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Thermal Conductivity of Complex Hydrocarbon Systems at Pressures Up To 1000 MPa

The thermal conductivity of five samples of crude oil and one sample of gas condensate was measured by the transient hot-wire technique. The measurements were made along isotherms (245, 250, 273, 295, 320, 336, and 373 K) in the pressure range from atmospheric pressure up to 1000 MPa and along isobars (at 0.1, 100, 200, 300, 400, 500, and 1000 MPa) in the temperature range 245–450 K. It was observed that the thermal conductivity of the samples investigated strongly depends on the pressure and rises with increasing pressure for all the temperatures. At a certain pressure, the temperature coefficient of thermal conductivity reverses from negative to positive. The pressure at which this reversal was observed varied in the range of 300–380 MPa.
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1 Introduction

Information on the high-pressure properties of crude oils can give new insight into the processes that take place in the depths of the Earth and that accompany the formation of hydrocarbons. This type of investigation is also interesting from the point of view of the physics of disordered multicomponent matter, because crude oils are usually complex liquid mixtures with a colloidal (microheterogeneous) structure. The investigation of the properties of hydrocarbon systems under high pressure is of great interest to the oil industry because it is related to the problem of oil recovery from deeply placed beds. This paper is a continuation of the series of papers published by the authors previously [1–4].

2 Experimental Details

The investigated oil and gas condensate samples were selected from different regions of Russia and have quite different characteristic properties (Table 1). All the samples were degassed and dried before investigation.

The transient hot-wire technique used to determine the thermal conductivity as functions of temperature and pressure was developed at the Department of Physics, Umeå University, Umeå, Sweden and was described previously [5,6]. The hot-wire is a transient dynamic technique based on the measurement of the temperature rise in a defined distance from a linear heat source embedded in the test material. The nickel wire (0.3 mm in diameter and with a length of 40 mm) was installed as a circular loop inside the teflon cell together with a sample of petroleum system investigated. The whole assembly was loaded into a piston–cylinder high-pressure apparatus, and the pressure was generated by a hydraulic press. Unaccuracy of pressure measurement was less than 50 MPa. The temperature was measured using a chromel–alumel thermocouple with accuracy of ±2.2 K.

The measurements of thermal conductivity were made along isotherms (245, 250, 273, 295, 320, 336, and 373 K) in the pressure range from atmospheric pressure up to 1000 MPa and along isobars (at 0.1, 100, 200, 300, 400, 500, and 1000 MPa) in the temperature range 245–450 K. In the isothermal measurements, the stabilization of temperature was performed after every change in pressure, and the temperature was determined with an accuracy of 1%. In the isobaric measurements, the temperature was increased at constant rate of approximately 0.01 K/s. The uncertainty of the determination of the thermal conductivity was not more than 2.5%. As demonstrated previously [7], for viscous liquids, the convection effects are negligible in this method.

3 Experimental Results

Figure 1 shows the pressure dependence of the thermal conductivity (λ) for Komsomolsk oil. The fact that the data obtained during the isothermal and isobaric experiments are the same

Table 1 Properties of samples investigated: 1—Usinsk oil, 2—Komsomolsk oil, 3—Kumkolsk oil, 4—Kalchinsk oil, 5—Verhozimskaya oil, and 6—Shtokman gas condensate

	Sample number					
Properties	1	2	3	4	5	6
Density at 293 K (kg/m^3)	962	942	813	871	939	792
Molecular mass	415	305	225	303	350	135
Initial boiling temperature (K)	404	480	298	346	371	—
Viscosity at 323 K (mm^2/s)	513	80.9	3.7	8.0	22.1	1.0
Content (%)						
Silica-gel pitches	22	14	10	11	22.5	0
Asphaltenes	11	1.3	<0.1	1.5	10.1	0
Petroleum wax	0.3	0.2	15	2.9	5.0	0
Fraction content (vol. %)						
Boiling below 100 °C	0	0	8	6	0	8
Boiling below 200 °C	5	0	28	20	1.5	70
Boiling below 300 °C	15	11	50	40	20	0

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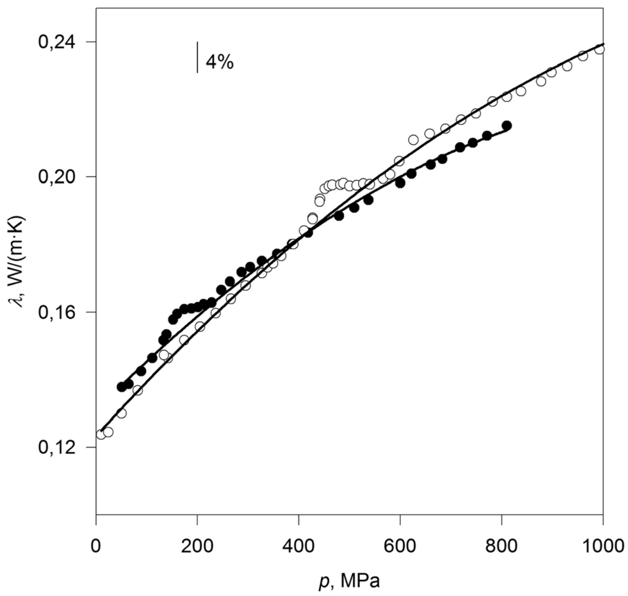

Fig. 1 Pressure dependence of λ for Komsomolsk oil at 295 K (filled circles) and at 245 K (open circles) oils

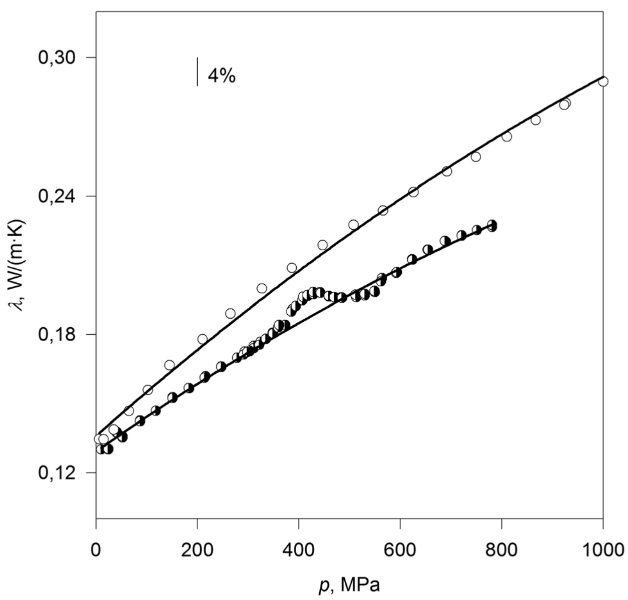

Fig. 2 Pressure dependence of λ for Usinsk (filled circles) and Kumkolsk (open circles) oils at 295 K

Table 2 Correlation coefficients in Eq. (1) for calculation of thermal conductivity at high pressure

Temperature (K)	a_1	a_2	a_3
Usinsk oil			
245	0.1365	0.1548	0.07484
295	0.1374	0.1772	0.06474
336	0.1260	0.1642	0.03950
Komsomolsk oil			
245	0.1334	0.1457	0.05759
295	0.1228	0.1745	0.05789
336	0.1225	0.1655	0.04091
Kumkolsk oil			
245	0.1551	0.1691	0.02043
295	0.1359	0.1944	0.0386
336	0.1306	0.2222	0.0862
Kalchinsk oil			
273	0.138	0.1536	0.02163
295	0.1319	0.1652	0.02932
336	0.1315	0.1518	0.02237
Verhozimskaya oil			
295	295	295	295
336	336	336	336
Shtokman gas condensate			
245	0.128	0.1203	0.0803
273	0.1275	0.1264	0.01718
295	0.1181	0.1594	0.04019

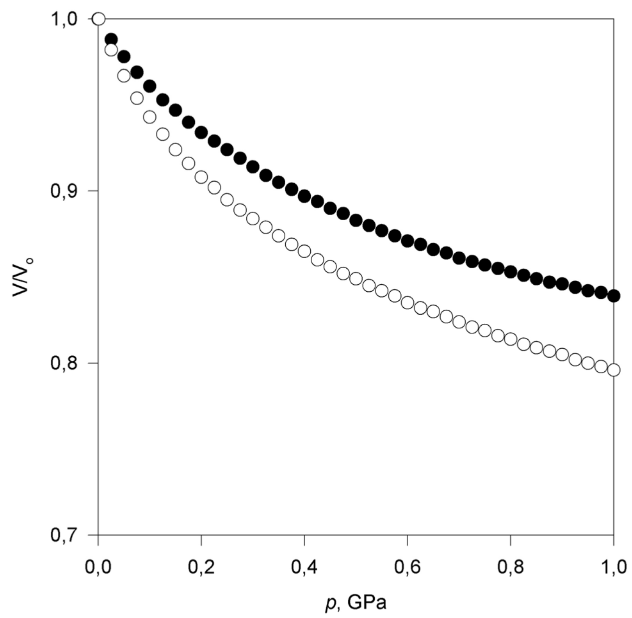

Fig. 3 Relative volume changes of Usinsk oil (filled circles) and Kumkolsk oils (open circles) at 295 K

within the measurement accuracy confirms the reliability of the results obtained.

As shown previously [5,8], the data for the maxima of λ are not equilibria but should be regarded as the consequence of structural relaxations in the crude oils with characteristic times comparable to the heat pulse duration. Thus, although the apparent maxima on the λ curves are typically indications of glass transitions when detected by the transient hot-wire method, the "true" values for λ are obtained only after subtracting these effects by using extrapolation. The resulting curves (solid lines in Figs. 1, 2, 4, and 5) show the change in the slope of the temperature and pressure dependencies of the thermal conductivity.

Several general regularities regarding the pressure dependence of the thermal conductivity of crude oil and gas condensate samples can be derived from the experimental data. Over the whole investigated range, the thermal conductivity rises with pressure (p). Within the experimental accuracy, the thermal conductivity can be approximized with the following equation:

$$\lambda = a_1 + a_2 \cdot p + a_3 \cdot p^2 \qquad (1)$$

where a_1, a_2, and a_3 are the correlation coefficients; their values for the investigated petroleum systems are given in Table 2.

The pressure dependence of the thermal conductivity is strongly influenced by isothermal compressibility. Higher isothermal compressibility leads to a higher λ–p slope, which is shown in Fig. 2

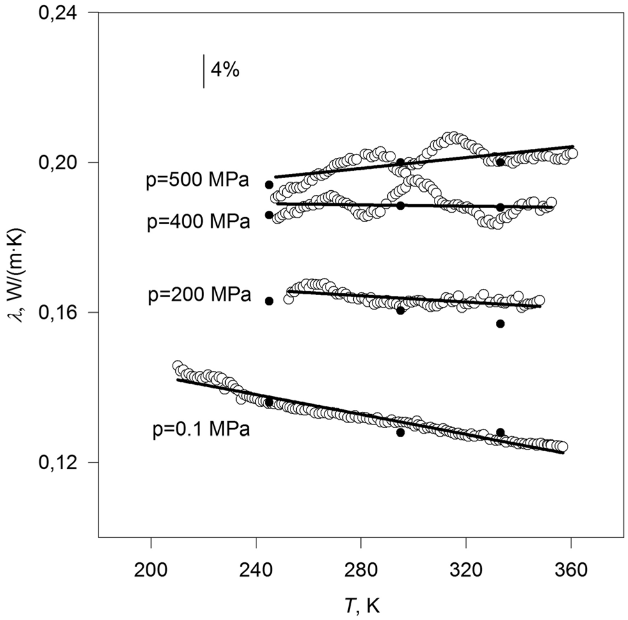

Fig. 4 Temperature dependence of λ for Usinsk oil at different pressures at isothermic (filled circles) and isobaric (open circles) experiments

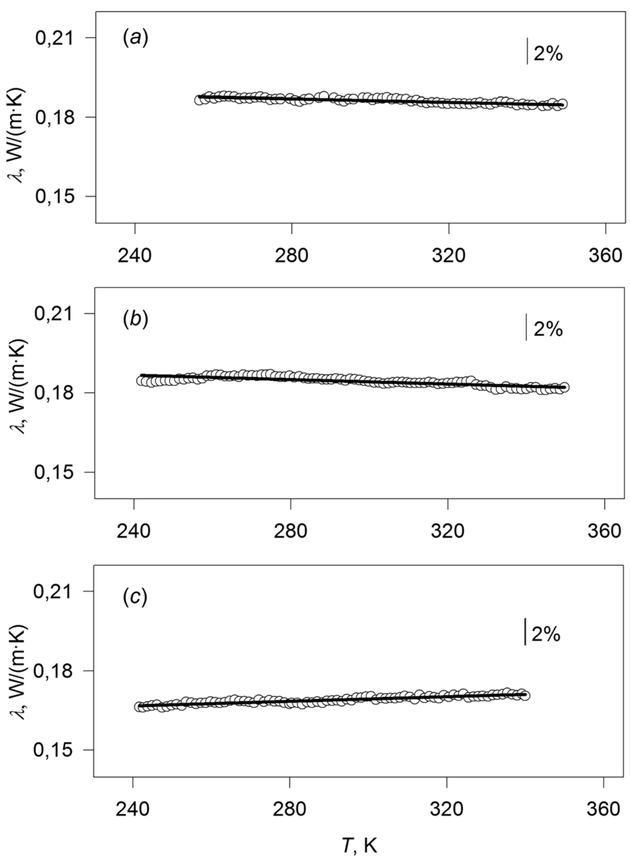

Fig. 5 Temperature dependence of λ for Kalchinsk oil (*a*), Verhozimskaya oil (*b*), and Shtokman gas condensate (*c*) at pressure of 300 MPa

for the examples of Usinsk and Kumkolsk oils. The relative volume changes of Usinsk and Kumkolsk oils at 295 K and the corresponding isothermal compressibility factors are given in Fig. 3.

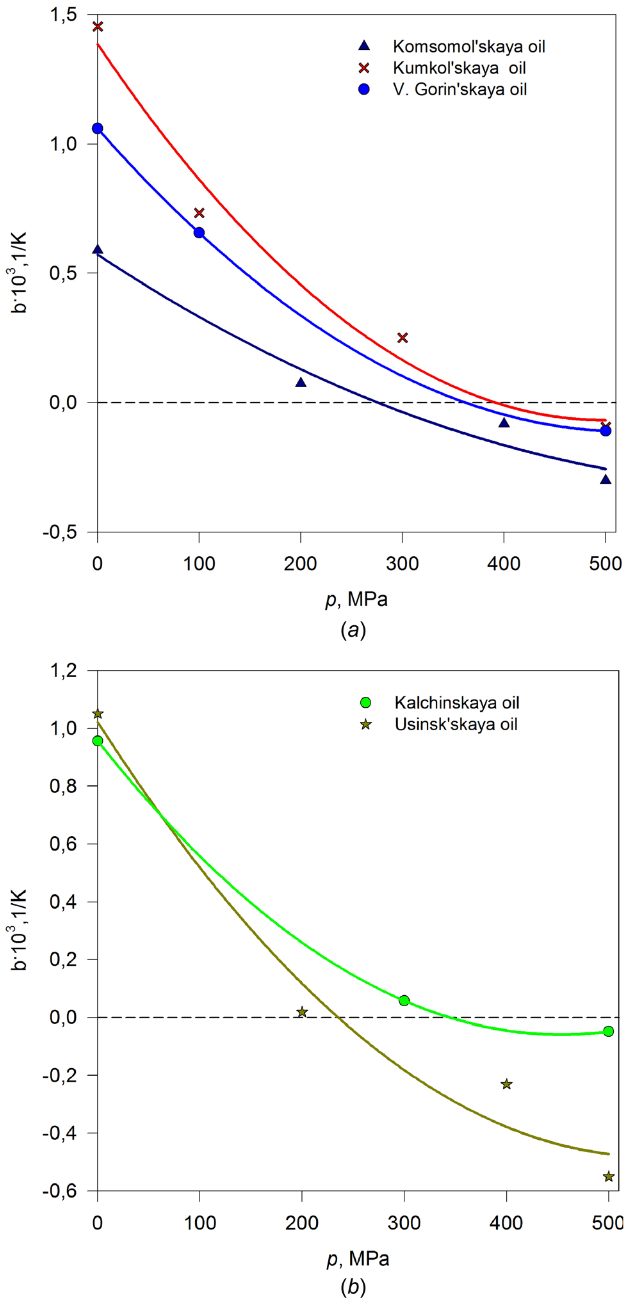

Fig. 6 Pressure dependence of *b* temperature coefficient in Eq. (2) for different hydrocarbon systems. Symbols represent experimental points, and solid lines are quadratic regression lines for correspondent experimental points.

The temperature dependence of λ for Usinsk oil is shown in Fig. 4. The thermal conductivity decreases linearly with increasing temperature at pressures up to 300 MPa.

At pressures below 300–380 MPa, the thermal conductivity of all the samples investigated decreases linearly with increasing temperature. In the pressure range of 300–380 MPa, λ does not depend on temperature (Fig. 5). At higher pressures, the thermal conductivity increases linearly with rising temperature.

4 Discussion

The experimental data obtained show the influence of isothermal compressibility on the pressure dependence of the thermal conductivity of petroleum systems. This corresponds to the theoretical conclusions of Kamal and McLaughlin [9], who showed a linear and always positive characteristic of the pressure influence on the thermal conductivity of the liquid.

The temperature dependence for the samples investigated at different pressures can be described by the linear function [10]

$$\lambda_T = \lambda_{293} \cdot [1 - b \cdot (T - 293)] \quad (2)$$

where λ_T and λ_{293} are the thermal conductivity at temperature T and temperature 293 K, respectively, W/(m·K); and b is the temperature coefficient of thermal conductivity at a given pressure, 1/K.

At pressures of 300–380 MPa, the temperature coefficient of thermal conductivity is reversed from negative to positive. This experimental result confirms the suggestion made by Bridgman [11] that the sign of the temperature dependence of thermal conductivity for liquids changes above 300 MPa and corresponds with the theoretical calculations of Horroks and McLaughlin [12]. Bridgman [11] explained this phenomena by the fact that for liquids, the thermal expansion at high pressure is greater at low temperature than at high temperature. Horroks and McLaughlin [12] using the vibrational theory of thermal conductivity confirmed the Bridgman suggestion. In Figs. 6(*a*) and 6(*b*), the change of temperature coefficient b with pressure for the investigated petroleum samples is shown.

5 Conclusions

The thermal conductivity of crude oil and gas condensate was investigated by the transient hot-wire method at pressures up to 1000 MPa in the temperature range of 245–450 K. It was observed that the thermal conductivity of the samples investigated increases with pressure at all the temperatures. The relative effect of pressure increases at higher temperature. The change with temperature is so large that at a certain pressure, the temperature coefficient of thermal conductivity reverses from negative to positive. The pressure at which this reversal was observed varied in the range of 300–380 MPa.

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