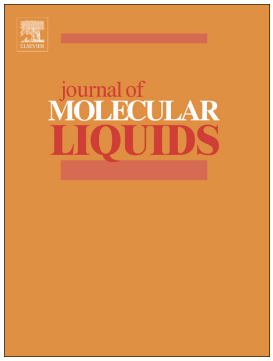

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Crystallization and Glass Transition in Crude Oils and their Fractions at Atmospheric and High Pressures

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A short review of up-to-date experimental data and theoretical notions concerning crystallization and the glass transition in complex hydrocarbon systems – crude oils and their fractions – is presented. Special attention is given to the behavior of crude oils and their fractions at high pressure. It is demonstrated that all oils may be approximately divided into two classes. For the first class of oils and fractions (with high initial viscosity), one can observe the onset of the non-equilibrium glassification process at decreasing temperature or increasing pressure. For those in the second class (with low viscosity), cooling or increased pressure leads to a multi-step crystallization process (mainly of n-alkanes) continuing up to the onset of main matrix glassification. For all oils and fractions investigated, crystallization does not influence the position of the glass transition line of the main matrix.

1. Introduction

Investigation of complex hydrocarbon systems permits a deeper insight into various physical phenomena. Being unique natural systems, crude oils and their fractions are multicomponent systems of hydrocarbon macromolecules that are heterogeneous on the nano- and meso-levels, and their response to changing external parameters (e.g., temperature and pressure) corresponds to that of a complex multiphase system. Thus, investigation of crude oils and their fractions at high thermobaric conditions is interesting in terms of the physics of disordered multicomponent matter. Moreover, this type of investigation could also be interesting from the point of view of application. During the production, transportation and refining of crude oils, their phase-change behavior and properties can change dramatically. Crystallization and glass transition processes can degrade flow properties and cause severe problems by plugging valves and flow lines, among other problems. Information on the high-pressure properties of crude oils can provide new insight into processes taking place deep in the Earth that have accompanied the formation of crude oil deposits.

In this paper, we present a short review of the current state of the investigations of crystallization and glass transition processes in crude oils and their fractions at atmospheric and high pressures.

2. Crystallization and glass formation during cooling and compression

For the continuous cooling of a liquid, there are two possible scenarios for solidification. The first one is crystallization, i.e., the formation of a regular crystal lattice with long-range order. In the second scenario, cooling to a certain temperature causes the liquid to vitrify, during which some of its physical characteristics, such as specific heat, compressibility, and heat expansion coefficient, change dramatically. The solid state achieved in this process is not the ordered one; similar to a liquid, there is only short-range and no long-range order. The crystallization is the equilibrium process; the glassification corresponds to the non-equilibrium state.

In the case of a one-component liquid, if crystallization has taken place, all molecules are present in the crystal lattice, and there will be no glassification upon further cooling. However, if the crystallization of the liquid is somehow impeded (as is often the case for polymer liquids) or/and the rate of cooling is sufficiently high, then the viscosity of the super-cooled liquid increases sharply, and it transforms to an amorphous solid state. The further transition of the glass to an equilibrium crystal is spontaneous but kinetically limited and is usually non-observable. Whereas the *glass state* is externally solid, it is essentially different from the crystal state. *First*, in the glass state, there is no long-range order of atomic position. Similar to the liquid state, *short-range order* exists; i.e., some atoms are grouped into small clusters. In the liquid state, the clusters are continuously changing their composition – some are destroyed, others are formed, and the mean cluster dimension is a function of temperature. In the glass state, the clusters behave as if frozen. The glass state structure may be described as a frozen copy of the liquid structure as it was at the onset of glassification. *Second*, the glass state is not the equilibrium one. If the glass temperature is not far below the glass

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