

Rheology of Crude Oils Containing Asphaltenes and Wax

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ABSTRACT

Rheological properties of three waxy crude oils with different asphaltene contents are investigated experimentally. The effect of interaction between wax and asphaltenes on the rheological properties is measured using oscillatory rheometry as well as viscosity measurements.

INTRODUCTION

Crude oils contain variable amount of asphaltenes. The asphaltene content of North Sea crude oils is typically less than 2%. Even with low asphaltene concentrations, serious production problems can arise from asphaltene precipitations. Problems have included extensive well maintenance work and even termination of oil production from a minor field several years earlier than expected.

Over the past decades, much effort has been spent to describe the chemistry of asphaltenes. As a result of the complexity of asphaltenes it is very difficult to describe their precise chemical structures. Due to the lack of an accurate structural description of the molecule, the petroleum industry applies an operational definition of asphaltenes:

Asphaltenes are a solubility class that is precipitated from petroleum and bitumens by addition of a minimum of forty volumes of the liquid n-pentane.

Asphaltenes are a polar fraction of petroleum, with a molecular weight in the range of 1000 - 5000. These molecules are normally stacked on top of each other like a deck of cards. Resin molecules act as dispersants for this deck of cards. The asphaltene-resin micelle is of colloidal size with a molecular weight of 10^3 - 10^5 . The

particle surface is covered by long paraffinic chains which make the particle soluble in a hydrocarbon fluid. The colloidal stability of the particle is dependent on several factors:

- Amount of resins.
- Hydrocarbon fluid composition.
- Pressure.
- Electrokinetic phenomena; the so-called streaming potential

Experience from different well sites around the world has shown that asphaltene flocculation occurs from the fluids bubble point pressure and below, in terms of depth.

The asphaltene particles have a strong affinity for metal surfaces. The particles that precipitate out of solution will adhere to the inside of production equipment or they might plug parts of the near-well reservoir.

In addition to asphaltenes most crude oils contain paraffinic wax. The paraffins in the oil having the highest molecular weights may form crystals at relatively high temperatures without affecting rheological properties significantly. When the temperature is reduced lighter paraffines will crystallize. Slightly above the pour point temperature of the crude oil, interactions between the wax crystals become important and the waxy crude oil develop a yield stress¹. The appearance of asphaltenes in crude oils is known to reduce the pour point temperature.

In the present study, steady shear and dynamic rheological properties have been determined for three crude oils with different amounts of wax and asphaltenes to investigate the interaction between wax and asphaltenes.

RHEOLOGICAL INSTRUMENTATION

A Bohlin VOR rheometer was used for

both oscillatory and steady shear measurements. Oil samples were poured into a C14 couette cell (inner diameter 14 mm; outer diameter 15.4 mm; bob height 21 mm). Temperature of the cell was controlled by a circulating water bath.

The steady shear viscosities, η , were measured at shear rates between 0.1 and 200 s^{-1} . The storage and loss shear moduli, G' and G'' , were determined by oscillatory measurements at a fixed temperature at frequencies between 0.001 and 20 Hz. The strain dependencies of G' and G'' were measured as a function of strain amplitude up to an amplitude of 0.20.

The temperature dependent properties of oils were investigated by cooling solutions from 40 °C at a cooling-rate of 0.5 °C/min in either steady shear, at a shear rate of 46 s^{-1} , or in oscillatory measurements at a frequency of 0.2 Hz.

THE OIL SAMPLES

Three different oils were tested. All of the oil samples had a relatively high wax content. The asphaltene content of the different samples was different. The wax and asphaltene properties of the oil samples are shown in Tables 1 and 2.

Table 1. Wax and asphaltene contents of oil samples

Sample	Wax content (%)	Asphaltene content (%)
A	15.1	14.2
B	13.4	5.1
C	9.8	0.2

Table 2. Crystallization and pour point temperatures of oil samples

Sample	Crystallization point (°C)	Pour point (°C)
A	33	6
B	35	-14
C	38	12

Interactions between the different wax crystals become important at temperatures far above the pour point. The pour points shown in Table 2 are measured on a high temperature and shear treated oil. The pour point as received may be significantly larger. For oil C the pour point as received is approximately 20°C. Wax crystal interference will occur

slightly above the pour point. The crystal interactions will create a structure in the fluid resulting in a yield stress formation.

RHEOLOGICAL MEASUREMENTS

It was anticipated that if the oil composition is held constant, except for the asphaltene content, an increase in viscosity should be observed with increasing asphaltene content. The viscosity measurements at temperatures higher than 30°C support this hypothesis as shown in Fig. 1. A significant increase in viscosity is observed with increasing asphaltene content. For these three oil samples the compositions of other components differ. However, the differences in asphaltene content are very large (see Table 1).

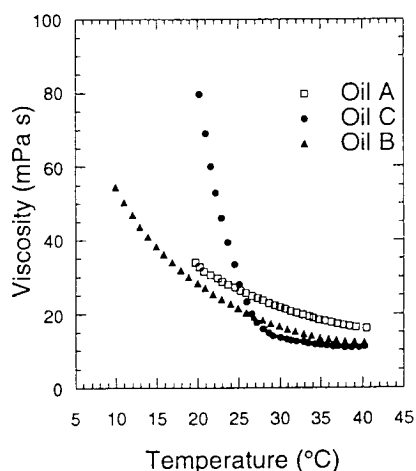


Figure 1. Viscosity measured at a shear rate of 46 s^{-1} for all oil samples at different temperatures

The viscosity will increase when the temperature of the crude oil approaches the pour point. This is illustrated by the viscosity curve belonging to crude oil C in Fig. 1. The viscosity exceeds the viscosity of the other two crude oils at temperatures less than 26°C even though the viscosity of crude oil C is the lowest at higher temperatures.

The formation of a structure, when the temperature is approaching the pour point temperature, can also be investigated using

dynamic rheological methods. A sharp increase in G' and G'' is observed for oil C, when the temperature was reduced to less than 23°C as shown in Fig. 2. At this temperature the interactions between the wax crystals become important even though the temperature is still slightly above the pour point. It is evident that the structure formation process proceeds as the temperature decreases as the G' and G'' values increase with several magnitudes.

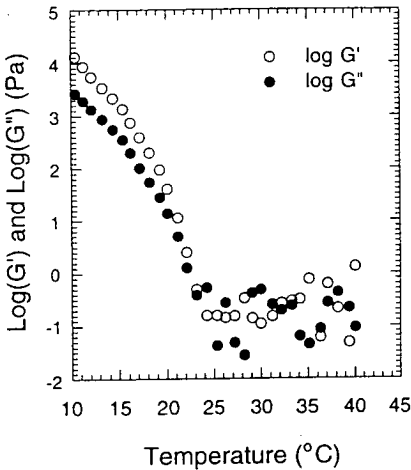


Figure 2. G' and G'' at 0.2 Hz for oil C in a cooling experiment between 40 and 10°C .

Frequency sweeps of oil C and of oils A and B at 5°C , are shown in Figs. 3 and 4, respectively. The values of G' for oil C are several magnitudes larger than those of oils A and B. Thus, a stronger wax structure exists in oil C than in A and B at this temperature.

The minimum pour points of oils A and B are reported to be 6°C and -14°C . However, the present oils are measured at conditions as received. Thus, a structure should have been formed for oil A and may have been formed for oil B. The G' and G'' values in Fig. 4 are seen to be parallel on a log/log plot. It has been suggested that parallel G' and G'' curves can be taken as an evidence of a gel point². Thus gel structures exist in all the oil samples at the measured temperature of 5°C . For oil A, the nearly constant G' and G'' values at low frequencies suggest that a yield stress exists at this temperature.

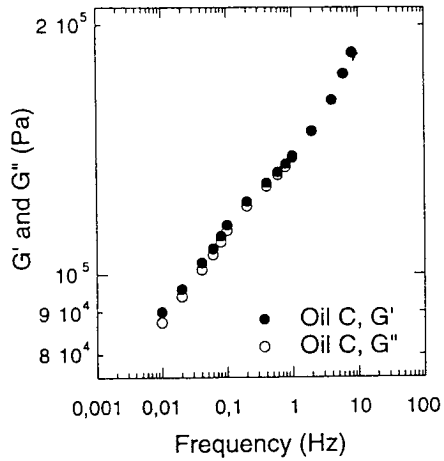


Figure 3. Frequency sweep of oil C at 5°C . G' (open circles) and G'' (filled circles).

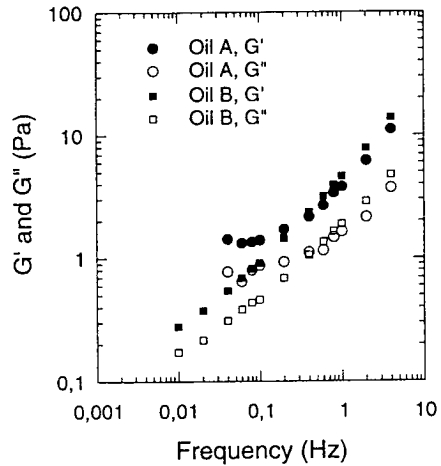


Figure 4. Frequency sweep of oils A and B measured at 5°C .

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