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Glass Transition in Crude Oil Under Pressure Detected by the Transient Hot-Wire Method

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The transition to the glassy state has been found in viscous crude oil with the transient hot-wire technique. The thermal conductivity and the specific heat per unit volume of the heavy Usinsk oil have been measured up to 1 GPa in the temperature range 200–400 K. The glass transition temperature was defined as the temperature of halfway change of the specific heat. It has also been found that the higher the pressure, the narrower the glass transition region, i.e., the steeper the specific-heat change in this region. The nature of glass transitions in crude oils is discussed.

KEY WORDS: crude oil; glass transition; high pressures; hot-wire method; specific heat; thermal conductivity.

1. INTRODUCTION

The behavior of crude oils under pressure is a subject of great interest in view of the problem of oil recovery from deeply located beds. Typically, heavy viscous oils are complex multicomponent liquid mixtures probably having a colloidal (microheterogeneous) structure. As the temperature decreases, the oils usually form a thixotropic gel-like structure induced by crystallization of paraffins. However, there are oils which contain practically no paraffins, and they can be cooled without crystallization down to very low temperatures. For such oils, one can expect the transition to the glassy state to be just like that for many other supercooled viscous liquids.

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2. EXPERIMENTAL DETAILS

The oil investigated was Usinsk oil (Permian Carboniferous horizon, Usinsk field, Komi region, Russia). Some characteristic properties of this oil are presented in Table I. It is characterized by an extremely low paraffin content and a high viscosity. After cooling by liquid nitrogen, the oil appears visually like a typical glass.

The oil was degassed and dried before investigation. The transient hot-wire technique used to determine the thermal conductivity and specific heat under pressure was developed in the Physics Department of Umeå University and has been described previously [1, 2].

Measurements of thermal conductivity λ and specific heat per unit volume ρc_p (ρ is density, c_p is mass specific heat) were made along three isotherms (at 245, 295, and 336 K) in the pressure range from atmospheric pressure up to 1.0 GPa and along four isobars (at 0, 0.2, 0.4, and 0.5 GPa) in the temperature range 150–360 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 $K \cdot s^{-1}$. The temperature rise of the Ni wire in each impulse was approximately 2 K. As demonstrated in Ref. 3, for viscous liquids the convection effects in this method are negligible. In addition, the specific-heat measurements have been performed at atmospheric pressure with a differential scanning calorimeter (details of the technique are given in Ref. 4). The rate of heating was 0.16 $K \cdot s^{-1}$.

3. THERMOPHYSICAL PROPERTIES OF USINSK OIL UNDER PRESSURE

Figures 1–7 show the thermal conductivity, λ, and the specific heat per unit volume, ρc_p, of Usinsk crude oil versus pressure and temperature. One

Table I. Properties of Usinsk Crude Oil

Density ($kg \cdot m^{-3}$)	962.0
Average molecular weight	415
Initial boiling point (K)	404
Kinematic viscosity ($10^{-6}\ m^2 \cdot s^{-1}$)	
$T = 293$ K	4820
$T = 323$ K	513
Content (%)	
Silica-gel pitches	22
Asphaltens	11
Paraffins	0.25

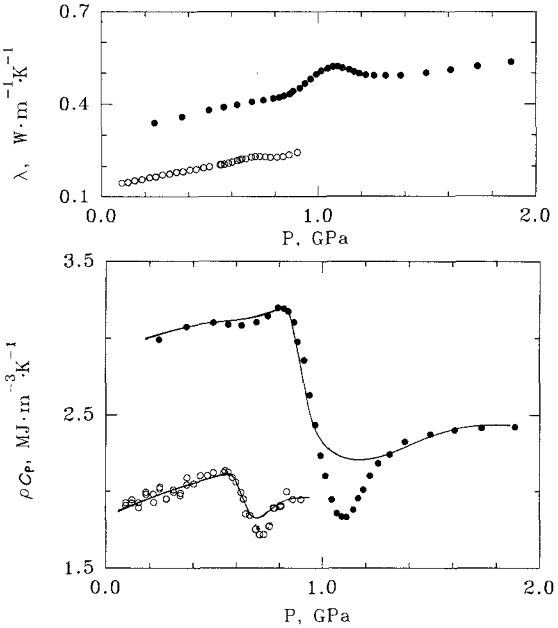

Fig. 1. Pressure dependence of λ and ρc_p for Usinsk oil at 336 K (open circles) and glycerol at 247 K (filled circles) [6].

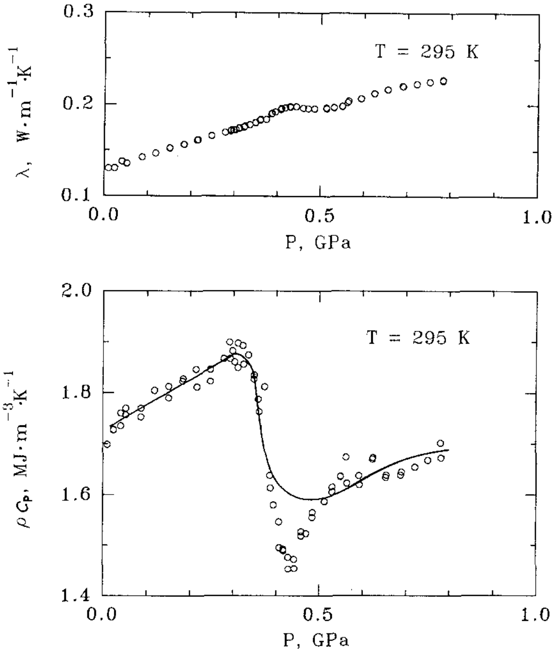

Fig. 2. Pressure dependence of λ and ρc_p for Usinsk oil at 295 K.

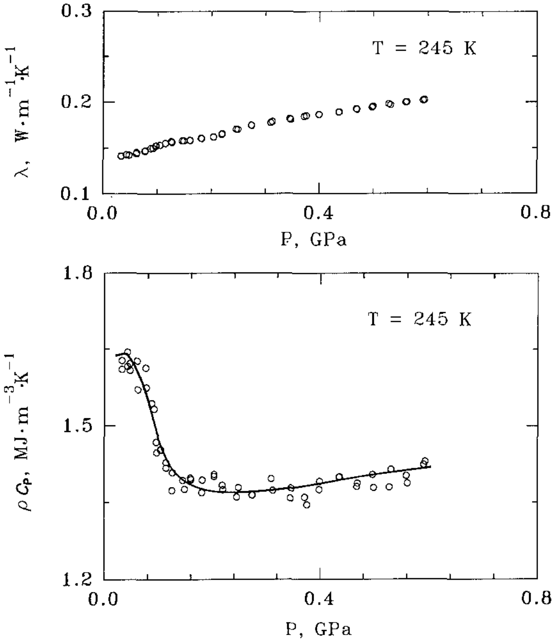

Fig. 3. Pressure dependence of λ and ρc_p for Usinsk oil at 245 K.

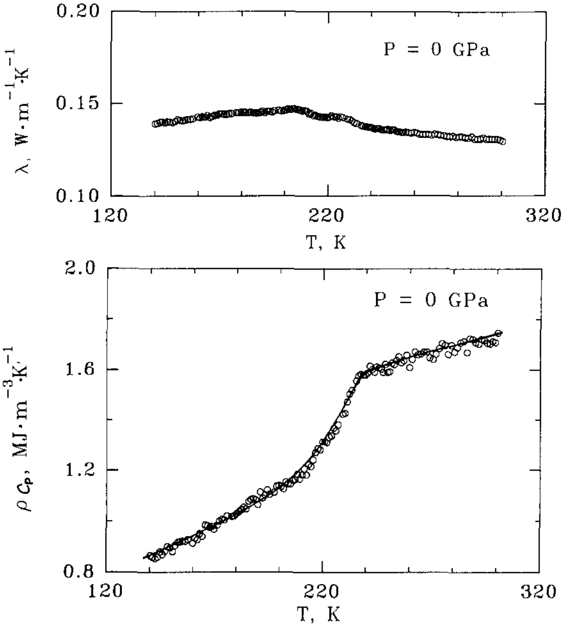

Fig. 4. Temperature dependence of λ and ρc_p for Usinsk oil at atmospheric pressure.

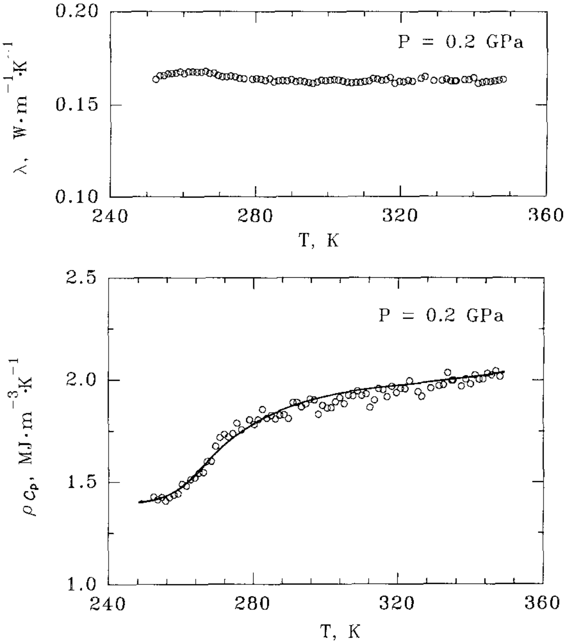

Fig. 5. Temperature dependence of λ and ρc_p for Usinsk oil at 0.2 GPa.

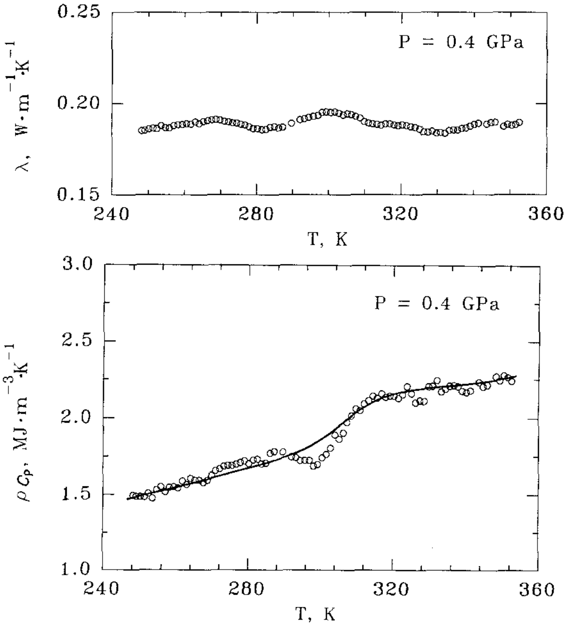

Fig. 6. Temperature dependence of λ and ρc_p for Usinsk oil at 0.4 GPa.

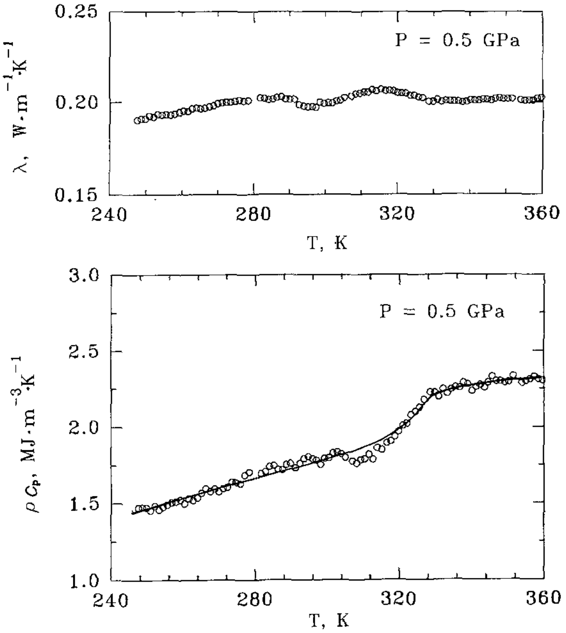

Fig. 7. Temperature dependence of λ and ρc_p for Usinsk oil at 0.5 GPa.

can compare the characteristic maximum of λ and the simultaneous step in ρc_p in the oil with those in glycerol (also presented in Fig. 1), where the glass transition is well established [5, 6]. As shown previously [1], the data at the maximum of λ and at the corresponding sharp minimum at the end of a step of ρc_p do not correspond to equilibrium but should be regarded as the consequence of structural relaxations in the material, with characteristic times comparable to the heat pulse duration. Thus although the apparent maxima on the λ curves and the near-the-step minima on ρc_p curves are typical indications of a glass transition when detected by the transient hot-wire method (see also Ref. 7), the "true" λ and ρc_p are obtained only after substracting these effects by extrapolation. The resulting curves (solid lines in Figs. 1–7) manifest the change of slope in the temperature and pressure dependence of the thermal conductivity and of the smoothed step of the specific heat.

The temperature dependence of the specific heat at atmospheric pressure as measured by a differential scanning calorimeter is shown in Fig. 8.

Since the transformation to the glass state is similar to but not a real second-order phase transition, the definition of the glass transition point is

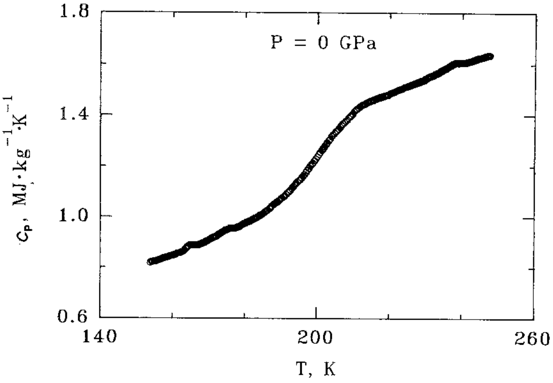

Fig. 8. Temperature dependence of a specific heat of Usinsk oil obtained by the DSC technique. Heating rate was 0.16 K·s^{-1}.

conventional. Following many authors (see, e.g., Ref. 8) we define a glass transition point as a point corresponding to half of the total change in specific heat in the transition region. Figure 9 shows the phase diagram of Usinsk oil. At atmospheric pressure, the data from both hot-wire and differential scanning calorimetry methods are presented. Figure 9 shows that the temperatures of the glass transition measured along isotherms and isobars correspond very well. The $T_g(P)$ dependence is represented as follows:

$$T_g = 223 + 251P - 102P^2 \tag{1}$$

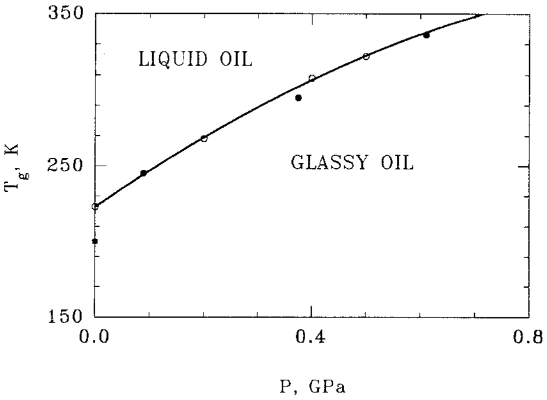

Fig. 9. Phase diagram of Usinsk oil. Filled circles show the glass transition points on isotherms; open circles, those on isobars. The filled square shows the result obtained with a differential scanning calorimeter.

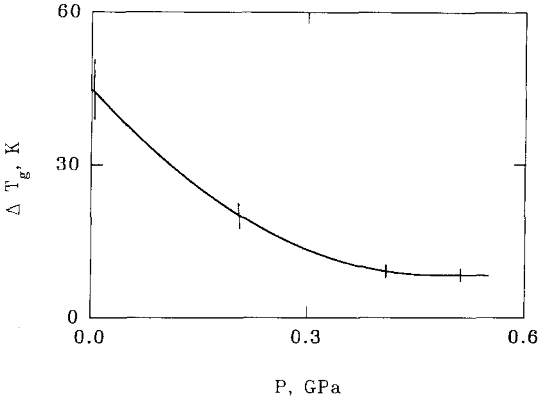

Fig. 10. Temperature width of the glass transition, ΔT_g, in Usinsk oil as a function of pressure.

where T is in K and P is in GPa. This equation is based on hot-wire data only.

4. DISCUSSION

It is well-known that the transition to the glassy state is a nonequilibrium process depending on the rate of cooling and heating, on the thermal prehistory of the sample, and on the degree of microscopic inhomogeneity [9, 10]. The latter factor often plays a dominant role; usually the more homogeneous the system, the narrower and steeper the glass transition [11].

According to Yonezawa [12], all glass-forming materials may be roughly divided into two categories: those showing a rapid but monotonic change in specific heat with temperature and those manifesting a sharp maximum of c_p at the glass transition. The representatives of the former category are liquids with a "strong" network structure such as SiO_2, while some nonnetwork and ostensibly ionic substances belong to the latter category. This difference in the c_p behavior reflects the difference in the degree of freedom of the molecular configuration, which can be largely restricted by the network structure.

As shown in Figs. 1–6, the glass transition in oils is rather smooth. The interpretation of the transition region is made difficult by the presence of many effects, physically very different, which distort the glass transition in the oil. On the one hand, it seems that viscous oils are closer to the category of the network-structure materials. On the other hand, the smoothness of the transition is not surprising, as the oil is a colloid-like microinhomogeneous mixture of hydrocarbons, asphaltens, and pitches. Such a system may possess several characteristic relaxation times. It is more interesting that the rise in pressure makes the glass transition in the oil much steeper (Fig. 10). Possibly, high pressure makes the structure of the oil more homogeneous by increasing, for example, the solubility of asphaltens. Another factor which should be taken into account is the temperature and pressure dependence of the oil viscosity. In this context, the independent study of oil structure and viscosity under pressure would elucidate the picture.

Using the Ehrenfest relation between steps of the specific heat and those of the thermal expansion coefficient $\alpha = (1/V)(\partial V/\partial T)_p$ yields

$$\frac{dT}{dP} = \frac{T\,\Delta\alpha}{\rho\,\Delta c_{\mathrm{p}}} \tag{2}$$

which holds for glass transitions only approximately [8]. From Eq. (2), one can evaluate the order of the change of α. As the ρc_{p} step does not depend on pressure, being $(0.3 \pm 0.05) \times 10^6\ \mathrm{J \cdot m^{-3} \cdot K^{-1}}$, the thermal expansion coefficient varies between $5 \times 10^{-4}\ \mathrm{K^{-1}}$ at room pressure and $1.2 \times 10^{-4}\ \mathrm{K^{-1}}$ at $P = 0.5$ GPa, the values typical for glass transitions.

5. CONCLUSION

In this work, we have reported the existence of a glass transition in a heavy viscous oil. Although the transition is rather smooth, the transition region becomes narrower with increasing pressure. Crude oils are complex multicomponent systems and cannot be described by a simple model. Therefore for a better understanding of the physical nature of phase transitions in oils, a systematic study of the separate fractions such as low molecular weight hydrocarbons, paraffins, asphaltens, and pitches should be carried out. The gel transition induced by paraffin crystallization is of a special interest. We intend to study this set of problems in the near-future.

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