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[*a shortened version of the title: Phase Diagram of Asphaltenes*]

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ABSTRACT

Comparative analysis of previously available and new experimental data reveals a complex structure of ambient pressure T-C phase diagram of asphaltenes in solutions, as well as in native petroleum. One of the characteristic properties of the diagram is an apparent series of temperature-controlled transitions between structural states in primary asphaltene nanoaggregates, presumably related to different types of intermolecular bonding. Hence, various earlier models of primary aggregates may be more closely related, than conventionally believed.

INTRODUCTION

Despite the importance of asphaltenes in petroleum reservoir development, transportation and refining, phase behavior measurement and modeling for asphaltenes and asphaltene-bearing media remains a complex task even after decades of scientific investigation. E. g., the formation/precipitation of an asphaltene solid phase during natural production process depends on pressure and temperature (Speight, 1998). This behavior is represented in a P - T phase diagram, where the onset points of asphaltene precipitation constitute stability boundaries (asphaltene precipitation envelope, APE). Experimental APEs are very scarce (Buenrostro-Gonzalez et al., 2004). For APE modeling thermodynamics' approaches are used which usually neglect complex processes of asphaltene molecular aggregation in an oil matrix. There is considerable evidence that within APE asphaltenes self-associate into various molecular aggregates of nanosized colloidal dimension. However, the nature and extent of the self-association is still widely debated (Yarranton, 2005; Maham et al., 2005). Hence, to model and predict/prevent eventual asphaltene precipitation, it is necessary to reveal phase behavior and phase boundaries of asphaltenes suspended in a fluid. In this paper, we illustrate apparent critical concentrations and specific temperatures (in systems at ambient pressure) and point out the new challenges faced in the creation of predictive models for asphaltene phase behavior.

DATA ACQUISITION FOR T-C PHASE DIAGRAM

It is a common practice to identify phase changes in studied systems by revealing "specific points" (singled out by step-like changes, extrema, inflections etc.) in experimental concentration/temperature dependencies of system's parameters. It is expected that in the absence of artefacts, these "specific points" should form well-defined lines (phase boundaries) on a T-C graph. With respect to asphaltene-containing systems, the T-C area of possible

practical importance is wide: from freezing temperatures to those of asphaltene decomposition/coking and from “infinitely diluted solutions” to solid asphaltenes. Over the past decades, a number of experimental groups have published a large volume of experimental data, which show a presence of “specific points” in various parts of the above T-C area for asphaltenes. E. g., our research group investigated concentration effects in dilute solutions with asphaltene contents from ~1 mg/l to ~1 g/l, mostly close to room temperatures (Evdokimov et al., 2001; 2003a,b; Evdokimov and Eliseev, 2005; Evdokimov and Losev, 2006). On the other hand, detailed studies of temperature effects in the range from -50°C to ~400°C (Maham et al., 2005; Masson et al., 2005; Zhang et al., 2004) have been performed with bitumen and precipitated asphaltenes, i. e. for asphaltene concentrations from ~140 g/l to ~1200 g/l. Some specific concentrations/temperatures were neither noticed, nor discussed in original publications, but the corresponding “specific points” are clearly seen in the published data plots. E. g., Roux et al., 2001, presented detailed concentration dependencies of the radii of gyration R_G in solutions of asphaltenes with concentrations 3.4 - 117 mg/l, at temperatures from 8°C to 73°C. They made a qualitative discussion of concentration/temperature effects, but did not specify obvious R_G maxima at concentrations ~5, ~20-22 and ~70 g/l. Moreover, their original data, being re-plotted on R_G vs T graph (cf. the plot for asphaltene concentration of 3.4 mg/l in Figure 1) clearly indicate the presence of “specific temperatures” of about 28-32°C.

To our knowledge, there have been no attempts to make a comparative analysis of all available information on “specific points” in asphaltene-containing media. In Figure 2 we present “raw experimental data” for such analysis. The “specific points” plotted on the T-C graph are those, discussed in original publications (specified in the following discussion), or those, obtained by further graphical/numerical analysis of the original experimental data. In a single journal paper it is impossible to make a complete list of all relevant references, hence

for the latter group of “specific points” we will present references only for the cases, principally important for interpretation of the phase boundaries.

As can be seen from Figure 2, the amount of currently available experimental evidence is sufficient for revealing some fairly well-defined phase boundaries in the T-C phase diagram.

CONCENTRATION-DEFINED PHASE BOUNDARIES

The upper boundary for molecular (monomeric) asphaltenes (line 1 in Figure 2).

The first experimental evidence for this primary aggregation stage at ca. 10 mg/l (for room temperatures) was obtained by measuring UV/vis absorption in toluene solutions of solid asphaltenes and of heavy crude oils (Evdokimov et al., 2003a,b). An appearance of asphaltene monomers below this boundary has been confirmed in our recent investigation of exponential slopes in the longer-wavelengths parts of the absorption spectra (Evdokimov and Losev, 2006). These slopes are related to the widths of states for two types of defects in asphaltene aromatic chromophores: 1) intrinsic structural defects insensitive to aggregation; 2) defects due to dangling bonds, liberated in asphaltene monomers. Figure 3 shows that massive appearance of dangling bonds is observed below the discussed phase boundary at ca. 10 mg/l. Attribution of this boundary to primary association of asphaltenes recently was also confirmed by fluorescence technique (Arteaga-Larios et al., 2005). Concentration-defined effects above this boundary and up to the next one were ascribed to appearance of various asphaltene oligomers (Evdokimov et al., 2003a,b).

Liquid-liquid demixing boundary (lines 2 in Figure 2). This boundary (ca. 100-150 mg/l at 20°C) has been revealed for solutions of solid asphaltenes and of heavy crudes by measurements of optical absorption (Evdokimov et al., 2003a,b), of kinematic viscosity (Priyanto et al., 2001), of ultrasonic velocity (Andreatta et al., 2005a), etc. Our interpretation

of the phase boundary was based mainly on the experimental relationship between dynamic viscosity η and NMR relaxation time T_2 for toluene solutions of heavy crudes (Evdokimov et al., 2003b). Figure 4 shows the respective data plot with some original data points removed to emphasize the basic trends. Positive values of $dT_2/d\eta$ for solution phases with asphaltene monomers and oligomers are indicative of strong interactions between these molecular species. Negative $dT_2/d\eta$ values above ca. 150 mg/l are typical for a phase of weakly interacting colloids/suspensions. The explanation for the observed behaviour was that at 100-150 mg/l the solution of asphaltene monomers/oligomers becomes inhomogeneous and starts to demix into an asphaltene-rich phase and a hydrocarbon-rich phase. However, no bulk phase separation follows as a result of this liquid-liquid phase transition, owing to the strongly non-equilibrium character of an asphaltene-rich phase (which may be regarded as supercooled below its glass temperature – cf. the following discussion). Hence, the emerging local regions of this phase quickly relax not by coalescence into a continuous bulk phase, but by nucleation into asphaltene “nanocolloids” with amorphous/glassy structure. A conclusion that asphaltenes may undergo a liquid-liquid phase separation into glassy non-coalescing "droplets" recently has been supported by other authors (Sirota, 2005).

“Former CMC” boundary (line 3 in Figure 2). This boundary at ~3-10 g/l is the most documented one, owing to a large magnitude of peculiarities (break points) in concentration dependencies virtually of all measurable parameters (Sheu, 1996). For many years, these break points have been interpreted by employing the concept of critical micellar concentration (CMC), projected from surfactant science into asphaltene science. Recently, it became clear that asphaltenes do not exhibit true CMC behavior (Merino-Garcia and Andersen, 2005), hence a new abbreviation was introduced - CNAC (critical nanoaggregate concentration) (Badre et al., 2006). Whatever the terminology, from the data of Figure 2 and from the above discussion it is clear that the “former CMC” boundary reflects a phase

transformation not in a primary system of asphaltene molecules, but in a secondary system of complex “nanocolloids” (glassy “droplets”), formed at the demixing boundary. Moreover, a well-known feature of demixing systems is closed-loop phase boundary at a T-C diagram (Jackson, 1991; Roberts et al., 1996). An inspection of Figure 2 shows that, indeed, phase boundaries 2 and 3 tend to form such loop, so that “former CMC” line may appear to be just a continuation of a demixing (liquid-liquid separation) boundary. It should be also noted, that characteristic attributes of closed-loop T-C diagrams are “upper” and “lower” “critical solution temperatures” (UCST and LCST) which has been observed in asphaltenes, as discussed below.

Highest-concentration boundaries (lines 4 and 5 in Figure 2).

Ramos et. al., 2001 in surface tension measurements have observed only the above “former CMC” phase boundary. However, by viscosity measurements, they registered additional strong effects at ~20-35 g/l (line 4 in Figure 2) which they ascribed to a “second aggregation concentration”. As a result of detailed SANS studies (Roux et al., 2001 and references therein), phase behavior in the highest-concentration range was interpreted as follows. In the “dilute concentration regime” (between boundaries 3 and 4 in Figure 2) asphaltene aggregates are stable independent entities with radii of gyration of a few nanometers. In the “semidilute concentration regime” (above boundary 3 in Figure 2) the internal structure of aggregates remains unchanged, but these aggregates overlap (interpenetrate) and form soft fractal objects (fractal dimension ≈ 2), imparting high solution viscosities. The “concentrated regime”, apparently above ~70-90 g/l (boundary 4 in Figure 2), is characterized by the appearance of a phase consisting of large ($>0.1 \mu\text{m}$) flocculated asphaltene domains, which may form “spatially-organized two-phase textures” (i. e., gel-like structures) and sedimentation of this phase may also occur. Hence, in simple solvents, boundary 4 may be regarded as a solubility limit (cf. Castillo et al., 2001). Higher asphaltene

concentrations apparently are encountered only in multicomponent highly viscous/gelled systems (bitumen).

It should be noted that Roux et al., 2001 expected “*that asphaltenes in crude oils or in the various industrially processed petroleum fractions also exhibit an overlap concentration above which the viscosity should increase very rapidly with asphaltene concentration*”.

Indeed, this expectation was confirmed by our recent analysis of databases for several hundreds of recovered (dead) world’s crudes (Evdokimov, 2005). Figure 5 shows a correlation of logarithm of 20°C viscosity (in cSt) with asphaltene content for ca. 200 crudes of various geographical/geological origin. Note a virtual absence of native free-flowing crude oils with asphaltene contents above a limit of ~70-75 g/l (phase border 4 in Figure 2) and rapid increases of viscosity at this limit and at ~20-30 g/l (cf. phase border 3 in Figure 2).

TEMPERATURE-DEFINED PHASE BOUNDARIES

In order to define some basic concepts for further discussion, we will first consider experimental data, obtained by differential scanning calorimetry (Masson et al., 2002; 2005; Puig et al., 2004; Zhang et al., 2004), SAXS and X-ray transmission (Maham et. al., 2005) for asphaltene-rich bitumen and for corresponding neat (solid) asphaltene fractions. Summarising, these experiments revealed the presence of several temperature-controlled phases of aggregated asphaltenes (as schematically illustrated at the highest-concentration part of Figure 2). At very low temperatures (not shown in Figure 2) asphaltenes exhibit a heat capacity consistent with that of an ordered solid, while at ca. -30°C they undergo a phase transition to an amorphous (glassy) phase, structurally controlled by interactions between polar alkane side chains, and dominant up to 25-30°C (denoted as α -phase in Figure 2). In a following phase transition asphaltenes acquire more dense structures, which are fairly stable up to ca. 100°C, and are controlled by bonding to pericondensed aromatic segments, (β phase in Figure 2). In

100-180°C temperature range there appear yet another asphaltene phase with some crystalline order (γ -phase in Figure 2). At higher temperatures, amorphous asphaltenes soften and liquefy, while crystalline domains melt at ~220-240°C. Finally, above ca. 350°C, asphaltenes decompose and form liquid crystalline mesophase, precursor of coke (Wiehe, 1993).

α - β phase boundary (line A in Figure 2). For asphaltene solutions, as well as for native crudes, the best documented specific temperatures are in this range of 25-35°C. E. g., a transition to a more dense (β) phase is manifested by noticeable shrinking of complex asphaltene aggregates (Roux et al., 2001), as illustrated in Figure 1. Another effect is a decrease of surface tension above 25°C in toluene solutions of C5I and C7I asphaltenes (Ramos et al., 2001). Among other effects is an increase of β -phase deposits from toluene solution of asphaltenes (Evdokimov and Eliseev, 2005) as illustrated in Figure 6.

Experimental results with maxima of asphaltene deposition/adsorption at α - β phase boundary may be also found in other publications (Escobedo and Mansoori, 1995; Guin and Geelen, 1996). Finally, temperature dependencies of critical concentrations (Priyanto et al., 2001) exhibit noticeable inflections at α - β phase boundary (cf. lines 2 and 3 in Figure 2). In support of the above discussed demixing phenomena, this boundary has been interpreted as “upper critical solution temperature” (UCST) both in bitumen (Masson et al., 2005) and in dilute asphaltene solutions (Neves et al., 2001).

β - γ phase boundary (line B in Figure 2). The corresponding “specific temperatures” are present in DSC results for native bitumen with 140-160 g/l asphaltenes (Masson et al., 2005). The presence of β - γ phase boundary also is indicated by yet another evident inflection in temperature dependencies of critical concentrations in asphaltene solutions (Priyanto et al., 2001) - cf. lines 2 and 3 in Figure 2.

Upper γ -phase boundary (line C in Figure 2). High-temperature experiments with asphaltene solutions are virtually non-existent. Hence, presently, in support of γ -phase

termination in non-solid asphaltenes we may supply only the above-quoted results of Priyanto et al., 2001. Namely, their two temperature dependencies of critical concentrations show an evident tendency of converging at an upper γ -phase boundary.

APPARENT POLYAMORPHISM OF ASPHALTENES

The apparent closed loop liquid-liquid demixing and the existence of several amorphous/glassy phases are characteristic attributes of the so-called “amorphous polymorphism” (frequently referred to as “polyamorphism”) in disordered systems, extensively investigated over the past decade (Poole et al., 1995; Roberts et al., 1996; Brazhkin et al., 2001). The data of Figure 2 show that temperature-driven transitions between α , β and γ phases are observed at all asphaltene concentrations above the demixing (liquid-liquid) boundary (line 2). Hence, apparently, these phases are inherent already to the primary asphaltene “nanoaggregates” and, most probably, their inner structures are controlled by different types of possible bonding of asphaltene monomers, as discussed above. In view of temperature- and thermal history-induced variations of structural “disorder parameter”, earlier proposed models of primary aggregates may be more closely related, than conventionally believed. Among these models are Yen’s “asphaltene crystallite” with some degree of order (Wong and Yen, 2000), more disordered Mullins’s “hairy tennis ball” (Andreatta et al., 2005b) and Yarranton’s “polymer structure” (Yarranton, 2005), liquid-like Sirota’s “glassy droplet” (Sirota, 2005).

CONCLUSIONS

Previously published experimental evidence and newly obtained results support a complex T-C phase diagram of asphaltenes in solutions, as well as in native petroleum (at ambient pressure). Some apparent, but unconventional features of this diagram are closed-

loop (demixing) area and temperature-controlled polyamorphism of asphaltenes. In view of obvious importance for prediction/prevention of asphaltene precipitation in industrial processes, the details of T-C phase diagram should be subjected to further experimental verification.

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FIGURES

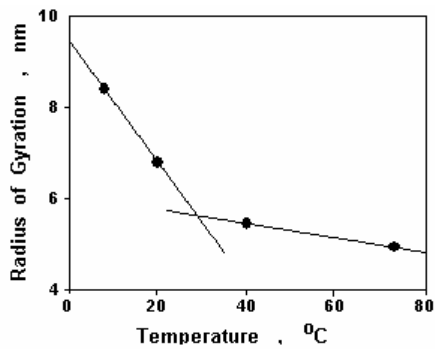


Figure 1. Noticeable change of the size of asphaltene particles at a “specific temperature” of ca. 30°C. (Re-plotted data of Roux et al., 2001).

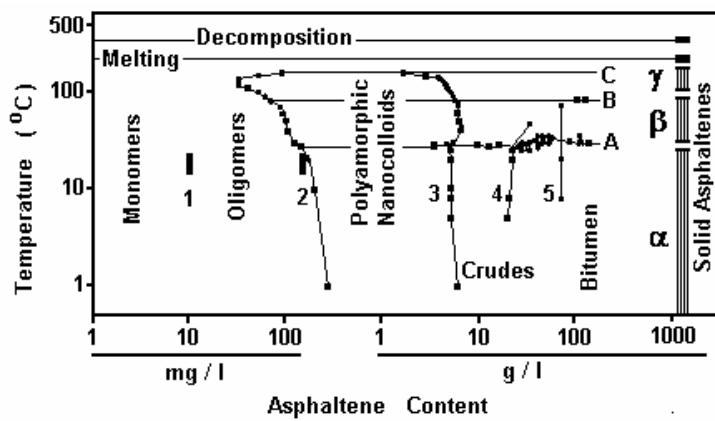


Figure 2. T-C plot of experimental “specific temperatures/concentrations”, related to noticeable changes in the measured properties of asphaltene-containing media.

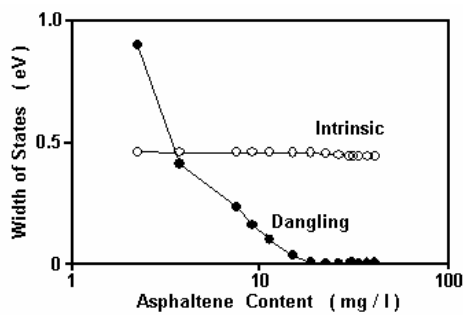


Figure 3. Massive appearance of asphaltene monomers with multiple dangling bonds below phase boundary (1) in Figure 2 (for details, cf. text).

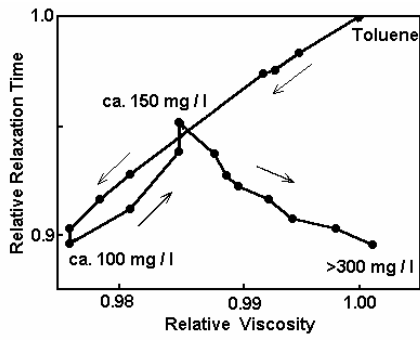


Figure 4. NMR relaxation time vs dynamic viscosity for toluene solutions of a heavy crude (adapted from Evdokimov et al., 2003b). Qualitative changes above phase boundary (2) in Figure 2 are indicative of a liquid-liquid phase separation (demixing).

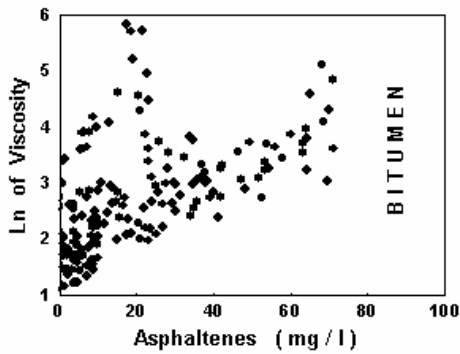


Figure 5. Viscosity vs. asphaltene content correlation for ca. 200 world's recovered crude oils (adapted from Evdokimov, 2005). Note viscosity peaking near phase boundaries 4 and 5 in asphaltene solutions (Figure 2).

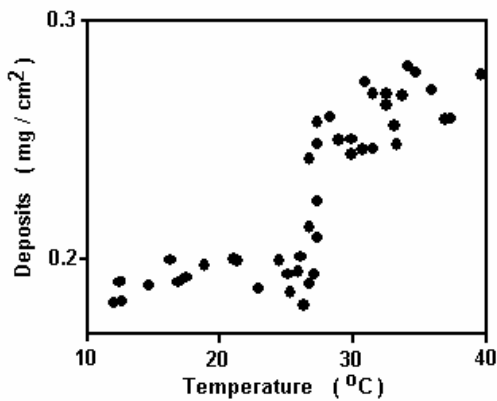


Figure 6. Temperature-dependent mass of deposits at a steel surface from a model oil with 12.3 g/l asphaltenes (adapted from Evdokimov and Eliseev, 2005).

FIGURE CAPTIONS

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