the shear thinning effect was observed in Sample (a), the viscosity of Sample (b) was independent of shear rate, demonstrated by the straight line across the shear rates. On the other hand, as Sample (a), the viscosity of Sample (b) decreased with increasing pressure until 80 bar. Above 80 bar the viscosity increased with increasing pressure.

Figure 6-14. Viscosity measurement for Sample (b) of diluted crude oil 4 with CO₂ at 50 °C and various shear rates in the second run. – – – lower shear rate limit; ●, 1 bar; ●, 20 bar; ●, 40 bar; ●, 60 bar; ●, 80 bar; ●, 100 bar; ●, 120 bar; ●, 140 bar; ●, 160 bar; ●, 180 bar; ●, 220 bar.
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Figure 6-15. The relative viscosity for Sample (b) of diluted crude oil 4 with CO₂ at 50 °C and various shear rates. — —, measurement fluctuation range; ◆, 1 bar; ◆, 20 bar; ◆, 40 bar; ◆, 60 bar; ◆, 80 bar; ◆, 100 bar; ◆, 120 bar; ◆, 140 bar; ◆, 160 bar; ◆, 180 bar; ◆, 220 bar.

Table 6-11. The rheology experiment data of Sample (b) of diluted crude oil 4 with CO₂ at temperature of 50 °C.

<table>
<thead>
<tr>
<th>P / bar</th>
<th>Ambient</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>120</th>
<th>140</th>
<th>160</th>
<th>180</th>
<th>220</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ / 1/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>24.06</td>
<td>17.89</td>
<td>32.24</td>
<td>17.83</td>
<td>43.2</td>
<td>17.82</td>
<td>11.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>57.89</td>
<td>17.79</td>
<td>11.32</td>
<td>7.27</td>
<td>7.83</td>
<td>8.333</td>
<td>9.054</td>
<td>9.952</td>
<td>11.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>139.3</td>
<td>17.7</td>
<td>11.11</td>
<td>7.04</td>
<td>5.135</td>
<td>3.025</td>
<td>6.823</td>
<td>7.801</td>
<td>8.462</td>
<td>9.207</td>
</tr>
</tbody>
</table>

The comparison between the viscosity measured at the highest shear rate of Sample (a) and that of Sample (b) is illustrated in Figure 6-13. In the viscosity reduction region the two samples show the same trend in pressure dependence. At 100 bar Sample (b) had a higher jump in the viscosity – its viscosity increased by 129% compared to 80 bar, while Sample (a) increased by 57%.

The cause of the difference in the rheological measurement of diluted crude oil 4 could be the difficulty in mixing the oil in the original bulk barrel. Given its extremely high viscosity, the original crude oil sample might be distributed into multiple layers of components after years of storage, due to sedimentation processes. When collected from the barrel and mixed with toluene, the composition of the original crude oil might be different in the two samples, and it consequently led to a difference in the compositions of the diluted samples. Therefore, the difference in the measurement results might be caused by the different compositions in the diluted samples.
Experimental Results for Heavy Crude Oil

6.2.2 Phase Behaviour Measurement

The view cell measurement, see Figure 6-16, of the original crude oil mixed with CO₂ showed a constant volume expansion in the oil rich phase at pressures up to 120 bar. Above 120 bar the volume of the oil rich phase continued to expand with pressure but at much lower rate. The phase behaviour measurement with diluted crude oil 3 is shown in Figure 6-17. From 1 bar to 40 bar, although CO₂ was dissolving into the diluted crude oil, the volume of the oil rich phase did not change. However, above 40 bar, the oil rich phase expanded considerably with pressure up to 100 bar. Above 100 bar, the volume of the oil rich phase was shrinking slightly with increasing pressure, so that the volume at 100 bar was the maximum volume within the measured pressure range. Both the original heavy crude oil and diluted crude oil 3 showed a correlation between the changes in oil rich phase volume and in viscosity: the trend in viscosity changed at the same pressure as that of the oil-rich phase volume.

The result of the phase behaviour experiment with Sample (b) of diluted crude oil 4 is illustrated in Figure 6-18. The experiment with Sample (a) was not performed due to insufficient sample volume. As the pressure increased to 80 bar, more and more CO₂ dissolved into the crude oil phase and the crude oil phase expanded. When the pressure reached 100 bar, a second less dense liquid phase appeared. It can be seen that this second liquid phase was brown and transparent, indicating that it contained some light components extracted from the diluted crude oil by the supercritical CO₂. The volume of the less dense liquid phase increased with pressure up to 160 bar. Faint banding in the images of the second liquid phase suggested that additional liquid phase may have formed.

The phase behaviour measurement also revealed the reason why the viscosity of diluted crude oil 4 experienced a change in pressure dependence. When the pressure reached 100 bar and above, more and more light components in the crude oil were stripped out from the crude oil mixture, increasing the heavy components concentrations in the oil rich phase. This led to a more condensed oil rich phase and increase in viscosity.
Figure 6-16. Phase behaviour at various pressures of CO₂ mixed with the original crude oil at 50 °C. The while dash line marks the level of the crude oil at 1 bar.
Figure 6-17. Phase behaviour at various pressures of CO$_2$ mixed with diluted crude oil 3 at 50 °C. The green dashed line marks the level of the crude oil at 1 bar.
Experimental Results for Heavy Crude Oil

<table>
<thead>
<tr>
<th>Ambient Pressure</th>
<th>10 bar</th>
<th>20 bar</th>
<th>30 bar</th>
<th>40 bar</th>
<th>50 bar</th>
<th>60 bar</th>
<th>70 bar</th>
<th>80 bar</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Images showing phase behaviour at various pressures of CO2 mixed with Sample (b) of diluted crude oil 4 at 50 °C.]

Figure 6-18. Phase behaviour at various pressures of CO2 mixed with Sample (b) of diluted crude oil 4 at 50 °C.
Experimental Results for Heavy Crude Oil

6.2.3 Solubility Measurement

6.2.3.1 Diluted Crude oil 1 and 2

All solubility measurements were performed by protocol 1, described in Section 5.2.2.1.1. Note that the equipment used to perform the solubility measurements on diluted crude oil 1 and 2 were the mixer and syringe pump in the circulation system [127]. At the time when these experiments were performed the view cell system was not constructed. Although the measurement principle was the same as protocol 1, the key difference between this setup and the view cell system was that the visual evidence of the phase behaviour was not available. The measurement procedure is based on the assumption of two phases and any CO$_2$ injected beyond that required to compress the (pure) CO$_2$ vapour into the oil phase. For diluted crude oil 1 and 2, a large amount of CO$_2$ had to be injected into the mixer for a small increase of pressure when the pressure approached 50 bar. As shown in Figure 6-19, this results in an apparent jump in the mass fraction of CO$_2$ assigned to the oil phase. We had a Liquid-Vapour (L-V) system at pressures below 50 bar consisting of a CO$_2$ rich vapour phase and an oil rich liquid phase and in this region the estimates of dissolved CO$_2$ mass fraction in the oil phase were reliable. However, although the saturated vapour pressure of pure CO$_2$ at 25 °C is 64 bar, when the pressure approached 50 bar, a second liquid phase was generated. In this region three phases occur – an oil rich liquid, a CO$_2$ rich liquid mixed with light hydrocarbons extracted from the crude oil, and a CO$_2$ rich vapour – a Liquid-Liquid-Vapour (L-L-V) system. The CO$_2$ rich liquid phase required a large amount of CO$_2$ and caused the jump in Figure 6-19 when the pressure is close to 50 bar. When the pressure was beyond the saturated vapour pressure of CO$_2$, 64 bar, the CO$_2$ was in the liquid phase and we observed a Liquid-Liquid (L-L) system. The phase change phenomena outlined above have also been reported by Orr et al. [25] in their study of the phase behaviour of CO$_2$ with crude oil and with alkanes.
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As mentioned in the literature, in the L-L-V phase, the extracted light hydrocarbons significantly increase the viscosity of the CO₂ rich liquid phase, while the CO₂ dissolved reduced the viscosity of the oil rich phase [25]. Therefore, at 60 bar the viscosity of the resulting mixture of these two liquid phases no longer followed the exponential decrease of the mixture viscosity with pressure increase, but decreases only slightly compared to the previous point which is for a mixture with a L-V phase. When the pressure is above the saturation point of CO₂, the viscosity measured was for a L-L system, and increased at higher pressure.

It is also worth pointing out that Figure 6-19 shows the CO₂ solubilities are different in the two oil mixtures. This is because the toluene mass fractions in the two diluted crude oils are different. As mentioned above the light fractions in the diluted crude oil were extracted in the CO₂ phase. The amount of these light fractions in CO₂ depended on the composition of the diluted crude oil and the toluene mass fraction in particular. The different composition in the CO₂ phase subsequently caused the different phase behaviour.

6.2.3.2 Diluted Crude Oil 3, 4 (Sample (b)) and The Original Crude Oil

The solubility measurements on the original crude oil, diluted crude oil 3 and 4 (Sample (b)) were performed in the view cell system described in Chapter 5.2, and protocol 1 in Section 5.2.2.1.1 was used as the measurement procedure. Figure 6-20 shows the solubility measurements of the original heavy crude oil, diluted crude oil 3 and diluted crude oil 4. The CO₂ solubility increased with increasing toluene content in the crude oil samples. The solubility of diluted crude oil 4 above 80 bar was not calculated, as the oil rich phase separated into two liquid phases (see Figure 6-18). However, this was not the case for the diluted crude oil 3 and the original heavy crude oil, which remained one liquid phase over the entire pressure range accessed. The CO₂ solubility in diluted crude oil 3 and the original crude
Experimental Results for Heavy Crude Oil

oil increased exponentially with pressure from 1 bar to 100 bar. Above 100 bar, the solubility in the original crude oil increased at a smaller rate and became almost linear with pressure, while for diluted crude oil 3 the CO$_2$ solubility above 100 bar became almost constant. The repeatability of the all the measurements was within 4%.

![Graph showing solubility of CO$_2$ in diluted and original crude oils](image_url)

Figure 6-20. The solubility of CO$_2$ in the diluted crude oils and original crude oil at 50 °C and pressure up to 220 bar. ▲, diluted crude oil 4 (Sample 2); ■, diluted crude oil 3; ●, original heavy crude oil.

The CO$_2$ solubility measurements with diluted crude oil 3 and the original crude oil give a further insight into the phenomenon observed through the view cell. As mentioned before, above 100 bar the volume of the oil rich phase of the original crude oil was independent of pressure, while the volume of the oil rich phase of diluted crude oil 3 decreased with pressure. On the other hand, above 100 bar the CO$_2$ solubility in the original crude oil increased with pressure, while that of diluted crude oil 3 showed a negligible increase. It indicates that, at pressures beyond 100 bar, the amount of CO$_2$ dissolved in the original crude oil was large enough to counter the compression effect, and thus to maintain the liquid level of the oil rich phase at the same level under increasing pressure. However, the amount of CO$_2$ dissolved in diluted crude oil 3 was too small to eliminate the compression effect, causing the shrinkage in the oil rich phase.

6.3 Correlations

As discussed above, in the viscosity decrease region the viscosity of the CO$_2$ and crude oil mixture reduced exponentially with increasing pressure, because of CO$_2$ dissolution. The pressure dependence can be described by

$$\ln(\eta_m) = -a_i P + b_i \quad @ \quad P \leq P_{\text{min}}$$

(6.1)
Experimental Results for Heavy Crude Oil

where $P_{\text{min}}$ is the pressure at which the mixture viscosity reaches the minimum. When the pressure is above $P_{\text{min}}$, the viscosity of the mixture increased linearly with pressure:

$$\ln(\eta_m) = a_2 P + b_2 \quad @ \quad P > P_{\text{min}}$$  \hspace{1cm} (6.2)

The values of the fitting parameters $a_1, b_1, a_2$, and $b_2$ are summarized in Table 6-12.

Table 6-12. The value of the fitting parameters in Equation (6.1), (6.2) and (6.4) for Zuata crude oil

<table>
<thead>
<tr>
<th>Component</th>
<th>$T / ^\circ\text{C}$</th>
<th>$a_1$</th>
<th>$b_1$</th>
<th>$a_2$</th>
<th>$b_2$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diluted Crude Oil 1</td>
<td>25</td>
<td>0.0473</td>
<td>5.1230</td>
<td>0.0017</td>
<td>2.9641</td>
<td>188.648</td>
</tr>
<tr>
<td>Diluted Crude Oil 2</td>
<td>25</td>
<td>0.0515</td>
<td>5.9299</td>
<td>0.0023</td>
<td>3.4989</td>
<td>174.302</td>
</tr>
<tr>
<td>Diluted Crude Oil 3</td>
<td>40</td>
<td>0.0417</td>
<td>6.2246</td>
<td>0.0033</td>
<td>3.4757</td>
<td>132.565</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.0366</td>
<td>5.7794</td>
<td>0.0021</td>
<td>3.0572</td>
<td>131.107</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.0320</td>
<td>5.6021</td>
<td>0.0037</td>
<td>2.9730</td>
<td>368.526</td>
</tr>
<tr>
<td>Diluted Crude Oil 4</td>
<td>50</td>
<td>0.0204</td>
<td>2.7372</td>
<td>0.0056</td>
<td>1.0518</td>
<td>284.190</td>
</tr>
<tr>
<td>Zuata Crude Oil</td>
<td>50</td>
<td>0.0458</td>
<td>8.6680</td>
<td>0.0013</td>
<td>4.1340</td>
<td>155.3312</td>
</tr>
</tbody>
</table>

Additionally, the viscosity data and CO$_2$ solubility were correlated using the equation reported by Shu [128], which is a modified version of the classic Arrhenius expression,

\[
\ln(\eta_m) = X_o \ln(\eta_o) + X_s \ln(\eta_s) 
\]  \hspace{1cm} (6.3)

with

\[
X_s = \frac{v_s}{\alpha v_o + v_s} 
\]  \hspace{1cm} (6.4)

\[
X_o = 1 - X_s 
\]  \hspace{1cm} (6.5)

where $v$ is volume fraction and the subscripts o, s, and m stand for diluted crude oil, CO$_2$ and CO$_2$/diluted crude oil mixture, respectively. The volume fraction is calculated by

\[
v_s = \frac{m_s/\rho_s}{m_s/\rho_s + m_o/\rho_o} = \frac{x_s\rho_s}{x_s\rho_s + x_o\rho_o} 
\]  \hspace{1cm} (6.6)

\[
v_o = 1 - v_s 
\]  \hspace{1cm} (6.7)

where $m_i$ is the mass of component $i$ in the mixture, $\rho$ the density and $x$ the mass fraction. From the solubility the amount of CO$_2$ dissolved in the crude oil can be worked out, and thus the CO$_2$ volume under the measurement condition. Assuming the crude oil has a constant density and the amount of crude oil in the oil rich phase is also a constant (i.e., the amount of crude oil components diffusing into
Experimental Results for Heavy Crude Oil

the CO₂ rich phase is negligible), the volume of crude oil in the mixture can be evaluated, and thus the volume fractions. The densities of the crude oil samples at ambient pressure were measured through a separate experiment. The viscosity and density of pure CO₂ as a function of temperature and pressure were obtained from the NIST Chemistry WebBook [105].

The empirical parameter $\alpha$ in Equation (6.4) has to be determined by fitting data via a nonlinear optimization that minimizes the absolute average relative deviation, $\Delta_{AAD,X}$

$$\Delta_{AAD,X} = \frac{1}{N} \sum_{i=1}^{X} \left| \frac{X_i - X_{i,\text{fit}}}{X_i} \right|$$ (6.8)

where $X_i$ is the experimental data, $X_{i,\text{fit}}$ calculated from the correlation applied at the same conditions, and $N$ the total number of points. The resulting values of the parameter $\alpha$ for crude oil samples are given in Table 6-12. The correlation results are illustrated in Figure 6-21, and the $\Delta_{AAD,X}$ for all the crude oil samples is 5.97%.

![Figure 6-21. The comparison between the correlation results from Equation (6.3) and measurements. ○, viscosity measurement for the original heavy crude oil at 50 °C; ◇, viscosity measurement for diluted crude oil 1; ▲, viscosity measurement for diluted crude oil 2; ◆, viscosity measurement for diluted crude oil 3 at 40 °C; ▄, viscosity measurement for diluted crude oil 3 at 45 °C; X, viscosity measurement for diluted crude oil 3 at 50 °C; ●, viscosity measurement for diluted crude oil 4 (Sample 2) at 50 °C; --, correlation.](image-url)
CHAPTER 7  EXPERIMENTAL RESULTS FOR LIGHT CRUDE OIL

7.1 Materials
Rheology and phase behaviour measurements have also been performed for a light crude oil provided by Shell. The crude oil was produced from an offshore platform at Gulf of Mexico (GoM). The crude oil has an API of 34.69, and Table 7-1 lists other properties of the crude oil. Since the crude oil is already low viscosity, no dilution was done. The experiments were performed at temperatures of 23 °C and 50 °C, and pressures up to 220 bar.

Table 7-1. The physical properties of the light crude oil from Gulf of Mexico

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity / mm²/s @ 60 F</td>
<td>12.59</td>
</tr>
<tr>
<td>Density / g/ml</td>
<td>0.8506</td>
</tr>
<tr>
<td>TAN / mg KOH/g</td>
<td>0.22</td>
</tr>
<tr>
<td>Nickel / ppm wt.</td>
<td>4.1</td>
</tr>
<tr>
<td>Vanadium / ppm wt.</td>
<td>1.2</td>
</tr>
<tr>
<td>Sulfur / %</td>
<td>0.23</td>
</tr>
<tr>
<td>Water / %</td>
<td>0.1</td>
</tr>
</tbody>
</table>

7.2 Measurement Results

7.2.1 Rheology Measurements
Figure 7-1 illustrates the rheological measurement of the GoM crude oil saturated with CO₂ at a temperature of 23 °C and pressures up to 160 bar. At all pressures the crude oil / CO₂ mixture behaved as a Newtonian fluid with a viscosity independent of shear rate. It should be pointed out that, at 50 bar, the mixture viscosity was so low that only the highest shear rate gives a reliable measurement.

Figure 7-2 shows the viscosity measurement of the GoM crude oil mixed with CO₂ at various shear rate at 50 °C and pressure up to 210 bar. Similar to the case of 23 °C, at ambient pressure the crude oil behaved as a Newtonian fluid, and its CO₂ saturated mixture did too. It should be pointed out that when the pressure was above 40 bar, the measured viscosity was below the measurement limit given by the manufacturer. In such a case, only the viscosity measured at the highest shear rate, 250 s⁻¹, is considered to be a reliable result. Therefore no flow curve can be given for pressures higher than 40 bar.
Experimental Results for Light Crude Oil

Figure 7-3 shows the relationship between the mixture viscosity and pressure. At 23 °C, as pressure increased, the dissolved CO₂ exponentially reduced the crude oil viscosity until 50 bar. Beyond 50 bar the logarithm of the mixture viscosity increased linearly with pressure. At 50 °C, the CO₂ dissolution also gave rise to an exponential decrease in the crude oil viscosity with increasing pressure, but with a gradient smaller than that at 23 °C. The lowest viscosity was reached at 90 bar. Above 90 bar, similar to the case at 23 °C, the logarithm of the mixture viscosity has a linear relationship with pressure.

![Graph showing viscosity measurement of GoM crude oil with CO₂ at 23 °C and various share rates.](image)

Figure 7-1. Viscosity measurement of GoM crude oil with CO₂ at 23 °C and various share rates. – – –, lower shear rate limit; ◆, 1 bar; ◆, 10 bar; ◆, 20 bar; ◆, 40 bar; ◆, 50 bar; ◆, 60 bar; ◆, 70 bar; ◆, 90 bar; ◆, 120 bar; ◆, 160 bar.

Table 7-2. The rheology experiment data of GoM crude oil with CO₂ at 23 °C

<table>
<thead>
<tr>
<th>$P = \text{Ambient}$</th>
<th>$P / \text{bar}$</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>90</th>
<th>120</th>
<th>160</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma / 1/s$</td>
<td>$\eta / \text{mPa}\cdot\text{s}$</td>
<td>$\gamma / 1/s$</td>
<td></td>
<td>$\eta / \text{mPa}\cdot\text{s}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1.825</td>
<td>2.147</td>
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</tr>
</tbody>
</table>
Experimental Results for Light Crude Oil

![Graph showing viscosity measurement of GoM crude oil with CO₂ at 50 °C and various shear rate.](image)

Figure 7-2. Viscosity measurement of GoM crude oil with CO₂ at 50 °C and various shear rate. ––, lower shear rate limit; ●, 1 bar; ●, 10 bar; ●, 20 bar; ●, 30 bar; ●, 40 bar; ●, 50 bar; ●, 60 bar; ●, 80 bar; ●, 90 bar; ●, 100 bar; ●, 120 bar; ●, 150 bar; ●, 180 bar; ●, 210 bar.

Table 7-3. The rheology experiment data of GoM crude oil with CO₂ at 50 °C

<table>
<thead>
<tr>
<th>$P$ / bar</th>
<th>Ambient</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>90</th>
<th>100</th>
<th>120</th>
<th>150</th>
<th>180</th>
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</thead>
<tbody>
<tr>
<td>$\gamma$ / 1/s</td>
<td>$\eta$ / mPa·s</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>124.2</td>
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<td>142.8</td>
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</tr>
<tr>
<td>164.3</td>
<td>3.375</td>
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<tr>
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<td>2.81</td>
<td>2.366</td>
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<td>1.247</td>
<td>0.903</td>
<td>0.824</td>
<td>0.9821</td>
<td>1.071</td>
<td>1.149</td>
<td>1.18</td>
<td>1.199</td>
</tr>
</tbody>
</table>
7.2.2 Phase Behaviour Measurement

The result of the phase behaviour measurements using the view cell for the GoM crude oil at 23 °C is shown in Figure 7-4. The dissolved CO\(_2\) expanded the oil rich phase volume, making the oil liquid level higher and higher. However, at 60 bar, when CO\(_2\) changed into a liquid phase, the oil rich phase started to shrink. It gave rise to a maximum volume of the oil rich phase at 50 bar, which corresponded to the pressure of the viscosity minimum. Since the CO\(_2\) solubility in the crude oil from 60 bar upward was constant (see Figure 7-6), the shrinkage in the oil rich phase was the result of the normal increase of density with pressure. Furthermore, at 220 bar, the CO\(_2\) density was higher than that of the oil mixture, which caused the CO\(_2\) phase to move down to the bottom of the view cell, as can also be seen in Figure 7-4.

Figure 7-5 shows the view cell measurement results for the GoM crude oil at 50 °C. Once again the CO\(_2\) dissolution led to the swelling of the oil rich phase and the maximum oil phase volume was reached at 100 bar. At pressures higher than 100 bar the oil phase started to shrink. As shown in Figure 7-6, the CO\(_2\) solubility in the GoM crude oil at 50 °C kept increasing with pressure, but the oil phase volume started to reduce above 100 bar. It is believed that, above 100 bar, pressure has a greater effect on the oil phase volume than CO\(_2\), causing the oil phase to shrink with increasing CO\(_2\) solubility. It is worth pointing out that when the CO\(_2\) reached the supercritical state (at 80 bar), the oil phase did not separate into two phases, which occurred in the 70% diluted Zuata crude oil (see Chapter 6.2.2).
Figure 7-4. The phase behaviour at various pressures of the GoM crude oil mixed with CO₂ at 23 °C
Experimental Results for Light Crude Oil

Figure 7-5. The phase behaviour at various pressures of the GoM crude oil mixed with CO₂ at 50 °C.
Experimental Results for Light Crude Oil

7.2.3 Solubility Measurement

All solubility measurements were performed using protocol 1 mentioned in Section 5.2.2.1.1 in the view cell system. As shown in Figure 7-6, the CO₂ solubility in the GoM crude oil at 23 °C was higher than that at 50 °C, especially when the pressure was above 40 bar. At 23 °C there was jump in the CO₂ solubility when the pressure was increased from 50 bar to 60 bar. After the jump the solubility levelled off. Given that the saturation pressure of CO₂ at 23 °C is 61.4 bar [105], it is likely that when the pressure reached 60 bar, a CO₂ rich liquid phase was formed by the extraction of light components from the crude oil. Because of the measurement principle (see Section 5.2.2.1.1), the CO₂ condensed after stirring was added to the measure of CO₂ dissolved into the crude oil, which resulted in the jump at 60 bar in the solubility measurement. On the other hand, at 50 °C the CO₂ solubility gradually rose with pressure until 100 bar. Beyond 100 bar, the solubility was increased at a much gentler gradient. Compared with the viscosity measurement, the trend of the CO₂ solubility was correlated with that of viscosity at both temperature levels.

Figure 7-6. The solubility of CO₂ in the GoM crude at pressure up to 220 bar. ◆, 23 °C; ●, 50 °C.

7.3 Correlations

The viscosity correlation with pressure can be described by Equation (6.1), (6.2) and (6.3) mentioned in Chapter 6.3. Table 7-4 shows the values of the parameters. The correlation results are illustrated in Figure 7-7, and the ΔAAD, X for Equation (6.3) is 43.37%.

Table 7-4. The value of the fitting parameters in Equation (6.1), (6.2) and (6.3) for GoM crude oil

<table>
<thead>
<tr>
<th>Component</th>
<th>T / °C</th>
<th>CO₂ Mixture</th>
<th>a₁</th>
<th>b₁</th>
<th>a₂</th>
<th>b₂</th>
<th>α</th>
</tr>
</thead>
<tbody>
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<td>23</td>
<td></td>
<td>0.0318</td>
<td>2.17443</td>
<td>0.00104</td>
<td>0.70372</td>
<td>43.0069</td>
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<td>GoM Crude Oil</td>
<td>50</td>
<td></td>
<td>0.0160</td>
<td>1.18914</td>
<td>0.00173</td>
<td>0.15557</td>
<td>16.2265</td>
</tr>
</tbody>
</table>
Experimental Results for Light Crude Oil

Figure 7-7. The comparison between the correlation results from Equation (6.3) and measurements of the GoM crude oil. ▲, 23 °C measurement; --, 23 °C, correlation; •, 50 °C, measurement; ---, 50 °C, correlation.
CHAPTER 8 EXPERIMENTAL RESULTS FOR HEAVY CRUDE OIL/WATER EMULSION

8.1 Materials

Rheology measurements were performed on an oil and water emulsion prepared using the Zuata crude oil, whose properties can be found in Chapter 6.1. The water used throughout these experiments was deionized and no interfacial agent was added during the emulsion preparation. The emulsion was prepared in a batch of about 600 g using a variable speed homogenizer (Silverson) to provide the necessary agitation and shearing of fluids. The emulsion contained 50 w% water and 50 w% Zuata crude oil. Due to the high viscosity of the crude oil, mixing at 25 °C did not result in an emulsion. Therefore, heating was carried out during the preparation, for which two protocols were used. Protocol one was to shear and heat up the liquids simultaneously to 50 °C and then maintain temperature and shearing for one hour. Protocol two was to heat up the liquids to 50 °C first, followed by shearing at 50 °C for 45 min. Only protocol two resulted in a stable emulsion. After the preparation one drop of the emulsion was placed in a beaker of water, and the emulsion droplet did not disperse into the water, indicating that the emulsion was water-in-oil, that is oil was the continuous phase. The emulsion obtained in this way remained stable for several days indicating that the Zuata crude oil contains components that can act as a stabiliser for the water/oil emulsion.

Figure 8-1 shows an image of the emulsion at ambient conditions scanned with a confocal laser-scanning microscope (CLSM) (LSM 700, Carl Zeiss, Germany) which was operated in the reflection mode using a 10× objective lens and a laser wavelength of 488 nm. The sample was prepared as follows: Two droplets were placed between a flat glass slide and a cover sheet (both obtained from Agar Scientific, Ltd., U.K.) and then mounted onto the CLSM stage.
Experimental Results for Heavy Crude Oil/Water Emulsion

Figure 8-1. The image of the oil/water emulsion taken by a confocal laser-scanning microscope at ambient conditions.

8.2 Rheology Measurement Results

8.2.1 Measurements at Different Temperatures without CO₂

The rheology measurement of the emulsion was first performed at ambient pressure without CO₂ and different temperatures, using a coaxial cylinder measuring system (Model No. CC27-SN20694) mounted on an Anton Paar rheometer (Model No. MCR301). The coaxial cylinder geometry has a measuring bob with a diameter of 27 mm and a measuring cup with a diameter of 29 mm, given a measuring gap of 1 mm. The temperature was controlled by an electrical heating device (Model No. C-ETD 200/XL) installed on the rheometer, which has a maximum heating rate of 8 K/min and temperature fluctuations of 0.02 °C. In a typical experiment, 19 ml of the emulsion was loaded in the measuring cup, and then the measuring cup was mounted on the rheometer. The rheometer
Experimental Results for Heavy Crude Oil/Water Emulsion

automatically adjusted the measuring bob to the designed position. Then the measuring system was brought to the desired temperature by the electrical heating device and held for 1 hour to ensure thermal equilibrium. Before each measurement, the emulsion was pre-sheared at 5 s⁻¹ for 0.5 min and at rest for 1 min. A different pre-shearing rate (10 s⁻¹) and resting time (5 min) were tested but showed no effect on the results. The rheological measurement was performed at shear rates from 10 s⁻¹ to 900 s⁻¹. The shear rate adjusting time was 0.5 min. From low to high shear rate, the measurement duration, excluding the shear rate adjusting time, lasted from 2 min to 1 min for each step with a logarithmic decrease. A descending shear rate measurement followed immediately after the ascending measurement. At each step of the descending measurement, the measurement duration was from 1 min to 2 min. The total measurement time for the ascending measurement was 58.8 min, while the descending measurement took the same amount of time. After the measurement at one temperature was completed, the temperature was adjusted to a higher level for the next measurement.

At each temperature level, after one ascending and descending flow curve was obtained, the sample was left at rest for one hour (while keeping the heating device on), and then a repeat measurement was performed (with the same pre-shear rate, resting time, and measurement duration). The results showed that only the ascending flow curves were repeatable while there were significant inconsistencies in the descending one. An example is shown in Figure 8-2, which illustrates two repeat measurements on the emulsion at ambient pressure and temperature of 45 °C. The ascending flow curves showed a good overlap between data points, while the points in the descending curves had considerable differences especially at shear rates lower than 100 s⁻¹. For all the temperature levels the overall repeatability of the ascending measurements was 4.1%, whereas that of the descending measurements was 40.3%. Therefore, only the results from the ascending flow curves were studied here.
Experimental Results for Heavy Crude Oil/Water Emulsion

Figure 8-2. Comparison of the results of two repeated flow curve measurements on the emulsion at ambient pressure and 45 °C. The filled points are for ascending measurements, while the empty points are for descending measurements. ⚫, measurement 1 (measured first) with ascending shear rate; ⚪, measurement 1 with descending shear rate; ▲, measurement 2 (measured second) with ascending shear rate; Δ, measurement 2 with descending shear rate.

Figure 8-3 and Figure 8-4 show the rheology measurement results at temperatures from 45 °C to 65 °C. As shown in Figure 8-3, the flow curve at each temperature can be separated into three regions. The first region was the low shear rate region, extending from the lowest shear rate measured to the shear rate just before the maxima in the flow curve. In this region, a weak shear thinning effect was observed in the viscosity measurements (Figure 8-4). In the second region a viscosity jump was observed, where the slope of the flow curve changed from positive to negative as the viscosity dramatically decreased to a lower value. This lower value was substantially below the viscosity of the oil phase indicating that the emulsion had undergone a phase inversion, becoming oil-in-water, although the viscosity remained at least an order of magnitude above that of water. Note that the stress at the end of the jump (Figure 8-3) was similar at all temperatures. This region extended from the stress maxima up to the end of the viscosity jump (see Figure 8-4). The third region was the high shear rate region, in which the viscosity was much lower than that in the low shear rate region, and the shear thinning effect was more pronounced. The viscosity, \( \eta \), in these three regions was fitted by the power-law model:

\[
\eta = K \gamma^{n-1}
\]

where \( \gamma \) is shear rate, \( n \) the power-law index, and \( K \) the fluid consistency. The fitting results are summarised in Table 8-1. The average absolute derivation (AAD) of the curve fitting for each region is also reported in Table 8-1.
Experimental Results for Heavy Crude Oil/Water Emulsion

Figure 8-3. The flow curve of the emulsion at atmospheric pressure and at different temperatures. –, the fitting curve by Equation (8.1); •, 45 °C; ◊, 50 °C; ▲, 55 °C; ■, 60 °C; ×, 65 °C. All the empty circles represented the points that may be measured at insufficient shearing time.

Figure 8-4. The viscosity measurement of the emulsion at atmospheric pressure and at different temperatures. –, the fitting curve by Equation (8.1); •, 45 °C; ◊, 50 °C; ▲, 55 °C; ■, 60 °C; ×, 65 °C. All the empty circles represented the points that may be measured at insufficient shearing time.

From Table 8-1 one can see that at the low shear rate region, the shear thinning effect was weaker at higher temperature, as the power-law index approached one with increasing temperature. The K value, however, was inversely proportional to temperature. In the viscosity jump region, the power-law index was considerably less than -1, which indicated an unstable condition in this shear rate range and suggested the shearing time may not have been sufficiently long to achieve steady state. Ideally these experiments should be repeated with a longer measurement time to refine the data. However, given the time available, such experiments were not performed. Therefore, only the maximum shear stress point and the end point of the viscosity jump will be analysed here, given that these two points are likely to
Experimental Results for Heavy Crude Oil/Water Emulsion

be approximations of steady state values. Finally, in the high shear rate region, both $n$ and $K$ were not correlated with the temperature. The means of $n$ and $\ln(K)$ were 0.2874 and 7.7092 with relative standard deviations of 19% and 4%, respectively. Furthermore, at each temperature, the power-law index in the high shear rate region was less than that in the low shear rate region. Since the shear thinning effect is more pronounced for values of $n < 1$, the smaller value of $n$ demonstrated that the shear thinning effect was stronger in the high shear rate region compared to the low shear rate region.

<table>
<thead>
<tr>
<th>Region</th>
<th>Low Shear Rate</th>
<th>Viscosity Drop</th>
<th>High Shear Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T / ^\circ C$</td>
<td>$n$</td>
<td>$\ln(K)$</td>
<td>$n$</td>
</tr>
<tr>
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<td>0.7945</td>
<td>10.4986</td>
<td>-5.3421</td>
</tr>
<tr>
<td>50</td>
<td>0.8913</td>
<td>9.6550</td>
<td>-3.9474</td>
</tr>
<tr>
<td>55</td>
<td>0.9164</td>
<td>9.0666</td>
<td>-4.4706</td>
</tr>
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<td>60</td>
<td>0.9217</td>
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<td>-3.6313</td>
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<tr>
<td>65</td>
<td>0.9325</td>
<td>8.2617</td>
<td>-4.8935</td>
</tr>
<tr>
<td>AAD</td>
<td>1.6%</td>
<td>51.8%</td>
<td>6.9%</td>
</tr>
</tbody>
</table>

It is worth pointing out that the viscosity corresponding to the flow curve maxima, $\eta_{\text{max }, T}$, and that at the end of the viscosity jump, $\eta_{\text{end }, T}$, can be correlated with temperature through the following equation:

$$\ln(\eta_{\text{max }, T}) = A + \frac{B}{T}$$  \hspace{1cm} (8.2)

Furthermore, the shear rate at the highest shear stress, $\gamma_{\text{max }, T}$, was proportional to temperature, and can be correlated by

$$\ln(\gamma_{\text{max }, T}) = A + B \times T$$  \hspace{1cm} (8.3)

$\eta_{\text{max }, T}$ is $\eta_{\text{max }, T}$ or $\eta_{\text{end }, T}$, and $A$ and $B$ are the fitting parameters. Note that the temperature, $T$, is in Kelvin. The average absolute derivations of the correlation for $\eta_{\text{max }, T}$, $\eta_{\text{end }, T}$ and $\gamma_{\text{max }, T}$ were 5.4%, 9.5%, and 0.1%, respectively. The curve fitting results are shown in Figure 8-5, and the values of $A$ and $B$ are summarised in Table 8-2. Since shear stress is the product of shear rate and viscosity, the competition between the shear rate and viscosity led to a minima among the highest shear stresses at different temperatures.
Experimental Results for Heavy Crude Oil/Water Emulsion

![Graph showing comparison between measurement and correlation results](image)

Figure 8-5. Comparison between the measurement and the correlation results given by Equation (8.2) and (8.3). The parameters used are given in Table 8-2. ◆, $\eta_{\text{max}, \text{T}}$; ▲, $\eta_{\text{end}, \text{T}}$; X, $\gamma_{\text{max}, \text{T}}$.

Table 8-2. The value of the fitting parameters in Equation (8.2) and (8.3)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\eta_{\text{max}, \text{T}}$</th>
<th>$\eta_{\text{end}, \text{T}}$</th>
<th>$\gamma_{\text{max}, \text{T}}$</th>
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</thead>
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<tr>
<td>$A$</td>
<td>-22.5604</td>
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<td>-25.2727</td>
</tr>
<tr>
<td>$B$</td>
<td>10231.07</td>
<td>8568.581</td>
<td>0.09051</td>
</tr>
</tbody>
</table>

8.2.2 Measurements at High CO₂ Pressures

Rheology measurements of the CO₂-saturated emulsion at 50 °C were performed in the circulation system described in Chapter 5.1. At each pressure, the equilibrium between CO₂ and the emulsion was reached through constantly stirring the mixer and flowing through the circulation loop for more than 24 hours. The equilibrium was confirmed by periodic measurements of both viscosity and pressure until no further changes were observed. Before a rheology measurement at a given pressure the circulation was stopped and the sample in the pressure cell was left at rest for one hour. The rheology measurement started with a 5 s⁻¹ pre-shearing for 0.5 min and then 1 min resting time. From low to high shear rate, the measurement duration at each shear rate step was logarithmically decreased from 2 min to 1 min (excluding the 0.5 min shear adjusting time), and it took totally 23.5 min for the entire shear rate range. Only ascending shear rate measurement was performed. After the measurement at a given pressure was finished, the gear pump and mixer were restarted to mix the CO₂ and emulsion for a 12 hour period at the next pressure, followed by a rheology measurement. If the results from different periods were the same, the mixture was confirmed to be at equilibrium, otherwise the mixing was continued. At the equilibrium stage between each measurement performed there was a one hour time gap to restore the sample. A different pre-shearing rate ($10$ s⁻¹) and resting time (5 min) were tested only at the equilibrium stage, but this had no effect on the results. At least two measurements with exactly the same setting
Experimental Results for Heavy Crude Oil/Water Emulsion

were performed at each equilibrium, and the overall repeatability was 3.1%. All measurement durations were the same as the one mentioned above.

Figure 8-6 and Figure 8-7 show rheological measurements of the emulsion saturated with CO\textsubscript{2} at different pressures, a constant temperature of 50 °C and shear rates from 10 s\textsuperscript{-1} to 500 s\textsuperscript{-1}. As expected from the previous measurements, at atmospheric pressure (with no CO\textsubscript{2}) and low shear rates the emulsion showed a weak shear thinning effect. As shown in Figure 8-6, when the shear rate reached 58 s\textsuperscript{-1}, the gradient of the flow curve changed from positive to negative and when the shear rate exceeded 104 s\textsuperscript{-1} the viscosity of the emulsion jumped to a much lower value. At the lower viscosity level (high shear rates) the shear thinning effect was still observed. The emulsion in equilibrium with CO\textsubscript{2} at 30 bar remained shear thinning at low shear rates, but a viscosity jump occurred at a higher shear rate and the high shear plateau was shifted above the accessible measurement range. At CO\textsubscript{2} pressures from 50 to 120 bar, the viscosity jump did not appear in the measurement range but changes in the shear thinning behaviour in the low shear rate regime could be observed.

![Figure 8-6. The flow curve of the crude oil/water emulsion and its saturated mixture with CO\textsubscript{2} at 50 °C and various pressure.](image)

Figure 8-6. The flow curve of the crude oil/water emulsion and its saturated mixture with CO\textsubscript{2} at 50 °C and various pressure. ●, ambient pressure; ○, 30 bar; ●, 50 bar; ●, 70 bar; ●, 90 bar; ●, 120 bar. All the empty circles represented the points that may be measured at insufficient shearing time. The solid lines are the fitting curves by Equation (8.1).
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Figure 8-7. The viscosity measurement of the crude oil/water emulsion and its saturated mixture with CO₂ at 50 °C and various pressure. ◆, ambient pressure; ○, 30 bar; ●, 50 bar; ▲, 70 bar; ▼, 90 bar; ▼, 120 bar. All the empty circles represented the points that may be measured at insufficient shearing time. The solid lines are the fitting curves by Equation (8.1).

The analysis of the high pressures experiment was similar to the one described in Section 8.2.1. The flow curves in Figure 8-6 were separated into three regions: low shear rate region, viscosity drop region and high shear rate region. The viscosities in these three regions (where they could be observed) were fitted with Equation (8.1), the power-law model. The fitting results are given in Table 8-3.

Table 8-3. The curve fitting results of Equation (8.1) for measurements shown in Figure 8-7. ln(K) is the natural logarithm of K.

<table>
<thead>
<tr>
<th>Region</th>
<th>Low Shear Rate</th>
<th>Viscosity Drop</th>
<th>High Shear Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/bar</td>
<td>n</td>
<td>ln(K)</td>
<td>n</td>
</tr>
<tr>
<td>Ambient</td>
<td>0.8784</td>
<td>9.7136</td>
<td>-2.5012</td>
</tr>
<tr>
<td>30</td>
<td>0.8892</td>
<td>8.9514</td>
<td>-4.6479</td>
</tr>
<tr>
<td>50</td>
<td>0.8863</td>
<td>7.6392</td>
<td>N/A</td>
</tr>
<tr>
<td>70</td>
<td>0.9205</td>
<td>7.1392</td>
<td>N/A</td>
</tr>
<tr>
<td>90</td>
<td>0.9472</td>
<td>6.4892</td>
<td>N/A</td>
</tr>
<tr>
<td>120</td>
<td>0.9451</td>
<td>6.0660</td>
<td>N/A</td>
</tr>
<tr>
<td>AAD</td>
<td>2.4%</td>
<td>70.5%</td>
<td>4.7%</td>
</tr>
</tbody>
</table>

As shown in Table 8-3, in the low shear rate region the power-law index, n, became closer to 1 as the CO₂ pressure increased, indicating that CO₂ weakened the shear thinning effect. During the viscosity jump, the mixture was unstable and led to values of n less than -1. As noted in the previous section, the shearing time may not be long enough in this region to achieve steady state. Additional experiments with a longer shearing time were not performed because of the limited time available.

An additional set of rheological measurements with a narrower pressure range (30 to 50 bar) and higher shear rates was also carried out to observe in more detail how CO₂ affected the jump and high shear
viscosity. The measurement procedure was the same as the one described in the first paragraph of Chapter 8.2.2, except that the shear rate was varied between 10 s\(^{-1}\) and 900 s\(^{-1}\). In the measurement with ascending shear rate, the measurement duration at each shear rate step was varied from 2 min to 1 min. It was immediately followed by a descending measurement with a step duration of 1 min to 2 min. The total measurement time was 58.8 min for both ascending and descending measurements. However, similar to the results in Section 8.2.1, significant inconsistency was found in the descending flow curves of two repeating measurements with the same setting (pre-shearing, resting time and measurement duration) at the same conditions. An example was given in Figure 8-8. The overall repeatability of the ascending and descending measurements were 4.0\% and 61.4\%, respectively. Therefore, only the results from the ascending flow curves were studied further.

![Graph](image.png)

**Figure 8-8.** Comparison of the results of two repeating flow curve measurements on the CO\(_2\) saturated emulsion at CO\(_2\) pressure of 32 bar and 50 °C. The filled points are for ascending measurements, while the empty points are for descending measurements. ◆, measurement 1 with ascending shear rate (measured first); ◇, measurement 1 with descending shear rate; ▲, measurement 2 with ascending shear rate (measured second); △, measurement 2 with descending shear rate.

Figure 8-10 and Figure 8-9 show rheological measurements for the emulsion saturated with CO\(_2\) at pressures between 30 and 50 bar and shear rates up to 900 s\(^{-1}\). At pressures of 30 to 32 bar, the emulsion once again jumped to a lower value and a high shear region could be observed. However, in contrast to the measurements at ambient pressure, the viscosity in the high shear rate region was independent of shear rate. As the pressure was increased further and more CO\(_2\) dissolved into the emulsion, the viscosity jump appeared at higher and higher shear rates and the high-shear plateau shifted above the observable region. However, the shear thinning effect before the occurrence of the viscosity jump was observable at each pressure level.
Experimental Results for Heavy Crude Oil/Water Emulsion

Figure 8-9. The flow curve of the crude oil/water emulsion and its saturated mixture with CO\(_2\) at 50 °C and various pressure. •, 30 bar; ●, 31 bar; ●, 32 bar; ●, 38 bar; ○, 45 bar; ○, 50 bar. All the empty circles represented the points that may be measured at insufficient shearing time. The solid lines are the fitting curves by Equation (8.1).

Figure 8-10. The viscosity measurement of the crude oil/water emulsion and its saturated mixture with CO\(_2\) at 50 °C and various pressure. •, 30 bar; ●, 31 bar; ●, 32 bar; ●, 38 bar; ○, 45 bar; ○, 50 bar. All the empty circles represented the points that may be measured at insufficient shearing time. The solid lines are the fitting curves by Equation (8.1).

Once again the measurement results in Figure 8-9 and Figure 8-10 were analysed using the method described in Chapter 8.2.1, and the viscosity measurement in Figure 8-10 were correlated using Equation (8.1). Table 8-4 summarises the calculated fitting parameters. In Table 8-4, the values of \(n\) and \(\ln(K)\) in the low shear rate and viscosity jump regions showed similar trends for increasing pressure compared to those in Table 8-3. The most significant information revealed by Table 8-4 was that in the high shear rate region, the power-law indices at pressures from 30 bar to 32 bar were around 1, demonstrating Newtonian fluid behaviour. It confirmed that in this pressure range the viscosity was independent of shear rate after the viscosity jumps, as shown in Figure 8-10.
Experimental Results for Heavy Crude Oil/Water Emulsion

Table 8-4. The curve fitting results of Equation (8.1) for measurements shown in Figure 8-10. \( \ln(K) \) is the natural logarithm of \( K \).

<table>
<thead>
<tr>
<th>Region</th>
<th>Low Shear Rate</th>
<th>Viscosity Drop</th>
<th>High Shear Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P / \text{bar} )</td>
<td>( n )</td>
<td>( \ln(K) )</td>
<td>( n )</td>
</tr>
<tr>
<td>30</td>
<td>0.8916</td>
<td>8.9279</td>
<td>-3.3376</td>
</tr>
<tr>
<td>31</td>
<td>0.8966</td>
<td>8.7272</td>
<td>-3.2738</td>
</tr>
<tr>
<td>32</td>
<td>0.8963</td>
<td>8.3943</td>
<td>-3.5298</td>
</tr>
<tr>
<td>38</td>
<td>0.9019</td>
<td>8.1457</td>
<td>-3.8896</td>
</tr>
<tr>
<td>45</td>
<td>0.9089</td>
<td>7.7546</td>
<td>N/A</td>
</tr>
<tr>
<td>50</td>
<td>0.9183</td>
<td>7.5366</td>
<td>N/A</td>
</tr>
<tr>
<td>AAD</td>
<td>3.3%</td>
<td>50.1%</td>
<td>1.5%</td>
</tr>
</tbody>
</table>

Although the shearing time may not be long enough in the region of the jump and the \( n \) and \( \ln(K) \) values here should be treated with caution, the maximum shear stress point and the end point of the viscosity jump were analysed further. At pressures up to 50 bar, the viscosity at the highest shear stress, \( \eta_{\text{max}, P} \), and the viscosity at the end of the viscosity jump, \( \eta_{\text{end}, P} \), can be correlated with pressure, \( P \), by the following equation:

\[
\ln(\eta_{\text{max}(P)}) = A + B \times P
\]  

(8.4)

Also the shear rate at the highest shear stress, \( \gamma_{\text{max}, P} \), can be related to the CO\(_2\) pressure by

\[
\ln(\gamma_{\text{max}, P}) = A + B \times P
\]  

(8.5)

where \( \eta_{\text{max}(P)} \) is \( \eta_{\text{max}, P} \) or \( \eta_{\text{end}, P} \), and \( A \) and \( B \) are the fitting parameters. The AAD of the correlations for \( \eta_{\text{max}, P} \), \( \eta_{\text{end}, P} \) and \( \gamma_{\text{max}, P} \) were 19.7%, 3.5% and 16.4%, respectively. The fitting results are shown in Figure 8-5, and the values of \( A \) and \( B \) are summarised in Table 8-2. The competition between the viscosity and shear rate leads to a maximum among the highest shear rates at different CO\(_2\) pressures.

Table 8-5. The value of the fitting parameters in Equation (8.4) and (8.5)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( \eta_{\text{max}, P} )</th>
<th>( \eta_{\text{end}, P} )</th>
<th>( \gamma_{\text{max}, P} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>9.289683</td>
<td>4.58399</td>
<td>3.97378</td>
</tr>
<tr>
<td>( B )</td>
<td>-0.04869</td>
<td>-0.00949</td>
<td>0.05492</td>
</tr>
</tbody>
</table>
Figure 8-11. Comparison between the measurement and the correlation results given by Equation (8.4) and (8.5). The parameters used are given in: $\eta_{\text{max}}$, $\eta_{\text{end}}$, $\gamma_{\text{max}}$, $\gamma_{\text{end}}$, $P$, $\sigma$.

Since, as in the case of the CO$_2$ free emulsions, the viscosity jumped to a value that was much lower than the viscosity of the oil phase, it is likely that a catastrophic decrease in viscosity was caused by phase inversion: at higher shear rates the water became the continuous phase.

**8.2.3 Comparison Between The Emulsion and Zuata Crude Oil at High CO$_2$ Pressures**

Figure 8-12 shows comparisons of the viscosity of the CO$_2$ saturated Zuata crude oil and that of the emulsion in equilibrium with CO$_2$ at the same pressures, all at a temperature of 50 °C. In Figure 8-12. The viscosity measurement of the Zuata crude oil at ambient pressure was taken directly from the data presented in Chapter 6.2.1, while other points were calculated using Equation (6.1) and (6.2) in Chapter 6.3, since direct measurements at those pressures were not available. Note that at pressures above 30 bar, the CO$_2$ saturated Zuata crude oil was a Newtonian fluid as shown in Chapter 6.2.1, while the emulsion remained slightly shear thinning.
Experimental Results for Heavy Crude Oil/Water Emulsion

**Figure 8-12. Comparison between the emulsion and Zuata crude oil viscosities at 50 °C and different CO₂ pressures.**

For the emulsion: ■, ambient pressure; ●, 30 bar; ▲, 50 bar; ○, 70 bar; ×, 90 bar; ✦, 120 bar. For Zuata crude oil: ○, ambient pressure; □, 30 bar; Δ, 50 bar; ●, 70 bar; ×, 90 bar; ✦, 120 bar.

The dispersed phase volume fraction and emulsion viscosity were analysed using the model developed by Pal [101]:

\[
\eta_r \left( \frac{2\eta_r + 5\lambda}{2 + 5\lambda} \right)^{\frac{1}{2}} = \exp \left( \frac{2.5\phi}{1 - \phi/\phi_m} \right) \tag{8.6}
\]

where \( \eta_r \) is the relative viscosity defined as the ratio of emulsion viscosity to continuous phase viscosity, \( \lambda \) the ratio of the dispersed phase viscosity to the continuous phase viscosity, \( \phi \) the dispersed phase volume fraction, and \( \phi_m \) the maximum packing volume fraction. Given that the emulsion contained 50 w% Zuata crude oil 50 w% water and the API of the crude oil was 9.28, the volume fraction of the dispersed phase was about 0.5. Since the CO₂ pressure had a limited effect on the oil volume (see Chapter 6.2.2 for detail), it was assumed that the dispersed phase volume fraction remained constant for different CO₂ pressures and also after phase inversion. It was also assumed that the water phase had a constant viscosity of 1 mPa·s. With these assumptions, \( \phi_m \) was used to fit Equation (8.6) to the viscosity of the emulsions at a shear rate of 10 s\(^{-1}\) for each CO₂ pressure.

The resulting maximum packing volume fractions, \( \phi_m \), are shown in Figure 8-13. These are rather scattered but show a decreasing tendency with increasing pressure. The values of \( \phi_m \) are large and even exceed 1, compared to the values of \( \phi_m \) for a monodisperse spherical solid suspension at 0.64 for random close packing and 0.74 for hexagonal close packing [129]. It is also worth mentioning that, \( \eta_r \), showed an upward trend with CO₂ pressure, whereas the emulsion viscosity was reduced with increasing CO₂ pressure. This is due to the fact that the dissolved CO₂ decreases the oil viscosity to a larger extent than that of the emulsion. As the key physical meaning of \( \phi_m \) is how the droplets fill space, it is strongly

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related to both the droplet size distribution and droplet deformability [130, 131]. As demonstrated by Desmond et al. [132], for a system of rigid spherical particles in which larger particles dominate, a decrease in $\phi_m$ means a wider droplet size distribution, while in a smaller particles dominated system the decrease in $\phi_m$ resulted from a narrower droplet size distribution. Furthermore, from the droplet deformation point of view, the decrease in $\phi_m$ can be accounted for the decrease in droplet deformability, since the packing becomes more efficient by “soft” droplets which distort easily to accommodate each other [131]. However, the decrease in $\phi_m$ observed in Figure 8-13 was a result of the combination of the polydispersity and deformability effects. Further interpretations of $\phi_m$ requires detailed morphological studies of the water droplets, which was not available in this work.

The values of $\phi_m$ at different shear rates before the phase inversion were also analysed. However, the resulting $\phi_m$ values at some pressure levels were much larger than 1, which is non-physical. This indicated that Equation (8.6) is not suitable to analyse the emulsion at different shear rates, given that Equation (8.6) was developed based on the theory for suspensions [101, 130].
Experimental Results for Heavy Crude Oil/Water Emulsion

Figure 8-14. The maximum package volume fractions of the emulsion after the phase inversion at 50 °C and various shear rates. ◆, ambient pressure; ▲, 30 bar.

Furthermore, the maximum packing volume fraction after the phase inversion was analysed. As shown in Figure 8-14, at ambient pressure the value of \( \phi_m \) in the emulsion increases with increasing shear rate. However, at 30 bar, with CO\(_2\) dissolution, the changes in \( \phi_m \) over the shear rate range were very small and thus \( \phi_m \) was considered to be a constant. The increase in \( \phi_m \) showed that, without CO\(_2\) addition, the oil droplets in the phase-inverted emulsion were rearranging, likely by deformation and/or breakup, to respond to shear. However, when CO\(_2\) was dissolved in the emulsion, there was no such rearrangement, so \( \phi_m \) was a constant.

An analysis applying the critical capillary number concept to the post phase inversion emulsion was also carried out. The critical capillary number, \( Ca_{em,cr} \), for a concentrated emulsion is given by [133],

\[
Ca_{em,cr} = \frac{\eta_{em} a_m \gamma}{\sigma_{IFT}}
\]

(8.7)

where \( \eta_{em} \) is the emulsion viscosity, \( a_m \) the maximum stable drop radius, \( \gamma \) the shear rate and \( \sigma_{IFT} \) the interfacial tension between the water and oil phases. For each viscosity ratio \( \lambda_{em} \) between the dispersed phase (oil phase viscosity, \( \eta_{oil} \)) and the emulsion, the droplet will break up if the capillary number is greater than \( Ca_{em,cr} \). As shown by Golemanov et al. [104], for a concentrated hexadecane-in-water emulsion, the critical capillary number was independent of \( \lambda_{em} \) and volume fraction. Therefore, it was assumed that the critical capillary numbers were the same in the post phase inversion emulsion at ambient pressure (no CO\(_2\) addition) and at a CO\(_2\) pressure of 30 bar, although the two emulsions had different \( \lambda_{em} \). Furthermore, as shown in Figure 8-15, in the high shear rate region, the viscosity of the phase-inversed emulsion with CO\(_2\) dissolution was higher than that without CO\(_2\). In addition, Poteau et al. [134] showed that the interfacial tension of an oil-in-water emulsion stabilised by asphaltene was
Experimental Results for Heavy Crude Oil/Water Emulsion

smaller in an acidic aqueous phase. Given that the CO\textsubscript{2} dissolution can reduce the water phase pH by generating carbonic acid, it was assumed that the interfacial tension in the CO\textsubscript{2} saturated phase-inversed emulsion was lower than that without CO\textsubscript{2} dissolution. With these arguments and applying Equation (8.7) at constant shear rate, one can compare the maximum stable drop radiuses for the two post phase inversion emulsions (see Table 8-6). It showed that \(a_m\) with CO\textsubscript{2} dissolution was smaller than \(a_m\) without CO\textsubscript{2}. The interpretation of this difference was that the mean droplet size in the post phase inversion emulsion without CO\textsubscript{2} addition was larger than that with CO\textsubscript{2} dissolution.

Table 8-6. Comparison between the critical capillary number of the post phase inversion emulsion without CO\textsubscript{2} dissolution and that with CO\textsubscript{2} dissolution.

<table>
<thead>
<tr>
<th>No CO\textsubscript{2}</th>
<th>With CO\textsubscript{2}</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\lambda_{em}=115.7) &gt; (\lambda_{em}=21.6)</td>
<td>(\lambda_{em}=\eta_{oil}/\eta_{em}) at shear rate of 500 s(^{-1})</td>
<td></td>
</tr>
<tr>
<td>(Ca_{em,cr} = ) (Ca_{em,cr})</td>
<td>Assumption according to [104]</td>
<td></td>
</tr>
<tr>
<td>(\eta_{em} &lt; \eta_{em})</td>
<td>See Figure 8-15</td>
<td></td>
</tr>
<tr>
<td>(1/\eta_{em} &gt; 1/\eta_{em})</td>
<td>See Figure 8-15</td>
<td></td>
</tr>
<tr>
<td>(\sigma_{IFT} &gt; \sigma_{IFT})</td>
<td>Assumption according to [134]</td>
<td></td>
</tr>
<tr>
<td>(\gamma = \gamma)</td>
<td>Compare at the same shear rate</td>
<td></td>
</tr>
<tr>
<td>(a_m &gt; a_m)</td>
<td>(a_m= Ca_{em,cr} \sigma_{IFT}/\eta_{em} \gamma)</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 8-15. Comparison between the viscosity of the emulsion without CO\textsubscript{2} dissolution and that with CO\textsubscript{2} dissolution at temperature of 50 °C. The data in this figure was taken from Figure 8-4 and Figure 8-10. ●, ambient pressure (no CO\textsubscript{2}); ○, 30 bar (CO\textsubscript{2} pressure).](image)

8.3 Discussion

8.3.1 The Mechanism of Phase Inversion

Because of the complex nature of the phase inversion phenomenon, there is little knowledge of the actual mechanism governing the inversion process. Drop dynamics has been proposed to play an
important role in phase inversion [53]. It has also been shown that the phase inversion based on drop coalescence is able to explain both transitional and catastrophic inversion [53]. We speculate that the shear-induced phase inversion occurred in this work was caused by coalescence of the water droplets.

The water droplets in the emulsion were covered by a layer of surface-active agents which stabilised the emulsion. Subject to shear, the droplets aggregated together to form bigger droplets, and at higher shear rate the droplets deformed into a film-like shape, as shown in Figure 8-16. Since the droplets were stretched by shear, the curvature of the interface layer changed from negative to zero. As reviewed by Perazzo et al. [54], in the phase inversion process, the transition from water droplets in an oil phase to oil droplets in a water phase can be attributed to a change of curvature of the interfacial monolayer from concave to concave passing through a flat stage, as shown in Figure 8-16. At this transition stage, the hydrophilic-lipophilic properties of the interface agent were balanced, and consequently a bicontinuous or lamellar structure was formed [135]. When the shear rate was further increased, the structures with zero curvature separated into metastable small droplets which contained the oil, leading to an oil-in-water emulsion. Because the water was now the continuous phase, the emulsion viscosity was much smaller than that with oil being the continuous phase. The sketch of the mechanism described above is given by Figure 8-16. Note that in Figure 8-16 the interface agent has been drawn as a surfactant for convenience; the actual interface agents can be surfactant molecules or small solid particles with a suitable wettability in the crude oil, or a mixture of both.

![Figure 8-16. The mechanism of the phase version proposed to explain the viscosity behaviour observed in the measurement. The red lines shown here are for the emulsion and CO₂ mixture at 50 °C and 30 bar.](image-url)
Experimental Results for Heavy Crude Oil/Water Emulsion

8.3.2 The Effect of CO₂ on Phase Inversion

As mentioned previously, after each flow curve measurement in Figure 8-4 to Figure 8-9, the sample was left to rest for one hour in the measuring cell before the flow curve measurement was repeated, with an overall repeatability of 3.73% for all the ascending measurements mentioned above. This indicated that after shearing the emulsion returned to its original viscosity after resting. In the cases where phase inversion occurred, the emulsion returning to its previous high viscosity demonstrated that the phase inversion was reversible. As noted by Norato et al. [136] phase inversion is generally an irreversible process, because there may be considerable differences in volume fraction and physical properties between the post phase inversion emulsion and the initial one. They also pointed out that in most cases, both shear rate (or agitation speed) and volume faction must be changed to cause the emulsion to revert back to the original dispersion – changing shear rate alone may be insufficient. However, one exception is given by Kato et al. [137]. In their study, the phase inversion of a hexane-in-water (O/W) emulsion was induced by a step increase in the agitation speed of a stirred vessel, leading to a water-in-hexane (W/O) emulsion. The resulting W/O emulsion could be inverted back to the O/W emulsion by a step decrease in the agitation speed. Norato et al. [53, 138] suggested that the experimental results from Kato et al, were caused by the fact that the volume fraction of the hexane/water emulsion was close to the intersection point of the two ambivalence curves of the emulsion, the cusp. An emulsion close to the cusp region does not require a large change in volume fraction to trigger phase inversion: a change in shear rate (or agitation speed) is enough (see Figure 8-17). Consequently the phase inversion is reversible with respect to shear rate (or agitation speed). Since our measurements show similar results as the one by Kato et al., our crude oil/water emulsion may have a volume fraction close to the cusp region, and the effect of CO₂ was to push the cusp to a higher shear rate.
Experimental Results for Heavy Crude Oil/Water Emulsion

Figure 8-17. A sketch of an ambivalence behaviour plot in terms of shear rate. The dash lines represent the ambivalence curves of an emulsion. \(v_{\text{water}}\) is water volume fraction, and \(\gamma\) is shear rate.

The dissolved CO\(_2\) can alter the critical shear rate of phase inversion through its effect on either the oil or water phase. The dissolution of CO\(_2\) in the oil phase reduced the continuous phase viscosity, thus it was easier for the water droplets to aggregate together and form bigger droplets at rest. These bigger droplets reduced the total surface area of the water phase, which resulted in the increased amount of interface agent per surface area. To coalesce, the water droplets needed to approach each other so close that the repulsion force dominated the interaction between droplets. Only when the force exerted by shearing overcame the repulsion force, could the coalescence be successful. With more interface agent around each droplet, the repulsion force became stronger, which led to the fact that the droplet coalescence was suppressed. The inverse proportionality between droplet size and coalescence rate in a particle stabilised emulsion was reported by Arditty et al. [139]. Therefore, a higher shear rate was required to overcome the larger repulsion forces and make the droplets coalesce and eventually form the water film, which was critical for phase inversion. Thus, the more CO\(_2\) dissolved, the lower the viscosity of the oil continuous phase and the higher the critical shear rate for phase inversion.

On the other hand, the dissolved CO\(_2\) can diffuse into the water phase and substantially change the water phase pH by the production of carbonic acid. Through altering the pH value, the dissolved CO\(_2\) could affect the performance of any charged interface agent representing the crude-oil/water interface. Strassner [140] showed that, in an asphaltene stabilised water-in-oil emulsion, the strength of the interface formed by asphaltenes was inversely proportional to the pH. Poteau et al. [134] also showed that for a water-in-oil emulsion stabilised by asphaltenes, the coalescence of water droplets was more important at neutral pH but very small at high or low pH. Thus, the dissolved CO\(_2\) lowered the pH,
enhanced the interface and decreased the coalescence rate. As a result, it required more energy to overcome the stronger interface in order to make the droplet curvature became zero. Therefore, CO₂ dissolution increased the critical shear rate for phase inversion. In other words, the more CO₂ dissolved the further the pH was altered, and thus the higher the critical shear rate for phase inversion.

8.3.3 The Effect of CO₂ on The High Shear Rate Region

Another phenomenon worth discussing is that the shear thinning effect in the high shear rate region disappeared as CO₂ dissolved into the emulsion. As one can see by comparing Figure 8-4 and Figure 8-7, at ambient pressure, the shear thinning effect can still be observed in the high shear rate region after the viscosity jump occurred. However, as shown in Figure 8-10, when CO₂ dissolved in the emulsion, the viscosity in the high shear rate region was independent of shear rate. An explanation of this phenomenon is proposed here. After the viscosity jump, the oil droplets formed in the emulsion without CO₂ dissolution were larger than those with CO₂. Without CO₂ dissolution, the larger droplets formed can deform under shearing, which gave rise to the shear thinning effect. The increase in the maximum packing fraction of the phase-inverted emulsion (see Figure 8-14) could be an indication of the oil droplet deformation. Similar morphological changes have been reported in the study by Lazo et al. [141]. They investigated the morphology development of a polystyrene and polyethylene blend at steady shear and constant temperature. In their experiment, a polymer blend with a polyethylene continuous phase was inverted to that with a polystyrene continuous phase. Through an electron microscope they observed that, after phase inversion, the polyethylene became the dispersed phase in the forms of drops, ellipsoids, fibres and fragments of strand network. With higher strain, the fragments were further thinned and eventually broke down to small drops. Although the viscosity measurement is not given in their paper, it was believed that the emulsion we studied shown a similar morphological change in the oil phase after the phase inversion, which resulted in the shear thinning effect.

On the other hand, the CO₂ in the oil phase provided additional surface active agents, because even at the pressure below the asphaltene precipitation point, the CO₂ dissolution can make the oil become a less good solvent for the asphaltenes which could push them onto the oil/water interface. This led to smaller oil droplets after phase inversion. As a result, a large number of small oil droplets were generated and they were too small to deform and break-up. The constant $\phi_m$ seen in Figure 8-14 can be an evidence. Therefore the post-phase-inversion emulsion behaved as a Newtonian fluid.
CHAPTER 9  CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

9.1 Conclusions of This Work

A rheology measurement system with circulation loop and a view cell system have been built in this work. These two systems allowed us to measure the rheology and phase behaviour of the CO\textsubscript{2} and crude oil mixtures. The crude oil samples studied included a light crude oil from Gulf of Mexico, Zuata heavy crude oil, and Zuata crude oil emulsion with water.

The dissolved CO\textsubscript{2} reduced the viscosity of the GoM light crude oil, but did not otherwise change the crude oil rheology: the CO\textsubscript{2} mixture viscosity was independent of the shear rate (Newtonian) as was the original crude oil. The oil viscosity first showed an exponential decrease with increasing CO\textsubscript{2} pressure, then an increase when the pressure was above the CO\textsubscript{2} saturation point. The phase behaviour of the GoM crude oil and CO\textsubscript{2} mixture was correlated with its viscosity. When brought to equilibrium with CO\textsubscript{2}, the oil rich phase expanded while its viscosity was decreasing and shrank while its viscosity was increasing. Similar correlations with the mixture viscosity can also be found with the CO\textsubscript{2} solubility (ref needed).

The CO\textsubscript{2} dissolution not only reduced the viscosity of the Zuata heavy crude oil, but also eliminated its shear thinning effect. With the exception of one crude oil sample, the toluene diluted Zuata crude oil and its saturated mixture with CO\textsubscript{2} behaved as a Newtonian fluid. The CO\textsubscript{2} saturated mixture of the diluted crude oil showed an exponential decrease in viscosity with increasing CO\textsubscript{2} pressure, but an increase in viscosity beyond the CO\textsubscript{2} saturation points. A correlation between the phase behaviour of the Zuata crude oil, original and diluted, mixed with CO\textsubscript{2} and the mixture viscosity can be observed. The volume of the oil rich phase was inversely proportional to the viscosity. The CO\textsubscript{2} solubility also showed a similar correlation with the mixture viscosity. However, at pressure from 30 bar to 60 bar, CO\textsubscript{2} dissolution caused a shear thinning effect observed in the diluted crude oil 4 sample (a), which was a Newtonian fluid without CO\textsubscript{2}. The reason of the shear thinning effect appearance in the CO\textsubscript{2} saturated sample (a) was not further investigated because the sample had been used up.

Finally, the Zuata crude oil emulsion without dissolved CO\textsubscript{2} was found to be slightly shear-thinning below a critical shear rate, above which the viscosity jumped to a much lower value. This critical shear rate was increased with increasing temperature. In the high shear rate, lower viscosity region, the shear...
Conclusions and Recommendations for Future Work

thinning effect was also observed. The CO$_2$ dissolution had three effects: first, it reduced the emulsion viscosity at low shear while preserving the shear thinning behaviour; second, increasing the pressure of CO$_2$ dissolution increased the critical shear rate at which the viscosity jump occurred; and third the CO$_2$ dissolution eliminated the shear thinning effect in the low viscosity region. At shear rates above the jump, the emulsion viscosity dropped to a lower level than that of the original continuous phase (oil). It is likely that the viscosity jump occurred due to phase inversion; however, this was difficult to observe directly. The dissolved CO$_2$ can influence the emulsion properties such as phase inversion through its action in both phases. The dissolution of CO$_2$ in the oil phase reduces its viscosity while dissolution into the water phase markedly changes pH and thereby the performance of any charged surface-active agent present in the crude oil.

A new method to evaluate Newtonian viscosity of hydrocarbons was also developed. In this method the hydrocarbon viscosity can be predicted from the knowledge of its density. This method requires only few experimental data to evaluate the model parameters. The proposed method is able to give a reliable viscosity prediction for pure alkanes, alkane mixtures and gas-saturated hydrocarbons.

9.2 Recommendations for Future Work

9.2.1 Further Investigations on The Emulsion Rheology Behaviour

More rheology measurements on the crude-oil/water emulsion and its CO$_2$ saturated mixture could be performed. Rheology measurements can be performed on the emulsion at different volume fractions of water phase, to study its effect on the rheology behaviour of the emulsion. In addition, rheology measurements can be carried out to investigate in detail the effect of the measurement duration at each shear rate step, especially in the shear rate range where phase inversion can be observed. Longer measurement duration can be applied to significantly shear the emulsion, and the results from different measurement duration can be compared to discover the minimum shearing time which results in steady state measurement. These experiments with different measurement durations can be carried out for both ascending and descending measurements, to study any thixotropic flow patterns.

9.2.2 Modification of The Rheometer System

The high pressure cell of the rheometer could be modified to allow the measurement of the electrical conductivity of the emulsion under shear. If a dramatic change in the electrical conductivity is observed at the critical shear rate of viscosity jump, it will be direct evidence of the phase inversion, because the electrical conductivity of water is much larger than that of oil [142]. The modification can be done by installing an electrical conductivity probe on the pressure cell. The probe should be mounted inside the wall of the pressure cell, and the sensor should be at the same surface of the wall, in order to prevent any disturbance to the flow pattern of the emulsion under shear. This would be the best modification plan because it allows the simultaneous measurements of the emulsion viscosity and electrical conductivity.
Conclusions and Recommendations for Future Work

conductivity. However, such delicate modification may only be done by the rheometer manufacturer, so co-operation would be necessary.

Another way to measure the electrical conductivity is to mount the electrical conductivity measuring probe on the tube connected to the outlet of the pressure cell, the closer to the outlet the better. When the viscosity jump occurs, the gear pump could be turned on for a while to push some fluid from the pressure cell to the outlet tube, in order to let the fluid contact with the electrical conductivity measuring probe. If the electrical conductivity shows a catastrophic change, it indicates that the continuous phase is water. However, when the emulsion is pushed into the outlet tube, the shear is also gone. As the measurement done in this work shows, the emulsion viscosity will increase and eventually restore to the viscosity value at rest. If the emulsion restores too fast and thus the measurement window is too small, the probe might fail to pick up significant changes in the electrical conductivity and consequentially, fail to detect the phase inversion. However, such modification is easy and can be done in-house.

Furthermore, the rheometer pressure cell can also be modified to introduce a morphology measurement device to study the droplets in the emulsion. The morphology measurement under shearing conditions could reveal the droplet size distribution and deformability, which is invaluable information to interpret the rheology measurements. The possible measurement techniques include light scattering and interferometric laser imaging [143].

It is also recommended to develop a digital control system for the circulation system. The gear pumps, syringe pump, and all valves will be connected to and operated through a computer. With such a control system, it is easy to develop a program which performs a status check of each unit before operation. It could significantly reduce the risk of equipment damage by wrong operation.

9.2.3 Study The Rheology of The CO₂/Oil Foam

Another field worth investigating with the rheometer system is the rheology properties of the crude oil after CO₂ is released from the saturated mixture. It could provide more useful knowledge for production well operation, since the crude oil in the production well will degas when it is transported to the surface. It is known that when CO₂ is released from the saturated crude oil, CO₂/crude oil foam will form. The rheology property of the CO₂ foam has drawn significant interest from industry, but no literature has provided such measurement. The rheometer system built in this work allows the rheology study of the CO₂/oil foam.
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