VISCOSITY OF SHALE OIL BINARY BLENDS

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The evaluation of the kinematic viscosity of shale oil binary blends is discussed. It is shown that the kinematic viscosity of shale oil originated light gas oil fraction, heavy gas oil fraction, commercial fuel oil and reduced shale oil blends can be evaluated by standard blending calculation technique, accepted for hydrocarbon oil blends. When the low viscosity component is the shale oil originated light "diesel oil" fraction, the experimental values of blend kinematic viscosity are always higher than calculated ones. For such blends difference between the logarithms of experimental and calculated values of kinematic viscosity can be described by a simple equation. Using this approach the binary blend kinematic viscosity can be evaluated with a great exactness.

In our previous paper [1] it was shown that for the Estonian kukersite shale oil distillates the temperature dependence of kinematic viscosity is described with great accuracy (correlation coefficient > 0.999) by a fundamental formula accepted for hydrocarbon oil blends [2, 3]:

$$\log \log Z = A - B \log T \qquad (1)$$

where Z is a function of the kinematic viscosity ν (mm²/s);
    T is the temperature (K);
    A and B are the viscosity characterization constants, whose values vary from one oil fraction to another.

Equation (1) holds true in spite of the fact that shale oils are mainly made up of the H-bond forming oxygen compounds which often exhibit non-Newtonian properties. It was also found that shale oil distillates are compatible amongst themselves: blends in whatever ratio are stable in a wide temperature range.

In this paper the evaluation of the kinematic viscosity of shale oil binary blends, including blends with a residual component, is discussed.

Oil Blending Calculations

Predicting the volume fractions of two given oils when blending to meet a specified kinematic viscosity at a given temperature is a common problem. For petroleum oils, a number of blending calculation techniques have been used. In any case, the required data are the kinematic viscosities of each component oil, as a minimum, at two temperatures and the desired kinematic viscosity of the oil blend at one temperature.

The Wright method [2, 3] is usually preferred since it automatically allows for the effects of oil type, molecular weight and viscosity-temperature dependence.

Graphically, the standard plotting technique [4] is as follows (see Fig. 1).
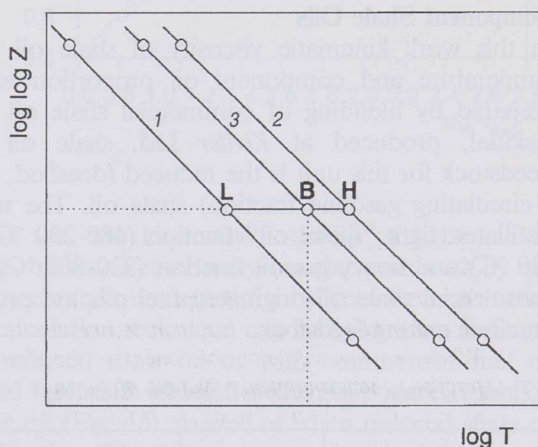

Fig. 1. Evaluation of two component blend kinematic viscosity:
1 - low viscosity oil,
2 - high viscosity oil,
3 - blend

The known data for each component oil are plotted on an ASTM viscosity - temperature chart (log log Z - log T chart). Straight lines through the points are drawn. The lines for component oils should extend beyond the blend kinematic viscosity required. The desired blend kinematic viscosity horizontal line is drawn through both the component oil lines. The distance LH between the lines for the two oils is measured where they intersect the line of the desired blend kinematic viscosity. On the same horizontal kinematic viscosity line the distance LB is read from the low viscosity oil line to the temperature desired. Dividing the latter by the first measurement between the two oil lines gives the volume fraction needed for the high viscosity oil:

$$\text{Volume fraction high viscosity oil } \varphi_H = \text{LB/LH.}$$

Then:

$$\text{Volume fraction low viscosity oil } \varphi_L = \text{BH/LH.}$$

The oil blends may be also calculated using a computer technique. We have been developed a blending program for personal computer, written in BASIC, similar to that described by Huggins [5]. It can calculate the blend viscosity when the component proportion is given and the component proportion to meet a specified viscosity. The basic data for calculations are

the viscosity characterization constants, A and B, for each component oil
with required temperatures, viscosities or component oil proportions. The
final displayed results give the viscosity characterization constants for the
binary blend as well.

We have used the Wright approach, originally developed for hydrocarbon
oil blending calculations, also for shale oils. Both viscosities and volume
fractions found using the described computer technique are further
interpreted as "calculated" values, contrary to the "experimental" ones
measured in laboratory.

Experimental and Results

Component Shale Oils
In this work kinematic viscosity of shale oil binary blends depending on
temperature and component oil proportion was studied. Oil blends were
prepared by blending of commercial shale oil fractions, both distillate and
residual, produced at *Kiviter* Ltd. shale oil distillation unit (Table 1).
Feedstock for this unit is the reduced (deashed, desalted and discharged from
a circulating gasoline fraction) shale oil. The unit produces ordinarily three
distillates: light "diesel oil" fraction (180-230 °C), light gas oil fraction (230-
320 °C) and heavy gas oil fraction (320-360 °C). By blending these fractions
commercial shale oil originated fuel oils are produced. Distillation residue is
usually a coking feedstock.

*Table 1.* **Shale Oil Fractions Used for Blending**

Component shale oil	Density at 20 °C, kg/m^3	Kinematic viscosity, mm^2/s						
		20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C
Light "diesel oil" fraction:								
Sample 1	841.4	1.798	1.507	1.289	1.122	0.991	0.888	0.804
Sample 2	848.0	1.712	1.442	1.239	1.083	0.960	0.863	0.783
Light gas oil fraction:								
Sample 1	956.8	36.48	20.56	12.74	8.506	6.024	4.473	3.451
Sample 2	973.0	60.07	31.91	18.83	12.08	8.274	5.974	4.501
Heavy gas oil fraction:								
Sample 1	1029.1	4957	1419	503.7	212.5	102.9	55.79	33.11
Sample 2	1027.4	4363	1219	426.5	178.7	86.38	46.86	27.89
Commercial fuel oil	992.8	275.2	125.5	64.98	37.25	23.19	15.43	10.84
Reduced shale oil	995.0	426.4	185.4	92.20	51.06	30.85	20.01	13.76

Methods
Kinematic viscosity for the component oils and their binary blends was
determined in glass capillary viscometers as established by generally accepted
standard specifications [6, 7]. For each blend viscosity was determined, as a
minimum, at 6-8 various temperatures. Compatibility of component oils and
stability of blends were determined using standard test procedure [8].

Fig. 2. Experimental (v_{exp}) and calculated (v_{calc}) values of kinematic viscosity (mm^2/s) for shale oil originated light gas oil fraction - heavy gas oil fraction blends.

Volume fraction high viscosity oil (φ_H):
1 - 0.21, *2* - 0.30,
3 - 0.42, *4* - 0.50,
5 - 0.62, *6* - 0.70,
7 - 0.80
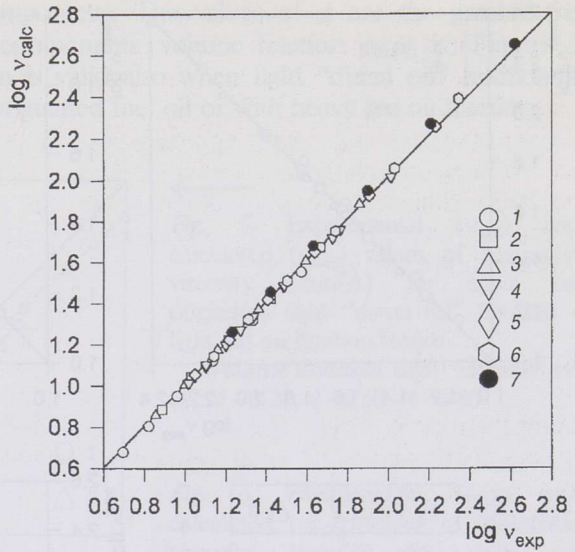
Results

From results obtained follows that the kinematic viscosity of light gas oil fraction blends with heavy gas oil fraction actually can be evaluated by the standard blending calculation technique, accepted for hydrocarbon oil blends (Fig. 2). The same blending calculation technique can be used when light gas oil fraction is blended with reduced shale oil or with commercial fuel oil (Fig. 3), and when commercial fuel oil is blended with heavy gas oil fraction (Fig. 4*a*) or with reduced shale oil (Fig. 4*b*), as well as when reduced shale oil is blended with heavy gas oil fraction (Fig. 4*c*).

All blends of oils under discussion, in whatever ratio are also stable in a wide temperature range. Blends, in which the low viscosity component is the shale oil originated light "diesel oil" fraction, having the kinematic viscosity at 20 °C as low as 1.5-2 mm^2/s, exhibit viscosity properties unlike to above-escribed.
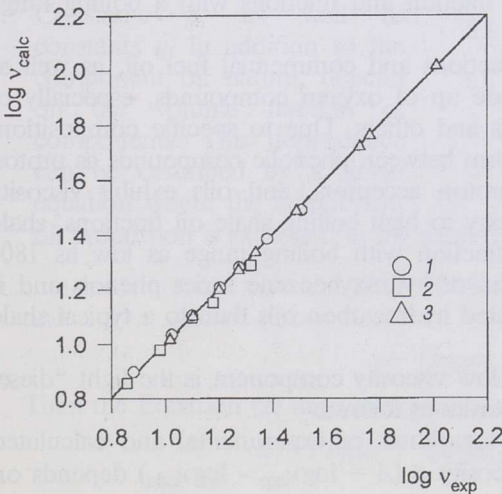

Fig. 3. Experimental (v_{exp}) and calculated (v_{calc}) values of kinematic viscosity (mm^2/s) for shale oil originated light gas oil fraction - reduced shale oil (*1*), light gas oil fraction - commercial fuel oil (*2*) and light gas oil fraction - heavy gas oil fraction (*3*) blends.
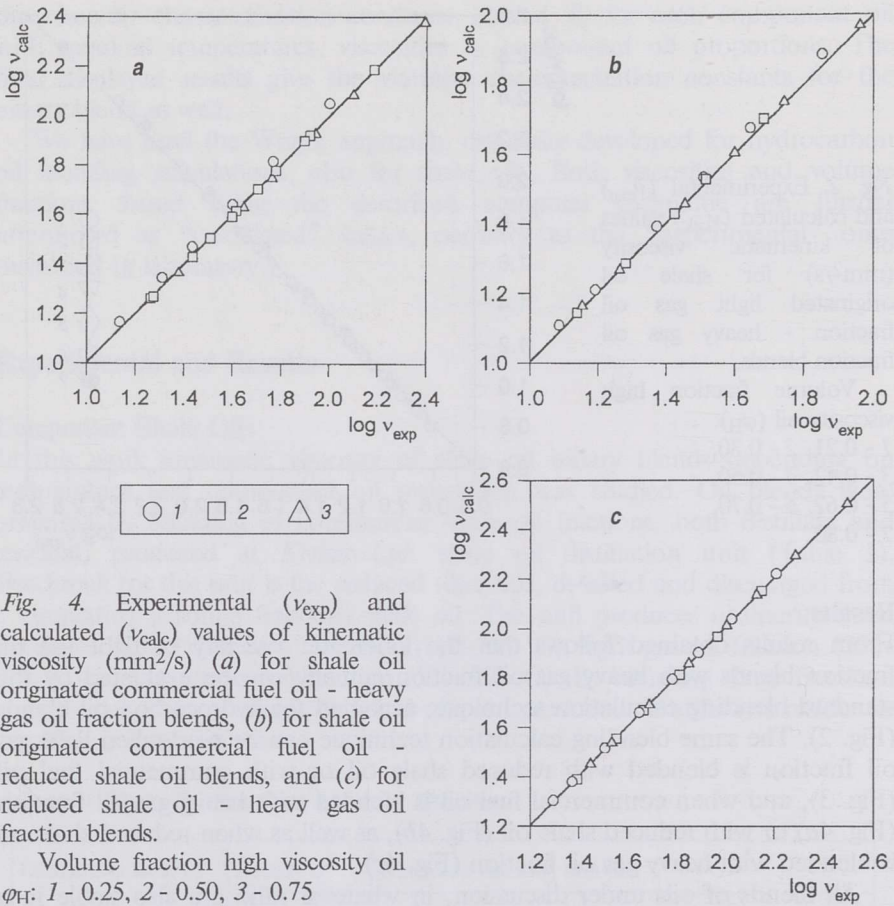
Volume fraction high viscosity oil $\varphi_H = 0.50$

Fig. 4. Experimental (v_{exp}) and calculated (v_{calc}) values of kinematic viscosity (mm^2/s) (a) for shale oil originated commercial fuel oil - heavy gas oil fraction blends, (b) for shale oil originated commercial fuel oil - reduced shale oil blends, and (c) for reduced shale oil - heavy gas oil fraction blends.

Volume fraction high viscosity oil φ_H: 1 - 0.25, 2 - 0.50, 3 - 0.75

As a rule, for these blends the experimental values of kinematic viscosity are always higher than the calculated ones.

This phenomenon can be explained as a result of different chemical group composition of light "diesel oil" fraction and fractions with a boiling range above 230 °C.

Shale oil originated gas oil fractions and commercial fuel oil, as well as reduced shale oil are mainly made up of oxygen compounds, especially of resorcinol series phenols, ketones and ethers. Due to specific composition, associates (H-bond complexes) form between phenolic compounds as proton donors and ketones/ethers as proton acceptors, and oils exhibit viscosity properties as a "polymer". Contrary to high boiling shale oil fractions, shale oil originated light "diesel oil" fraction with boiling range as low as 180-230 °C consists only a low amount of hydroxybenzene series phenols and is more similar to petroleum originated hydrocarbon oils than to a typical shale oil distillate.

Shale oil blends in which the low viscosity component is the light "diesel oil" fraction exhibit viscosity properties as follows:
1. The difference between the logarithms of experimental and calculated values of blend kinematic viscosity Δ ($\Delta = \log v_{exp} - \log v_{calc}$) depends on

volume fraction of components. The values of Δ are the greater the higher the product of components' volume fraction $\varphi_H\varphi_L$ is (Figures 5 and 6). This conclusion is valid also when light "diesel oil" fraction is blended with shale oil originated fuel oil or with heavy gas oil fraction.
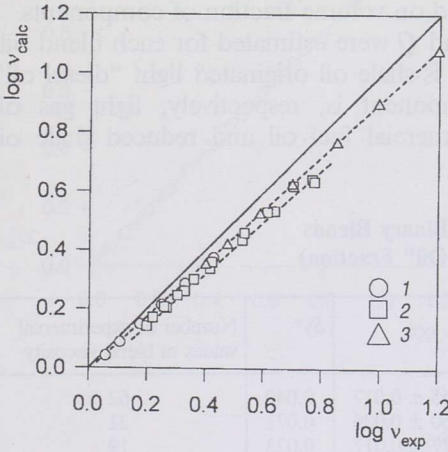
Fig. 5. Experimental (v_{exp}) and calculated (v_{calc}) values of kinematic viscosity (mm²/s) for shale oil originated light "diesel oil" fraction - light gas oil fraction blends.

Volume fraction high viscosity oil φ_H: *1* - 0.20, *2* - 0.50, *3* - 0.80

Fig. 6. Experimental (v_{exp}) and calculated (v_{calc}) values of kinematic viscosity (mm²/s) for shale oil originated light "diesel oil" fraction - reduced shale oil blends.

Volume fraction high viscosity oil φ_H: *1* - 0.25, *2* - 0.50, *3* - 0.75

2. The values of Δ depend on v_{exp}; for blends having constant value of $\varphi_H\varphi_L$ the dependence of Δ on v_{exp} measured at different temperatures may be expressed by the following equation

$$\Delta = p + q\log v_{exp} \qquad (2)$$

where p and q are constants.

3. Constants p, as well as constants q, in addition to the component oil nature, depend on the volume fraction of components. This dependence can be described by a linear equation where the component oil proportion is expressed in the form of product $\varphi_H\varphi_L$ as follows:
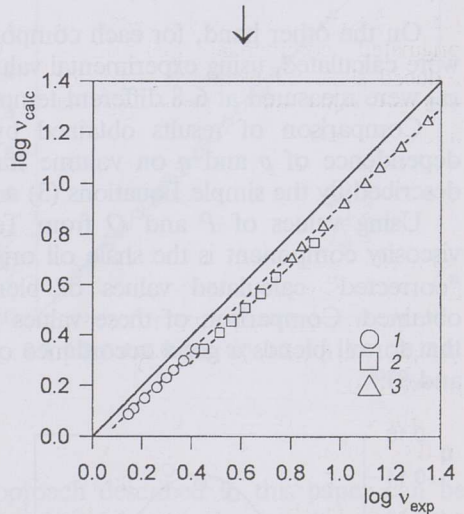
$$p = P\varphi_H\varphi_L \qquad (3)$$

and

$$q = Q\varphi_H\varphi_L \qquad (4)$$

Then the Equation (2) may be expressed:

$$\Delta = P\varphi_H\varphi_L + Q\varphi_H\varphi_L\log v_{exp} \qquad (5)$$

or

$$\frac{\Delta}{\varphi_H \varphi_L} = P + Q \ \log v_{\exp}, \qquad (6)$$

where P and Q are constants which depend on chemical nature of blend components, but do not depend on volume fraction of components.

Using Equation (6), constants P and Q were estimated for each blend oil, in which the low viscosity component is shale oil originated light "diesel oil" fraction and the high viscosity component is, respectively, light gas oil fraction, heavy gas oil fraction, commercial fuel oil and reduced shale oil (Table 2).

Table 2. **Constants P and Q for Shale Oil Binary Blends (Low Viscosity Component: Light "Diesel Oil" Fraction)**

High viscosity component	P	Q	Sy^*	Number of experimental values of blend viscosity
Light gas oil fraction	0.096 ± 0.010	0.565 ± 0.017	0.040	62
Heavy gas oil fraction	0.352 ± 0.032	0.360 ± 0.036	0.071	21
Commercial fuel oil	0.321 ± 0.011	0.017 ± 0.017	0.023	19
Reduced shale oil	0.297 ± 0.010	0.223 ± 0.014	0.023	23

$^* y = \Delta/\varphi_H \varphi_L$.

On the other hand, for each component oil proportion constants p and q were calculated, using experimental values of viscosity which at every value of φ_H were measured at 6-8 different temperatures.

Comparison of results obtained by these two ways certifies that the dependence of p and q on volume fraction of components can in fact be described by the simple Equations (3) and (4) (Fig. 7).

Using values of P and Q from Table 2 for blends in which the low viscosity component is the shale oil originated light "diesel oil" fraction, the "corrected" calculated values of blend kinematic viscosity (v_{ccalc}) were obtained. Comparison of these values with the experimental ones confirms that for all blends a good accordance of results has been reached (Figures 8 and 9).
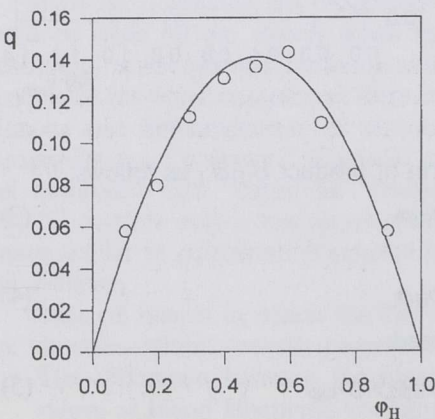

Fig. 7. Dependence of q on φ_H for shale oil originated light "diesel oil" fraction - light gas oil fraction blends.

Curve - calculated using constants P and Q from Table 2, points - calculated for blends, using at each φ_H values of $v_{\exp}$ at 6-8 various temperatures
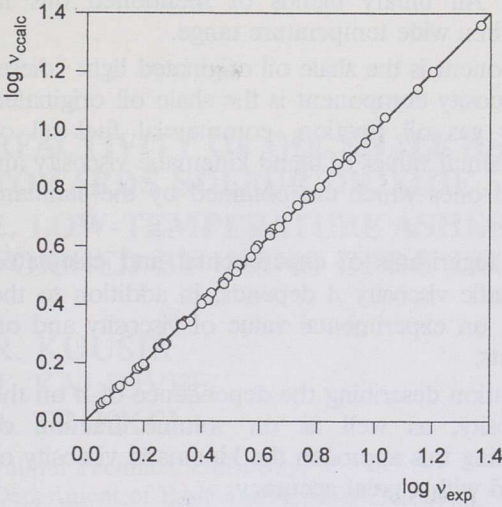
Fig. 8. Experimental (ν_{exp}) and "corrected" calculated (ν_{ccalc}) values of kinematic viscosity (mm^2/s) for shale oil originated light "diesel oil" fraction - light gas oil fraction blends.

Volume fraction high viscosity oil φ_H varies from 0.10 to 0.90

Fig. 9. Experimental (ν_{exp}) and "corrected" calculated (ν_{ccalc}) values of kinematic viscosity (mm^2/s) for shale oil originated light "diesel oil" fraction - reduced shale oil (*1*), light "diesel oil" fraction - commercial fuel oil (*2*) and light "diesel oil" fraction - heavy gas oil (*3*) blends.

Volume fraction high viscosity oil φ_H varies from 0.25 to 0.75
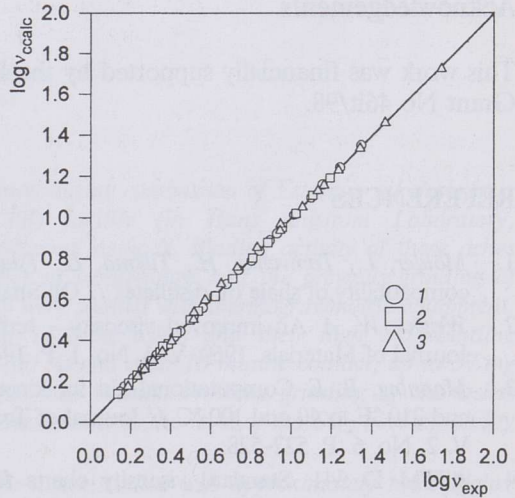
It is authors' opinion that the approach described in this paper can be used also for the evaluation of binary blend kinematic viscosity when the blends are made up of both a shale oil originated component and a petroleum oil originated component. Viscosity and stability of such blends will be discussed in our next paper.

Conclusions

1. The kinematic viscosity of shale oil originated light gas oil fraction, heavy gas oil fraction, commercial fuel oil and reduced shale oil binary blends can be evaluated by standard blending calculation technique, accepted

for hydrocarbon oil blends. All binary blends of mentioned oils in whatever ratio are also stable in a wide temperature range.

2. When the low viscosity component is the shale oil originated light "diesel oil" fraction and the high viscosity component is the shale oil originated light gas oil fraction, heavy gas oil fraction, commercial fuel oil or reduced shale oil, the experimental values of blend kinematic viscosity are always higher than calculated ones which are obtained by the standard calculation technique.

3. The difference between the logarithms of experimental and calculated values of binary blend kinematic viscosity Δ depends, in addition to the nature of blend components, on experimental value of viscosity and on volume fraction of components.

4. It is shown that a simple equation describing the dependence of Δ on the experimental value of viscosity, as well as on volume fraction of components, can be used. Using this approach the kinematic viscosity of binary blends can be evaluated with a great accuracy.

Acknowledgements

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