The effect of CO₂ dissolution on the rheology of a heavy oil/water emulsion

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KEYWORDS
Rheology, heavy crude oil, emulsion, carbon dioxide, viscosity, non-Newtonian fluid

ABSTRACT

During the later stages of flow from an oil well, water inevitably appears in the produced fluids. When crude oil and water are energetically mixed by constrictions in the production tubing, emulsions can form. Heavy crude oils may also contain surface-active agents that can stabilise the emulsion, resulting in persistent flow problems. If carbon dioxide is injected into such a reservoir (e.g. for CO₂ EOR), then the CO₂ will dissolve into both oil and water phases affecting the emulsion properties, however this aspect has been neglected in the literature so far.
This paper presents a study of the rheology of oil/water emulsion altered by carbon dioxide. The emulsion was prepared by blending 50 wt% water and 50 wt% Zuata heavy crude oil in a high shear mixer (Silverson), resulting in a water-in-oil emulsion. The emulsion was subsequently stable at ambient conditions for several weeks without the addition of any surfactants. A high pressure rheometer system coupled to a mixing vessel and fluid circulation loop allowed the emulsion to be brought into equilibrium with CO$_2$ and its rheology was then measured at a temperature of 50 °C and at pressures from ambient to 120 bar. The emulsion without dissolved CO$_2$ was found to be slightly shear thinning below a critical shear rate, above which the viscosity jumped to a much lower value. The CO$_2$ dissolution had two effects: first, it reduced the emulsion viscosity at low shear while preserving the shear thinning behaviour; second, increasing the CO$_2$ pressure in equilibrium with the emulsion increased the critical shear rate at which the viscosity jump occurred. At shear rates above the jump, the emulsion viscosity dropped to a level lower 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 jump was reversed (with some hysteresis) as the shear rate was reduced again. 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 reduced the viscosity of the oil while dissolution into the water phase markedly changed pH and thereby the performance of any charged surface-active agents present in the crude oil.

1 Introduction

Crude oil is usually not produced alone; it is normally mixed with formation water, 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 [1]. 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 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 flow 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 lead to a number of operational challenges. One of the challenges 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 [1]. Dewatering is a necessary operation for the upstream oil producers, but the formation of a stable emulsion prevents easy water/oil separation and increases the cost of the surface facilities.

Most literature on the rheology of crude oil emulsions has focussed on how the rheological properties are affected by water content, surface agent properties, droplet behaviour and dynamics, and operation conditions [2-7]. The rheology of the crude oil emulsions reported in these study were predominately measured at ambient pressure, without any gas dissolution. In the real situation, the crude oil emulsion produced could contain dissolved gas, which could play a significant role in determining the rheological properties of the emulsion. Einar et al. developed a wheel-shaped flow simulator to measure the viscosity of live crude oil emulsions, in which the dissolved gas was composed of natural gas components [8]. However, they measured the viscosity at a constant rotational speed thus the viscosity response at different shear rate was not studied. In this paper, using an innovative rheometer system, we report on the effect of CO₂ dissolution on the rheology of a water/oil emulsion.
2 Experimental Section

Material

The water/oil emulsion was prepared using the Zuata crude oil, whose properties can be found in Table 1.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>API Gravity</td>
<td>9.28</td>
</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 H₂S Content (ppm)</td>
<td>-</td>
</tr>
<tr>
<td>Potential H₂S 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>
</tbody>
</table>

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 (at around 4000 rpm). The emulsion contained 50 w% water and 50 w% Zuata crude oil (50:50 emulsion). Emulsions with different water contents were not studied because of the limited time available. Due to the high viscosity of the crude oil, mixing at 25 °C did not result in an emulsion and heating was required during the preparation. The liquid was heated up to 50 °C, followed by shearing at 50 °C for 45 min. 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 a water-in-oil emulsion. The emulsion obtained in this way remained stable for several weeks when left static at room temperature and no free water or oil layers developed (see Figure 1), indicating that the Zuata crude oil contains the components that can act as a stabiliser for the water/oil emulsion.
Experiment Setup and Procedure

The rheology measurement of the 50:50 emulsion was first performed at ambient pressure without CO2 addition 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, giving 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 temperature fluctuations of less than 0.02 °C. In a typical experiment, 19 ml of the emulsion was loaded in the measuring cup and the measuring system was brought to the desired temperature by the electrical heating device and held for 1 hour to ensure thermal equilibrium. In each measurement, the emulsion was pre-sheared at 5 s\(^{-1}\) for 0.5 min and then held at rest for 1 min before the flow cure was measured. 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. Only ascending measurement was performed. After the measurement at one temperature was completed, the temperature was adjusted to a higher level for the next measurement.

A high pressure circulation rheometer system (see Figure 2) was built to perform the rheology measurements on the 50:50 emulsion in equilibrium with CO₂ and a detailed description can be found in our previous paper [9]. In a typical experiment, the emulsion was first loaded in the mixer and the entire system primed. After any air remaining in the system was removed by a vacuum pump, the CO₂ was introduced into the mixer from the syringe pump, which controlled the overall system pressure. After the temperature and pressure reached the set-points, the stirrer and the gear pump were turned on. At each pressure, the equilibrium between CO₂ and the emulsion was reached through constantly stirring in the mixer and flowing through the circulation loop. The equilibrium was confirmed by periodic measurements of both viscosity and volume remaining in the pump until no further changes were observed. At equilibrium, the difference between two continuous measurements was less 1% for pump volume and 4% for viscosity. Before the rheology measurement was performed at a given pressure, the sample in the pressure cell was left at rest for one hour (the gear pump was turned off). The rheology measurement started with a 5 s⁻¹ pre-shearing for 0.5 min and then 1 min resting time, identical to the ambient pressure measurement. 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. 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). Only ascending shear rate measurement was performed. After the measurement at a given pressure was finished, a new set-point was input to the syringe pump.
When the new pressure level was reached and stabilised, the gear pump and mixer were restarted for the mixing and equilibration step before the new measurement.

3 Results

Measurements at ambient pressure

Figure 3 shows an image of the 50:50 water/oil 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.

![Image](image.png)

**Figure 3.** The image of the water/oil emulsion taken by a confocal laser-scanning microscope at ambient conditions.

Figure 4 and Figure 5 show the results at ambient pressure and temperatures from 45 °C to 65 °C plotted as shear stress and viscosity respectively. At each temperature the flow curve in Figure 4 can be broken down into three regions. The first region being the low shear rate region, extended from the lowest shear rate measured to the shear rate just before the flow curve maxima. In this region, a weak shear thinning effect was observed in the viscosity measurements (see Figure 5). In the second region a viscosity jump was observed in Figure 5, as the viscosity dramatically decreased to a lower value. In this region, as shown in Figure 4, the slope of the flow curve changed from positive to negative. This lower value of viscosity was substantially below the viscosity of
the oil phase (5380 mPa·s at 50 °C and ambient pressure [10]), indicating that the emulsion may undergo a phase inversion.

Figure 4. The flow curve of the emulsion at ambient pressure and at different temperatures. —, the fitting curve by Equation (1); ●, 45 °C; ○, 50 °C; ▼, 55 °C; ●, 60 °C; •, 65 °C. All the empty circles represent the points that may be measured at insufficient shearing time.

Figure 5. The viscosity measurement of the emulsion at ambient pressure and at different temperatures. —, the fitting curve by Equation (1); ●, 45 °C; ○, 50 °C; ▼, 55 °C; ●, 60 °C; •, 65 °C. All the empty circles represent the points that may be measured at insufficient shearing time.
Phase inversion is the phenomenon whereby a phase interchange occurs in a liquid-liquid emulsion [11]. In this case, the water-in-oil emulsion probably inverted to an oil-in-water emulsion at high shear. Note that the stress at the end of the jump was similar at all temperatures, which can be observed from Figure 4. This viscosity jump region extended from the stress maxima up to the end of the region in which measured stress decreased with increasing shear rate. Finally, 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:

$$\eta = K \dot{\gamma}^{n-1}$$

(1)

where $\dot{\gamma}$ is shear rate, $n$ the power-law index, and $K$ the fluid consistency. The fitting results are summarised in Table 2. The average absolute derivation (AAD) of the curve fitting for each region is also reported in Table 2.

Table 2. The curve fitting results of Equation (1) for measurements shown in Figure 5. $\ln(K)$ is the natural logarithm of $K$.

<table>
<thead>
<tr>
<th>Region</th>
<th>Low Shear Rate</th>
<th>Viscosity Jump</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>
<td>45</td>
<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>
<tr>
<td>60</td>
<td>0.9217</td>
<td>8.6538</td>
<td>-3.6313</td>
</tr>
<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>

From Table 2 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 (less than 2 min) may not have been sufficiently long.
to achieve steady state. Therefore, only the maximum shear stress point and the end point of the
viscosity jump were analysed, given that these two points were likely to 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 much lower 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 $n$ corresponds to a
stronger shear thinning effect in the high shear rate region compared to the low shear rate region.

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

$$\ln(\eta_{\text{max } (T)}) = A + \frac{B}{T}$$

(2)

Moreover, the shear rate at the maximum shear stress, $\dot{\gamma}_{\text{max } \sigma, T}$, was proportional to temperature,
and can be correlated by

$$\ln(\dot{\gamma}_{\text{max } \sigma, T}) = A + B \times T$$

(3)

$\eta_{\text{max } (T)}$ is $\eta_{\text{max } \sigma, T}$ 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 $\eta_{\text{max } \sigma, T}$, $\eta_{\text{end } T}$ and $\dot{\gamma}_{\text{max } \sigma, T}$
were 5.4%, 9.5%, and 0.1%, respectively. The curve fitting results are shown in Figure 6, and the
values of $A$ and $B$ are summarised in Table 3. 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.
Figure 6. Comparison between the measurement and the correlation results given by Equation (2) and (3). The parameters used are given in Table 3.

\[ \bullet, \eta_{\max, \sigma, T}; \quad \triangle, \eta_{\text{end}, T}; \quad \times, \gamma_{\max, \sigma, T}. \]

Table 3. The value of the fitting parameters in Equation (2) and (3).

<table>
<thead>
<tr>
<th>Parameter ( A )</th>
<th>( \eta_{\max, \sigma, T} )</th>
<th>( \eta_{\text{end}, T} )</th>
<th>( \gamma_{\max, \sigma, T} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -22.5604 )</td>
<td>(-22.1546)</td>
<td>(-25.2727)</td>
<td></td>
</tr>
<tr>
<td>( B )</td>
<td>( 10231.07 )</td>
<td>( 8568.581 )</td>
<td>( 0.09051 )</td>
</tr>
</tbody>
</table>

**Measurements at High CO\(_2\) Pressures**

Figure 7 and Figure 8 show the rheological measurements of the 50:50 emulsion saturated with CO\(_2\) at different pressures, a constant temperature of 50 °C and shear rates from 10 s\(^{-1}\) to 500 s\(^{-1}\). As expected from the previous measurements, at atmospheric pressure (with no CO\(_2\) addition) and low shear rates the emulsion showed a weak shear thinning effect (see Figure 7). At ambient pressure, when the shear rate reached 58 s\(^{-1}\), the gradient of the flow curve changed from positive to negative, as shown in Figure 7; when the shear rate exceeded 104 s\(^{-1}\) the viscosity of the emulsion jumped to a much lower value and the shear thinning effect was still observed at high shear rates, as shown in Figure 8. The emulsion in equilibrium with CO\(_2\) at 30 bar remained shear thinning at low shear rates, but had a viscosity jump that occurred at a higher shear rate and the
A high shear plateau was shifted above the measurement range. At CO₂ 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 7. The flow curve 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. The solid lines are the fitting curves by Equation (1). All the empty circles represent the points that may be measured at insufficient shearing time.

Figure 8. 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. The solid lines are the fitting curves by Equation (1). All the empty circles represent the points that may be measured at insufficient shearing time.
The analysis of the high pressure experiment was similar to that described above for the ambient measurements. The flow curves in Figure 7 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 (1), the power-law model. The fitting results are given in Table 4.

**Table 4.** The curve fitting results of Equation (1) for measurements shown in Figure 7. ln(K) is the natural logarithm of K.

<table>
<thead>
<tr>
<th>Region</th>
<th>Low Shear Rate</th>
<th>Viscosity Jump</th>
<th>High Shear Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>ln(K)</td>
<td>n</td>
</tr>
<tr>
<td>P / bar</td>
<td></td>
<td></td>
<td></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>
</tbody>
</table>

AAD: 2.4% | 70.5% | 4.7%

As shown in Table 4, 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 this led to values of n less than -1. As noted in the previous section, the shearing time (less than 2 min) may not be long enough in this region to achieve steady state.

An additional set of rheological measurements, with a narrower pressure range and higher maximum shear rates, was carried out to observe in more detail how CO₂ affected the jump and high shear viscosity. Figure 9 and Figure 10 show this set of measurements for the 50:50 emulsion saturated with CO₂ at pressures between 30 and 50 bar, temperature of 50 °C 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 plateau 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 CO₂ pressure was
increased further and more CO₂ 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.

![Flow curve of the crude oil/water emulsion and its saturated mixture with CO₂ at 50 °C and various pressure.](image1)

Figure 9. The flow curve of the crude oil/water emulsion and its saturated mixture with CO₂ at 50 °C and various pressure. ○, 30 bar; ●, 31 bar; ●, 32 bar; ●, 38 bar; ●, 45 bar; ●, 50 bar. The solid lines are the fitting curves by Equation (1). All the empty circles represent the points that may be measured at insufficient shearing time.

![Viscosity measurement of the crude oil/water emulsion and its saturated mixture with CO₂ at 50 °C and various pressure.](image2)

Figure 10. The viscosity measurement of the crude oil/water emulsion and its saturated mixture with CO₂ at 50 °C and various pressure. ○, 30 bar; ●, 31 bar; ●, 32 bar; ●, 38 bar; ●, 45 bar; ●, 50 bar. The solid lines are the fitting curves by Equation (1). All the empty circles represent the points that may be measured at insufficient shearing time.
Once again the measurement results in Figure 9 and Figure 10 were analysed using the method described in the previous section, and the viscosity measurement in Figure 10 were correlated using Equation (1). Table 5 summarises the calculated fitting parameters. In Table 5, in the low shear rate region, the value of $n$ approached to one with increasing CO$_2$ pressure, showing that the shear thinning effect was weakened by CO$_2$ addition, while the $K$ value was inversely proportional to CO$_2$ pressure. The most significant information revealed by Table 5 is 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 confirms that in this pressure range the viscosity was independent of shear rate after the viscosity jump, as shown in Figure 10.

Table 5. The curve fitting results of Equation (1) for measurements shown in Figure 9. $\ln(K)$ is the natural logarithm of $K$.

<table>
<thead>
<tr>
<th>Region</th>
<th>Low Shear Rate</th>
<th>Viscosity Jump</th>
<th>High Shear Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$/bar</td>
<td>$n$ $\ln(K)$</td>
<td>$n$ $\ln(K)$</td>
<td>$n$ $\ln(K)$</td>
</tr>
<tr>
<td>30</td>
<td>0.8916 8.9279</td>
<td>-3.3376 31.2466</td>
<td>1.0215 4.0849</td>
</tr>
<tr>
<td>31</td>
<td>0.8966 8.7272</td>
<td>-3.2738 32.9987</td>
<td>1.0224 4.1216</td>
</tr>
<tr>
<td>32</td>
<td>0.8963 8.3943</td>
<td>-3.5298 35.1334</td>
<td>1.0083 4.0946</td>
</tr>
<tr>
<td>38</td>
<td>0.9019 8.1457</td>
<td>-3.8896 38.0084</td>
<td>N/A N/A</td>
</tr>
<tr>
<td>45</td>
<td>0.9089 7.7546</td>
<td>N/A N/A</td>
<td>N/A N/A</td>
</tr>
<tr>
<td>50</td>
<td>0.9183 7.5366</td>
<td>N/A N/A</td>
<td>N/A N/A</td>
</tr>
<tr>
<td>AAD</td>
<td>3.3% 50.1%</td>
<td>1.5%</td>
<td></td>
</tr>
</tbody>
</table>

The maximum shear stress point and the end point of the viscosity jump were also analysed. 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:

$$\ln(\eta_{\text{max},P}) = A + B \times P$$

(4)

Also the shear rate at the highest shear stress, $\dot{\gamma}_{\text{max},P}$, can be related to the CO$_2$ pressure by

$$\ln(\dot{\gamma}_{\text{max},P}) = A + B \times P$$

(5)
where $\eta_{\text{max}(P)}$ is $\eta_{\text{max} \sigma, P}$ or $\eta_{\text{end}, P}$, and $A$ and $B$ are the fitting parameters. The AAD of the correlations for $\eta_{\text{max} \sigma, P}$, $\eta_{\text{end}, P}$ and $\dot{\gamma}_{\text{max} \sigma, P}$ were 19.7%, 3.5% and 16.4%, respectively. The fitting results are shown in Figure 11, and the values of $A$ and $B$ are summarised in Table 6. The competition between the viscosity and shear rate led to a maximum in the highest observed shear stress as CO$_2$ pressures were increased.

![Figure 11](image)

**Figure 11.** Comparison between the measurement and the correlation results given by Equation (4) and (5). The parameters used are given in. $\bullet$, $\eta_{\text{max} \sigma, P}$; $\times$, $\dot{\gamma}_{\text{max} \sigma, P}$; $\Delta$, $\eta_{\text{end}, P}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\eta_{\text{max} \sigma, P}$</th>
<th>$\eta_{\text{end}, P}$</th>
<th>$\dot{\gamma}_{\text{max} \sigma, P}$</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>

Since, as was 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 was likely that the catastrophic decrease in viscosity was caused by phase inversion: at higher shear rates the water became the continuous phase.

**Comparison Between The Emulsion and Zuata Crude Oil at High CO$_2$ Pressures**
Figure 12 shows the relative viscosity between the CO₂ saturated mixture with the 50:50 emulsion and that with Zuata crude oil at the same CO₂ pressures, temperature of 50 °C, and shear rate of 10 s⁻¹. In Figure 12, the viscosity data of the Zuata crude oil was taken from our previous paper [10]. Note that at pressure above 30 bar, the CO₂ saturated Zuata crude oil was a Newtonian fluid [10], while the emulsion remained slightly shear thinning.

![Figure 12. The relative viscosity $\eta_r$ between the emulsion and Zuata crude oil at 50 °C and different CO₂ pressures, at shear rate of 10 s⁻¹.](image)

The dispersed phase volume fraction and emulsion viscosity were analysed using the model developed by Pal [12]:

$$\eta_r = \frac{(2\eta_c + 5\lambda)^{3/2}}{2 + 5\lambda} \exp \left( \frac{2.5\phi}{1 - \phi/\phi_m} \right)$$  \hspace{1cm} (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 density of the crude oil was 1.0051 g/ml, the volume fraction of the dispersed phase was around 0.5. Since the CO₂ dissolution
had a limited effect on the oil volume [10], it was assumed that the dispersed phase volume fraction remained constant for different CO₂ pressures as well as after phase inversion. It was also assumed that the water phase had a constant viscosity of 1 mPa·s. With these assumptions, ϕₘ was used to fit Equation (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, ϕₘ, are shown in Figure 13. These are rather scattered but show a decreasing tendency with increasing pressure. The values of ϕₘ are large and even exceed 1, compared to the values of ϕₘ for a monodisperse spherical solid suspension at 0.64 for random close packing and 0.74 for hexagonal close packing [6]. It is also worth mentioning that, η_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 viscosity decrease by CO₂ dissolution in the crude oil was larger than that in the emulsion. As the key physical meaning of ϕₘ is how the droplets fill space, it is strongly related to both the droplet size distribution and droplet deformability [13, 14]. As demonstrated by Desmond et al., for a system of rigid spherical particles in which larger particles dominate, a decrease in ϕₘ means a wider droplet size distribution, while in a smaller particles dominated system the decrease in ϕₘ resulted from a narrower droplet size distribution [15]. Furthermore, from the droplet deformation point of view, the decrease in ϕₘ 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 [14]. However, the decrease in ϕₘ observed in Figure 13 was probably a result of the combination of the polydispersity and deformability effects.
The values of $\phi_m$ at other 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 (6) is not suitable to analyse the emulsion at different shear rates, given that Equation (6) was developed based on the theory for suspensions [12, 13].
Furthermore, the maximum packing volume fraction after the phase inversion was analysed. As shown in Figure 14, at ambient pressure the value of $\phi_m$ in the emulsion increased 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.

This behaviour can be rationalised by applying the critical capillary number concept to the post phase inversion emulsion. The critical capillary number, $Ca_{em,cr}$, for a concentrated emulsion is given by [16],

$$Ca_{em,cr} = \frac{\eta_{em}a_m\dot{\gamma}}{\sigma_{IFT}}$$

where $\eta_{em}$ is the emulsion viscosity, $a_m$ the maximum stable drop radius, $\dot{\gamma}$ 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. [17], 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, 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. showed that the interfacial tension of an oil-in-water emulsion stabilised by asphaltene was smaller in an acidic aqueous phase [18]. Given that the CO$_2$ dissolution can reduce the water phase pH by generating carbonic acid, we speculate that the interfacial tension in
the CO₂ saturated phase-inversed emulsion was lower than in that without CO₂ dissolution. With these arguments and applying Equation (7) at constant shear rate, one can compare the maximum stable drop radiiuses for the two post phase inversion emulsions (see Table 7). It showed that $a_m$ with CO₂ dissolution was smaller than $a_m$ without CO₂. The interpretation of this difference is that the mean droplet size in the post phase inversion emulsion without CO₂ addition was larger than that with CO₂ dissolution.

Table 7. Comparison between the critical capillary number of the post phase inversion emulsion without CO₂ dissolution and that with CO₂ dissolution

<table>
<thead>
<tr>
<th>No CO₂</th>
<th>With CO₂</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{em}=115.7$</td>
<td>$\lambda_{em}=21.6$</td>
<td>$\lambda_{em}=\eta_{oil}/\eta_{em}$ at shear rate of 500 s$^{-1}$</td>
</tr>
<tr>
<td>$Ca_{em,cr}$</td>
<td>$Ca_{em,cr}$</td>
<td>Assumption according to [17]</td>
</tr>
<tr>
<td>$\eta_{em}$</td>
<td>$\eta_{em}$</td>
<td>See Figure 5 and Figure 10</td>
</tr>
<tr>
<td>$1/\eta_{em}$</td>
<td>$1/\eta_{em}$</td>
<td>See Figure 5 and Figure 10</td>
</tr>
<tr>
<td>$\sigma_{IFT}$</td>
<td>$\sigma_{IFT}$</td>
<td>Assumption according to [18]</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>$\dot{\gamma}$</td>
<td>Compare at the same shear rate</td>
</tr>
<tr>
<td>$a_m$</td>
<td>$a_m$</td>
<td>$a_m=Ca_{em,cr}\sigma_{IFT}/\eta_{em}$</td>
</tr>
</tbody>
</table>

4 Discussions

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. Droplet dynamics has been proposed to play an important role in phase inversion [11]. It has also been shown that the phase inversion based on drop coalescence is able to explain both transitional and catastrophic inversion [11]. 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 15. Since the droplets were stretched by shear, the curvature of the interface agent layer changed from negative to zero. As reviewed by Perazzo et al., 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 15 [19]. 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. Note that in Figure 15 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 15. The mechanism of the phase version proposed to explain the viscosity behaviour observed in the measurement [20]. The red lines shown here are for the emulsion and CO$_2$ mixture at 50 °C and 30 bar.

*The Effect of CO$_2$ on Phase Inversion*
After the measurement of each flow curve shown in Figure 4, Figure 7 and Figure 9, the sample was left to rest for one hour in the measuring cell and then the flow curve measurement was repeated. The overall average difference two repeating measurements was 3.73%. This indicated that 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. phase inversion is generally an irreversible process, because there may be considerable differences in the volume fraction and physical properties between the post phase inversion emulsion and the initial one [21]. 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. [22]. 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. suggested that the experimental results from Kato et al., were caused by the fact that the volume faction of the hexane/water emulsion was close to the intersection point of the two ambivalence curves of the emulsion, the cusp [11, 23]. 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 16). 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 might have a volume fraction close to the cusp region, and the effect of CO₂ was to push the cusp to a higher shear rate.
The dissolved CO₂ can alter the critical shear rate of phase inversion through its effect on either the oil or water phase. The dissolution of CO₂ 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 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. [24]. 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 CO₂ 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 CO₂ 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 CO₂ could affect the performance of any charged interface agent representing the crude-
oil/water interface. Strassner showed that, in an asphaltene stabilised water-in-oil emulsion, the
strength of the interface formed by asphaltenes was inversely proportional to the pH [25]. Poteau
et al. 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 [18]. Thus, the
dissolved CO₂ 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.

**The Effect of CO₂ on The High Shear Rate Region**

Another interesting phenomenon is the disappearance of shear thinning effect in the high shear
rate region as CO₂ dissolved into the emulsion. As one can see from Figure 5, 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 10, when CO₂ dissolved in the emulsion, the viscosity in
the high shear rate region was independent of shear rate. After the viscosity jump, the oil droplets
formed in the emulsion without CO₂ dissolution were probably larger than those with CO₂. These
larger droplets can deform under shearing, which gave rise to the shear thinning effect. Note that
the increase in the maximum packing fraction of the phase-inverted emulsion (see Figure 14) is
also consistent with oil droplet deformation. Similar morphological changes have been reported in
the study by Lazo et al. [26]. 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
our emulsion without CO₂ addition 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 could have provided additional surface active agents,
because even at the pressure below the asphaltene precipitation point, the CO₂ dissolution would
make the oil become a less-good solvent for the asphaltenes pushing 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 as evidenced by the
constant \( \phi_m \) seen in Figure 14. Therefore the post-phase-inversion emulsion behaved as a
Newtonian fluid.

5 Conclusions

In conclusion, the Zuata crude oil 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.
This critical shear rate increased with increasing temperature. In the high shear rate, lower
viscosity, region the shear thinning effect was also observed. Furthermore, the CO₂ dissolution
had three effects: first, it reduced the emulsion viscosity at low shear while preserving the shear
thinning behaviour; second, increasing the pressure of CO₂ dissolution increased the critical shear rate at which the viscosity jump occurred; and third the CO₂ dissolution eliminated the shear thinning effect in the low viscosity region. At shear rates beyond the jump, the emulsion viscosity reached to a level that was much lower than the viscosity 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 CO₂ can influence the emulsion properties such as phase inversion through its action in both oil and water phase. The dissolution of CO₂ in the oil phase reduced its viscosity while dissolution into the water phase markedly changed pH and thereby the performance of any charged surface-active agent present in the crude oil.

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Notes

The authors declare no competing financial interest.

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