

Glass Transition in Crude Oils Under Pressure

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The transition to the glassy state in crude oil has been investigated at high pressures by the transient hot-wire method and differential scanning calorimetry. The nine samples investigated represent the most common types of crude oils and their fractions. The range of pressures was from atmospheric to 2 GPa in the temperature range of 150–370 K. The pressure dependence of the glass transition in crude oils and oil fractions (dT_g/dp) depends upon the viscosity of the system.

KEY WORDS: crude oils; glass transition; high pressure; oil fractions.

1. INTRODUCTION

Information on phase transitions in crude oils at high pressure has practical importance for many processes in oil industry, such as recovery, transport, refining, etc. Furthermore, this information is also interesting from the point of view of the physics of disordered multicomponent systems. We have investigated six different crude oils and one condensate. Our specimens were from different oil fields in Russia and Kazakhstan. Properties of the samples are shown in Table I. The specimens were degassed and dried before the investigations. We have also made measurements for heavy fractions of Usinsk oil and Kumkolsk oil, both of which have boiling temperatures higher than 523 K. These samples are designated, respectively, “Heavy 1” and “Heavy 2.” The viscosity of a heavy fraction distilled from a crude oil is much higher than the viscosity of a crude oil itself. For example, the viscosity of Kumkolsk oil (sample 3) at 323 K (ν_{50})

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Table I. Properties of Crude Oils

Properties	Number of oil sample ^a						
	1	2	3	4	5	6	7
Density at $T = 20^\circ\text{C}$ ($\text{kg} \cdot \text{m}^{-3}$)	962	942	813	871	832	939	792
Average molar mass	415	285	225	303	262	350	135
Initial boiling point (K)		404	480	298	346	359	371
Viscosity at $T = 50^\circ\text{C}$ ($\text{mm}^2 \cdot \text{s}^{-1}$)	513	80.9	3.7	8	5.7	83.6	0.97
Content (%)							
Silica-gel pitches	22	14	10	11	4.5	22.5	0
Asphaltenes	11	1.3	<0.1	1.5	0.8	10.1	0
Petroleum wax ^b	0.3	0.2	15	2.9	3.7	5.0	0
Fractions content (%)							
boiling below 100°C	0	0	8	6	3	0	8
boiling below 200°C	5	0	28	20	26	1.5	70
boiling below 300°C	15	11	50	40	46	20	0

^a 1—Usinsk oil, 2—Komsomolsk oil, 3—Kumkolsk oil, 4—Kalchinsk oil, 5—Vostochno-Gorinsk oil, 6—Verhozimsk oil, 7—Shtokman condensate.

^b Total amount of wax was determined by the method of low temperature deparaffinization (State Standard of Russia No. 11851–85).

is $3.7 \text{ mm}^2 \cdot \text{s}^{-1}$, while the viscosity of its heavy fraction is $25.8 \text{ mm}^2 \cdot \text{s}^{-1}$. Therefore, the experiments with heavy fractions were carried out to investigate the influence of the viscosity of an oil system on the glass transition process.

2. EXPERIMENTS

Using the transient hot-wire method [1], we measured the thermal conductivity λ and specific heat capacity per unit volume ρc_p of the samples along three isotherms (at 275, 295, and 320 K) in the pressure range from atmospheric pressure to 2 GPa and along isobars (at 0, 0.1, 0.3, 0.5, and 1.0 GPa) in a temperature range of 250–330 K. In isothermal measurements, the temperature was stabilized after every change in pressure. In isobaric measurements, the temperature was increased at a constant rate of approximately $0.01 \text{ K} \cdot \text{s}^{-1}$. The temperature rise of the Ni wire in each measurement event was about 2 K during a time of 1 s (so the corresponding rate of the temperature rise was of the order of $1 \text{ K} \cdot \text{s}^{-1}$). Each experiment was repeated. The difference between repeated experiments was less than the uncertainty of the method. As demonstrated in Ref. 2, the effects of natural convection are negligible for viscous liquids in this method. The

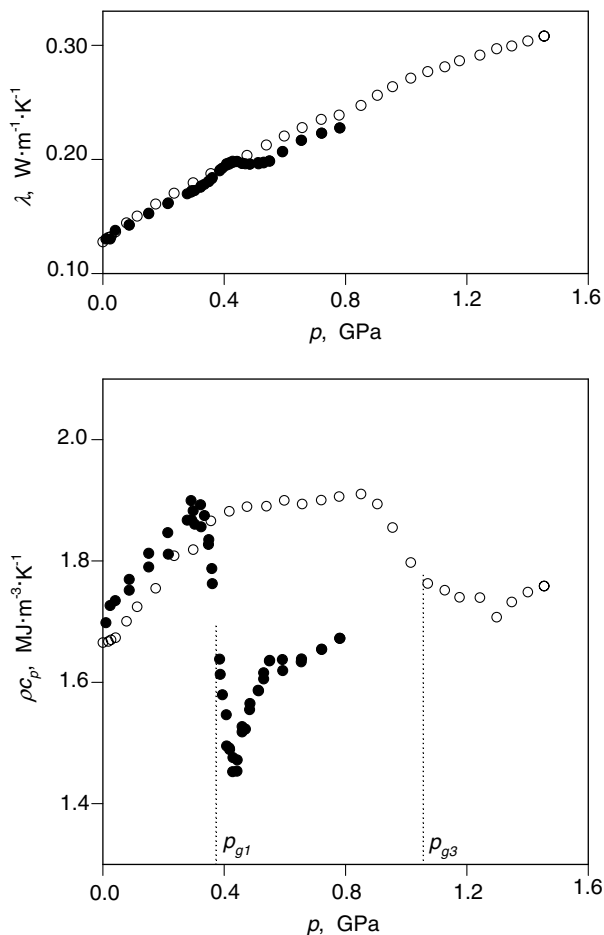


Fig. 1. Pressure dependence of λ and ρc_p at 295 K for Usinsk-sample 1 (filled circles) and Verhozimsk-sample 3 (open circles) oils.

method and the experimental arrangement have been fully described in Refs. 1 and 3. As shown in Ref. 2, the uncertainty of the determination of λ and ρc_p for organic liquids is 2.5 and 4%, respectively.

A Perkin-Elmer DSC-2 calorimeter was used for the measurements of the specific heat capacity c_p . To ensure complete dissolution of precipitated hydrocarbons, we heated all samples to 340 K in closed agitated containers for 15 min. Then the samples were left to cool to room temperature and put into standard aluminum capsules. Beginning at room temperature we heated capsules in the calorimeter up to 340 K at a rate of $10 \text{ K}\cdot\text{min}^{-1}$

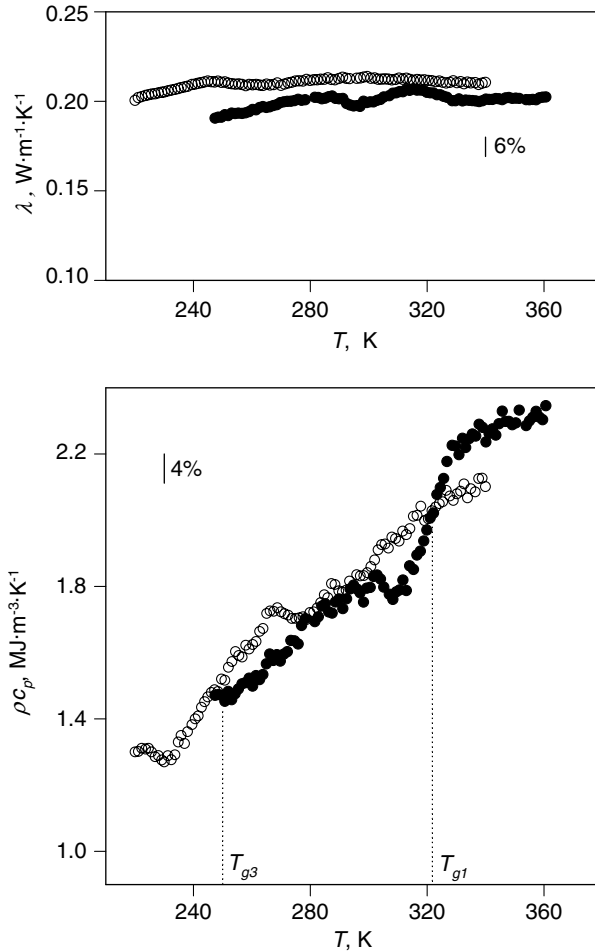


Fig. 2. Temperature dependence of λ and ρc_p at 0.5 GPa for Usinsk-sample 1 (filled circles) and Verhozimsk-sample 3 (open circles) oils.

and then started the cooling experiment. The measurements were made in a temperature range of 130 – 340 K at a rate of $10 \text{ K}\cdot\text{min}^{-1}$, both for the cooling and heating experiments at atmospheric pressure. The potential to use this method for cooling experiments was shown in Ref. 4. Full details, including a calibration of the calorimeter for cooling experiments, were described in Ref. 4. The uncertainty in the determination of c_p was not more than 2%.

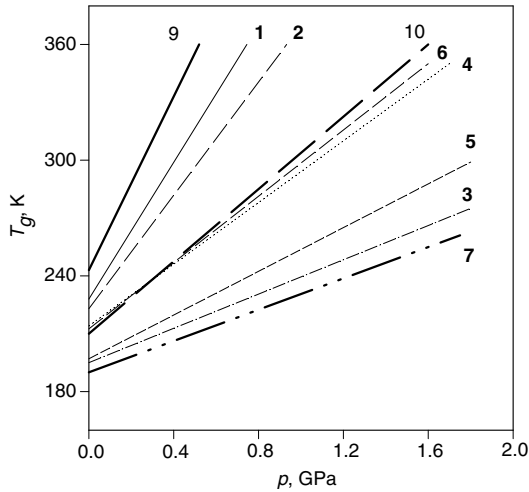


Fig. 3. T - p diagram of oils investigated. Line numbers correspond to the numbers of the samples: 1- Usinsk oil, 2- Komsomolsk oil, 3- Kumkolsk oil, 4- Kalchinsk oil, 5- Vostochno-Gorinsk oil, 6- Verhozimsk oil, 7- Shtokman condensate, 9 – Heavy 1, 10– Heavy 2.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show λ and ρc_p of Usinsk (sample 1) and Verhozimsk (sample 3) crude oils versus pressure and temperature, respectively. It is possible to compare the characteristic maximum of λ and the simultaneous step in ρc_p in the oils with those in glycerol, whose glass transition is well established [5]. As shown previously [6], the data at the local maximum of λ and the corresponding sharp minimum at the end of a step of ρc_p are typical indications of a glass transition when detected by the transient hot-wire method. A T – p diagram of oils investigated is presented in Fig. 3. The glass transition points for this diagram are defined in a traditional manner: as a temperature (pressure) half-step change in ρc_p . Both isothermal and isobaric data have been used for the diagram. By decreasing the temperature or with increasing pressure, the viscosity of a liquid increases; and, if it does not crystallize on the way, the liquid solidifies to an amorphous glass. The approach of the glass transition is manifested by a dramatic increase of the viscosity. In our investigations, we sought a correlation between dT_g/dp and certain physical properties of the oils. By comparing the values of the viscosity of the oil samples at 323 K from

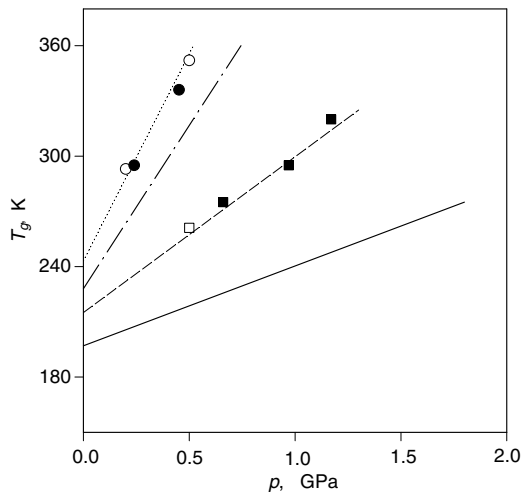


Fig. 4. T - p diagram for Usinsk oil (dashed-dotted line) and its heavy fraction—Heavy 1 (dotted line and circles), for Kumkolsk oil (solid line), and its heavy fraction—Heavy 2 (dashed line and squares). Filled circles and squares show the glass transition points on isotherms; open circles and squares, those on isobars.

Table I (ν_{50}) and the T - p diagram in Fig. 3, it is possible to conclude that there is a correlation between dT_g/dp and the viscosity of the oils (ν_{50}).

This conclusion was confirmed by the experiments with heavy fractions. The investigation of the Heavy 1 [7] and Heavy 2 oil fractions has demonstrated the presence of the glass transition in these fractions as well, but shifted toward higher temperatures (lower pressures) compared with crude oils themselves (Fig. 4). This shift was explained by the higher value of ν_{50} in the case of the heavy fractions. A correlation between dT_g/dp and ν_{50} is shown in Fig. 5.

4. CONCLUSION

The glass transition process in different complex oil systems over a wide temperature–pressure range has been investigated by two different thermophysical methods. We have constructed the “phase” diagram for the oil systems investigated, and observed the correlation between dT_g/dp and the viscosity of the oil systems.

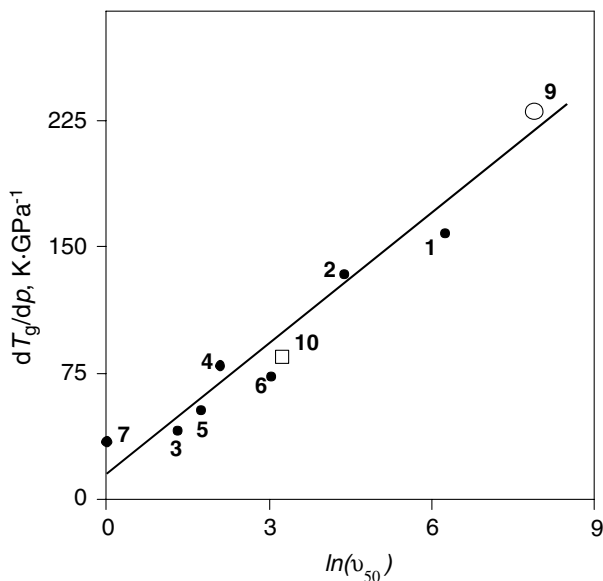


Fig. 5. Correlation between dT_g/dp and the viscosity at 323 K (ν_{50}) of the systems investigated. Point numbers correspond to the numbers of the samples as in Fig. 3.

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