Some Compositional Viscosity Correlations for Crude Oils from Russia and Norway

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ABSTRACT
The current work is based on experimental viscosity and compositional data of about 200 crude oil samples from various part of Russia and Norwegian continental shelf. Data analyses were performed to estimate correlations between viscosity and density values, as well as concentrations of main components from the crude oils of different origin. It appeared that in some cases it is possible to establish a general correlation of viscosity increase along with growing asphaltene, resin, and aromatics contents, but also a decrease in viscosity with increasing saturates content. The spread of the data points can be rather wide for the oils of different origin. It was observed that asphaltenes from all the crude oil samples acted as promoters of the viscosity growth at rather low concentrations, while resins and aromatics effectively increased viscosity in higher concentration range. The effect of asphaltenes on the viscosity of real crude oils seems to be more important than when dissolved in a model solvent (xylene). This means that either the asphaltenes have a different solvation state in crude oils compared to xylene, or asphaltenes are not solely responsible for the high viscosity of the crude oils.

Key words: crude oil, viscosity, density, asphaltenes, resins, aromatics, saturates
1. INTRODUCTION

Both Norway and Russia are known as major oil and gas producers. Russian production is almost exclusively onshore (North-Western Siberia), while Norway’s resources are predominantly located in the North Sea. For the past few decades both countries had focus on research and development in the crude oil sector and gathered valuable knowledge and technology that can be used to solve upcoming production challenges. After signing an Arctic border agreement in 2010, the two countries have been joining forces in the offshore development of the Barents Sea region.

Crude oil transport, widely referred to as flow assurance, is always a challenge for any new development. The term flow assurance indicates sustained economic delivery of hydrocarbons from a geologic reservoir to the market. Successful transport largely depends on technology developed based on the knowledge of various crude oil properties. One of the most important properties is oil viscosity. Viscosity of crude oil determines its process characteristics, and largely depends on the oil composition. It is not a trivial task to establish a correlation between oil composition and viscosity since the composition of crude oils is very complex, and it is almost impossible to take into account the contribution of each separate component. Crude oils generally exhibit Newtonian behavior even in case of heavy crude oils i.e., the viscosity is independent of shear rate with the exception of waxy crude oils below their pour point.

Since the pioneering work by Mack in 1932, asphaltenes are widely recognized as a major contributor to crude oil viscosity. Asphaltenes is the fraction of crude oil insoluble in n-alkane but soluble in organic solvents like toluene. It is obtained by precipitation from crude oil using n-alkane, however several standards and procedures exist. Asphaltenes self-associate to form nanoaggregates, which are considered to be responsible for the high viscosity of heavy crude oils. Asphaltene’s viscosity is mainly studied using model systems: asphaltenes are extracted from crude oil and dissolved in model solvents like toluene. Some studies also report viscosity data of samples prepared by addition of precipitated asphaltenes into deasphalted oils. The viscous behavior of asphaltene dispersions is typically described by two approaches/models:

1. Based on the assumption that asphaltenes behave as polymers in solutions, two viscosity domains termed dilute and concentrated are defined. In the latter the asphaltenes overlap inducing a dramatic increase of the solution viscosity.
2. Based on assumption that asphaltenes may behave as solid particles (hard sphere models). Hard sphere equations, initially developed to fit the viscosity of particle
dispersions, are used to fit viscosity of asphaltene solutions. These models predict asymptotic viscosity in the region where the particle volume fraction approaches the dense random packing volume fraction $\phi_m$. One of these models, the Quemada equation\textsuperscript{13}, is based on dissipated energy minimization by viscous effect and is used to fit the data of asphaltene solutions in model solvents:

\[
\eta_{rel} = \left(1 - \frac{\phi_v}{\phi_m}\right)^{-2}
\]

where $\eta_{rel}$ is a relative viscosity and $\phi_v$ is a volume fraction of particles.

Other examples of hard sphere equations proposed to fit asphaltene viscosity are the Mooney\textsuperscript{14} and Krieger-Dougherty equations\textsuperscript{15}. The Pal and Rhodes equation\textsuperscript{16} was initially developed to fit viscosity data of emulsions, but have also been applied for asphaltenic systems\textsuperscript{10}. Barré et al.\textsuperscript{12} compared viscosity and Small-angle X-ray scattering (SAXS) data obtained from asphaltene solutions in toluene. Their results suggested that asphaltenes could be considered as fractal objects. They successfully applied a flat disc model for description of SAXS data, but the model failed to explain the viscosity values.

Resins, the second most polar fraction of petroleum crude oil, is known to increase the solubility of asphaltenes in oil and also contribute to dispersion of asphaltene nanoaggregates\textsuperscript{17,18}. Pfeiffer and Saal, as early as in 1940, proposed a model in which the resins peptize the asphaltenes to disperse them in crude oil\textsuperscript{19}. The data obtained by Pierre et al.\textsuperscript{11} show that resins reduce the effect of asphaltenes on viscosity through reducing the size of asphaltene aggregates.

In this work we aim to compare knowledge on viscosity from the compositional properties of the crude oil samples from both Russia and Norwegian continental shelf. Two sets of data, both available in the literature, were studied:

1\textsuperscript{st} group - crude oils mainly from the Norwegian continental shelf with some additional samples from West Africa and France\textsuperscript{20}. The publication by Navre Aske et al. (Norway)\textsuperscript{20} is devoted to study the stability of crude oil emulsions, but also contains systematic results for the determination of crude oil composition by SARA (saturates, aromatics, resins, asphaltenes) protocol. Physico-chemical properties (including viscosity values) of 21 crude oil samples and condensates are described in the publication.

2\textsuperscript{nd} group - crude oils from different regions of Russia. The second group of experimental data is adopted from a Russian Handbook “Crude oils of the USSR”, an additional
volume devoted to the physico-chemical characteristics of a large number of crude oils\textsuperscript{21}. Some unpublished new data for a heavy crude oil from Tatarstan is also included in this group. The volume contains information about several hundreds of oils. 174 oil samples were chosen to be included in the current publication based on availability of the asphaltene viscosity data. Among those are the oils from the following Russian regions: Tatarstan, Bashkortostan, Udmurtia, Perm, Komi, Eastern Siberia, and Western Siberia. These samples are representative for oil fields in Russia with regard to compositional variation.

2. MATERIALS AND METHODS

2.1. Materials

The two groups of published experimental results from Norway (group 1) and Russia (group 2) were analyzed and the summary of the analysis is presented in Table 1.

Additional rheological measurements on asphaltenes dissolved in a model solvent (xylene) were carried out using asphaltenes precipitated from a specific heavy crude oil sample from the Norwegian continental shelf. Solvents used for this asphaltene precipitation are: n-pentane (98%), n-hexane (≥95%) n-heptane (99%) and n-octane (98%) were all reagent grade purchased from Sigma-Aldrich.

Table 1. Dead crude oil samples and their origin

<table>
<thead>
<tr>
<th>Source</th>
<th>Number of samples</th>
<th>Markers on the graphs</th>
<th>Symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Eastern Siberia</td>
<td>8</td>
<td>Purple square</td>
<td></td>
</tr>
<tr>
<td>2 Western Siberia</td>
<td>57</td>
<td>Navy triangle with a right tip</td>
<td></td>
</tr>
<tr>
<td>3 Komi</td>
<td>8</td>
<td>Dark cyan circle</td>
<td></td>
</tr>
<tr>
<td>4 Perm</td>
<td>32</td>
<td>Magenta triangle with an up tip</td>
<td></td>
</tr>
<tr>
<td>5 Udmurtia</td>
<td>5</td>
<td>Violet triangle with a down tip</td>
<td></td>
</tr>
<tr>
<td>6 Bashkortostan</td>
<td>42</td>
<td>Olive rhomb</td>
<td></td>
</tr>
<tr>
<td>7 Tatarstan</td>
<td>21</td>
<td>Blue triangle with a left tip</td>
<td></td>
</tr>
<tr>
<td>8 North Sea and others\textsuperscript{20}</td>
<td>21</td>
<td>Red hexahedron</td>
<td></td>
</tr>
<tr>
<td>9 New data for heavy oil from Ashalchinskoe field (Tatarstan)</td>
<td>1</td>
<td>Black star</td>
<td>⭐</td>
</tr>
</tbody>
</table>
2.2. Asphaltene preparation

The procedures used to determine the SARA contents in the oils considered in this article are the following:

1st group of crude oils: SARA contents was determined by asphaltene precipitation. The crude oil was heated to 60°C for at least 1 hour, shaken vigorously to ensure homogeneity before sampling before being diluted in proportion of 1:40 (g/mL) by n-hexane and stirred for 24 h. The diluted mixture was filtered with a 0.45 μm HVLP type Millipore filter membrane and washed with hexane until the filtrate became colorless. The filter cake was dried under nitrogen for almost 24 hours. The maltenes were then separated into saturates, aromatics and resins on a chemically bonded silica-NH₂ column using n-hexane and trichloromethane.

2nd group of crude oils: The chemical composition of all oils was determined according to a procedure similar to SARA protocol. Precipitation from oils was done by the 40-fold excess of n-heptane. The oil solutions were filtered after 40 hours and followed by extraction of co-precipitated resins and paraffin waxes by heptane. Resins were adsorbed onto silica gel while passing the deasphaltenated oil solution in gasoline with further washing of silica gel by gasoline and gasoline/toluene (6/1) mixture. The resins were then desorbed by washing the silica gel with a toluene/methanol (1/1) mixture. Paraffin waxes were precipitated from the deasphaltenated and resin-free oil by a mixture with 10-fold excess of acetone/toluene (35/65) at -20°C.

Asphaltenes prepared in this work were obtained from a North Sea crude oil according to a procedure similar to the one used by Aske et al. Different alkanes were used to incorporate different amounts of resins. The yields of asphaltenes precipitated with different solvents are presented in the Table 2. The table shows that the resin content in the sample increases when the alkane chain length decreases (the trend typically expected from previous work).

<table>
<thead>
<tr>
<th>n-alkane</th>
<th>Yield, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane</td>
<td>4.0</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>3.2</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>2.5</td>
</tr>
<tr>
<td>n-Octane</td>
<td>1.6</td>
</tr>
</tbody>
</table>
2.3. Rheology (viscosity measurements)

1st group of crude oils: The viscosity values were obtained using a stress-controlled Anton Paar (USD 200) in combination with a Lauda temperature bath. The characterization was done at the shear rate of 100 s\(^{-1}\) and 25°C\(^{20}\).

2nd group of crude oils: The viscosity was measured according to the National standard (GOST 33-82) as the kinematic viscosity measured with Ubbelohde (or similar) glass viscometers at 20°C. The tabulated values (expressed in cSt) were recalculated into dynamic viscosity (in Pa s).

The viscosity data for the asphaltene model solutions were obtained using an Anton Paar MCR 301 (Austria) fitted with a DG-26 geometry at 25°C. After a 2-minute rest period, the flow curves were determined by first increasing the shear rate from 1 to 1000 s\(^{-1}\) (during 5 minutes) and then decreasing it from 1000 to 1 s\(^{-1}\) (again during 5 minutes).

3. RESULTS AND DISCUSSION

There are two alternative methods for establishing correlation between crude oil viscosity and its composition. One is to prepare model solutions containing varying concentrations of single components and follow viscosity changes as a function of concentration. For example, synthetic model oils were prepared and the influence of asphaltene concentration on the viscosity of solutions was measured\(^{11}\). Xylene was used as model oil in this work. The second possibility is to go beyond the analysis of model oils by investigating real crude oil systems. In this case, different components can simultaneously provide their input to the viscosity. In the current work, both options have been considered.

3.1. Asphaltenes dissolved in a model solvent

3.1.1 Flow Curves

Flow curves (viscosity as a function of shear rate) for different concentrations of n-heptane-precipitated asphaltenes in xylene are shown in Fig. 1. The solutions (dispersions) showed Newtonian and non-thixotropic behavior at the maximum tested concentration of 7-8 wt%. It should be noted that the asphaltenes have moderate abilities to act as vicosifying agents as the viscosity of a 7-8 wt% asphaltene solution is only about 60 % higher than the viscosity of the pure solvent.
3.1.2 Viscosity-concentration relationship

Figure 2 shows viscosity as a function of asphaltene concentration in xylene for 4 asphaltene samples differing in their resin content. It can be noticed that the viscosity increases linearly with the concentration at low asphaltene concentrations. The viscosity measured at the highest concentrations however show an increase in the slope of the curve indicating a non-linear behavior.

The curve also shows that there is no, or little, influence of the n-alkane used to precipitate asphaltenes on the asphaltene viscosifying properties in xylene. This result was unexpected considering the important difference in resin amounts between n-pentane- and n-octane-precipitated asphaltenes (yield ratio of 2.5, Table 2). This result also deviate from the conclusion obtained by Pierre et al.\textsuperscript{11} for the asphaltenes extracted from a Venezuelan extra heavy crude oil. The difference could be explained by the limited range of asphaltene concentrations investigated.
Figure 2. Newtonian viscosity as a function of the asphaltene concentration in xylene for asphaltenes obtained by precipitation in various n-alkanes

The intrinsic viscosity $[\eta]$ was then determined using the Huggins equation:

$$\left(\frac{\eta_{\text{rel}}-1}{\phi_v}\right) = [\eta] + k_H [\eta]^2 \phi_v$$  \hspace{1cm} (2)$$

where the $\eta_{\text{rel}} = \frac{\eta}{\eta_{xylene}}$, $k_H$ is the Huggins coefficient and $\phi_v$ is the asphaltene volume fraction.

The volume fractions were calculated from the asphaltene mass fraction and by using an asphaltene density of 1.135 g/mL determined by measuring densities of hexane-precipitated solutions in toluene and extrapolating the density to a 100 % content of asphaltenes. The Huggins plot is shown on Figure 3. The determined intrinsic viscosity is dimensionless (7.6) and in a good agreement with the values obtained by other authors$^{12,25}$. This value, higher than 2.5 and typical for hard sphere, indicates that the asphaltenes form solvated objects in solution.
Figure 3. Huggins plot for n-hexane-precipitated asphaltenes in xylene

The viscosity data were also fitted with the Quemada equation requiring only one fitting parameter (1). Figure 4 shows that this model provides a good data fit. By taking into account the solvation of asphaltenes, using an effective volume fraction $\phi_{v,eff}$ equal to a maximum packing volume fraction of 0.87:

$$\phi_{v,eff} = \phi_v \times \frac{[\eta]}{25}$$  \hspace{1cm} (3)

It must be noted that this value is obtained from a large extrapolation and is, therefore, not completely accurate. The value is somewhat higher than the value typically found for the random packing spheres (0.64).
The data presented and discussed here should be considered complementary to Ilyin et al\textsuperscript{27}, where a detailed analysis of asphaltenes precipitated by various solvents is given. It is shown that the viscosity of the pristine crude oil and corresponding asphaltenes depend on the solvent used for flocculation.

3.2 Crude oil viscosity

3.2.1 Density-viscosity relationship

The relationship between viscosity and density of crude oils is shown in Figure 5. The majority of the Russian crude oil samples exhibited the individual wax melting points in the range from 43 to 63°C. The viscosity data may, therefore, be affected by the presence of the wax crystals as the viscosity was measured at a lower temperature of 20 °C.

Figure 4. Comparison of experimental data and the Quemada equation for asphaltenes extracted with different alkanes $\eta_0 = 0.58 \text{ mPa} \cdot \text{s}$. The density of the different asphaltene samples was assumed to be equal to the value determined for n-hexane precipitated asphaltenes (1.135 g/mL at 25°C)
The existence of viscosity versus density correlation is rather evident in the viscosity range exceeding 4 decimal orders. However, the diversions of two points (presented by Aske et al.\textsuperscript{20}) with the same density (close to 0.84 g/cm\textsuperscript{3}) is unexpectedly large – more than 35 times.

The results shown in Figure 5 can be well approximated by the power law as shown in Figure 6.
The fit in the Figure 6 can be described by the following equation:

\[
\eta = \frac{3.2 \times 10^{-3}}{(1 - \rho)^{4.18}} \text{ (in mPa·s)}
\]  

(4)

Other complex equations have been proposed to fit the relationship between viscosity and density/or API.28,29,30

3.3. Contributions from the crude oil components

3.3.1. Viscosity as a function of the asphaltene concentration

Figure 7 presents viscosity variations of Russian crude oils as a function of the asphaltene mass fraction. It can be seen that the viscosity increases non-linearly with the asphaltene concentration. It can be noticed that the Western Siberian oils (Navy triangle with a right tip) form a separate group in comparison with others. They present higher viscosity for asphaltene contents comprised between 2 and 3 wt%. In addition, asphaltenes are practically absent in the 8 crude oils samples from Eastern Siberia, but the viscosity varies from 0.7 to 20 mPa·s confirming that the asphaltenes are not the only components responsible for the viscosity fluctuations.

The Quemada equation (1) was used to fit the viscosity data. The mass fraction was approximated to be equal to volume fraction in absence of density data. The “solvent” viscosity, in this case the viscosity of the deasphalted crude oil, was considered as a second fitting parameter. The results of the fitting procedure are displayed in Figure 7.
Figure 7. Comparison of Russian data with the Quemada fit. $\eta_0 = 7.0854 \text{ mPa} \cdot \text{s}$ and $\phi_m=0.095$ (using mass fraction in equation (1))

As seen in the figure, although the spread of the data is large, the trend of the data follows the Quemada equation. The fitted apparent maximum packing fraction is quite low (0.095) compared to the asphaltene model solutions (0.37 if mass fractions are used in the Equation 1). This means that either the asphaltenes have a different solvation state in crude oils compared with xylene, or asphaltenes are not the only compound responsible for the high viscosity of crude oil.

So, the conclusion is that the increase in asphaltene concentration may promote the viscosity increase, but the general correlation between viscosity and the asphaltene concentrations is not evident.

3.3.2. Viscosity as a function of the asphaltene and resin concentrations

It might be reasonable to expect that viscosity will be more dependent on the total concentration of asphaltenes and resins, since both fractions contain all the polar compounds from crude oil. General trend of viscosity versus total asphaltene and resin concentration is presented in the Figure 8. The linear fit here is described by the following equation:

$$\eta = 2 \times 10^{(6 \pm 0.2) [C]} \text{ (in mPa} \cdot \text{s)}$$ (5)
where \([C]\) is the wt% total concentration of asphaltenes and resins.

![Graph showing viscosity vs. total asphaltenes and resins concentration](image)

**Figure 8.** Viscosity vs. total asphaltenes and resins concentration

The general tendency exists for the full concentration-viscosity ranges. The shape of the curve is similar to the one in Figure 7 (where only asphaltenes are considered). Then it would be interesting to compare the relative influence of resin and asphaltene concentrations for crude oil samples of the same origin. Figure 9 mainly shows data adopted from Aske et.al. Two points in this figure sharply deviate from the general tendency. It was established that these points belong to the oils originated not from the North Sea wells. It is interesting that the viscosity versus the asphaltene concentration dependence for the Western Siberian oils (Fig. 7) overlaps with the data for the North Sea oils. Then we could assume that these oils have similar compositions even though the methods used to determine the asphaltene and resin contents in two studies are different.
Figure 9. Comparison of the relative influence of asphaltenes and resins on the oil viscosity for the data adopted from Aske et al.\textsuperscript{20} and data for the Western Siberia oils.

The linear fit of both series of data is described by the following equations:

For asphaltenes: \[ \eta = 0.6 \times 10^{(110\pm40)[C]} \] (6)

For resins: \[ \eta = 0.6 \times 10^{(11\pm4)[C]} \] (7)

where [C] is the wt\% concentrations of asphaltenes or resins.

Figure 9 demonstrates that the presence of asphaltenes has a dominant influence on the viscosity even at rather low concentration, while a larger content of resins is necessary in order to have an influence of the crude oil viscosity (mainly in the range above 10 wt\%).

3.3.3. Viscosity as a function of aromatic component’s concentration

Aromatic compounds are the next group of components, which should be taken into account in comparison of viscosities of different crude oils. It should be mentioned that we are not only dealing with the pure effect of aromatics, but also other components present in the oils. The complete experimental data sets necessary for the comparison are collected only for the 1\textsuperscript{st} group of crude oils\textsuperscript{20}. A single new experimental point was obtained for the new Tatarstan oil. The results and corresponding fit are presented in Figure 10.
3.3.4. **Viscosity as a function of the saturated component’s concentration**

In general, it is expected that an increase in the concentration of saturated compounds should lead to a decrease in oil viscosity. **This is observed experimentally and shown in Figure 11 (corresponding fit is included).**
Figure 11. Viscosity versus concentration for the saturated compounds according to the data adopted from Aske et al.\textsuperscript{20} and heavy oil from a new Tatarian source.

The figure also shows how oil viscosity depends on the concentration of the saturated compounds and that the viscosity can be only be slightly higher than 1 mPa·s (close to water). The viscosity therefore corresponds well to the presence of low molecular weight hydrocarbons in the oil.

It is interesting to mention that the paraffins (high molecular weight hydrocarbons) present in almost all samples did not exceed several percent\textsuperscript{21}. However, their role is rather difficult to estimate because paraffinic oils (even at low levels of paraffin content) are visco-plastic non-Newtonian fluids with thixotropic behavior\textsuperscript{2} and their viscosity cannot be estimated for comparison. This is seen in Figure 12. No reasonable correlation can be obtained from the data. This might be due to the behavior and crystallization of waxes at different temperatures.
Conclusions
The viscosity values for approximately 200 samples of oils from different origins have been compared. Correlations between viscosity-density, and between viscosity-concentration of the main groups of compounds typically present in the crude oils, have been established. In some cases, the correlations merely represent a general trend while in other cases they provided a good correlation for oils of different origins. An increase in asphaltenes, resins, and aromatics leads to an increase in viscosity, while an increase in saturates results in a steep drop in viscosity. Small concentrations of asphaltenes effectively contributes to an increase in viscosity, while much higher concentrations of resins and aromatics are necessary in order to cause a significant increase of viscosity.

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