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Measurement of Viscosity of Hydrocarbon Liquids Using a Microviscometer

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The viscosity of normal alkanes, their mixtures, and true boiling point (TBP) fractions (C_6−C_{19}) of four North Sea petroleum reservoir fluids have been measured by use of an automatic rolling ball microviscometer at 20 °C. The equipment is specially suited for samples of limited amount as only 120 to 2500 μL is required depending on the viscosity range. The densities of the fluids were also determined. The accuracy of these measurements is ascertained and compared with literature data on *n*-alkane mixtures. The data reported for reservoir fluids includes molecular weights as well as density. Finally, generalized viscosity correlations for the C_6 to C_{19} fractions are discussed.

Introduction

All equations expressing flow of fluids, whether flow in porous media or in wells or pipes, contain the viscosity of the fluid. In Newtonian fluids the velocity of the fluid is inversely proportional to its viscosity. Viscosity therefore plays a very important role in various engineering calculations.

The viscosity of hydrocarbon mixtures and petroleum reservoir fluids is commonly measured by either the rolling ball viscometer or the capillary tube viscometer. Other nonconventional methods include the laser light scattering (Dorshow, 1991) and the piezoelectric quartz crystal (Pallas, 1990) techniques. In the rolling ball viscometer, the time required by the steel ball to travel through the fluid is correlated to its density and viscosity.

The apparatus described in this paper uses the principle of the rolling ball. The time required by the ball to travel a fixed distance through a glass capillary filled with the test fluid is directly proportional to its viscosity and density. A small sample volume is required to carry out each measurement, and the apparatus is completely automated. This makes the apparatus particularly attractive for application to viscosity measurement of the true boiling point (TBP) fractions of petroleum reservoir fluids, where normally a limited amount of sample is available. To the best of our knowledge, the data reported here with regard to viscosity measurements on TBP fractions of North Sea oils has never been reported before. However, a large amount of data has been published on TBP fractions of various Arab crude oils (Amin and Beg, 1994), Alberta bitumen (Miadoyne et al., 1994), and Saskatchewan heavy oils (Singh et al., 1994).

Apparatus

The apparatus was designed and manufactured by Anton-Paar KG of Austria to measure the viscosity of liquids at atmospheric pressure and for temperatures from 6 to 80 °C suitable for a viscosity range of 0.5 to 800 mPa·s. Different types of measuring systems are available with the microviscometer. Up to 10 measurement programs and calibration tables for angles ranging from 15 to 90° can be stored in the memory of the microviscometer.

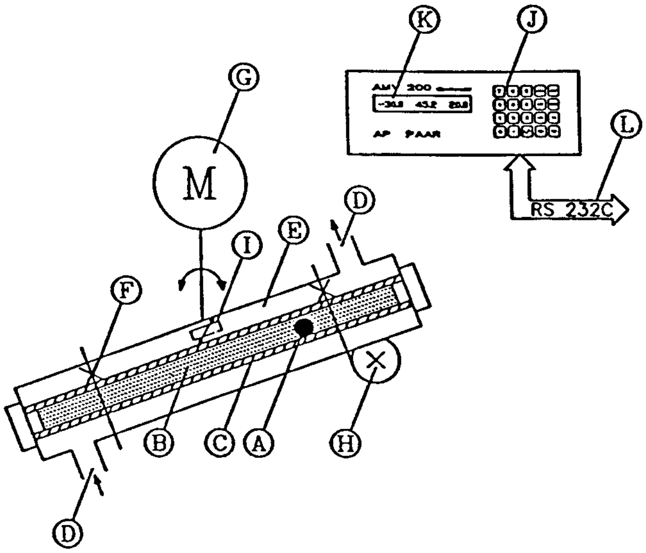

Figure 1. Schematic diagram of the microviscometer.

A schematic drawing of the microviscometer is shown in Figure 1. The gold-covered steel ball (A) rolls down inside the glass capillary (C), which is filled with the sample (B). The capillary is placed in the thermostated (D) capillary block (E). Two magnetic sensors (F) detect the rolling time of the ball. The desired inclination angle can be adjusted through a stepper motor (G). Zero balancing is performed for each inclination angle by means of the reference sensor (H). A temperature sensor (I) measures the temperature within the capillary block close to the surface of the capillary. Communication with the instrument takes place via the keyboard (J) and the alphanumeric display (K). The built-in RS 232 C serial interface (L) allows interfacing of the microviscometer to a printer or a PC.

Calibration of the Viscometer. Accurate determination of the viscosity requires careful calibration of the apparatus. The calibration constant has to be determined for each inclination angle used for measurement. In this work the viscometer was calibrated at 20 °C for angles ranging from 15 to 80°.

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Table 1. Densities and Viscosities of Calibration Standards, Supplied by Cannon and Haake

viscosity standard	composition	ρ (20 °C)/g·cm^{-3} lit.	ρ (20 °C)/g·cm^{-3} this work	η (20 °C)/mPa·s
N.4 (Cannon)	100% *n*-hexane	0.6665[a]	0.6675	0.3210[a]
N.8 (Cannon)	mixture of xylenes	0.8659[a]	0.8660	0.6657[a]
N1.0 (Cannon)	mixed hydrocarbons	0.7950[a]	0.7949	1.0850[a]
NF2 (Haake)	unknown	0.7420[b]	0.7438	1.2790[b]
NF4 (Haake)	unknown	0.8040[b]	0.8058	4.4980[b]
NF10 (Haake)	unknown	0.8550[b]	0.8551	8.8750[b]

[a] From Cannon. [b] From Haake.

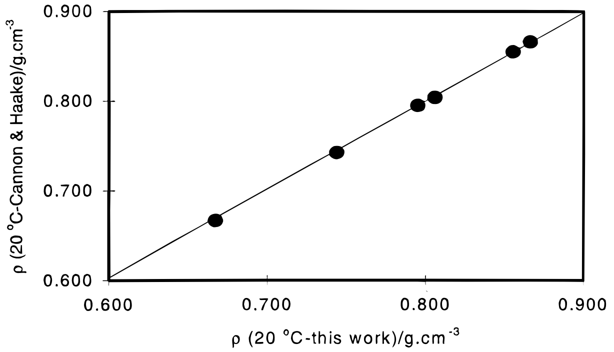

Figure 2. Comparison of density data for various viscosity standards.

Viscosity standards supplied by Cannon Instruments Co. and Haake Medingen GmbH were employed. The viscosity range considered was 0.4 to 10 mPa·s. The relevant data for the viscosity standards is provided in Table 1. Calibration constants for each inclination angle were automatically determined by the viscometer according to the following equation:

$$K(a) = \eta/t\cdot\Delta\rho$$

where $K(a)$ = calibration constant, η = viscosity of standard liquid, $\Delta\rho$ = difference in density of the ball and the standard liquid, and t = the rolling time of the ball. A comparison of the density data measured in this work and that reported for the viscosity standards is shown in Figure 2. An excellent agreement is clearly seen.

Experimental Procedure

Materials. All the normal alkanes used for the viscosity measurements were of analytical grade and were purchased from Aldrich Chemical Co. No further purification of the reagents was carried out. The true boiling point (TBP) fractions were obtained by distilling four stabilized crude oil samples, which is described in the following section.

Preparation of Solutions and Distillation of TBP Fractions. All the normal alkane mixtures were prepared by carefully weighing each component in a Sartorius Analytic balance with a stated precision of 0.0001 g. Mixture compositions were accurate to 0.005 wt %.

A Fischer distillation apparatus equipped with an HMS 500 Spaltrohr column with 90 theoretical plates was employed to distill four samples of stabilized crude oils (oils A−D) from the North Sea. The TBP fractions were designated as follows: C_n, where n represents the highest normal alkane in the fraction; e.g., C_{14} means the fraction collected between 0.5 °C above the boiling point of nC$_{13}$ and 0.5 °C above the boiling point of nC$_{14}$. All the oils were distilled at atmospheric pressure up to 151.3 °C (C_9 fraction), and a pressure of 2.66 kPa was applied to C_{10} to C_{19} fractions.

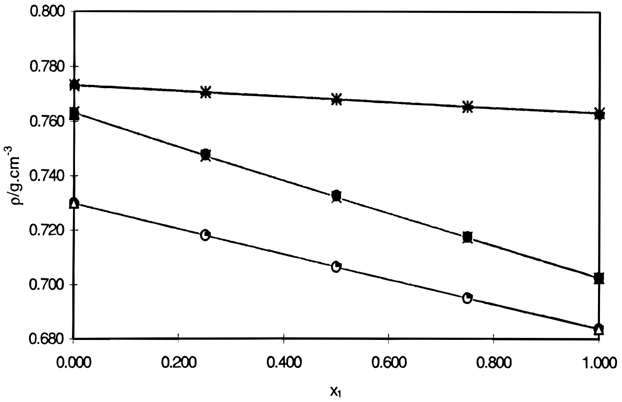

Figure 3. Comparison of density data for various mixtures: − ○ −, *n*C7(1) + *n*C10(2), this work; ■; *n*C7(1) + *n*C10(2), Cooper; △, *n*C7(1) + *n*C10(2), TRC; − × −, *n*C8(1) + *n*C14(2), this work; ●, *n*C8(1) + *n*C14(2), Cooper; ▲, *n*C8(1) + *n*C14(2), TRC; − * −, *n*C14(1) + *n*C16(2), this work; —, *n*C14(1) + *n*C16(2), Cooper; ◆, *n*C14(1) + *n*C16(2), TRC.

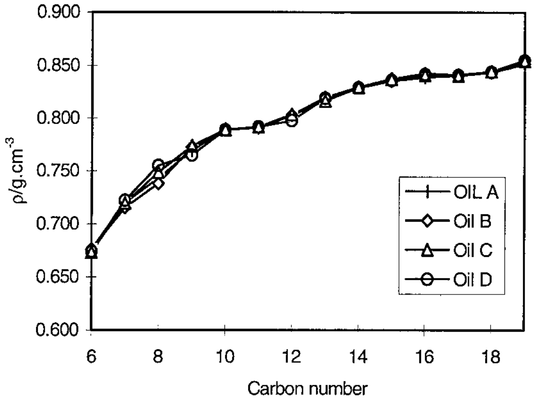

Figure 4. Density data for the TBP fractions of oils A−D.

Density and Molecular Weight Measurements. The density data for pure normal alkanes, their mixtures, and the various TBP fractions were measured by the Anton−Paar densitometer (DMA 58). The densitometer was calibrated with air and double-distilled, degassed water.

A freezing point depression apparatus (wide-range CRYETTE 5009), with *p*-xylene as a solvent, was employed to measure the molecular weights of all the TBP fractions.

Results and Discussion

A comparison of the measured density results for all the pure normal alkanes and their mixtures is given in Figure 3. The data agrees to within 0.05% and 0.07% with that reported by Cooper and Asfour (1991) and that reported in the TRC Tables (1986), respectively. The density data for the TBP fractions is presented in Figure 4 and Table 2.

All the viscosity measurements reported in this paper were carried out at 20 °C. The temperatures were mea-

Table 2. Densities, Molecular Weights, and Viscosities of True Boiling Point (TBP) Fractions[a]

carbon no.	b_p/°C	oil A			oil B			oil C			oil D			generalized viscosity values
		ρ	MW	η	ρ	MW	η	ρ	MW	η	ρ	MW	η	
6	69.2	0.676	82.5	0.323	0.676	90.9	0.321	0.673	91.1	0.317	0.674	84.7	0.320	0.320
7	98.9	0.720	88.0	0.463	0.715	101.3	0.459	0.719	96.6	0.459	0.722	93.8	0.450	0.458
8	126.1	0.743	100.4	0.551	0.738	116.2	0.517	0.749	106.8	0.571	0.755	109.8	0.520	0.540
9	151.3	0.769	119.5	0.690	0.773	140.4	0.719	0.774	125.7	0.720	0.765	122.3	0.890	0.755
10	174.6	0.790	134.2	0.941	0.789	150.8	0.964	0.789	139.3	1.020	0.789	136.9	0.890	0.954
11	196.4	0.791	146.0	1.180	0.791	160.9	1.150	0.792	147.5	1.210	0.792	147.2	1.090	1.158
12	217.2	0.803	157.3	1.470	0.803	176.6	1.490	0.804	157.9	1.420	0.798	163.1	1.420	1.450
13	235.9	0.817	169.2	1.910	0.820	189.9	1.930	0.817	172.3	1.802	0.819	174.4	1.950	1.898
14	253.9	0.829	182.7	2.483	0.830	205.0	2.480	0.830	185.1	2.468	0.829	188.3	2.440	2.468
15	271.1	0.836	193.1	3.106	0.837	219.8	3.218	0.837	199.4	3.253	0.836	202.2	3.160	3.184
16	287.3	0.839	208.3	3.992	0.843	236.0	4.218	0.841	203.7	4.270	0.842	215.4	4.060	4.135
17	303.0	0.841	215.8	4.952	0.841	254.0	5.560	0.840	214.0	5.563	0.841	231.2	5.270	5.336
18	317.0	0.844	227.3	6.521	0.845	272.0	7.515	0.845	231.8	7.614	0.844	246.3	6.730	7.095
19	331.0	0.852	245.9	8.776	0.855	280.2	9.406	0.854	257.5	9.089	0.855	260.9	8.930	9.050

[a] ρ, density in g·cm^{-3} at 20 °C; MW, molar mass; η, viscosity in mPa·s.

Table 3. Densities and Viscosities of Pure Normal Alkanes and Their Mixtures

mass fraction (A)	ρ (20 °C)/g·cm^{-3}			η (20 °C)/mPa·s		
	this work	lit.[a]	lit.[b]	this work	lit.[a]	lit.[b]
		n-Heptane (A) + *n*-Decane (B)				
0.000	0.730	0.730	0.730	0.910	0.916	0.926
0.250	0.718	0.719	*c*	0.725	0.727	*c*
0.500	0.707	0.707	*c*	0.584	0.590	*c*
0.750	0.695	0.696	*c*	0.489	0.489	*c*
1.000	0.684	0.684	0.684	0.417	0.411	0.417
		n-Octane (A) + *n*-Tetradecane (B)				
0.000	0.763	0.763	0.763	2.292	2.304	2.334
0.250	0.747	0.748	*c*	1.501	1.472	*c*
0.500	0.732	0.733	*c*	1.003	1.009	*c*
0.750	0.717	0.718	*c*	0.753	0.726	*c*
1.000	0.703	0.703	0.703	0.542	0.541	0.545
		n-Tetradecane (A) + *n*-Hexadecane (B)				
0.000	0.773	0.773	0.774	3.425	3.447	3.475
0.250	0.771	0.770	*c*	3.067	3.099	*c*
0.500	0.768	0.768	*c*	2.789	2.796	*c*
0.749	0.766	0.765	*c*	2.529	2.532	*c*
1.000	0.763	0.763	0.763	2.292	2.304	2.334

[a] Cooper and Asfour (1991). [b] TRC Tables (1986). [c] Only pure component data is available.

sured with an accuracy of 0.01 °C. The measuring system used consisted of a capillary with an inside diameter of 1.6 mm and an internal volume of 400 μL. The calibration constants calculated by means of the equation described in the section Calibration of the Viscometer were used to determine the viscosity from the roll times. The roll times measured at all the angles were considered for the viscosity calculation. The roll times were measured with a stated precision of ±0.01 s. The measured viscosity data for all the pure normal alkanes and their mixtures is presented graphically in Figure 5 and Table 3. The percentage error from the average viscosity values as a function of the measurement angle for the binary mixture of octane and tetradecane is shown in Figure 6. The values measured in this work agree to within 0.9% and 1.2% with those reported by Cooper and Asfour (1991) and those reported in the TRC Tables (1986), respectively. The results, thus, clearly indicate the reliability of the microviscometer for measuring the viscosity of liquids by use of very small sample volumes.

After the successful application of the microviscometer to measure the viscosity of pure normal alkanes and their mixtures, the viscosities of various TBP fractions of four stabilized crude oil samples (oils A−D) were measured. The measurement system was the same as above. The measured densities, molecular weights, and viscosities for all the TBP fractions for the oils A−D are given in Table 2. For all the oils the viscosity values are quite similar for all the TBP fractions. A set of generalized values based on these measurements on the oils is also presented in Table 2. Similarly, a plot of the viscosities vs the carbon number of all the TBP fractions is shown graphically in Figure 7.

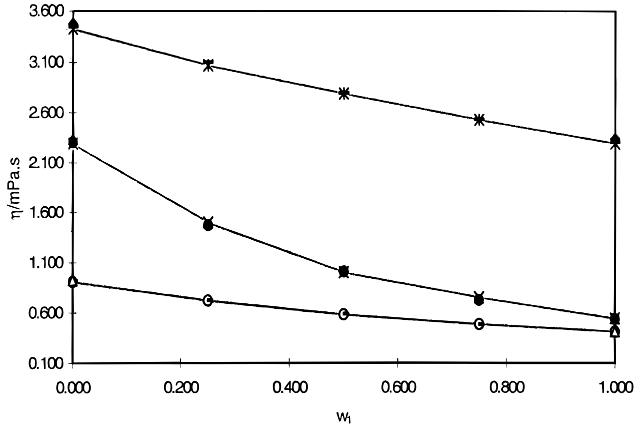

Figure 5. − ○ −, *n*C7(1) + *n*C10(2), this work; ■; *n*C7(1) + *n*C10(2), Cooper; △, *n*C7(1) + *n*C10(2), TRC; − × −, *n*C8(1) + *n*C14(2), this work; ●, *n*C8(1) + *n*C14(2), Cooper; ▲, *n*C8(1) + *n*C14(2), TRC; − * −, *n*C14(1) + *n*C16(2), this work; −, *n*C14(1) + *n*C16(2), Cooper; ◆, *n*C14(1) + *n*C16(2), TRC.

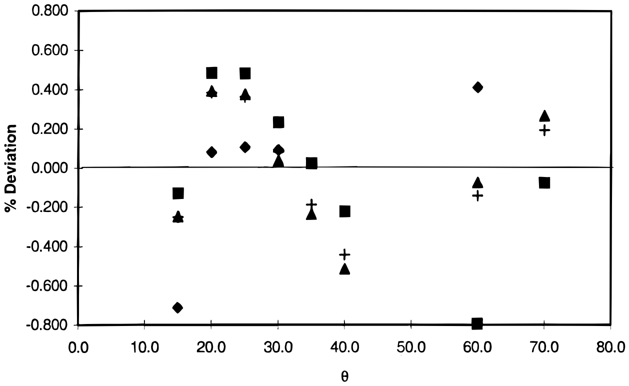

Figure 6. Effect of measurement angle θ on the measured viscosity: ◆, 1.00nC8 + 0.00nC14 (0.5 mPa·s); ■, 0.75nC8 + 0.25nC14 (0.7 mPa·s); ▲, 0.50nC8 + 0.50nC14 (1.0 mPa·s); +, 0.25nC8 + 0.75nC14 (1.5 mPa·s).

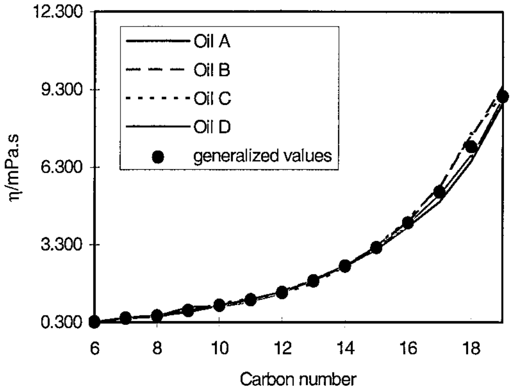

Figure 7. Carbon number vs viscosity for the TBP fractions of oils A−D.

TBP fractions consist of mixtures of hydrocarbons having a similar boiling point range. However, in terms of molecular weight, there may be a significant range of sizes and structures as the size of molecules of the same boiling point increases from aromatics to alkanes. This is observed in the properties and the behavior of the fractions. Another point that may be considered is the so-called purity of the fraction. This is related to the fact that, within the distribution of compounds in a fraction C_n, compounds belonging to the C_{n-1} and the C_{n+1} fractions may be observed by gas chromatography (Rønningsen et al., 1989). Detailed comparison of oils has indicated that samples with similar properties may indeed have markedly different composition (Stewart et al., 1989). Measurements of the viscosity of the TBP fractions can be highly desirable and beneficial as an input parameter, augmented by the specific gravity and refractive index, to predict the fractional composition of paraffins, naphthenes, and aromatics contained in these fractions. This approach has been described in detail by (Riazi and Daubert, 1980) and makes it possible to treat each TBP fraction in terms of separate subfraction as paraffinic, naphthenic, and aromatic content. Thus a rather detailed description of the entire reservoir fluid is allowed for. Moreover, it has already been demonstrated that such an approach using a detailed description of the reservoir fluid significantly enhances the quality of phase-behavior calculations (Rønningsen et al., 1989; Pedersen et al., 1984).

Conclusions

A microviscometer on the basis of the principle of a rolling ball is described. The apparatus is capable of measuring viscosities of liquids at atmospheric pressure and at temperatures from 6 to 80 °C suitable for a viscosity range of 0.5 to 800 mPa·s. A wide range of measuring systems (in terms of internal volumes of the capillaries and the viscosity range desired) are available. It has made possible a considerable reduction of the sample volume compared to conventional rolling ball viscometers, and a high degree of automation has been incorporated. The performance of the microviscometer is illustrated by comparing results from viscosity measurements on pure normal alkanes and their mixtures with previously reported data. In addition to these data, viscosity measurements on the true boiling point (TBP) fractions of four stabilized crude oil samples from the North Sea are also presented. It is believed that such data will be useful for the development of more accurate and reliable methods for predicting the viscosity. It is also believed that measurements of the viscosity of TBP fractions will improve the reservoir fluid description (in terms of PNA analysis) to enhance the accuracy of phase-behavior calculations.

Acknowledgment

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