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A Study on the Heavy Crude Oil Viscosity Reduction with the Dissolution of Nitrogen and Carbon Dioxide

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A Study on the Heavy Crude Oil Viscosity Reduction with the Dissolution of Nitrogen, Carbon dioxide and a mixture of Nitrogen and Carbon dioxide

Thesis

submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering

Master of Engineering (Chemical)

at

The City College of New York

of the

City University of New York

by

Abdurahman Ajumobi

May 2015

Approved:

______________________________
Dr. Marco J. Castaldi, Advisor

______________________________
Professor Jeff Morris, Chairman
Department of Chemical Engineering
Notations And Symbols

A = dimensionless parameter, cubic equations of state
a = parameter, cubic equations of state
B = dimensionless parameter, cubic equations of state
b = parameter, cubic equations of state
\( \hat{f} \) = fugacity of specie in a mixture
\( \mathcal{H} \) = Henry’s constant
P = Pressure
\( P_c \) = critical pressure
\( P_{\text{vap}} \) = vapor (saturation) pressure
\( P_r \) = reduced pressure
R = gas constant
T = Temperature
\( T_c \) = critical temperature
\( T_r \) = reduced temperature
V = Volume
\( \omega \) = acentric factor
Z = compressibility factor
Acknowledgment

Many thanks to my advisor, Prof. Castaldi for the opportunity I have under him working on this project. He provided an intellectual support all through the course of the study in a unique way. Whether far away or near, he was always there. I am equally thankful to Prof. Jeff Morris (the Chair, Chemical Engineering Department) for given me the opportunity to carry out this experiment in his laboratory. My appreciation also goes to Jeff LeBlanc and Mike Nyce (both of the Chemical Engineering Department) for their time and great support. It seems they were there always waiting to render help when called upon. They provided great support towards the success of the study. Lastly, putting my data together within the limited timeframe I had would never have been possible without the help of my wife, Medinat Ajumobi. Her contribution made all the difference, and I will forever be indebted.
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Abstract

World’s energy challenges would be greatly improved upon if half of the world’s heavy oil and extra heavy oil could be made to flow in pipelines. Viscosity reduction of heavy oils is the key to solving this problem. In this study, aside from injecting pure nitrogen and pure carbon dioxide separately into the oil, two different compositions of the mixture of the two gases were also injected. In the first mixture, varied quantities of the two gases were used; 62.5%, 82.2% and 86.4% of the mixture was nitrogen while 37.5%, 17.8% and 13.6% was carbon dioxide at total test pressures of 100, 300 and 500 psi. The second mixture was composed of equal composition of the two gases at the three different pressures listed above. Against the expectation that the mixed gas effect on the heavy oil should be additive of the constituent gases and further reduce the oil viscosity, it was discovered that the viscosity of the oil increased compared to having pure carbon dioxide as the only injected gas. Using carbon dioxide at 40°C reduced the oil viscosity from 10.248 Pa.s to an average value of 2.2718 Pa.s, while the mixture of CO₂ and N₂ at the same temperature only reduced the viscosity to an average value of 2.4435 Pa.s. Nitrogen, being classified as a non-condensable gas, has a negligible solubility in the heavy oil as shown in the data, and when it is mixed with carbon dioxide, it caused a decrease in the carbon dioxide solubility in the oil. The main reason that is believed to contribute to the reduction of carbon dioxide solubility in the oil is the decrease in the carbon dioxide partial pressure due to the presence of nitrogen [4]. Thus, the higher the nitrogen content in the mixture, the lower is the carbon dioxide partial pressure and its solubility and, hence, an increase would be observed in the viscosity of the heavy oil.
1 Introduction

The depletion in the production of low-viscosity oils has initiated a growing interest in the use of non-conventional heavy oil resources to produce fuels and petrochemicals. Non-conventional oil as defined by the US Energy Information Administration is a petroleum produced by means that do not meet the criteria for conventional production. Being two different oil types, the processes involved in their production, transportation, and refining are substantially different. Heavy oil is defined by the US Department of Energy as a petroleum which has density between 10 and 20 API (American Institute Petroleum) gravity. The incorporation of heavy oil to energy markets presents important challenges that require significant technological developments in the production chain. The transportation of heavy oils presents many operational difficulties that limit their economic viability, but for countries like USA and China or Japan with growing energy demands, the restructuring of its refining industries to handle this non-conventional crude is imperative. Heavy oil is cheaper than conventional petroleum, and the refining margin can be bigger if properly handled with higher profits per barrel. Transportation and distribution through pipelines is the most convenient means for the transportation of crude oils and derived products continuously and economically. However, transportation of heavy crude oils through pipeline is difficult due to the low mobility and flowability of the crude leading to wax and asphaltene deposition on pipeline wall surfaces.

The production of heavier crude oil and it associated flow assurance issues bring the employment of a variety of enhanced oil recovery techniques. Gas injection is widely used for heavy oil viscosity reduction, contributing to a higher oil recovery. Among the different types of gases used in this process, carbon dioxide ($CO_2$) is known as a very effective viscosity reducer because of its high solubility at relatively low pressures in heavy oil. The dissolution of $CO_2$ in heavy oil expands the volume of the heavy oil and increases the elastic energy to improve the recovery of heavy oil. Another benefit associated with the use of $CO_2$ in heavy oil reduction is for $CO_2$ sequestration to reduce green house gas emissions.
On the other hand, using $CO_2$ for heavy oil viscosity reduction presents some technical and economical challenges. From a technical perspective, asphaltene precipitation during $CO_2$ injection is a common occurrence that can undermine the success of this method and cause severe problems such as formation damage, wettability alteration, flow interruption in the reservoir, and surface facilities [10]. There are also corrosion problems associated with the use of $CO_2$ in saline brine environments (particularly in the presence of dissolved oxygen). On the economic point of view, limited availability of $CO_2$ in some areas of the world add enormously to the operating cost of the method.

Owing to the aforementioned problems, which may be associated with the $CO_2$ injection method, some companies are reluctant to use $CO_2$ as an injection gas [10]. Although with sufficient design and experimental work conducted prior to the implementation of $CO_2$ injection in heavy oil reservoir, many uncertainties can be eliminated and future operational problems reduced. In the past two decades, nitrogen has emerged as a competitive gas injection alternative for dilution and displacement of heavy oils from matured oil reservoir [10]. Nitrogen could be separated from air, produced from natural nitrogen gas reservoirs, or from the combustion of the heavy oil. Both the $CO_2$ and the $N_2$ alongside with the heat could be obtained as products of the in-situ combustion of the oil as given by the equation below:

$$Oil + (O_2 + 3.76N_2) \rightarrow CO_2 + H_2O + N_2 + \text{heat}$$

In spite of all the disadvantages associated with using $CO_2$ as a heavy oil diluent, it is still known as the most soluble non-hydrocarbon gas in heavy oil. Also, its employment in the heavy oil viscosity reduction provides a good use of unwanted environmental $CO_2$. Consequently, in this study, both carbon dioxide and nitrogen were used in the heavy oil viscosity reduction to study how they separately impact the viscosity of the oil. The mixture of the two gases was also injected in the oil. The aim of doing this was to marry the benefits in the usage of both gases and determine its effect on the heavy oil viscosity reduction. The secondary motivation for this study is the abundant global reserves of untapped heavy oils,
which are potential energy sources that could contribute to the ever-growing world’s energy needs. As shown in the diagram below, heavy, extra heavy oils, and bitumen make up 70% of the world’s oil reserves.

Figure 1.1. - Distribution of Total World Oil Reserves by Classification Oilfield Review, (2006)
2 Literature Review

Historically, demand for heavy oils has been marginal because of their high viscosity and composition complexity that make them difficult and expensive to produce, transport, and refine. Dilution is one of the oldest and preferred methods for reducing the viscosity of heavy oils\textsuperscript{7}. Since the 1930s, dilution was mainly done by the addition to heavy oil of lighter liquid hydrocarbons, typically condensates from natural gas production, but lighter crude oils are also used\textsuperscript{7}. Using lighter liquid hydrocarbon as heavy oil diluent is an effective option to reduce oil viscosity and facilitate its mobility in the pipeline since a ratio of 20-30\% of solvent is often enough to avoid high-pressure drops or the need for high temperatures\textsuperscript{5}. However, the dilution option has some challenges that made it less attractive. It requires substantial investments in pumping and pipelines due to the increase of the transport volume and the need to separate at some point the solvent, processes it and subsequently returns it to the oil production site. Also, experience has shown that in order to meet pipeline viscosity specifications, more diluent is used than necessary to meet the API gravity specifications which may affect the required oil/solvent ratio. Special attention must be accorded to asphaltene and paraffins stability, since condensate or light oil addition may cause precipitation and pipeline clogging \textsuperscript{[5]}.

In 2006, Van den Bosch and Schrijvers\textsuperscript{5} presented a combined dilution-upgrading method based in the in situ production of the solvent by separation, distillation and thermal cracking of a part of the heavy oil feed to produce one or more light fractions and one or more heavy fractions. The feed of the heavy oil is split in two, half is sent to the aforementioned process and the other half is diluted with the mix of all light fractions of the processed heavy oil while the obtained heavy fractions are used to generate heat and/or power. Thus a pipeline-transportable syncrude is formed which is easier to refine and presents less problems than completely upgraded syncrudes.

Within the same period in 2006, Iqbal et al\textsuperscript{5}. presented a variety of schemes that can allow the transport and process of heavy oils with different salts and water contents, acidity and
API gravity less than 15. They proposed an integrated approach to the dilution-upgrading-transportation process thus reducing initial capital requirements and operating costs. First, the dilution of the heavy oil is done with a light liquid hydrocarbon in 1:10 ratio; the mixture is then transported via pipeline to a solvent deasphalting unit which can be at a remote location. The deasphating process produces an asphaltene fraction, a deasphalted oil fraction essentially free of asphaltenes that is ready for further refining, and the solvent fraction that can be recovered and recycled as the extraction solvent or returned for heavy oil dilution.

A simpler alternative transport method for heavy oils was developed by Argilier et al (2006). Here, asphaltene are precipitated by n-alkanes and re-incorporated to the oil to obtain a slurry, i.e a suspension of non-colloidal particles with low viscosity that fluidizes the oil. Considering that the structure of heavy oils behaves like a viscous colloidal suspension, breaking the colloid system through asphaltene precipitation will have a definitive effect in its viscosity. The resulting morphology change of the crude in suspension form actually leads a viscosity decrease.

In 2007, Henaut et al proposed the use of dimethyl ether (DME) under pressure as solvent to adjust heavy oil viscosity and pressure drop in the pipeline. Moreover, the recovery of DME in the refinery, as opposed to other solvents, is much easier. Other solvents that are being researched are alcohols, i.e pentanol is doubly effective in reducing the viscosity of heavy oil in comparison to kerosene, due to hydrogen bond interactions with the hydroxyl groups that feature some of the asphaltene.

Since viscosity decreases very rapidly with increasing temperature, several works have been done in applying heating methods to improve the flow properties of heavy crude oils [5]. A famous example is the Alyeska pipeline in Alaska which transports crude oil at approximately 50°C. However, designing a heated pipeline is not simple since is involves many considerations; expansion of the pipelines, number of pumping/ heating stations, heat losses etc. Other significant issues are the high costs and greater corrosion rate of the internal pipe due the temperature [5]. Moreover, a recent study by Evdokimov et al. showed that
heat treatment could induce changes in the colloidal structure of the crude oils and worsen their rheological properties [5].

Currently, nitrogen gas, naphtha or light crude oil are an interesting alternative to the use of natural gas condensates due to its high API gravity and efficiency in the dilution of heavy oil.
3 Theoretical Background And Experimental Apparatus

3.1 Solubility of the gases in the heavy oil.

A knowledge of the solubility of gases in liquid is of crucial use in this experiment. The solubility of gases in the oil is the main mechanism associated with the heavy oil viscosity reduction. Gas solubility in heavy oil can be modeled using Henry’s law. Henry’s law assumes that at constant temperature, the gas-phase fugacity is proportional to the liquid mole fraction $x_i$.

$$ f_i = \mathcal{H} x_i $$

where,

- $f_i$ = fugacity of component i
- $\mathcal{H}$ = constant of proportionality (Henry’s constant)
- $x_i$ = mole fraction of species i in the liquid phase
  (generally termed as the solubility of species i)

This assumption is not only valid when $x_i \to 0$, but also when the species entering the liquid phase do not react or dissociate [3]. Henry’s law constant has a unit of pressure, and it depends on temperature and on pressure to a lesser degree. At low pressures, the impact of Henry’s constant can be neglected. At high pressures, however, the effect is not negligible and therefore, its variation with pressure is necessary. Starting with the equation that gives the change in fugacity with pressure:

$$ \left( \frac{\partial \ln f_i^L}{\partial P} \right)_{T,X} = \frac{V_2^L}{RT} \quad (1) $$

where $f_i^L$ = fugacity of species i in the liquid phase

- $V_2^L$ = partial molar volume of species i in the liquid phase

Taking the limit of both sides as $x_i \to 0$

By the properties of derivatives and limits, the left hand side (LHS) is given as
\[ \text{LHS} = \lim_{x_i \to 0} \left( \frac{\partial \ln f_i^L}{\partial P} \right)_{T,X} = \left( \frac{\partial \ln (\lim_{x_i \to 0} f_i^L)}{\partial P} \right) \equiv \left( \frac{\partial \ln (\lim_{x_i \to 0} x_i \mathcal{H}_i)}{\partial P} \right) \]

\[ \lim_{x_i \to 0} = \left( \frac{\partial \ln (x_i \mathcal{H}_i)}{\partial P} \right)_{T,X} \]

Assuming \( x_i \) is a constant, that is, independent of \( P \)

\[ \lim_{x_i \to 0} = \left( \frac{\partial \ln (x_i \mathcal{H}_i)}{\partial P} \right)_{T,X} = \left( \frac{\partial \ln (\mathcal{H}_i)}{\partial P} \right)_T \to \text{no longer dependent on } x_i \quad \text{(2)} \]

Proof: \( \frac{d \ln (a f(x))}{dx} = \frac{d \ln (f(x))}{dx} \); if \( a = \text{constant} \)

\[ \frac{d \ln (a f(x))}{dx} = \frac{1}{a f(x)} \frac{df(x)}{dx} = \frac{a}{f(x)} \frac{df(x)}{dx} = \frac{1}{f(x)} \frac{df(x)}{dx} = \frac{d \ln f(x)}{dx} \]

Taking limit as \( x_i \to 0 \), right hand side (RHS) of equation (1) becomes

\[ \text{RHS} = \lim_{x_i \to 0} \frac{V_i^L}{RT} = \frac{V_i^L}{RT} = \text{defining } V_i^\infty = \lim_{x_i \to 0} V_i^L \]

where \( V_i^L \) = partial molar volume of species \( i \) in the liquid phase at infinity.

Hence,

\[ \text{LHS} = \text{RHS} \]

\[ \left( \frac{\partial \ln (\mathcal{H}_i)}{\partial P} \right)_T = \frac{V_i^\infty}{RT} \quad \text{(3)} \]

Integrating both sides with respect to \( P \) from \( P' \) (an arbitrary reference pressure) to \( P \)

\[ \int_{P'}^{P} \left( \frac{\partial \ln (\mathcal{H}_i)}{\partial P} \right)_T \, dp = \int_{P'}^{P} \frac{V_i^\infty}{RT} \, dp \]

\[ \text{RHS} = \int_{P'}^{P} \frac{V_i^\infty}{RT} \, dp = \frac{1}{RT} \int_{P'}^{P} V_i^\infty \, dp \]
LHS = \int_{p^r}^{p} \frac{\partial \ln(H_i)}{\partial P} \, dp = \ln(H_i) \mid_{p^r}^{p} = \ln(H_i(p)) - \ln(H_i(p^r))

By definition,

\[ H_i(p) = \lim_{x_i \to 0} \frac{f_i^{L}}{x_i} \]
\[ H_i(p^r) = H_i(p^r) \]

LHS = RHS

\[ \ln \lim_{x_i \to 0} \frac{f_i^{L}}{x_i} - \ln H_i(p^r) = \frac{\int_{p^r}^{p} V_{L}^{\infty} \, dp}{RT} \]

As \( x_i \to 0 \), \( \lim_{x_i \to 0} \frac{f_i^{L}}{x_i} = \frac{f_i}{x_i} \)

Therefore,

\[ \ln \frac{f_i}{x_i} = \ln H_i(p^r) + \frac{\int_{p^r}^{p} V_{2}^{\infty} \, dp}{RT} \] \hspace{1cm} (4)

If the solution temperature is well below the critical temperature of the solvent, it is assumed that \( V_{2}^{\infty} \) is independent of pressure\(^1\). Letting \( i = 2 \) (solute) and \( P^r = P^s \) (saturation vapor pressure), the last equation becomes:

\[ \ln \frac{f_2}{x_2} = \ln H_2^{(p^r)} + \frac{\int_{p^r}^{p} V_{2}^{\infty}(P - P^s) \, dp}{RT} \] \hspace{1cm} (5)

This equation is known as Krichevsky-Kasarnovsky equation and it is remarkably useful for representing solubilities of sparingly soluble gases to very high pressure. Krichevsky and Kasarnovsky made the following assumptions:

(i) \( x_2 \ll 1 \)

(ii) \( V_{2}^{\infty} \) is independent of pressure
And when the vapor pressure of the solvent is negligible, i.e \( P_{1}^{\text{vap}} \simeq 0 \), Krichevsky-Kasarnovsky equation reduces to:

\[
ln \left( \frac{f_2}{x_2} \right) = ln H_2^{(p')} + \frac{V_2^{L∞}}{RT} P
\]  

(6)

Both of these assumptions hold in this experiment and therefore, equation 6 was used.

An illustration of the use of the above equations is drawn from the work of Yuan et al. [3], where solubilities of carbon dioxide was reported in 2-hydroxyl ethylammonium formate as a function of pressure. Although, the compound 2-hydroxyl ethylammonium formate is not similar to heavy oil but the example illustrated how Henry’s constant is obtained from a given data. Same method was employed in this study. Estimation of the Henry’s law constant and the partial molar volume of \( CO_2 \) at infinite dilution were done using the following data:

<table>
<thead>
<tr>
<th>( x_2 )</th>
<th>( P ) (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0304</td>
<td>5.1</td>
</tr>
<tr>
<td>0.0831</td>
<td>16.0</td>
</tr>
<tr>
<td>0.1001</td>
<td>19.8</td>
</tr>
<tr>
<td>0.1099</td>
<td>22.2</td>
</tr>
<tr>
<td>0.1796</td>
<td>43.3</td>
</tr>
<tr>
<td>0.2101</td>
<td>58.6</td>
</tr>
<tr>
<td>0.2428</td>
<td>74.6</td>
</tr>
<tr>
<td>0.2437</td>
<td>90.9</td>
</tr>
<tr>
<td>0.2468</td>
<td>86.9</td>
</tr>
</tbody>
</table>

Table 1

The fugacity of pure carbon dioxide at different pressures was calculated using Soave-Redlich-Kwong equation and the results are given in the following table:
\[
\ln\left(\frac{f_2}{x_2}\right) = P \quad (\text{bar})
\]

Table 2

<table>
<thead>
<tr>
<th>(x_2)</th>
<th>(f_2)</th>
<th>(\ln(\frac{f_2}{x_2}))</th>
<th>(P \text{ (bar)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0304</td>
<td>5</td>
<td>51.02751</td>
<td>5.1</td>
</tr>
<tr>
<td>0.0831</td>
<td>14.9</td>
<td>5.189072</td>
<td>16</td>
</tr>
<tr>
<td>0.1001</td>
<td>18.2</td>
<td>5.203007</td>
<td>19.8</td>
</tr>
<tr>
<td>0.1099</td>
<td>20.2</td>
<td>5.213867</td>
<td>22.2</td>
</tr>
<tr>
<td>0.1796</td>
<td>35.7</td>
<td>5.292174</td>
<td>43.3</td>
</tr>
<tr>
<td>0.2101</td>
<td>44.7</td>
<td>5.360145</td>
<td>58.6</td>
</tr>
<tr>
<td>0.2428</td>
<td>52.2</td>
<td>5.3706</td>
<td>74.6</td>
</tr>
<tr>
<td>0.2437</td>
<td>57.2</td>
<td>5.458371</td>
<td>90.9</td>
</tr>
<tr>
<td>0.2468</td>
<td>56.2</td>
<td>5.428094</td>
<td>86.9</td>
</tr>
</tbody>
</table>

Figure - 3.1.

The plot of \(\ln\left(\frac{f_2}{x_2}\right)\) versus \(P\) was made and given above. The slope and the intercept of the straight line are \(3.668 \times 10^{-3}\) and 5.121 respectively. Thus,
\[ \mathcal{H}_2 = \exp(5.121) = 167.5 \text{ bar} \]
\[ \overline{V}_2^{L_\infty} = (83.14)(313)(3.668 \times 10^{-3}) = 95.45 \text{ cm}^3/\text{mol} \]

### 3.2 Experimental Apparatus

The experimental apparatus comprised of a high pressure rheometer (AR 2000EX), a pressure transducer, and gas cylinders. The choice of geometry used on a rheometer is determined by degree of the viscosity of the sample. The pressure cell cup is not only suitable for this experiment because of the viscosity of the sample but also, it allows the for the external pressurization of the cup through the injection of gas. Other geometries include concentric cylinders, cone and plate, and parallel plate etc. These are not suitable choices for this experiment.

*The high pressure rheometer*

The term rheometer comes from the Greek word rheo, meaning flow, and rheometer is a device for measuring flow. To keep track of the heavy oil viscosity changes on the injection of gas under varying conditions, a rheometer was used. The pressure cell is a TA instrument pressure cell designed for use at temperatures up to 150\(^o\)C and pressures up to 138 bar (2000psi). The pressure cell is used with the standard concentric cylinder, peltier-controlled heating jacket. The pressure cell has a self pressuring mode in which the pressure is produced by the volatility of the sample, as well as an external pressurization mode. The external pressurization mode was used for this experiment.

*Pressure Cell Components*

The pressure cell consists of 4 main components assemblies. The components include the pressure cell cup, the concentric cylinder rotor, the magnet assembly and the pressure manifold.

A schematic cross section of the pressure cell cup, rotor, and magnetic assemblies is shown in the Fig below:
The pressure cell cup contains the sample fluid. It is inserted into the peltier jacket, which mounts on the rheometer using the smart swap\textsuperscript{TM} connection. A copper sheath ensures good heat transmission between the jacket and the cup. There are three ports on the cup: the inlet port, which is used in the external pressurization mode, the pressure gauge port, and the safety relief port. The inlet port is where the compressed gas is introduced to the cup. The pressure gauge port is fitted with a pressure gauge to indicate the pressure within the cell, and the safety relief port is only intended to be used when the pressure from the cell cannot be relieved in the usual way. The safety relief port is equipped with a rupture disk.
assembly that is designed to relieve excessive cup pressure.

The rotor and the magnetic assembly are shown below. The rotor assembly contains the concentric cylinder rotor, which is mounted on a shaft that is radically supported by two sapphire bearings located under the rotor assembly cap. The magnet assembly attaches to the rheometer’s rotating spindle and then lowers over the rotor assembly.
The pressure manifold is a high pressure manifold assembly that is connected to the rheometer frame. It also includes necessary valves and gauges for safety pressurizing and depressurizing the cell. It is a critical part of the pressure cell assembly and the pressure cell could not be operated without the manifold in place.
4 Experimental Method

The heavy oil used in this study was obtained from Innoveering. Characterization of heavy oil is based on two properties; the API gravity and its viscosity value. These two properties were determined for this sample at the initial stage of the study. To determine the specific gravity of the oil, a small container with volume of 11.3 mL was used. The mass of the container was measured using an electronic digital balance. The container was then filled with the oil sample and the new mass was taken and recorded. The difference between the mass of the container plus the sample and the mass of the container yields the mass of the sample. The density of the sample was then determined from its mass and volume as shown below. The ratio of the density of the oil to that of water gives the specific gravity of the oil. The API gravity was then determined from the specific gravity. The calculations are given below:

Mass of container = 6.586g
Mass of container + sample = 17.172g
Volume of the sample = 11.3ml

Density of the sample = \( \frac{\text{Mass of sample}}{\text{Volume of sample}} \)

= \( \frac{10.586g}{11.3ml} = 0.937g/ml \)

Specific gravity of the oil sample = \( \frac{\text{Density of oil}}{\text{Density of water}} \)

= \( \frac{0.937g/ml}{1g/ml} = 0.937 \)

API gravity of the oil sample = \( \frac{141.5}{S.G} - 131.5 \)

= \( \frac{141.5}{0.937} - 131.5 = 19.5^0 \text{ API} \)
In comparing the obtained value of 19.5\(^{0}\) API with the graphical representation of API definitions below, it is confirmed that the sample oil is indeed heavy oil.

![Heavy Oil Classification](image1)

Figure 4.1. - Heavy Oil Classification.

The viscosity of the sample was determined using a rheometer and shearing the sample between 1 and 100 l/s at room temperature. A plot of the viscosity and the shear rate was made and given below:

![Shear rate vs Viscosity](image2)

Figure 4.2. - Shear rate vs Viscosity.
Over the shearing rate, the viscosity remains fairly constant with an average value of 10,248 cP (10.248 Pa.s). This value which is >10,000 cP also qualifies the sample as heavy oil as graphically defined above.

4.1 Oil sample viscosity variation with temperature

Having ascertained that the oil sample is heavy and its viscosity determined, the effect of temperature on the viscosity was also established. The sample’s viscosity was measured between 25°C and 50°C at atmospheric pressure, and a plot between the viscosity and temperature was generated and given below:

![viscosity vs temperature](image_url)

Figure 4.3. - A plot of viscosity vs temperature.

4.2 Viscosity variation with temperature and pressure

The viscosity of the oil was measured again but this time with the injection of nitrogen at different pressures. A plot was generated showing the viscosity at different temperatures and pressures, and it was observed that the viscosity was steady as the pressure increases except for at 25°C where a sharp drop in viscosity was recorded between 100 and 200 psi. The impact of the temperature on the oil viscosity was again reflected in this experiment. At
lower temperature, (25°C), a slight reduction was observed in the viscosity from 9.66 Pa.s at 100 psi to 8.94 Pa.s at 400 psi. As the temperature increases, increase in pressure was observed to increase the oil viscosity. At 40°C (100 psi), the viscosity was 2.91 Pa.s and as the pressure was increased to 400 psi, the viscosity was seen to rise to 2.97 Pa.s.

![Viscosity of oil at different temp. & pressure](image)

Figure 4.4. - A plot of viscosity vs pressure at different temperatures.

### 4.3 Equipment set up

Operating the rheometer requires learning and paying attention to minute details during operation. At the initial stage of the experiment, some external connections were required to prepare for the targeted experiments. The tubing between the pressure manifold and the gas cylinder was set up using a metal pipe tube to sustain the high pressure between the two units. A picture for the connection is shown below:
All the NPT valves were replaced and the teflon reinforced to guarantee that they are leak proof. This was confirmed by conducting pressurizing leak tests.  

A pressure transducer with a millivolt output was used in the experiment. The pressure drop in the process of the saturation of the oil was monitored with the aid of the transducer. The pressure transducer had to be connected to the cup housing the sample and the gas on one end. A multimeter was connected to the power supply which gives the output readings of the pressure drop in voltage. A picture of the connection is shown below:
Figure 4.6. - Connection of power supply to the multimeter.

The calibration of the transducer was done and a plot showing a straight line relationship between the output voltage on the multimeter and the pressure was obtained and given below:

Figure 4.7. - Plot of voltage vs pressure (left), Plot of residuals vs pressure (right).
Pressure values were determined from the equation of the straight line

\[ P = \frac{V - 0.0275}{0.0016} \]

A check on the linearity of the relationship was carried out by plotting the pressure versus the residual. With the residual scattered all over the plot in fig-b and not able to detect a pattern proves the linearity of the relationship. Upon completion of installing the pressure transducer for a more accurate reading, calibrating and demonstrating linearity, the system was ready for continued experimentation. This new more accurate installation enabled the change in pressure to be used to determine the amount of gases dissolved in the oil.

4.4 Pressure cell calibration

Once the experimental arrangement had been set up as schematically shown below:-

![Diagram of the experimental setup](image)

Figure 4.8. - A schematic diagram of the experimental set up.

the pressure cell required calibration prior to running experiments.

(i) Pressure cell geometry was selected in the AR-2000EX software and the gap zero position determined. From the zero gap, the rotor assembly and the upper magnet was raised to a gap of 3500 micrometer as required in the equipment manual.
(ii) At this geometry gap of 3500 micrometer, bearing friction calibration was done. A required value for the pressure cell is between 8 and 15 micrometer/(rad/s).

NOTE - At the start of this experiment, the bearing friction calibration could not be passed. Manually input values were recorded each time to get beyond this stage. At a point a decision was reached to try out a different geometry to confirm if the problem would persist with cone plate geometry, the calibration was successful. This outcome confirmed that the equipment was not broken but the calibration steps had to be reviewed. In the process of repeated calibration, it was discovered that prior to setting the zero gap, the required 5mm distance between the upper magnet and the shoulder of the cup could not be significantly off. When this distance is not close to the required value, it hinders the rotation of the spindle and hence disrupts the subsequent bearing friction calibration. Once this was mastered, passing the bearing friction calibration was not an issue in the calibration process. To further authenticate the data from the pressure cell a viscosity test was done on two geometries; the pressure cell and the cone plate. It could be observed from the plot that the viscosity values from the two geometries are in agreement as shown below:
(iii) The rotational mapping of the air bearing is done at this stage.

### 4.5 Detailed Procedure

1. All the experiments were conducted at two different temperatures ($40^\circ C$ and $60^\circ C$) and at three different pressures (100psi, 300psi and 500psi). The gas was left overnight to soak in the oil and the oil saturation was confirmed by no further changes in the pressure reading over a period of 2-3 hours.

2. The solubility of each gas dissolving in the heavy oil between the initial and saturation pressure was determined using the mole balance:

   \[
   n_{gas \text{ (dissolved)}} = n_{gas \text{ (initial)}} - n_{gas \text{ (final)}}
   
   = \frac{P_i V}{Z_i RT} - \frac{P_f V}{Z_f RT}
   
   = \frac{V}{RT} \left[ \frac{P_i}{Z_i} - \frac{P_f}{Z_f} \right]
   \]
3. Redlich-Kwong equation of state was used in determining the fugacity of the pure gases in the form below:

\[
\ln f = \ln \frac{RT}{v-b} + \frac{a}{bRT^{3/2}} \ln \frac{V}{v+b} + \frac{b}{v-b} - \frac{a}{RT^{3/2}(v+b)}
\]

where

\[a = 0.42748R^\frac{2}{3}T^2 \quad b = 0.08664R^\frac{2}{3}T^2\]

4. A plot of \(\ln \left(\frac{f_2}{x_2}\right)\) vs \(P\) was generated where the exponent of the intercept gives the Henry’s constant.

5. For the gas mixture, Peng-Robinson equation of state was used in calculating the fugacity coefficient of each gas and then their fugacity. This worked better with binary mixture [2]. The Peng-Robinson equation was used in the form:

\[
\ln \varphi = -\ln(Z-B) - \frac{A}{B\sqrt{8}} \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B}\right] + Z - 1
\]

fugacity was calculated from the fugacity coefficient using the equation.

\[f = \varphi P\]

\(Z\) was evaluated from:

\[
Z = \frac{1}{(1-B/Z)} - \frac{A}{B} \cdot \frac{B/Z}{1 + 2B/Z - (B/Z)^2}
\]

where \(A \equiv \frac{aP}{R^2T^2}\) and \(B \equiv \frac{bP}{RT}\)
and \( a \equiv a_c \alpha; \quad a_c \equiv 0.45723553 \frac{R^2 T^2}{P_c} \quad b \equiv 0.07779607R \frac{T_c}{P_c} \)

\[
\alpha \equiv [1 + \kappa(1 - \sqrt{T_c})]^2 \quad \kappa \equiv 0.37464 + 1.54226\omega - 0.26992\omega^2
\]

\( T_c, P_c \) and \( \omega \) are reducing constants according to the principle of corresponding states [2] and their values for each gas were given in the calculation table.

6. The mole fraction of each gas in the mixture dissolving in the heavy oil was calculated from the already determined Henry’s constant from the equation.

\[
f_i = \mathcal{H}.x_2
\]

\[
\Rightarrow x_2 = \frac{f_i}{\mathcal{H}}
\]

### 4.6 Calculations

The experiments involving pressurizing with the gases (\( N_2, CO_2 \) and \( N_2+CO_2 \)) in this study are done at three different pressures; 100psi, 300psi and 500psi and at two different temperatures; 40\(^\circ\)C and 60\(^\circ\)C. The calculations for the determination of the amount of moles of \( N_2, CO_2 \), and \( N_2 + CO_2 \) that dissolved in the heavy oil at 40\(^\circ\)C are shown below for 100psi. For 300 and 500psi, the calculations are given in the Appendix. To do these calculations, the critical properties and the acentric factors of the gases are required. These values are obtained from Elliot and Lira [2] and are tabulated below:

<table>
<thead>
<tr>
<th>Gas</th>
<th>( T_C(K) )</th>
<th>( P_C(bar) )</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2 )</td>
<td>126.2</td>
<td>33.94</td>
<td>0.040</td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>304.2</td>
<td>73.76</td>
<td>0.225</td>
</tr>
</tbody>
</table>

Table 3

The subscript \( i \) denotes initial, while subscript \( f \) denotes final.
\[ P_r = \text{reduced pressure} \]
\[ T_r = \text{reduced temperature} \]

4.6.1 \textit{N}_2 \text{ dissolution in the oil at } 40^0C

At 100psi,

\[ P_i = \frac{0.1884 - 0.0275}{0.0016} = 100.6 \text{psi} \]

\[ P_f = \frac{0.1879 - 0.0275}{0.0016} = 100.25 \text{psi} \]

\[ P_r = \frac{P}{P_c} \]

\[ P_{r(i)} = \frac{(100.6/14.504) \text{bar}}{33.94 \text{bar}} = 0.204 \]

\[ P_{r(f)} = \frac{(100.25/14.504)}{33.94} = 0.20 \]

In calculating the reduced temperature \((T_r)\), the experimental temperature has to be converted from \(^{\circ}C\) to Kelvin by adding 273.15 before dividing by the critical temperature as shown below:

\[ T_r = \frac{T}{T_c} \]

\[ T_r = \frac{313.15K}{126.2K} = 2.48 \]

The compressibility values for both initial and final; \(Z_i\) and \(Z_f\) were read from the compressibility chart and are given below. To obtain these values, the calculated reduced pressures and temperatures were used.
\[ Z_i = 0.998 \quad Z_f = 0.998 \]

\[ n_{N_2(\text{dissolved})} = n_{N_2(i)} - n_{N_2(f)} \]

\[
n_{N_2} \text{ (dissolved)} = \frac{P_iV}{Z_iRT} - \frac{P_fV}{Z_fRT} \]

\[
= \frac{V}{RT} \left[ \frac{P_i}{Z_i} - \frac{P_f}{Z_f} \right] \]

\[
n_{N_2} \text{ (dissolved)} = \frac{14.2}{83.14 \times 313.15} \left[ \frac{6.94}{0.998} - \frac{6.91}{0.998} \right] \]

At 100 psi, \(1.64 \times 10^{-5}\) moles of \(N_2\) dissolved in the oil.

The plot of the oil viscosity against pressure is given below:

![Viscosity of N2 vs P at 40°C](image)

**Figure 4.10. - A plot of \(N_2\) viscosity vs pressure.**

With the obtained mole fraction \(x_2\), the fugacities of \(N_2\) were calculated at the 3 different pressures using Redlich-Kwong equation of state (RKEOS) in the form:

\[
\ln f = \ln \frac{RT}{v - b} + \frac{a}{bRT^{3/2}} ln \frac{V}{v + b} + \frac{b}{v - b} - \frac{a}{bRT^{3/2}(v + b)}
\]
where \( a = 0.42748R^2\frac{T_c^{2.5}}{P_c} \)

\[ \text{b} = 0.08664R\frac{T_c}{P_c} \]

Using matlab, the RKEOS was solved for the fugacities of \( N_2 \) at different pressures and the results are given below:

\[
\begin{aligned}
    f_2 &= 6.9184 \text{ bar at 6.93 bar (100 psi)} \\
    f_2 &= 20.6199 \text{ bar at 20.7 bar (300 psi)} \\
    f_2 &= 34.3408 \text{ bar at 34.5 bar (500 psi)}
\end{aligned}
\]

A straight line plot of \( \ln(f_2/x_2) \) vs P was generated as shown below:

Figure 4.11. - A plot of \( \ln (f_2/x_2) \) vs pressure.
The intercept of the above plot is 13.2 and from this value, Henry’s constant was obtained thus:

\[ H_2 = \exp(13.2) = 5.37 \times 10^5 \text{ bar} \]

Having determined experimentally the solubilities of \( N_2 \) at 100, 300 and 500 psi, \( x_2 \) at other pressures could be predicted.

The experimental values for the number of moles of \( N_2 \) dissolved were compared with the calculated values and plotted as shown below. The calculated values are significantly different from the observed solubilities.

![Graph showing viscosity values for both experimental and calculated vs pressure at 40°C for \( N_2 \).](image)

Figure 4.12. - A plot showing viscosity values for both experimental and calculated vs pressure at 40°C for \( N_2 \).

It is observed that there is a large divergence between the experimental and calculated values. The main reason that might be associated with this observation is the negligible solubility on of \( N_2 \) in the oil. The experimental values reflect this almost insoluble state of \( N_2 \) in the oil, while the equation of state used in obtaining the calculated values did not reflect the true solubility of the gas in the oil.
4.6.2 \textit{CO}_2\ \text{dissolution in the oil at 40^\circ C}

At 100psi,

\[ P_i = \frac{0.1888 - 0.0275}{0.0016} = 100.8\text{psi} = 6.95\text{bar} \]

\[ P_f = \frac{0.1677 - 0.0275}{0.0016} = 87.6\text{psi} = 6.04\text{bar} \]

\[ P_{r(i)} = \frac{P_i}{P_c} = \frac{(100.8/14.504)}{73.82} = 0.094 \]

\[ P_{r(f)} = \frac{P_f}{P_c} = \frac{(87.6/14.504)}{73.82} = 0.08 \]

\[ T_r = \frac{T}{T_c} = \frac{313.15}{304.2} = 1.029 \]

The respective \( Z_i \) and \( Z_f \) values are read off the chart and are given as:

\[ Z_i = 0.9668 \quad \quad Z_f = 0.9712 \]

\[ n_{(\text{CO}_2)}\,\text{(dissolved)} = n_{\text{CO}_2(i)} - n_{\text{CO}_2(f)} \]

\[ = \frac{PV}{Z_iRT} - \frac{P_fV}{Z_fRT} \]

\[ = \frac{V}{RT} \left[ \frac{P_i}{Z_i} - \frac{P_f}{Z_f} \right] \]

\[ n_{\text{CO}_2}\,\text{(dissolved)} = \frac{14.2}{83.14 \times 313.15} \left[ \frac{6.95}{0.9668} - \frac{6.04}{0.9712} \right] \]

At 100psi, \( 5.29 \times 10^{-4} \text{mole} \) of \( \text{CO}_2 \) dissolved in the oil.

A plot of the oil viscosity vs pressure is shown below:
Here, it is observed that the viscosity of the oil drops as the pressure of CO₂ increases in the cup. This is in contrast to what was observed in the case of N₂. The viscosity of the oil and the gas solubility possess an inverse proportionality relationship. Because CO₂ dissolves more in the oil than N₂, it reduces the oil viscosity significantly.

Having determined the mole quantity of CO₂ that dissolved in the oil at different pressures, the gas fugacities at these pressures were calculated by using the Redlich-Kwong equation and the results are given below:

\[
\ln f = \ln \left( \frac{RT}{v-b} + \frac{a}{bRT^{3/2}} \right) + \ln \left( \frac{V}{v+b} + \frac{b}{V-b} - \frac{a}{RT^{3/2}(v+b)} \right)
\]

\[
f_2 = 6.7505 \text{ bar at 6.95 bar (100psi)}
\]
\[
f_2 = 19.0355 \text{ bar at 20.7 bar (300psi)}
\]
\[
f_2 = 30.2609 \text{ bar at 34.5 bar (500psi)}
\]

A straight line plot of \(\ln(f_2/x_2)\) vs P was generated as shown below:
Figure 4.14. - A plot of $\ln \left( \frac{f_2}{x_2} \right)$ vs pressure.

The intercept of the plot above is 7.4959 and from this value, Henry’s constant was obtained thus:

$$H_2 = \exp(7.4959) = 1800.6 \text{ bar}.$$  

The experimental values for the number of moles of $CO_2$ dissolved were compared with the calculated values and plotted as shown below. The calculated values were higher than those from the experiments and more divergence was observed at higher pressures.
Figure 4.15. - A plot showing viscosity values for both experimental and calculations vs pressure at 40°C for CO₂.

In the plot above, there is a better agreement between the experimental and calculated values as compared to that obtained for N₂. More CO₂ dissolves in the oil as its quantity increases in the cup. This singular factor gave a good input for the equation of state used to determine the calculated values.

4.6.3 N₂ + CO₂ mixture in the oil at 40°C

In the mixture of N₂ and CO₂, higher proportion of N₂ was used at 40°C. The fugacity of each gas at their respective pressure was calculated using Peng-Robinson equation of state:

The Peng-Robinson equation at each pressure was solved using matlab and the results are given below:-

1a. \( P_{(N₂)} = 7.6 \) bar, fugacity = \( 11.87 \) bar

1b. \( P_{(CO₂)} = 4.6 \) bar, fugacity = \( 11.64 \) bar
2a. \( P(\text{N}_2) = 21.2 \text{ bar}, \text{fugacity} = 11.83 \text{ bar} \)
2b. \( P(\text{CO}_2) = 4.6 \text{ bar}, \text{fugacity} = 11.64 \text{ bar} \)

3a. \( P(\text{N}_2) = 30.2 \text{ bar}, \text{fugacity} = 11.81 \text{ bar} \)
3b. \( P(\text{CO}_2) = 4.8 \text{ bar}, \text{fugacity} = 11.63 \text{ bar} \)

From the previous experiments done with each gas at 40\(^\circ\)C, the Henry’s constants were determined and are given for the two gases below:

\( \mathcal{H} \) for \( \text{N}_2 \) at 40\(^\circ\)C = \( 5.37 \times 10^5 \text{ bar} \)
\( \mathcal{H} \) for \( \text{CO}_2 \) at 40\(^\circ\)C = 1800.6 \text{ bar} 

The mole fraction of each gas dissolving in the oil was calculated using:

\[ f_i = \mathcal{H} x_2 \]
\[ x_2 = \frac{f_i}{\mathcal{H}} \]

Therefore,

1a. \( x_{\text{N}_2} = \frac{11.87}{5.37 \times 10^5} = 2.21 \times 10^{-5} \)

1b. \( x_{\text{CO}_2} = \frac{11.64}{13100} = 8.98 \times 10^{-4} \)

2a. \( x_{\text{N}_2} = \frac{11.83}{5.37 \times 10^5} = 2.20 \times 10^{-5} \)

2b. \( x_{\text{CO}_2} = \frac{11.64}{13100} = 8.98 \times 10^{-4} \)

3a. \( x_{\text{N}_2} = \frac{11.81}{5.37 \times 10^5} = 2.20 \times 10^{-5} \)

3b. \( x_{\text{CO}_2} = \frac{11.63}{13100} = 8.97 \times 10^{-4} \)

In each experimental run, the amount of injected \( \text{CO}_2 \) was kept fairly constant while the
amount of $N_2$ in the mixture was increased each time. More of the $CO_2$ got dissolved in the oil in spite of its lesser composition in the mixture. On the contrary, as the amount of $N_2$ in the mixture increases, its solubility does not rise but instead dropped. A plot showing the number of moles of the mixture dissolved in the oil for calculated and experimental values was made, and there was no agreement between the two values as revealed in the plot below. The presence of $N_2$ in the mixture could be largely associated with this observed disagreement. Its negligible solubility also impacted $CO_2$ solubility in the mixture [4].

![A plot showing experimental vs calculated values of dissolved gas mixture.](image)

Figure 4.16. - A plot showing experimental vs calculated values of dissolved gas mixture.

### 4.7 Solubilities of the gases under the same conditions

In comparing the solubilities of the three different gases ($N_2$, $CO_2$ and $N_2 + CO_2$) at $40^\circ C$, a plot was made showing the quantity of each gas dissolved under the same conditions. With $CO_2$ being the most soluble, its solubility increases with its quantity in the oil. In the gas mixture, the quantity dissolved was observed to be higher than that of $N_2$ only but lower as compared to $CO_2$ only. It was also observed that the solubility was fairly constant in the three pressure ranges. $N_2$ showed the least solubility with an insignificant rise between 100 and 500 psi. The plot is given below:
Figure 4.17. - A plot showing no. of moles of $N_2$, $CO_2$ and $N_2 + CO_2$ dissolved at 40°C.

A final plot was made comparing how the viscosity of the heavy oil was impacted by the three gases ($N_2$, $CO_2$ and $N_2 + CO_2$) at 40°C and given below:

Figure 4.18. - A plot for viscosity vs pressure for $N_2$, $CO_2$ and $N_2 + CO_2$ at 40°C.
5 Results And Discussions

As seen in section 4.2, with increased temperature, the viscosity of the oil was reduced by 85.4% between 25 and 50°C. This confirmed that temperature is a very potent means of reducing heavy oil viscosity. When both temperature and pressure were varied, as plotted in figure 4.4, it was observed that the oil viscosity was fairly constant at different temperatures as N₂ gas pressure in the oil was increased between 100 - 400 psi. By contrast, as the temperature was increased between 25 - 40°C, the viscosity was reduced by 70% at 100psi where the highest viscosity drop was observed. Figure 4.15 revealed a fair agreement between the calculated and the experimental data initially yet diverged at higher pressures for CO₂ at 40°C. As stated earlier, more CO₂ dissolves in the oil as its quantity increases in the cup. This progression in the dissolved quantity CO₂ gave a more meaningful input for the equation of state used to determine the calculated values. On the other hand, figure 4.16 showed a poor agreement between the calculated and the experimental data for the gas mixture at 40°C. The presence of N₂ not only lead to a pressure build up in the cup as a result of its negligible solubility, but also lowers the partial pressure of CO₂ leading to a reduction in its solubility as well [4]. The curve for the experimental values is largely controlled by the ratio of the mixture, whereas, the calculated values barely respond to the ratio of the mixture. This explains the disagreement between the two curves.

In section 4.6.3., where the mixture of the two gases was used in diluting the oil, it was observed that the oil viscosity did not respond as expected. By using the two gases in the mixture, their impacts on the oil viscosity was expected to be additive of the individual gas but instead, there was a rise in the oil viscosity as compared to the values obtained from using pure CO₂ as plotted in figure 4.18. It was discovered that increasing the N₂ content in the mixture only increases the viscosity of the oil. The main reason behind this observation is that N₂ not only has a negligible dissolution in the oil but also contribute to the decrease in the solubility of CO₂ and since viscosity reduction is directly related to the amount of gas dissolved in the oil, the result could not be otherwise. With more N₂ in the mixture, the
partial pressure of $CO_2$ was further reduced and from Henry’s equation, its concentration in the oil was as well reduced.

In the graph in figure 4.18, where the viscosities of the three gases were plotted against pressure. It could be read from the graph that it is only with $N_2$ that the viscosity slightly increases as the pressure increases. This is because the solubility of $N_2$ does not significantly increase as more of it was introduced in the oil, and when this happens, the increase pressure as a result of density rise causes increase to the viscosity. Also from the graph, under the same conditions, $CO_2$ impacted the oil viscosity the most.
Conclusion

The viscosity of the heavy oil used in this study was determined at the start of the study to be 10.248 Pa. On the basis of the results obtained by the dilution with pure nitrogen, pure carbon dioxide and a mixture of nitrogen and carbon dioxide, the following conclusions can be drawn:

1. In all the gases ($N_2$, $CO_2$ and $N_2+CO_2$) injected in the oil, $CO_2$ is the most soluble and as a result reduces the oil viscosity the most by 77.8% on the average at 40°C. While at the same temperature, $N_2$ and $N_2+CO_2$ reduced the oil viscosity by 73.4% and 75.8% on the average respectively.

2. The experimental results for pure nitrogen in the oil show different pattern from that of pure $CO_2$. As the nitrogen pressure increases in the cup, a pressure build up lead to a rise in the viscosity. This happens because of the negligible solubility of $N_2$ in the oil and since viscosity reduction is a function of the gas solubility in the oil, the rise in the oil viscosity is understood.

3. In the experimental results from the gas mixture, at 100 psi where the dissolved mole of $N_2$ was $2.21 \times 10^{-5}$, the viscosity was 2.56 Pa.s. At 300psi, although same quantity of $CO_2$ was observed to dissolve in the oil as in 100psi mixture, the amount of dissolved $N_2$ slightly decreased. With the slight decrease in $N_2$, the viscosity of the oil was observed to drop by 3.5%. In comparing the oil viscosity values obtained from the injection of the gas mixtures to that from the pure gases, the impact of the gas mixture on the oil viscosity was not additive of the two gases. The presence of nitrogen with carbon dioxide led to an increase in the viscosity of the oil-gas mixture. This behavior has been observed and reported in literature. Nguyen and Farouq [4] in their work on the effect of nitrogen on the solubility and diffusivity of carbon dioxide into oil and oil recovery by the immiscible WAG process gave the most probable reason for this behavior. It was stated that because of the negligible solubility of $N_2$ in the heavy crude oil, its presence in the gas mixture reduces the partial pressure of $CO_2$ in the mixture, and hence its solubility in the oil. Thus, the higher the nitrogen content in
the mixture, the lower is the carbon dioxide partial pressure; as a result, the solubility of $CO_2$ will be lowered and hence, the oil viscosity increases.
Appendix

$N_2$ at 300 psi, and 40°C,

\[ P_i = \frac{0.508 - 0.0275}{0.0016} = 300.9\text{psi} \]

\[ P_2 = \frac{0.503 - 0.0275}{0.0016} = 297.2\text{psi} \]

\[ P_{r(i)} = \frac{(300.9/14.504)}{33.94} = 0.611 \]

\[ P_{r(f)} = \frac{(297.2/14.504)}{33.94} = 0.604 \]

And the respective Z values are:

\[ Z_i = 0.995 \quad Z_f = 0.995 \]

\[ n_{N_2\text{ (dissolved)}} = \frac{14.2}{83.14 \times 313.15} \left[ \frac{20.75}{0.995} - \frac{20.49}{0.995} \right] \]

At 300 psi, $1.096 \times 10^{-4}$ moles of $N_2$ dissolved in the oil.

At 500 psi, and 40°C,

\[ P_i = \frac{0.829 - 0.0275}{0.0016} = 500.9\text{psi} \]

\[ P_f = \frac{0.826 - 0.0275}{0.0016} = 499.1\text{psi} \]

\[ P_{r(1)} = \frac{(500.9/14.504)}{33.94} = 1.02 \]

\[ P_{r(2)} = \frac{(499.1/14.504)}{33.94} = 1.01 \]

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And the Z values are:

\[ Z_i = 0.993 \quad Z_f = 0.993 \]

\[ n_{N_2} \text{ (dissolved)} \] = \[ \frac{14.2}{83.14 \times 313.15} \left[ \frac{34.5}{0.993} - \frac{34.4}{0.993} \right] \]

At 500 psi, \(2.765 \times 10^{-4}\) moles of \(N_2\) dissolved in the oil.

**For CO\textsubscript{2} gas,**

At 300 psi, and 40\(^\circ\)C,

\[ P_i = \frac{0.508 - 0.0275}{0.0016} = 300.8 psi = 20.7 \text{bar} \]

\[ P_f = \frac{0.473 - 0.0275}{0.0016} = 278.4 psi = 19.2 \text{bar} \]

\[ P_{r(i)} = \frac{P_i}{P_c} = \frac{20.7}{73.82} = 0.28 \]

\[ P_{r(f)} = \frac{P_f}{P_c} = \frac{19.2}{73.82} = 0.26 \]

And from the above, \(T_r = 1.029\)

The calculated Z values are:

\[ Z_i = 0.8980 \quad Z_f = 0.9058 \]

Applying the mole balance,

\[ n_{C O_2} \text{ (dissolved)} \] = \[ \frac{14.2}{83.14 \times 313.15} \left[ \frac{20.7}{0.8980} - \frac{19.2}{0.912} \right] \]
At 300psi, \(= 1.09 \times 10^{-3}\) moles of \(CO_2\) dissolved in the oil.

At 500psi, and 40°C

\[
P_i = \frac{0.829 - 0.0275}{0.0016} = 500.9\text{psi} = 34.5\text{bar}
\]

\[
P_f = \frac{0.774 - 0.0275}{0.0016} = 466.6\text{psi} = 32.2\text{bar}
\]

\[
P_r(i) = \frac{P_i}{P_c} = \frac{34.5}{73.82} = 0.47
\]

\[
P_r(f) = \frac{P_f}{P_c} = \frac{32.2}{73.82} = 0.44
\]

\[T_r = 1.029\]

\[Z_i = 0.8234 \quad Z_i = 0.8363\]

Applying the mole balance,

\[
n_{CO_2} \text{ (dissolved)} = \frac{14.2}{83.14 \times 313.15} \left[ \frac{34.5}{0.8234} - \frac{32.2}{0.8363} \right]
\]

At 500psi, \(1.85 \times 10^{-3}\) moles of \(CO_2\) dissolved in the oil.

\(N_2\) dissolution in the oil at 60°C

At 100psi,

\[P_i = 6.97\text{ bar}\]

\[P_f = 6.95\text{ bar}\]

\[Z_i = Z_f = 0.9990\]

\[T = 333.15\text{K}\]
\[ T_r = \frac{T}{T_c} = 2.64 \]

Applying mole balance,
\[ n_{N_2} \text{ (dissolved)} = \frac{14.2}{83.14 \times 333.15} \left[ \frac{6.97}{0.999} - \frac{6.95}{0.999} \right] \]
\[ = 1.027 \times 10^{-5} \text{ moles} \]

At 300psi,
\[ P_i = 20.8 \text{ bar} \]
\[ P_f = 20.7 \text{ bar} \]
\[ Z_i = Z_f = 0.9978 \]
\[ n_{N_2} \text{ (dissolved)} = \frac{14.2}{83.14 \times 333.15} \left[ \frac{20.8}{0.9978} - \frac{20.7}{0.9978} \right] \]
\[ = 5.14 \times 10^{-5} \text{ moles} \]

At 500psi,
\[ P_i = 34.5 \text{ bar} \]
\[ P_f = 34.1 \text{ bar} \]
\[ Z_i = Z_f = 0.9975 \]
\[ n_{N_2} \text{ (dissolved)} = \frac{14.2}{83.14 \times 333.15} \left[ \frac{34.5}{0.9975} - \frac{34.1}{0.9975} \right] \]
\[ = 2.057 \times 10^{-4} \text{ moles} \]
Figure A1. - A plot of N2 viscosity vs pressure at 60°C.

The intercept of the plot = 13.02 $\mathcal{H} = \exp^{13.02} = 4.53 \times 10^5$ bar.
REFERENCES


