

Observation of liquid crystals in heavy petroleum fractions

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In this work we report for the first time the observation of liquid crystalline domains of circa 100 μm diameter in heavy fractions of petroleum. Precipitated solids from several bitumen and heavy oil samples exhibited the characteristic optical patterns of liquid crystals when observed under cross-polarized light.

Liquid crystals are a state of matter with molecular order between that of a solid and an isotropic liquid. In normal liquids, the molecules are completely disordered, or isotropic, while in crystalline solids the molecules are ordered in three dimensions. In liquid crystals the molecules have partial positional and orientational order. Liquid crystals are usually divided into two categories, thermotropic and lyotropic. Thermotropic liquid crystals are formed by a change of temperature, while lyotropic liquid crystals are observed by addition of a suitable solvent. Some liquid crystals can show both lyotropic and thermotropic phases which are called amphotropic or amphitropic [1].

Samples examined in this study included asphaltenes precipitated from Athabasca, Cold Lake bitumen (Canada), Maya heavy crude oil (Mexico), and Safaniya crude oil (Saudi Arabia), and a maltene fraction of Athabasca bitumen extracted with supercritical n-pentane. Powdered samples were placed on a yttrium-aluminium-garnet (YAG) window and inserted at the bottom of a temperature and atmosphere controlled cell. An inverted reflective microscope was used to observe the samples.

The liquid crystal domains in asphaltenes appeared at ~ 330 K in a nitrogen atmosphere, and disappeared at ~ 430 K. For asphaltenes at approximately 330 K a phase transition occurred and the first liquid-crystal domains appeared as droplets with Maltese crosses (Figure 1). The Maltese crosses (or disclinations with four dark brushes) rotate in the direction of the polarizer and analyzer rotation, as observed in concentric lamellar liquid crystals [2]. Once the liquid crystal phase appeared upon heating 330 K, it remained stable upon cooling, at least for a period of days. When samples are heated beyond 430 K for asphaltenes and then cooled, however, liquid crystal domains did not reappear over a period of days.

The domains also appeared in the presence of toluene vapour. Exposure of asphaltene powder to toluene vapour at room temperature for circa 10 min gave transient appearance of liquid-crystal domains, which then disappeared after 30 min of exposure. This combination of thermal and solvent interactions

with the liquid crystalline domains was consistent with amphotropic liquid crystals. Petroleum solids are the first naturally occurring example of this type.

The microscopy results are consistent with the previous studies of asphaltene phase transitions using differential scanning calorimetry and phase angle measurements. Heavy oil and bitumen undergo complex transitions from solid like behaviour to liquid behaviour over the temperature interval 150 K to 520 K and have been shown to exhibit a minimum of three phases over much of this interval. The asphaltene fraction gives a broad reversible endothermic transition spanning the 330 K to 500 K temperature interval and centred at about 430 K, which is the temperature for disappearance of these liquid crystals. Another endothermic transition occurs at about 330 K which is roughly the temperature for the formation of these liquid crystals [3].

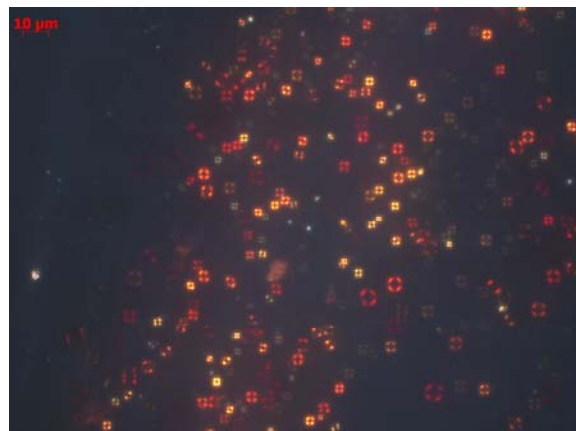


Fig. 1. Liquid crystal spheres with Maltese crosses in Athabasca asphaltenes (C5) at 358 K.

Asphaltenes appear to comprise a minimum of three phases in the temperature interval 330 K to 430 K; a liquid phase, a solid phase, and a liquid crystal phase. This observation of liquid crystal domains in precipitated samples from bitumen and heavy oils suggests that molecular self assembly may enable new separation methods for components of petroleum.

References

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