Thermophysical properties and phase-behaviour of asphaltene-containing petroleum fluids

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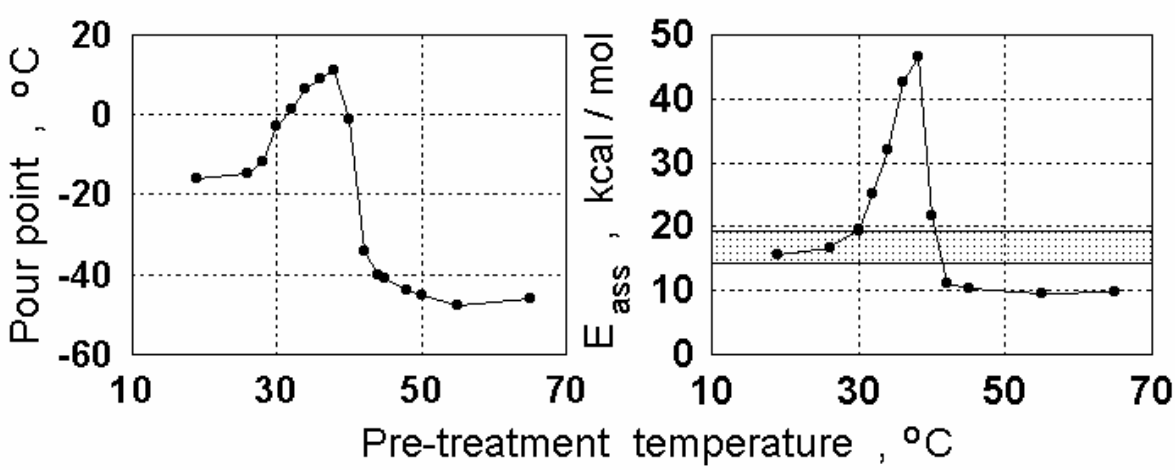
It is well known that in petroleum fluids transition of the asphaltene sub-system from a molecular-solution phase to that of a suspended-solid one may trigger the processes of percolation, flocculation and precipitation which cause troubles in the petroleum production, transportation and processing [1]. In turn, the system of suspended-solid asphaltenes may exhibit various structural transformations [2], so that it may have a complex (*P,C,T*) phase diagram, related to that of discotic liquid crystals.

In our recent studies [3-5] we have investigated the thermophysical properties of model petroleum fluids (toluene + vacuum residue) and observed thermal anomalies which were attributed to a previously unreported structural phase transition in the asphaltene subsystem. It was concluded that this transition is defined by specific molecular interactions of asphaltenes, viewed as true chemical species, but not as just as a solubility class. Hence, the characteristics of the transition point should be almost insensitive both to the geographical/geological origin of asphaltene species and to the nature of the bulk petroleum fluid.

In the present study, we have measured thermal effects on the flow properties of an unprocessed virgin crude oil, collected directly from a wellhead at Romashkinskoye reservoir (Tatarstan). After water-separation, the crude contained 3.5 wt.% asphaltenes. Prior to the flow measurements, oil samples were subjected to thermal pre-treatment for 1 hour at a constant temperature from 15^0C (room temperature) to 65^0C, followed by cooling to 8^0C at the rate of $1{,}5^0$C per minute. The rheological parameters have been investigated at 8-30^0C, for shear rates up to 150 s^{-1} , in a Brookfield Programmable DV-II+ Viscometer (Brookfield Eng. Labs., Inc.) equipped with a temperature control. From the temperature dependencies of Bingham's plastic viscosity and apparent yield stress, we calculated the Arrhenius activation energies which, according to [2] were interpreted as asphaltene association/interaction energies Eass. The pour points of oil samples were determined as temperatures at which the measured or extrapolated plastic viscosities reached the value of 10 Pa·s (as recommended by the XI's World Petroleum Congress, London 1983).

One of the main results of the present studies is that the above discussed structural transition (at temperatures close to 37^0C) in the microscopic asphaltene sub-phase may lead to a macroscopically observed transformation of the bulk of a crude oil to a new metastable (but long-lived) state. This transformation may be registered by monitoring various thermophysical parameters of the oil samples. For example, such technologically important parameter as the pour point, dramatically increases from –16.2 ^{0}C to +11.2 ^{0}C after thermal pre-treatment of oil at temperature of 37^0C, as shown at the left-side figure. Such *increase* of the pour point is quite unexpected from the point of view of conventional technological recommendations, where heating of crude oils is expected, in all cases, to *decrease* the pour

points. Our data, presented in the figure, show that such decrease is observed only after thermal pre-treatment at temperatures exceeding 40-45^{0}C.



The precise nature of the observed pour point variations is still being investigated. A working model is the formation (at temperatures ≤37 ^{0}C) of gel-like oil "islands" reinforced by extended networks of asphaltene nanoparticles. At lower temperatures these "islands" interconnect, leading to gelation of the entire oil volume.

The transition to extended asphaltene networks is facilitated by a noticeable increase of the asphaltene association (interaction) energy Eass from 16-17 kcal/mol to 46 kcal/mol, as shown in the right-side figure. The shaded strip denotes the range of Eass reported in other (low-resolution) asphaltene studies with temperature increments not less than 10-15 ^{0}C (cf.[2]). In turn, the lambda-shaped Eass(T) dependence we regard (cf.[5]) as indicative of a specific structural phase transition involving Yen's [2] quasispherical "nanocrystallites", which have effective diameters of 1.5-2 nm, are composed of four flat asphaltene molecules (with MW=750-1000) and are held together primarily by the π-π and the dipole-dipole interactions.

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