International Journal of Thermophysics, Vol. 15, No. 1, 1994

Glass Transition in Viscous Crude Oils Under Pressure

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Received June 17, 1993

The transitions to the glassy state in viscous crude oils have been investigated at high pressures by the transient hot-wire method, by differential scanning calorimetry, and by equation-of-state measurements. The range of pressures investigated was up to 1.2 GPa in the temperature interval 150–370 K. The glass transition in crude oils is a common phenomenon and occurs due to the viscosity increase on decreasing the temperature or increasing the pressure. The actual transition coordinates depend not only on physical properties but also on the characteristic experimental time.

KEY WORDS: bulk modulus; crude oil; glass transition; heat capacity; high pressure; thermal conductivity.

1. INTRODUCTION

This work is the third in an experimental series concerned with the investigation of complex oil systems. In the present work, we report the results of measurements of thermophysical properties over a wide pressure–temperature region for Komsomolsk crude oil and also for light and heavy fractions of Usinsk oil. In our discussion, the present results are compared with our previous data for Usinsk crude oil [1, 2].

In the present work, Komsomolsk crude oil is referred to as sample 1 and light and heavy fractions of Usinsk oil as samples 2 and 3, respectively. The light fraction corresponded to a boiling temperature $T_b < 523$ K and the heavy fraction to $T_b > 523$ K.

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Table I. Properties of Crude Oils

Property	Usinsk oil	Komsomolsk oil
Density ($kg \cdot m^{-3}$)	962	942
Average molecular weight	415	—
Initial boiling point (K)	404	480
Kinematic viscosity ($10^6 m^2 \cdot s^{-1}$)		
$T = 293$ K	4820	—
$T = 323$ K	513	80.9
Content (%)		
Silica-gel pitches	22	14.
Asphaltenes	11	1.3
Petroleum wax[a]	0.25	0.21

[a] Total amount of wax determined by the method of low-temperature deparaffinization (State Standard of Russia No. 11851-85).

2. PHYSICO-CHEMICAL PROPERTIES OF OILS UNDER INVESTIGATION

Properties of the oils (as determined at the Russian Institute of Oil Refining) are shown in Table I. Usinsk oil is much more viscous than Komsomolsk oil and they both contain practically no petroleum wax. The specimens were dehydrated before the investigations. Light and heavy fractions were obtained by distillation following a standard method (State Standard of Russia No. 11011-85).

3. EXPERIMENTS

We used the transient hot-wire method to measure both the thermal conductivity λ and the heat capacity per unit volume ρc_p. The method and experimental arrangement are fully described in Refs. 3 and 4. Some additional information has also been given in Ref. 1.

We also made equation-of-state measurements at room temperature in a piston-cylinder device with an internal diameter of 15 mm. The piston displacement was measured with two calibrated linear variable differential transformers. The force was measured with a load cell and pressure was calculated as force over cylinder area. All measurements were corrected for piston compression (by calibration) and the mean-area expansion was calculated from theory [5]. The specimen was enclosed in an indium capsule 30 mm high and with a wall thickness of 0.5 mm, to prevent leakage and ensure low friction. All volume data were calculated as the average of values taken under conditions of increasing and decreasing pressure, and the friction was not more than ±2.5% of the load. Testing the equipment on indium showed the inaccuracy in relative volume to be less than 0.1%. After each change in pressure we waited long enough for the volume to stabilize after any volume relaxation which might have occurred. We have also used a differential scanning calorimeter [6] to measure the specific heat capacity c_p.

We have measured λ and ρc_p of sample 1 along three isotherms (at 245, 295, and 336 K) at pressures up to 1.2 GPa and along four isobars (at 0, 0.2, 0.4, and 0.5 GPa) in the temperature range 150–360 K. Similar measurements were made for sample 3 along three isotherms (at 249, 295, and 336 K) at pressures up to 1 GPa and along two isobars (at 0.2 and 0.5 GPa) in the temperature range 250–370 K. We have also measured the relative volume $V(p)/V(0)$ of samples 2 and 3 at room temperature (295 K) at pressures up to 1 GPa. The specific heat capacity c_p of sample 1 was also measured at atmospheric pressure by DSC technique in the temperature range 150–250 K.

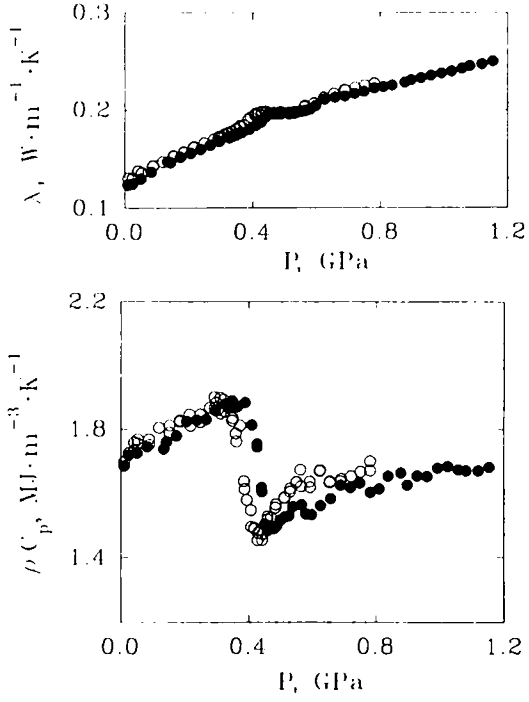

Fig. 1. Pressure dependence at 295 K of λ and ρc_p for Usinsk (open circles) [1] and Komsomolsk (filled circles) oils.

4. RESULTS

Hot-wire results for λ and ρc_p of Usinsk and Komsomolsk crude oils are presented and compared in Figs. 1 and 2, for p and T dependencies, respectively. The data at the weak local maximum of λ and the corresponding sharp minimum at the end of a step of ρc_p are reflections of structural relaxation in the material with characteristic times comparable to the heat-pulse duration [1]. These features are typical indications of a glass transition when detected by the transient hot-wire method (see, e.g., the data for glycerol [7], where the glass transition is well established [8]). As a glass transition is not a "real" phase transition but a relaxation-induced phenomenon, the definition of the glass-transition point inside the transition interval is only conventional and is strongly dependent on the experimental procedure . We define a glass transition point as detected by

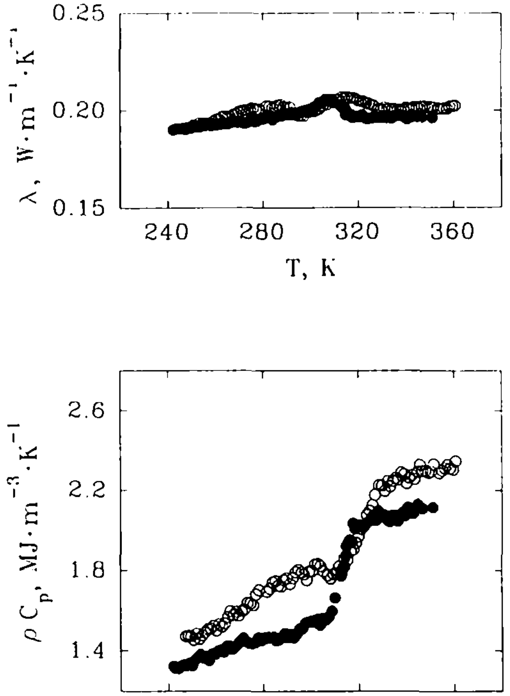

Fig. 2. Temperature dependence at 0.5 GPa of λ and ρc_p for Usinsk (open circles) [1] and Komsomolsk (filled circles) oils.

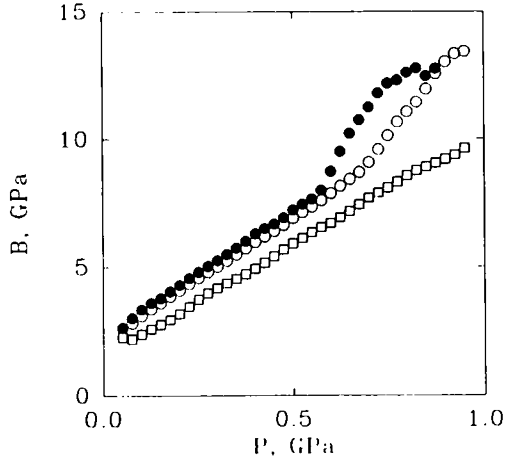

Fig. 3. Pressure dependence at 295 K of isothermal bulk modules B_T for Usinsk oil (open circles) [2] and its heavy fraction (filled circles) and light fraction (open squares).

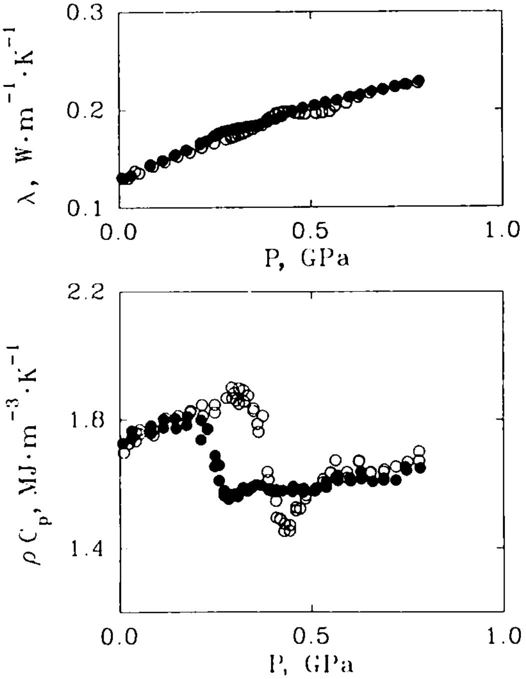

Fig. 4. Pressure dependence at 295 K of λ and ρc_p for Usinsk oil (open circles) [1] and its heavy fraction (filled circles).

the transient hot-wire technique to be a point corresponding to half of the total change in ρc_p in the transition region.

Figure 3 gives results deduced from volumetric $V(p)$ measurements. We have differentiated our data for $V(p)$ to obtain isothermal bulk modules B_T as a function of p. This plot reveals clearly pronounced changes of slope in $B_T(p)$ for Usinsk crude oil and its heavy fraction but not for the light fraction. According to Rehage and Borchard [9], the point where the change in slope of B_T versus p occurs corresponds to the beginning of a glass transition interval. The end of this interval and the onset of the glassy state itself are associated with the reverse change of slope to a value which appears to be nearly the same as that found for the liquid. We have taken the glass transition in the crude oil and the heavy fraction to correspond to the midpoint of the sloping step in $B_T(p)$. This yields glass transition pressures of about 0.80 GPa for Usinsk crude oil and about 0.65 GPa for its heavy fraction.

Hot-wire results for λ and ρc_p of Usinsk crude oil as well as its heavy fraction are presented and compared in Figs. 4 and 5, for p and T dependencies, respectively.

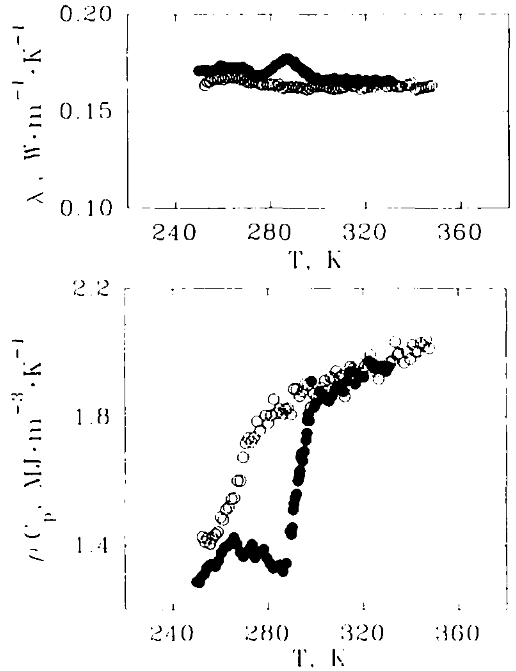

Fig. 5. Temperature dependence at 0.2 GPa of λ and ρc_p for Usinsk oil (open circles) [1] and its heavy fraction (filled circles).

5. DISCUSSION

Figures 6 and 7 show the *T–p* diagrams of Usinsk and Komsomolsk crude oils, respectively. The solid lines are polynomial fits to transition coordinates deduced with the transient hot-wire method. The transition points obtained from the DSC measurements at atmospheric pressure are presented in the same figures for comparison. The transition point obtained from the volumetric measurements at room temperature is shown in Fig. 6. The broken lines in Figs. 6 and 7, drawn through glass transition points as detected by the DSC or the volumetric method, have also been drawn parallel to the glass transition line as determined by the hot-wire method. That these lines should be parallel is, of course, an assumption on the basis of our present data. However, we contend that such an assumption is reasonable, as discussed further in the following paragraph, and we are also expecting to undertake an investigation in the future in order to establish this parallelism experimentally for the volumetric method.

Since the onset of a glass transition usually corresponds to the point where the structural relaxation time τ_s is about equal to the characteristic experimental time τ_e, one would expect the points corresponding to a

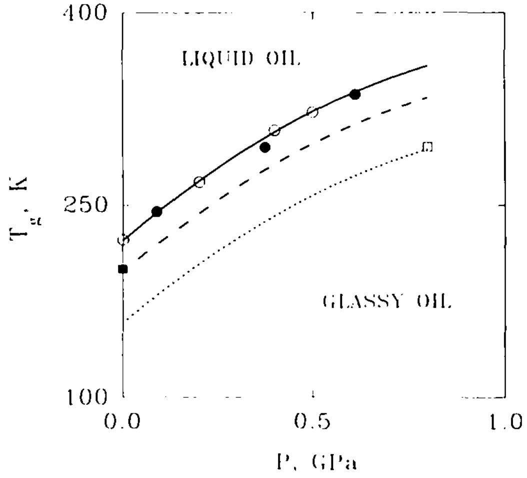

Fig. 6. *T–p* diagram of Usinsk oil. Filled circles show the glass transition points on isotherms; open circles, those on isobars. The filled square shows the result obtained with a differential scanning calorimeter. The square corresponds to the glass transition point obtained with the equation-of-state measurements. The broken lines show possible positions of glass transition lines.

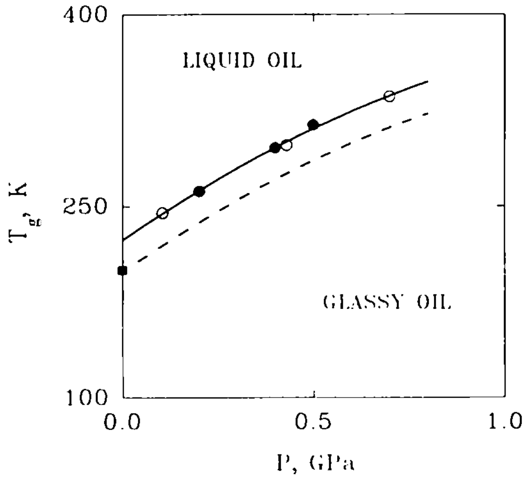

Fig. 7. *T–p* diagram of Komsomolsk oil. Filled circles show the glass transition points on isotherms; open circles, those on isobars. The filled square shows the result obtained with a differential scanning calorimeter. The dashed line shows the possible position of a glass transition line.

slower experiment to lie on a lower curve. This is consistent with the three types of results presented in Fig. 6: for the transient hot-wire technique τ_e is ~ 1 s, for the DSC technique τ_e ~ 10 s, and for $V(p)$ measurements $\tau_e > 10^3$ s in a glass transition region. The corresponding shift of transition curves is in agreement with the weak logarithmic dependence of the glass-transition temperature T_g on τ_e which is expected from theory [10].

As we can see from Fig. 3, there is no trace of any phase transformations in the light fraction of Usinsk oil in the investigated range of parameters. This may not be surprising as this substance contains, on the one hand, no petroleum wax or other crystallization-inducing components, and on the other hand, the viscosity of the light fraction is not large enough for a glass transition to occur in the temperature and pressure ranges under investigation. In fact, light gasoline is often used as a pressure transmitting liquid at high pressures due to the high value of its solidification pressure.

All data presented in Figs. 4 and 5 reveal the presence of a glass transition in the heavy fraction of Usinsk crude oil. The relative position of the glass transition point as detected by different methods falls into the same pattern as it did in the case of the crude oil itself (see the previous discussion). There is an evident shift of the glass transition in the direction of higher temperatures (lower pressures) compared with the crude oil (see Figs. 4 and 5). This means that a glass state is more easily accessible in the case of the heavy fraction than for the unfractioned crude oil. As the viscosity of heavy fractions is noticeably higher than that of the crude oil, such a tendency is quite understandable in view of the isoviscous character of the glass transition.

Both oils contain a comparatively large proportion of pitches and asphaltenes, and due to this a very high viscosity is observed even under normal conditions. On increasing the pressure or decreasing the temperature, the viscosity of a liquid increases and, if for some reason it does not crystallize on the way, the liquid solidifies to an amorphous glass. The glass transition temperature (pressure) may be obtained from measuring any property which undergoes a noticeable change in this transition. Figure 8 illustrates the definition of the glass transition point from enthalpy measurements. The glass transition point is dependent on the rate of cooling or heating, and so its definition is only conventional. A variety of data (see, e.g., the review in Ref. 10) shows that at a glass transition point, all glass-forming liquids have approximately the same value of viscosity (this justifies the often-used isoviscous definition of glass transition point). Accordingly, the more viscous liquids are expected to glassify more easily. The initially high value of viscosity is also an important factor in frustrating the onset of crystallization, as in more viscous liquids the nucleation rates are slower. To avoid crystallization it is usually necessary to maintain a sufficiently high cooling (pressure increasing) rate in the supercooled (superpressed) region. As the oils investigated do not crystallize even with a comparatively slow change of these parameters (in transient hot-wire and especially in volumetric measurements), they may be ranged amid the so-called "true" amorphous substances, which have a very low tendency to crystallize due to some intrinsic constraints against forming sufficiently large ordered regions. In this particular case the situation is favored by the nearly complete absence of petroleum wax, which can crystallize very easily due to the regular chemical structure [11].

The data obtained on oils do not permit us to decide whether they belong to the class of "strong" or "fragile" liquids—for this purpose one should analyze the temperature dependence of viscosity. However, there exists a correlation between strong and fragile viscosity behavior and the value of a specific heat capacity change Δc_p in the glass transition region (see, e.g., Ref. 12). For inorganic liquids such as SiO_2 and GeO_2, which have a strong network structure, the viscosity for many decades follows a simple Arrhenius behavior for temperatures above the glass transition, and at the glass transition point Δc_p is very small. This indicates the stability of their structure and a small contribution of structural degrees of freedom

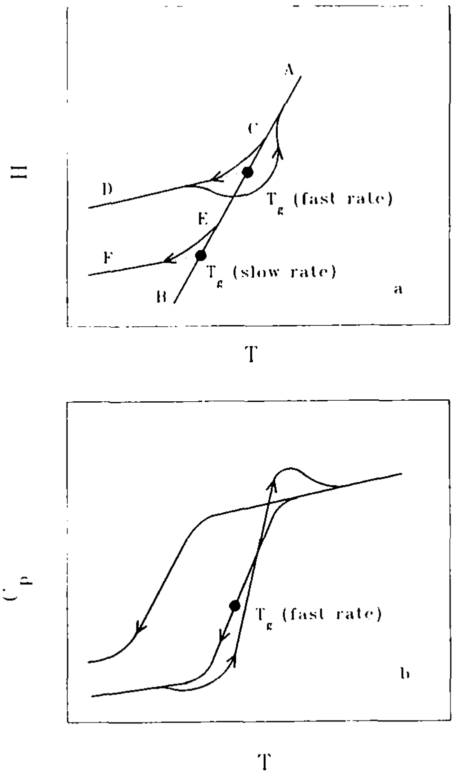

Fig. 8. Definition of a glass transition point T_g from enthalpy (or volume) measurements with a constant cooling (heating) rate (a). AB is a metastable liquid curve; CD and EF are the glassy states obtained with different cooling rates. A lower cooling rate would yield a lower value of T_g. Hysteresis during the heating reveals itself as a sharp overshot in the heating curve for c_p (b). For transient hot-wire measurements the hysteresis effects should be considerably less pronounced (see text).

(which are frozen at T_g) to the specific heat capacity. Since the specific heat capacity changes Δc_p for the oilds in the present work are of the same order of magnitude as for typical fragile organic liquids, one would expect them to belong to this class. This could mean that the structure of these multicomponent liquids undergoes considerable changes in passing through the glass transition region.

We must emphasize an important feature of the transient hot-wire method, as compared with constant-rate measurements. There are *two* characteristic time scales connected with the hot-wire method: a slow one for changing of temperature or pressure (in isobaric measurements the rate of temperature change is $0.01\ \mathrm{K \cdot s^{-1}}$) and a fast one for the temperature rise in a measurement event (rate, $\sim 1\ \mathrm{K \cdot s^{-1}}$). We detect a glass transition at the point corresponding to the fast rate, when the structure and diffusive degrees of freedom become too slow to be excited during the time of the measurement event (see, in this connection, the "two-mode" analysis in Ref. 7). However, between measurement events the rate of temperature (pressure) change is very slow and structural relaxation on this scale is rapid enough to maintain the liquid in its quasi-equilibrium state. This is illustrated in Fig. 8: if a high cooling rate were maintained all the time, the liquid would fall at point C from its "equilibrium" line AB to the glassy line CD; in hot-wire measurements the liquid remains for some time on line AB, but the values of λ and ρc_p obtained from the "quick" measurement events are nearly the same as in a glassy-state CD. This feature of the hot-wire method may have some clear experimental consequences. For example, in this situation one should not expect the appearance of an overshot peak in the upper end of a slope in ρc_p curves, often obtained during fast heating, as this peak is of a pure kinetic origin [10] (it is due to the retarded structural relaxation during heating; see Fig. 8). Thus we have to conclude that the "T–p transition lines" to the glassy state presented in Figs. 6 and 7 are undoubtedly method dependent. However, a universal diagram can probably be plotted after appropriate frequency-dependent scaling of the glass transition temperature. To be able to create such a diagram we need more experimental information about the glass transition taking place at slow changes of temperature and pressure.

6. CONCLUSION

We have investigated some phenomena in crude oils and their fractions. We observed a transition to the glassy state in the oils investigated and in the heavy fraction of Usinsk oil. This transition is a common phenomenon in oils and occurs due to the viscosity increase on decreasing the temperature or increasing the pressure. We have detected that the glass transition in crudes depends not only on the physical properties of a system but also on the characteristic experimental time.

ACKNOWLEDGMENTS

This work was supported by the Swedish Ministry of Education. We are grateful to Professor Gunnar Bäckström for his advice and interest in this work.

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