

# “FINE PHASE TRANSFORMATIONS” IN PETROLEUM - THE BASIS FOR EMERGING NANOTECHNOLOGIES

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Published as

**Chapter 11** in: *Petroleum Science Research Progress*, Editor, K. L. Montclair, Nova Science Publishers, Inc., New York, 2008. p.235-259

The book may be obtained from the publisher at:

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**ABSTRACT.** Understanding petroleum phase composition at every stage of the production processes helps optimize resource exploitation. Initially, thermodynamical descriptions of petroleum “phase composition” have been limited to simplest two-phase models of vapor-liquid equilibria. Practical industry requirements are more complex in having possible solid phases. While there has been a considerable progress in modeling liquid-solid phase boundaries for hydrates and waxes, phase behavior of asphaltenes is still poorly understood. For example, thermodynamic theories presume that asphaltenes dissolve in solution; hence solid asphaltene precipitation is fully reversible; colloidal theory holds that asphaltenes disperse in solution and predicts irreversible precipitation. A common feature of both theories is an implication of two phase behavior of asphaltenes with a single phase boundary.

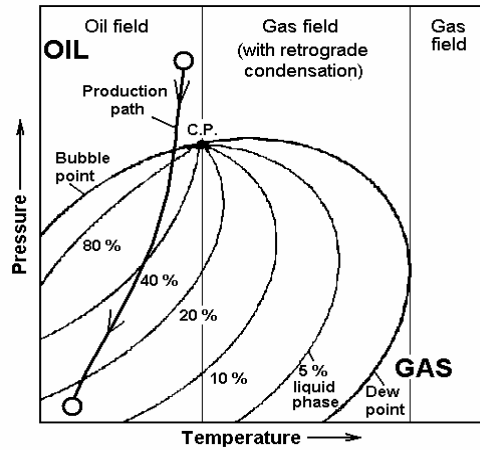
However, comparative analysis of previously available and of new experimental data reveals complex “fine phase transformations” of asphaltenes in solutions, as well as in native petroleum. E.g., there are multiple well-defined phase boundaries at ambient pressure T-C phase diagram of asphaltenes. Our experimental results definitely show that in course of traditional technological operations, macroscopic properties of petroleum media (viscosity, density, pour point, etc.) may undergo abrupt changes caused by currently uncontrolled microscopic phase transitions in asphaltene nanocolloids. In particular, petroleum fluids may practically solidify at RT after a short-time residence at a temperature-defined phase boundary of ca. 28-35°C; native crudes of diverse origin exhibit sharp viscosity/density peaking at several composition-defined phase boundaries which are relevant to compatibility problems.

We conclude that now there is enough factual evidence to consider native crude oils as “association nanofluids”. Hence, we suggest that conventional/emerging technologies for reservoir engineering should become “nanotechnologies” in a sense that they should be optimized/designed with an account for (still under-investigated) complex phase diagrams of intrinsic petroleum nanocolloids, primarily those formed by asphaltenes. At the least, this would help to preserve a delicate inner structure of native crudes (the approach which may be regarded as “petroleum nanoecology”).

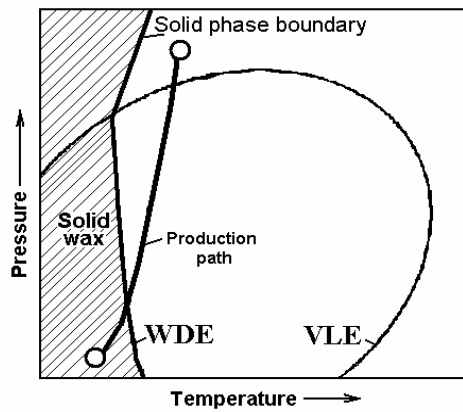
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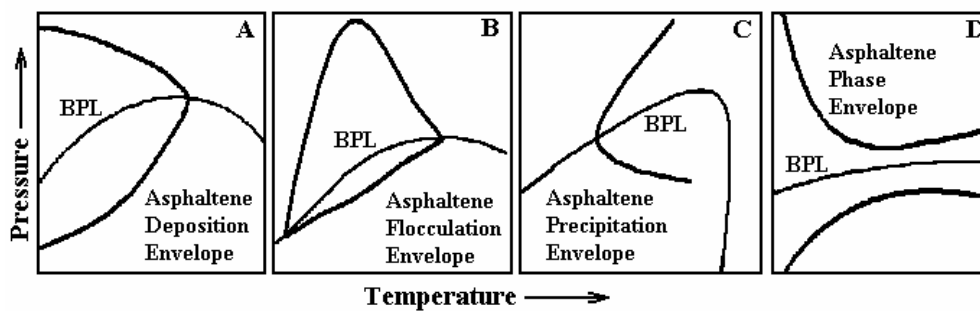
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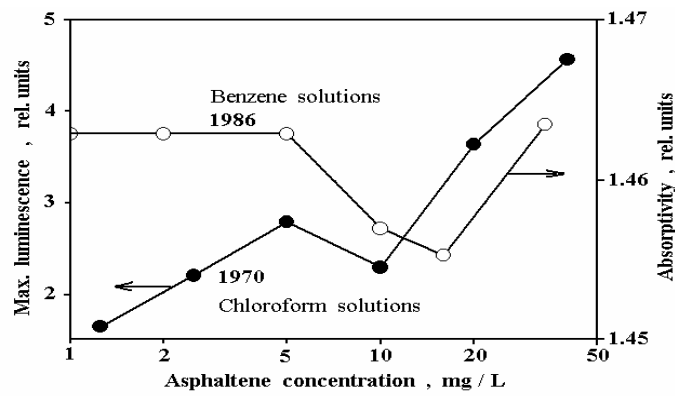
**Figure 1.** A typical P-T phase diagram demonstrating the effects of pressure and temperature on recovered petroleum. Bubble and dew point lines constitute a “Vapor-Liquid Envelope” (VLE)



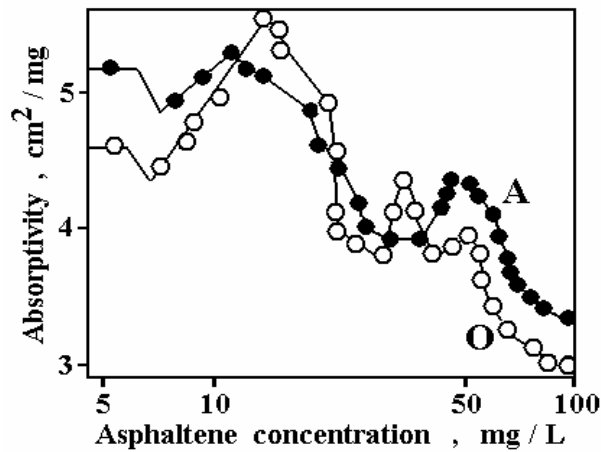
**Figure 2.** A schematic P-T phase diagram of petroleum with a “Wax Deposition Envelope” (WDE)



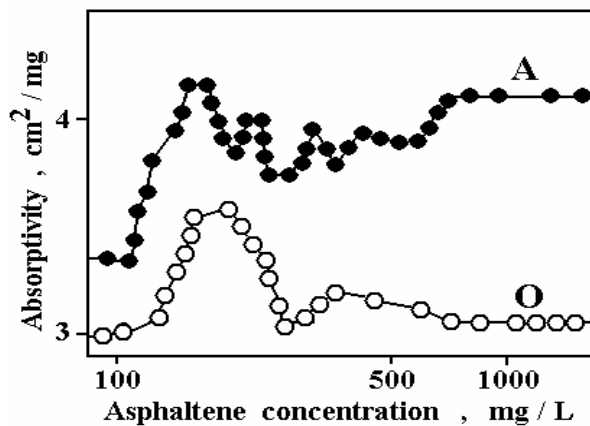
**Figure 3.** A variety of “Asphaltene Envelopes”, modeled by different research groups. A – after Leontaritis, 1996; B – after INFOCHEM, 2006; C - after Almehaideb, 2003; D – after Verdier, 2006



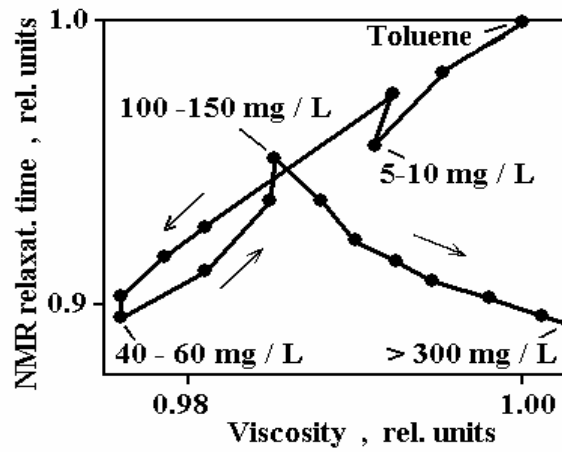
**Figure 4.** Early experimental evidence of asphaltene aggregation at concentrations, three orders of magnitude lower than conventional “CMC” (Kazakova and Koretskij, 1970; Yokota et al., 1986)



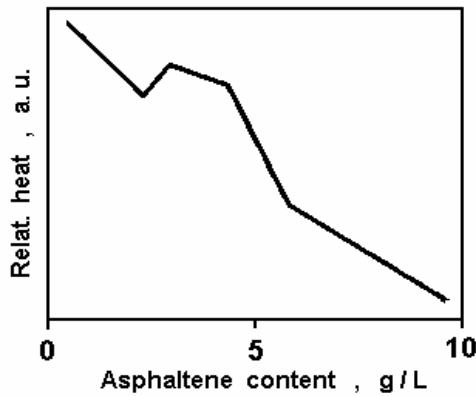
**Figure 5.** Primary asphaltene aggregation and consecutive formation of various oligomers in toluene solutions as revealed by measurements of optical absorptivity (after Evdokimov et al., 2003b)



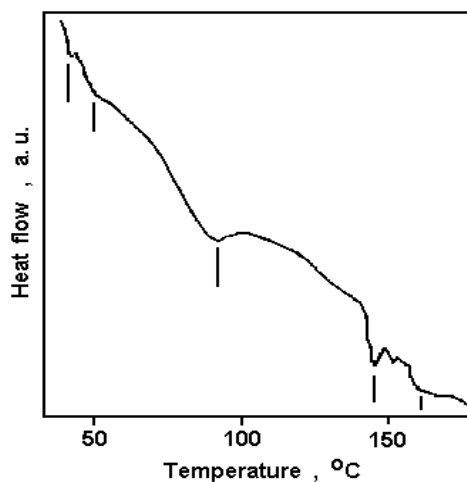
**Figure 6.** Higher-concentration continuation of the data in Fig. 5 with abrupt variations of optical absorptivity attributed to formation (precipitation) of solid asphaltene nanocolloids (after Evdokimov et al., 2003b)



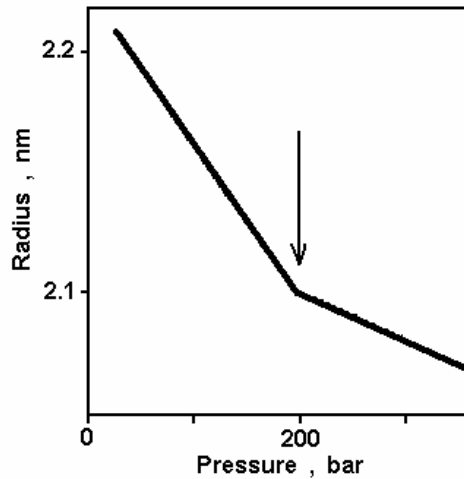
**Figure 7.** Qualitative changes of fluid's properties associated with formation of nanocolloids at asphaltene concentrations of 100-150 mg/L (after Evdokimov et al., 2003c)



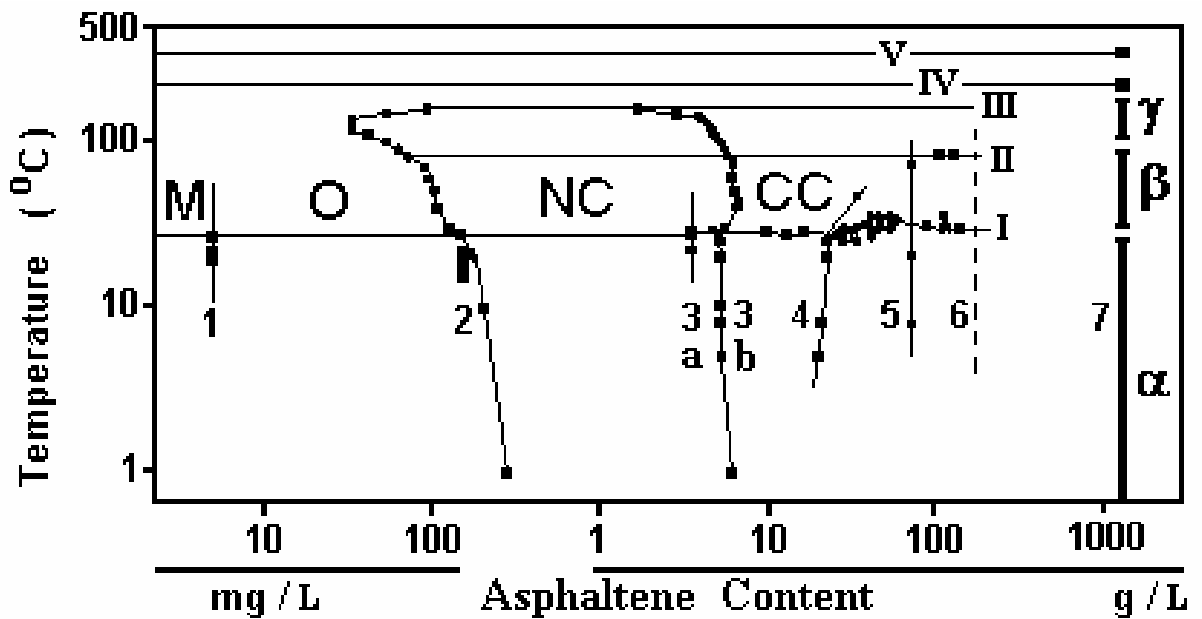
**Figure 8.** Multiple asphaltene phase boundaries in the concentration range of “former CMC” as measured by calorimetry (after Andersen and Christensen, 2000; experimental points not shown)



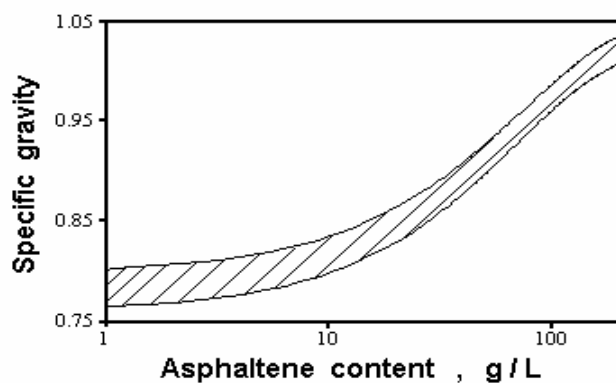
**Figure 9.** Evidence for multiple temperature-induced phase transitions in asphaltene colloids in a thermal curve of West African crude oil with 21 wt.% asphaltenes (after Ekulu et al., 2005)



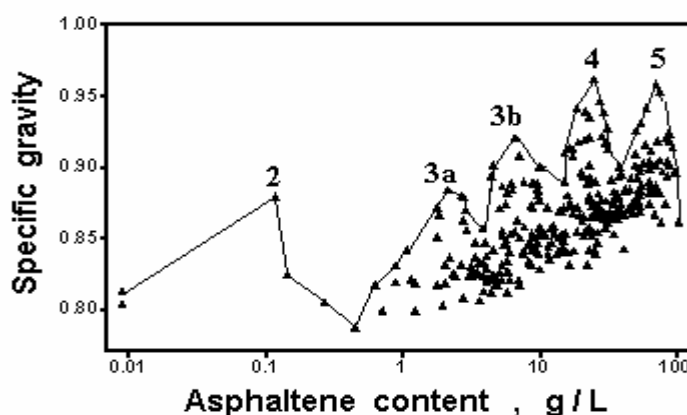
**Figure 10.** Pressure effect on the apparent radius of gyration of colloidal nanoparticles in a crude oil solution with asphaltene concentration close to 60 g/L (after Carnahan et al., 1993, experimental points not shown)



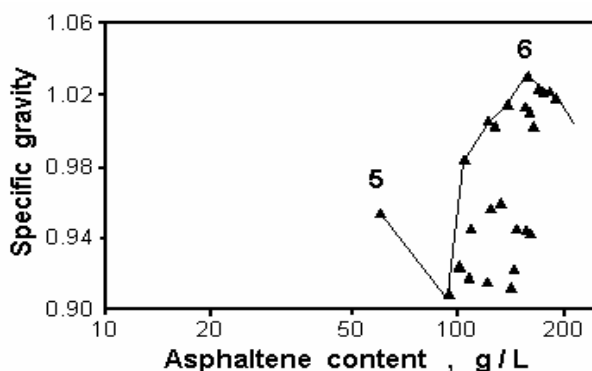
**Figure 11.** A complex T-C phase diagram for asphaltenes in petroleum (at ambient pressure), constructed on the basis of currently available data. 1-6 – concentration-defined phase boundaries in asphaltene-containing fluids. 7 – solid asphaltenes with  $\alpha$ ,  $\beta$  and  $\gamma$  phases discussed in Section 2.4. I-V - temperature-defined phase boundaries. Types of asphaltene species in petroleum: M – monomers; O – oligomers; NC – nanocolloids; CC – colloidal clusters



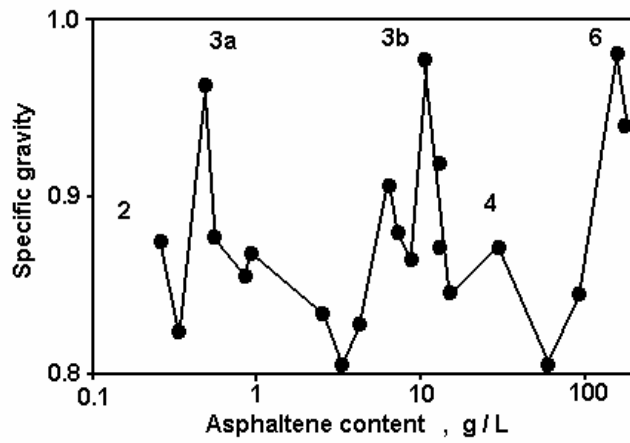
**Figure 12.** A conventionally assumed monotonous relationship of the specific gravity of world's crude oils to their asphaltene content (after Speight, 1999)



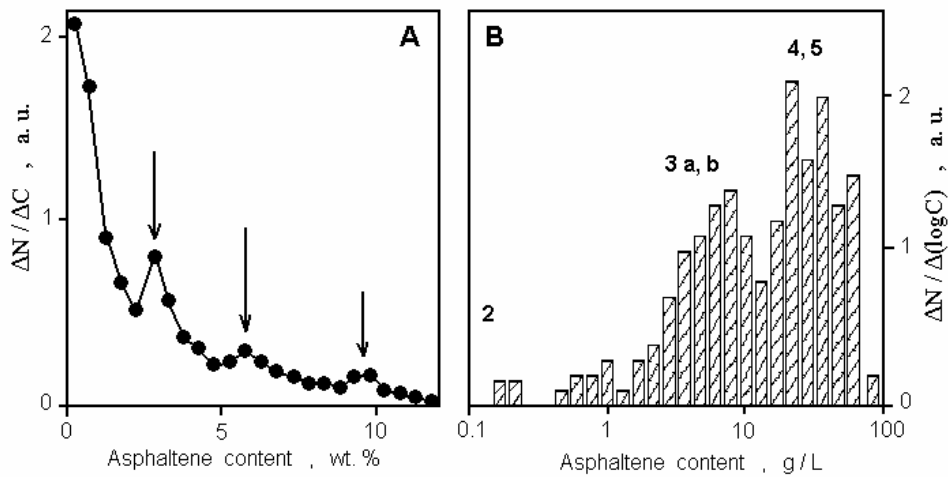
**Figure 13.** The evident non-monotonous relationship of the specific gravity to asphaltene content in a database of world's free-flowing crude oils (after Evdokimov, 2005). The numbered extrema of specific gravity coincide with the respective concentration-defined asphaltene phase boundaries of Fig. 11



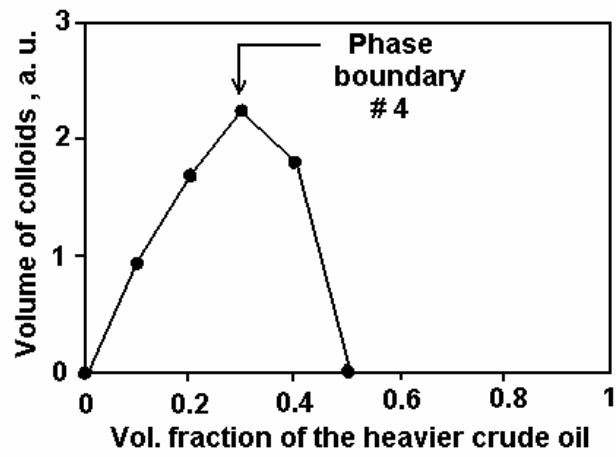
**Figure 14.** The non-monotonous relationship of the specific gravity to asphaltene content in a database of highly viscous heavy oils and bitumen (after Speight, 1999). The evident extremum of specific gravity was regarded as an indication of highest-concentration asphaltene phase boundary 6 in Fig. 11



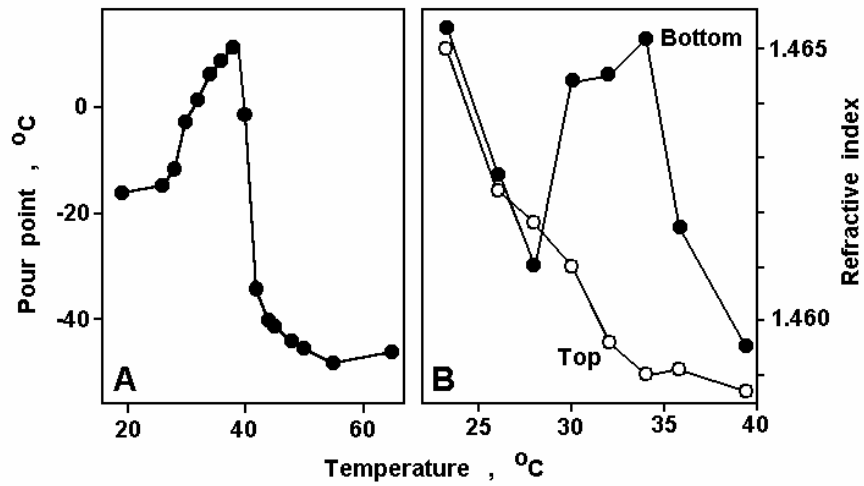
**Figure 15.** “Asphaltene nanophase” effects on specific gravity in a limited collection of world’s crude oils (after Ryder et al., 2003)



**Figure 16.** Frequency distributions of world’s crude oils with respect to their asphaltene content. Equal histogram intervals on: A – linear wt. % scale (after Evdokimov, 2005), B - logarithmic g/L scale



**Figure 17.** Compatibility problems in crude oil blends with asphaltene contents close to a nanophase boundary (after Mason and Lin, 2006)



**Figure 18.** Strong variation of native crude oil properties at a temperature-defined nanophase boundary (after Evdokimov et al., 2003d; 2006b)