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Crystallization and Glass Transition in Crude Oils and Their Fractions at High Pressure

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Two sequential phase transitions, a wide-range crystallization and glass transition, were detected for crude oils and their fractions at high pressures by the transient hot-wire method and at atmospheric pressure by differential scanning calorimetry. The range of pressures investigated was up to 1.2 GPa in the temperature interval of 150–370 K. The presence of the glass transition in the oil and heavy fractions after the crystallization leads to a conclusion that crystallization does not lead to the formation of a continuous crystalline network, but rather to many separate crystalline regions. These regions are present in a liquid matrix, which after the sequential change of pressure/temperature undergoes the glass transition.

KEY WORDS: crude oil; crystallization; glass transition; heat capacity; high pressure; oil fractions; thermal conductivity.

1. INTRODUCTION

Information on the phase and glass transitions in complex oil systems at different pressures and temperatures is of great value to the oil industry. At the same time, these results are interesting from the point of view of the physics of disordered multicomponent matter, oils being complex liquid mixtures with a colloidal structure.

The characteristics of phase and glass transitions strongly depend on the chemical content of the oil system. One can expect the specific role of different components in the formation of these transitions. For example, *petroleum wax* can easily form crystalline clusters and precipitate

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from solution. On the other hand, low concentrations of light components should lead to an increase in viscosity, which is of great importance for the onset of the glass transition. In order to understand more clearly the influence of chemical composition on transitions in oil systems, one should investigate not only crude oils, but also their different fractions.

In previous experiments, we have investigated viscous oils with a very low concentration of petroleum wax [1, 2]. The main reason for this choice of samples was to exclude the influence of wax crystallization, and to investigate the pure glass transition in crude oils and their fractions. Our investigations covered two representatives of crude oils with very low wax content: Usinsk oil and Komsomolsk oil. The glass transition in these oils was detected and investigated by the transient hot-wire method. This method enables measurement of the thermal conductivity and heat capacity per unit volume at high pressures and different temperatures [3, 4]. We have also carried out equation-of-state $V(p)$ measurements at room temperature and detected the glass transition at high pressure [5]. In addition, the glass transition at atmospheric pressure was investigated by heat-capacity measurements using a differential scanning calorimeter (DSC) [6].

A similar investigation of the *heavy fraction* of Usinsk oil [1] has demonstrated the presence of the glass transition in this fraction as well, but shifted towards higher temperatures (lower pressures) as compared with the crude oil itself. This shift was explained by the higher value of viscosity in the case of this heavy fraction.

The phase diagrams for the glass transition in Usinsk and Komsomolsk oils and a heavy fraction of the Usinsk oil, have been developed in Ref. 2. It has been demonstrated that the position of the glass transition line was not universal, but depended strongly on the type of experiment used to determine it. More precisely, the phase diagram depends on the characteristic experimental time as a consequence of the dynamic nonequilibrium character of a glass transition.

In this paper we present the results of our investigation of transitions in crude oil with quite different properties as compared with the previously investigated samples. First of all, this oil has a considerably lower value of viscosity, which is due to the higher content of light components. This should result in more difficult access to the glass transition, i.e., this transition should take place at higher pressures and lower temperatures. But the most important difference consists of considerably higher content of easily crystallizable components—petroleum wax. As a result, these oil systems undergo a many-step first-order phase transition, which includes the crystallization of hydrocarbons with different molar masses and occurs over a wide temperature/pressure interval. As this crystallization process takes place, before the onset of the glass transition (at decreasing temperature or increasing pressure), one should investigate the influence of the presence of the crystalline phase on the glassification process. There are several possibilities for consideration. If the crystalline network occupied the whole volume of a forming sample, for example, as some sort of molecular crystal [7], this would drastically diminish the degree of configurational mobility of molecules in the noncrystallized part of the oil matrix. In this case, one should expect the strong influence of crystallization on the position and properties of the glass transition (including the possibility of its total suppression). However, this overall crystallization occurs usually only at high concentrations of crystallizing components. The fact that in low-viscosity crude oils at atmospheric pressure the crystallization of petroleum wax is accompanied by the precipitation process indicates that molecules of petroleum wax form many separate crystalline clusters rather than one overall network [8]. The last assumption is in agreement with earlier experimental evidence that the glass transition in oil systems at atmospheric pressure is nearly independent of wax content [9–11]. If this is also true at high pressures, then the crystallization would not have a great influence on the glass transition.

As representatives of crude oils with high content of petroleum wax, we have chosen Kumkolsk oil (Kazakhstan), which will be referred to as sample 1. Physico-chemical properties of this oil are given in Table I. We

Table I. Properties of Kumkolsk Crude Oil

Properties	Value
Density ($kg \cdot m^{-3}$)	813
Average molar mass	225
Initial boiling point (K)	298
Viscosity ($mm^2 \cdot s^{-1}$)	
$T = 303\,K$	7.1
$T = 323\,K$	3.7
Content (mass%)	
Silica-gel pitches	10
Asphaltenes	< 0.1
Petroleum wax[a]	15
Content (vol%) of fractions with boiling temperature	
below 100°C	8
below 200°C	28
below 300°C	50

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

have also made measurements for two heavy fractions of Kumkolsk oil. The first heavy fraction is a mixture of the fractions of Kumkolsk oil that have boiling temperatures higher than 523 K—sample 2. By removing asphaltenes and pitches from sample 2 (method of deasphaltization, State Standard of Russia No. 11865-66) and then removal of petroleum wax (method of low-temperature deparaffinization, State Standard of Russia No. 11851-85), we obtained sample 3—heavy fraction without asphaltenes, pitches, and petroleum wax. In addition to the above-mentioned samples, we have investigated petroleum wax extracted from Kumkolsk oil (sample 4) and one model oil (sample 5). To prepare the model oil, we have taken Komsomolsk oil that was investigated in our previous work [2] and added 10 mass% of petroleum wax extracted from Kumkolsk oil. All samples were degassed and dried before the investigations.

2. EXPERIMENTAL DETAILS

We measured the thermal conductivity λ and heat capacity per unit volume ρc_p using the transient hot-wire method. The experimental arrangements of this method have been described in Refs. 3 and 4. The uncertainties of determinations of λ and ρc_p were estimated to be 2.5% and 4%, respectively.

Measurements of λ and ρc_p were made along four isobars (0, 0.1, 0.3, and 0.5 GPa) for all samples in the temperature range of 245–373 K. We have also measured λ and ρc_p along five isotherms (249, 295, 320, 353, and 373 K) for the crude oil and along three isotherms (275, 295, and 320 K) for the heavy fractions.

A Perkin-Elmer DSC-2 calorimeter was used for the measurements of the specific heat capacity c_p. Since the DSC data will be very important for subsequent discussion, we give a description of some experimental details here. To ensure complete dissolution of precipitated hydrocarbons, we have heated all samples to 340 K in closed containers for 15 min with agitation. Then samples were left to cool to room temperature and put into standard aluminum capsules. Starting from room temperature, we have heated the filled capsules in the calorimeter up to 340 K at a rate of $10\,\mathrm{K \cdot min^{-1}}$ and then started the cooling experiment. The measurements were made in the temperature range of 130–340 K at a rate of $10\,\mathrm{K{\cdot}min^{-1}}$ both for cooling and heating experiments. All experiments were repeated three times. We used liquid N_2 cooling. The sample compartment was purged with He. Cyclohexane, *n*-octane, and indium were used for calibration. The uncertainty of the determination of the specific heat capacity c_p was not more than 2%. Full details are described in Ref. 6.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Typical experimental curves for hot-wire measurements of λ and ρc_p for Kumkolsk crude oil (sample 1) and its heavy fraction (sample 2) are presented in Figs. 1–3. We have detected the presence of two subsequent phase transitions for Kumkolsk oil and for both heavy fractions investigated. These transitions were detected both for isobaric and for isothermal measurements. We have interpreted the first transition as a wide-range crystallization and the second one as a glass transition. This identification was made on the basis of comparison of our results with characteristic examples for the hot-wire method [7]. We define a point of the beginning of crystallization as detected by the hot-wire method to be a

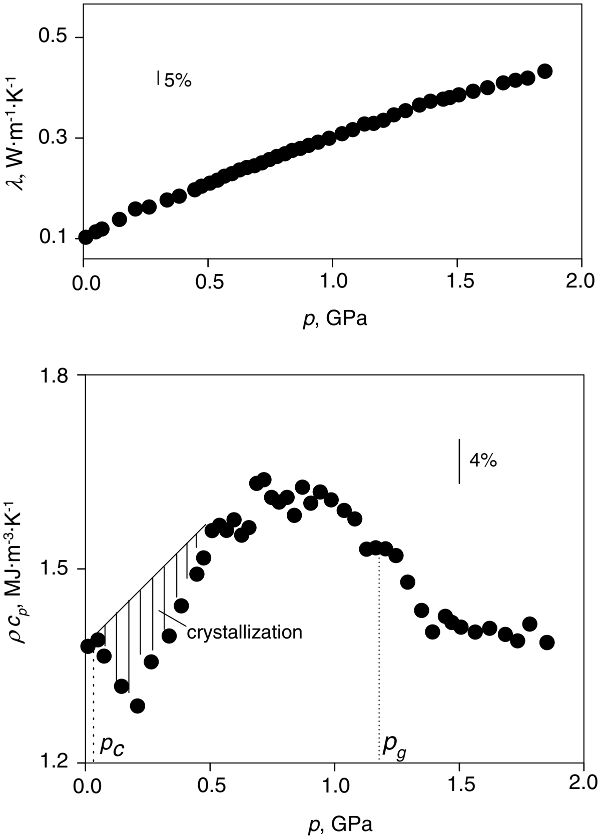

Fig. 1. Pressure dependence (at increasing pressure) of λ and ρc_p at 250 K for Kumkolsk oil.

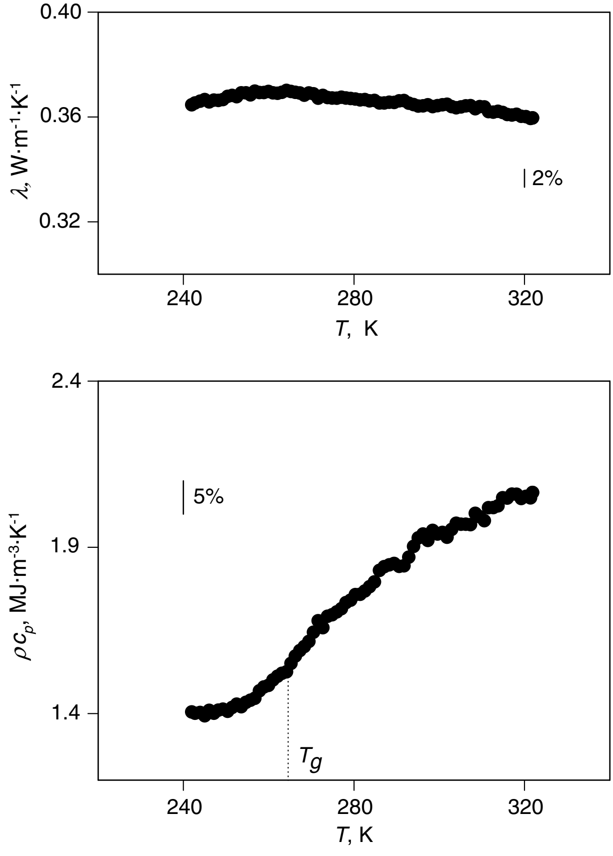

Fig. 2. Temperature dependence (at increasing temperature) of λ and ρc_p at 1.5 GPa for Kumkolsk oil.

point corresponding to the beginning of the rapid change in ρc_p in the phase transition region. As a glass transition point we take the value of pressure (temperature) corresponding to the middle point of the ρc_p step. DSC data, presented in Fig. 4, confirm the results of the hot-wire experiments: wide-range crystallization was observed as well as the glass transition in Kumkolsk oil.

The phase diagram for Kumkolsk oil is presented in Fig. 5. The hot-wire measurements were used for this diagram. In contrast to the phase diagrams of Usinsk and Komsomolsk oils discussed in Refs. 1, 2, and 5, there are two transition lines, corresponding to the glass transition and the beginning of crystallization.

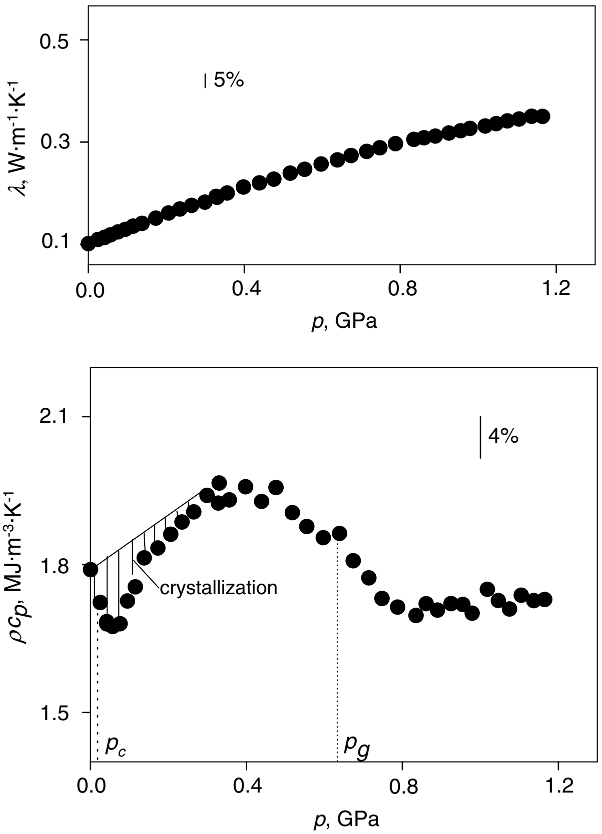

Fig. 3. Pressure dependence (at increasing pressure) of λ and ρc_p at 275 K for sample 2.

The phase diagrams for the two heavy fractions (samples 2 and 3) based on the hot-wire measurements are shown in Fig. 6. We would like to emphasize the important feature of these plots; each transition line is determined by both isobaric and isothermal data.

The presence of the glass transition in the oil and heavy fractions after crystallization leads to a conclusion that crystallization does not lead to the formation of a continuous crystalline network but rather to many separate crystalline regions. These regions are inserted in the liquid matrix, which after the subsequent change of pressure/temperature, undergoes the glass transition. The similar sequence of phase transitions has been observed before for different systems [8]. This conclusion is supported by the fact that the glass transition line is identical for both of the

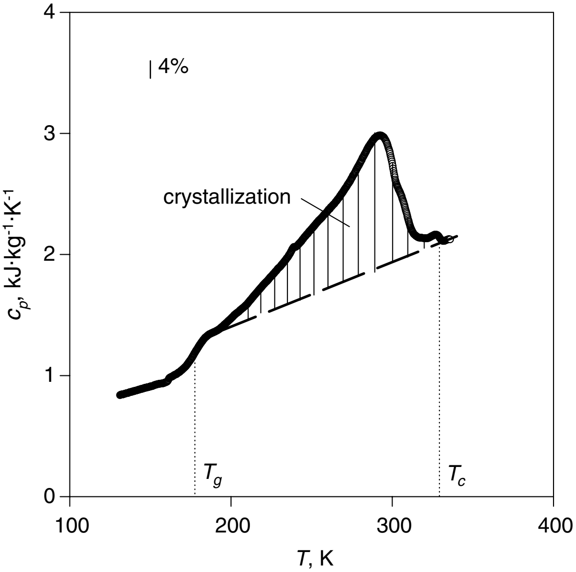

Fig. 4. DSC data for Kumkolsk oil (cooling measurements).

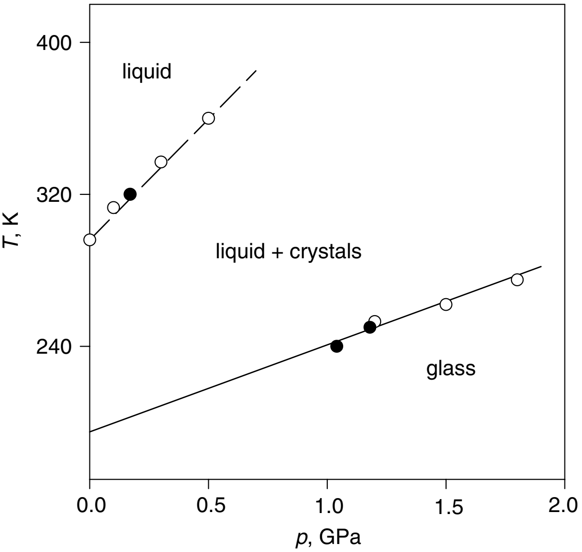

Fig. 5. Phase diagram for Kumkolsk oil. Filled circles show points on isotherms; open circles, those on isobars. Solid line corresponds to the position of glass transition line; dashed line corresponds to the position of the beginning of crystallization line.

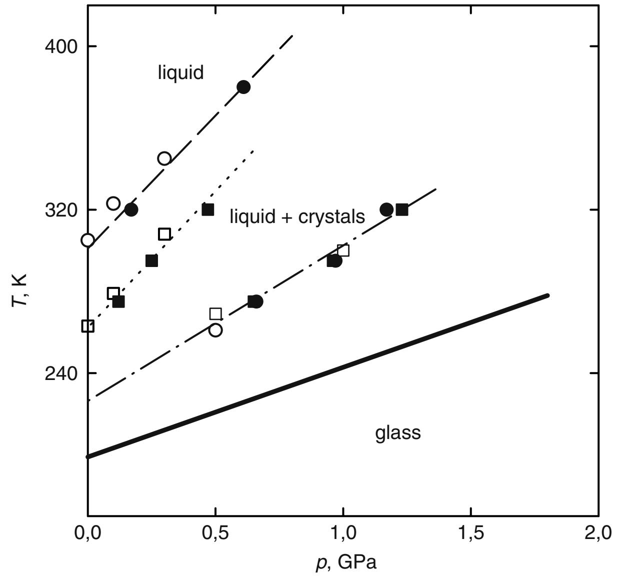

Fig. 6. Phase diagram for samples 2 (circles) and 3 (squares). Filled symbols show points on isotherms; open symbols, those on isobars. Solid line corresponds to the position of glass transition line for Kumkolsk oil. Dashed line corresponds to the position of the beginning of crystallization line for sample 2, dotted line, that for sample 3.

heavy fractions of Kumkolsk oil and, at the same time, the crystallization lines have quite different positions. To understand this, note that the difference between these fractions is the presence of petroleum wax in one of them and its absence in the other. During the crystallization, the waxes are crystallized together with other crystallizing components and, in this way, are removed from the remaining liquid matrix. Hence, the crystallization in these cases is different (it involves the crystallization of wax in one case) but the glass transition should be practically the same. More than this, one can conclude that the presence of crystallized wax should not change noticeably the viscosity, because the value of the viscosity is the decisive factor for the position of the glass transition. These conclusions are supported by the DSC data (Fig. 7). The DSC curves show that two heavy fractions (samples 2 and 3) have different temperatures of the beginning of crystallization (T_{c2} and T_{c3}) yet they have the same glass transition temperature T_g.

We would like to emphasize that both hot-wire and DSC measurements were performed with both increasing and decreasing temperature

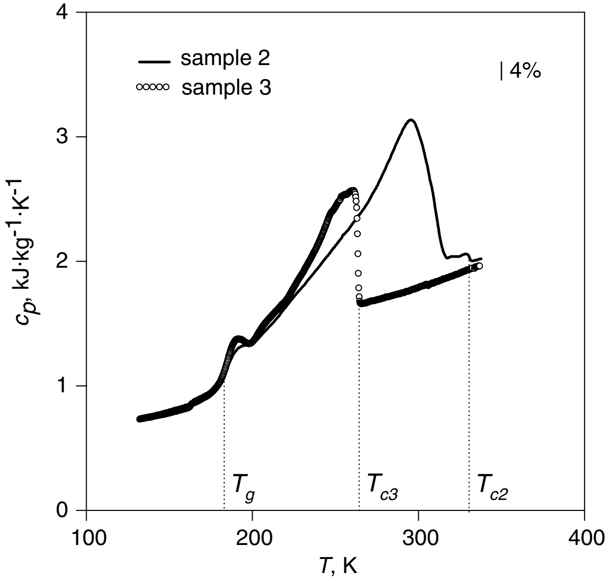

Fig. 7. Temperature dependence of the specific heat of samples 2 (solid line) and 3 (circles) obtained by the DSC technique (cooling measurements).

(pressure), and there was no hysteresis observed. A detailed discussion of the dependence of the glass transition point on the experimental rate was presented in Ref. 2.

As one can see from Fig. 6, the positions of glass transition lines of Kumkolsk oil and its heavy fractions are quite different. The main reason for this difference is due to the increase in system viscosity after removal of low viscosity light fractions from Kumkolsk oil. A detailed investigation of the influence of the light fraction composition on the phase behavior of oil systems will be presented elsewhere.

We measured the specific heat capacity of a sample of petroleum wax extracted from Kumkolsk oil and a sample of the model oil by DSC at atmospheric pressure in a temperature range of 130–370 K. The wide-range crystallization was detected in the petroleum wax, and we did not observe a glass transition (Fig. 8). The investigation of the model oil system serves to verify that the glass transition temperature of the oil system is changed by dilution with wax. The DSC curve for the model oil (Fig. 9) shows the apparent crystallization process which, however, does not influence the glass transition temperature. The DSC experiments with

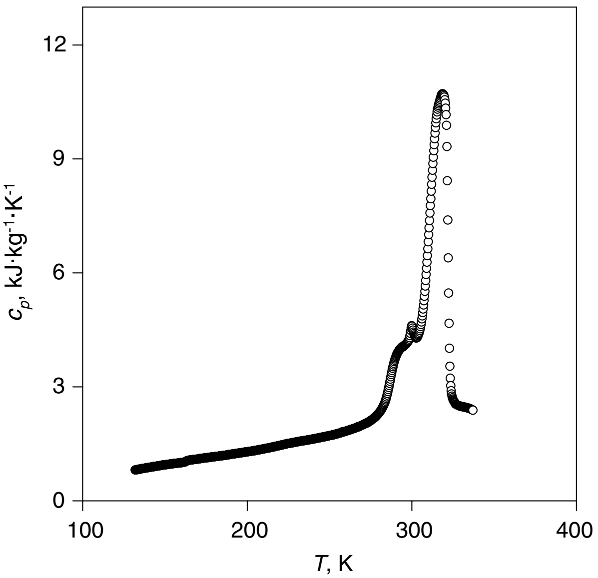

Fig. 8. DSC data for petroleum wax extracted from Kumkolsk oil—sample 4 (cooling measurements).

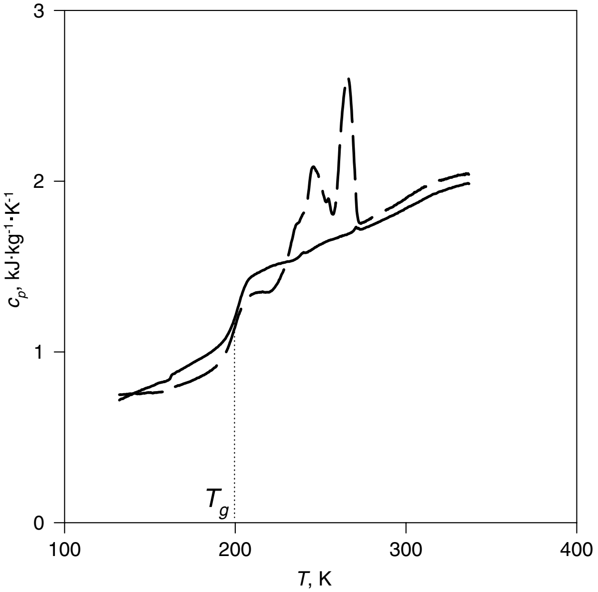

Fig. 9. DSC data for Komsomolsk oil (solid line) and the model oil—sample 5 (dashed line).

the model oil system confirm observations of different authors [9, 10] that the glass transition should not depend on the change of wax content.

4. CONCLUSION

Crystallization and the glass transition processes in different complex oil systems over a wide temperature–pressure range have been investigated by two different thermophysical methods. We have constructed the "phase" diagram for the oil systems investigated, and observed that the crystallization process does not influence the glass transition temperature. Our experiments confirm observations of different investigators that the glass transition does not depend on the change of wax content.

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