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## Emerging Petroleum-Oriented Nanotechnologies for Reservoir Engineering

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### **Abstract**

The paper describes experimental/analytical research aimed at modification of petroleum technologies to “nanotechnologies” by accounting for molecular processes in nanocolloids of native petroleum fluids.

Our results show that in course of traditional technological operations, macroscopic properties of petroleum media (viscosity, density, pour point, etc.) may exhibit abrupt changes caused by currently uncontrolled microscopic phase transitions in nanocolloids. In particular, our experiments provided phase diagrams of

petroleum nanocolloids, which show critical parameters, highly unfavorable for industrial processing of petroleum. E.g., petroleum fluids may practically solidify at RT after a short-time residence at the 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. Contrary to widespread assumptions, the current properties of petroleum nanocolloids (and, hence, the current properties of petroleum fluids) are not defined solely by current technological parameters. Of equal/decisive importance are the details of a preceding history of reservoir development.

We conclude that proper recovery “nanotechnologies” should be designed and performed with an understanding of importance of the complex nanophase diagrams of petroleum fluids. Such technology should include specifically designed processes (employ specifically selected parameters) to purposely avoid/instigate particular phase transformations in petroleum nanocolloids in order to improve (or, at least, not to ruin) the practically important bulk properties of petroleum. With respect to immediate practical applications, it should be emphasized that the discussed phase diagrams contain only “the most obvious” nanophase boundaries, reflect our *current knowledge* of structural transformations in petroleum and should be subjected to further investigation.

## **Introduction**

Nanotechnology has been making its presence felt in the industry for some time, and many applications are already standard in petroleum refining. E.g., nanostructured zeolites are now used to extract up to 40% more gasoline than the catalysts they replaced.<sup>1,2</sup> The most obvious application of nanotechnology for upstream operations is development of better materials.<sup>3,4</sup> The oil industry needs strong, stable materials in virtually all of its processes. By building up such substances on a nanoscale, it could produce equipment that is lighter, more resistant, and stronger. Nanotechnology could also help develop new metering techniques with tiny

sensors to provide improved information about the reservoir.<sup>3,4</sup> Other emerging applications of nanotechnology in oil reservoir engineering are in the sector of developing new types of “smart fluids” for improved/enhanced oil recovery, drilling, etc.<sup>4-7</sup> Among these are new nanoformulations of surfactants/polymers, microemulsions, colloidal dispersion gels (CDG), biliquid foams (aphrons). More recent developments deal with so-called “nanofluids”.<sup>6,7</sup> These are designed by introducing small volumetric fractions of nanosized solid particles to a liquid phase in order to enhance or improve some of the fluid properties. Nanofluids can be designed to be compatible with reservoir fluids/rocks and be environmentally friendly. Some newly developed nanofluids have shown extremely improved properties in such applications as drag reduction, binders for sand consolidation, gels, products for wettability alteration, and anticorrosive coatings.<sup>6,7</sup> Presently, the term “nanofluid” is used mainly to define suspensions of *solid* nanoparticles, though there is noticeable tendency to extend it to nanoparticles of any nature.<sup>8</sup> In the following this term will be used in the latter, general meaning.

In the present publication we will discuss a lesser investigated subject of upstream nanotechnologies for petroleum fluids proper. The discussion is based on our original experimental studies and on other published experimental data. In support, we analyze available databases of the properties of world (dead) crudes. The main conclusion is that native crude oils may be classified as “association nanofluids”. Hence, all conventional/emerging technologies for reservoir engineering should be optimized/designed with an account for (still under-investigated) complex phase diagrams of intrinsic 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”).

The discussion begins with necessary descriptions of some concepts in “nanotechnologies” and “petroleum colloids”, which are frequently misinterpreted or misused.

## What is nanotechnology?

### Sources of confusion about nanotechnology

Some persistent “nanomyths” apparently became widespread in 1966, when Isaac Asimov’s science fiction novel, “Fantastic Voyage” was made into a movie featuring adventures of the crew of a miniaturized submarine which is injected into the blood stream of a defecting scientist in order to melt an inoperable blood clot in his brain. Moreover, in 1986, Eric Drexler publishes a book<sup>9</sup> with a scientist’s idea of nanotechnology using programmed molecular sized robots called “*nanobots*” – machines that could assemble individual atoms and molecules into required structures. Fig. 1 shows an artist’s impression of nanobot (image from [http:// www . thelensflare . com/ gallery / p\\_nanobot\\_223.php](http://www.thelensflare.com/gallery/p_nanobot_223.php)).



Fig. 1. Mechanical nanorobot for molecular *forced assembly*.

In our opinion, nanotechnologies for petroleum industry have little to do with building nanobots, though a popular website **Wired.com** quotes one report that says tiny nanorobots will “patrol the pores of an oil or gas reservoir, monitor how hydrocarbons are flowing, decide how to maximize recovery, and dictate which other robots in the wells and zones should produce at that moment and which should inject water.” Moreover, a concept of nanorobots has been a subject of some recent presentations at petroleum-oriented conferences.<sup>10,11</sup>

Currently, there are no universally accepted “precise” definitions which would allow distinguishing between “true” nanotech-



nologies and other domains of atomic and molecular science/engineering. The fairly representative definitions are:<sup>12</sup> “*Nanoscience* is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale.” “*Nanotechnologies* are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale.”

Note that these definitions do not refer to any specific methods/devices like nanobots. The reason is that, in fact, there are two fairly distinct branches of nanotechnology. More commonly, the term “nanotechnology” is used interchangeably with “molecular nanotechnology” (MNT), which exploits the concept of mechano-synthesis based on positionally-controlled molecular manipulation (*forced assembly*), guided by machine systems - scanning probe devices (STM, AFM) or Drexler’s nanobots.

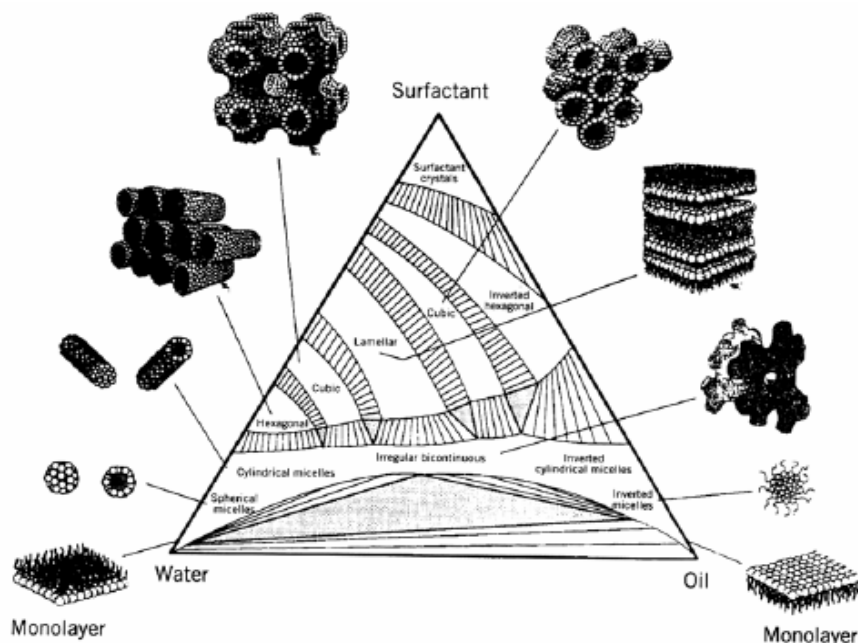


Fig. 2 Molecular nanostructures by *self-assembly*.

As indicated, we do not expect that in the foreseeable future this type of nanotechnology will be of any importance for upstream operations. The other branch of nanotechnology evolved as su-

pramolecular chemistry with a fundamental concept of molecular *self-assembly* without guidance or management from an outside source. In self-assembly all final nanostructures are “encoded” in the shapes and properties of the molecules that are employed. The particular desired structures of suspended supramolecular nanoparticles may be realised by subtle changes of macroscopic system parameters, e.g. system’s composition, as illustrated in the phase diagram of Fig. 2 (from Ref. 13).

In turn, phase changes in evolving nanocolloids may notably affect macroscopic properties of the bulk nanofluid. In petroleum, the majority of self-assembling molecules belong to the solubility-defined fraction of “asphaltenes”.<sup>14-17</sup>

## **Colloidal Suspensions and Association Nanocolloids in Petroleum**

Specialists in the subject may argue that there is no novelty in importance for petroleum properties of native colloids (either micrometer- or nanometer-sized). Indeed, this importance has been emphasized several decades ago, firstly with respect to bitumen.<sup>18,19</sup> Later, it was recognized that any petroleum medium represents a colloid system with dispersed colloidal phase constituted predominantly of asphaltenes. The details of asphaltene colloid characterization have been reported in numerous references. The important milestones in this research were publications of a book based on materials of 1993 International Symposium on the Characterization of Petroleum Colloids<sup>20</sup> and of a Russian-language book on disperse systems in petroleum.<sup>21</sup>

However, neither earlier, nor more recent models of asphaltene colloids in petroleum include a concept of asphaltene self-assembly into a variety of (nano)colloidal configurations with a well-structured phase diagram.

In most models (cf. Ref. 22 and multiple references therein), asphaltenes from the start are regarded as *solid* (quasispherical) colloidal particles with diameters of 2–10 nm. Under evolving conditions these colloids may coagulate/flocculate via diffusion- or re-

action–limited processes into larger and larger aggregates until these loose buoyancy and precipitate out of the liquid. Evidently, in these essentially continuous schemes there are no complex phase diagrams of hard sphere colloids, the only “critical boundary” being not a specific phase transformation, but a precipitation onset.

Just one additional “critical boundary” appears in colloidal models where colloidal particles are not permanently present in petroleum but are formed from molecular solutions of asphaltenes at certain critical conditions as a result of some association processes which, for a long period of time, were regarded to be similar to micellization phenomena of simple surfactants. “Critical micellization concentration” (“CMC”) of asphaltenes has been the subject of numerous publications,<sup>23</sup> though now it is realized that some processes other than textbook “micellization” should be responsible for this particular structural transformation of asphaltene (nano)colloids.<sup>24</sup>

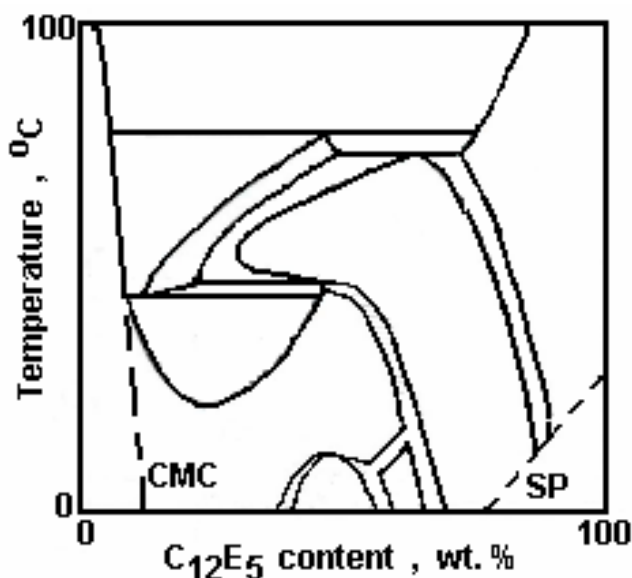


Fig. 3. A complex T-C phase diagram for association colloids in a binary surfactant/water system. Dashed critical boundaries are those for conventional “micellization” (CMC) and for solid precipitation (SP) (*adapted from Refs. 26,27*).

Apparently, it never has been realized that the assumption of “micellization” places asphaltenes into a principally different class of disperse systems. A system of solid particles dispersed in a liq-

uid is classified as a “colloidal suspension”,<sup>25</sup> while systems with particles which are formed by reversible “micellization” are classified as “association colloids”<sup>25</sup> which usually exhibit a very rich phase behavior ranging from the simplest isotropic micellar phases to highly organized supramolecular nanostructures.<sup>26</sup>

As an example, Fig. 3 shows a complex temperature concentration (T–C) phase diagram for nonionic surfactant penta-ethyleneglycol dodecyl ether (C<sub>12</sub>E<sub>5</sub>) in water.<sup>27</sup> Note the appearance of enclosed phase domains (“closed loops”) at the phase diagram, representative of a so-called reentrant phase behaviour.<sup>28</sup> For further discussion it is important that “closed loops” are indicative of polymorphism of a system;<sup>29</sup> these loops originate in liquid-liquid immiscibility phenomena and are characteristic signatures of directional noncovalent (e.g. hydrogen) bonding in associating species.<sup>30</sup>

It is amazing that after introducing a concept of “micellization” for nanoparticles of asphaltenes, the petroleum researchers remained content with the obsolete notion of a single critical concentration (CMC) in surfactants. Consequently, a possible analogy with known complex properties of association colloids (rich phase diagram, hence multiple critical concentrations/temperatures) has not been investigated, though, as shown in the following sections, well known published experimental results and recent publications provide multiple data in support of the concept of asphaltenes being “*association nanocolloids*”.

### **T-C Phase Diagram of Asphaltenes in Petroleum – Data Accumulation**

Phase changes in asphaltene-containing systems can be identified by revealing “specific points” (singled out by steplike changes, extrema, inflections etc.) in experimental concentration and temperature dependencies of system’s parameters. Fig. 4 shows an example from our publication on concentration and temperature effects on Herschel–Bulkley’s rheological parameters in asphaltene-rich model oils.<sup>31</sup>

In the absence of artifacts, the above “specific points” may be expected to form well-defined phase boundaries on a T–C graph. The T–C area of possible practical importance is wide: from pour point temperatures to those of asphaltene decomposition/coking and from “infinitely diluted petroleum 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  $\sim 1$  mg/l to  $\sim 1$  g/l, mostly close to room temperatures.<sup>32-34</sup>

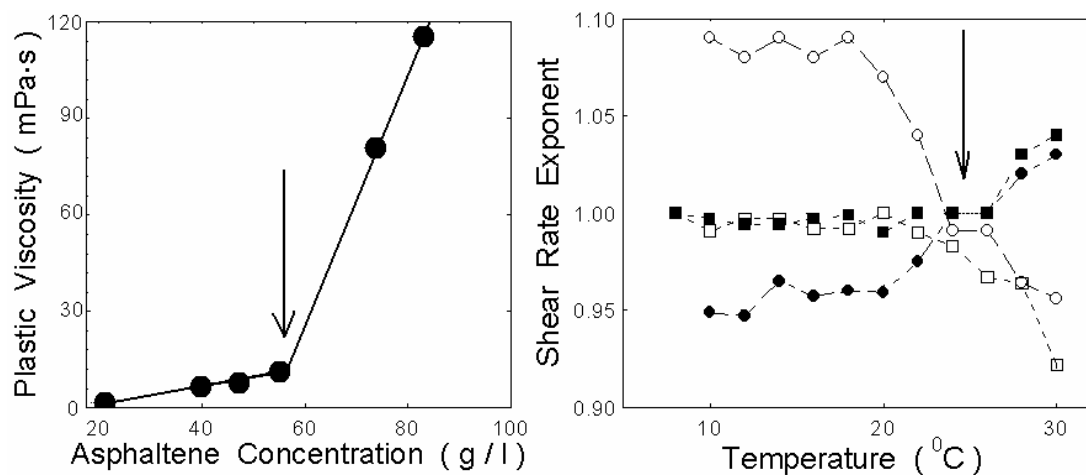


Fig. 4. Identification of specific/critical points for asphaltene phase diagram in experimental data sets (adapted from Ref. 31).

On the other hand, detailed studies of *temperature* effects in the range from  $-50^{\circ}\text{C}$  to  $\sim 400^{\circ}\text{C}$  have been performed<sup>35-37</sup> with bitumen and precipitated asphaltenes, i.e. for asphaltene concentrations from  $\sim 140$  g/l to  $\sim 1200$  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., SANS study of asphaltene aggregation<sup>38</sup> provided 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 to  $73^{\circ}\text{C}$ . The authors made a qualitative discussion of concentration/temperature effects, but did

not specify obvious  $R_G$  maxima at concentrations  $\sim 5$ ,  $\sim 20$ – $22$  and  $\sim 70$  g/l. Moreover, their original data, being re-plotted on  $R_G$  vs  $T$  graph clearly indicate the presence of “specific temperatures” of about  $28$ – $32^\circ\text{C}$ . In a single journal paper it is impossible to make a complete list of all relevant references; other sources of “specific points” used for constructing the  $T$ – $C$  phase diagram will be listed in a forthcoming publication.

### **T-C Phase Diagram of Asphaltenes in Petroleum – Current Version**

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 Fig. 5 we present a first cumulative  $T$ – $C$  plot of all “specific points” obtained as described in the previous section. As can be seen from the figure, currently available experimental evidence already is sufficient for revealing some fairly well-defined phase boundaries in the  $T$ – $C$  phase diagram. However, the still limited amount of data does not allow any statistical analysis; hence all below discussed numerical values of “critical” parameters should be regarded as approximate and will be subjected to further investigation.

### **Concentration-Defined Phase Boundaries**

**Primary aggregation boundary** (line 1 in Fig. 5). The first experimental evidence for this primary aggregation stage at ca.  $7$ – $10$  mg/l (at  $20^\circ\text{C}$ ) was obtained by measuring UV/vis absorption, viscosity and NMR relaxation in toluene solutions of solid asphaltenes and of heavy crude oils.<sup>32-34</sup> Attribution of this boundary to primary association of asphaltenes monomers recently was also confirmed by fluorescence technique.<sup>39</sup>

**Liquid-liquid demixing boundary** (line 2 in Fig. 5). This boundary (ca.  $100$ – $150$  mg/l at  $20^\circ\text{C}$ ) has been revealed for solutions of solid asphaltenes and of heavy crudes by measurements of optical absorption,<sup>32-34</sup> of NMR relaxation,<sup>33,34</sup> of viscosity,<sup>33,34,40</sup> of ultrasonic velocity,<sup>41</sup> etc. A well-known feature of demixing sys-

tems is a closed-loop phase boundary at T–C diagram.<sup>28-30</sup> An inspection of Fig. 5 shows that, indeed, phase boundaries 2 and 3 tend to be parts of such loop. Other characteristic boundaries of closed-loop T–C diagrams are “upper” and “lower” “critical solution temperatures” (UCST and LCST) which, apparently, also are present in Fig. 5.

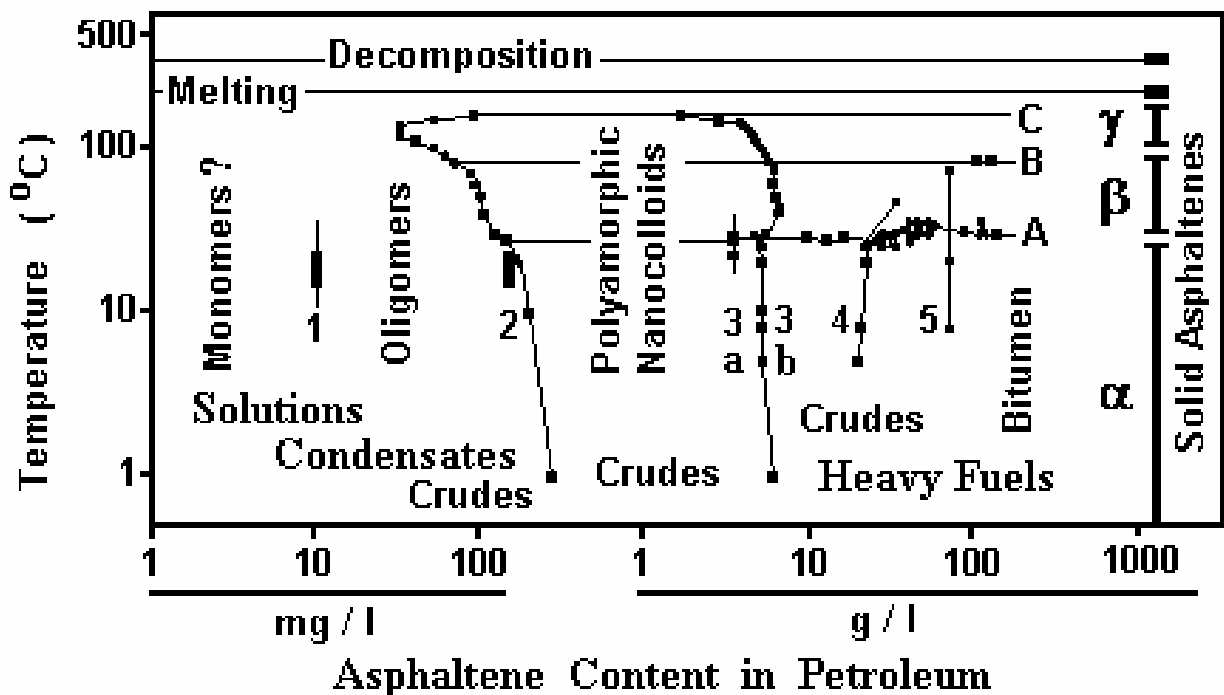


Fig. 5. A complex T–C phase diagram for association nanocolloids of asphaltenes in petroleum media, constructed on the basis of the (limited) currently available data.

“Former CMC” boundaries (lines 3a and 3b in Fig. 5). “Specific points” at ~1–10 g/l are the most documented one, owing to a large magnitude of abrupt changes in concentration dependencies virtually of all measurable parameters.<sup>42</sup> More detailed inspection shows that published “CMC” data tend to concentrate at two sub-ranges, namely at ~1–3 g/l and at ~7–10 g/l. As discussed above, for many years, these specific points have been interpreted by employing the concept of CMC, projected from surfactant science. When it became clear that asphaltenes do not exhibit true CMC behavior, a new abbreviation was introduced – CNAC (*criti-*

*cal nanoaggregate concentration*).<sup>43</sup> Fig. 5 shows that the “former CMC” boundaries reflect phase transformations not in primary systems of asphaltene molecules, but in secondary systems of complex nanocolloids formed at the demixing boundary. Moreover, as indicated above, at least one of “former CMC” lines may appear to be just a continuation of a demixing (liquid-liquid separation) closed loop.

**Highest-concentration boundaries** (lines 4 and 5 in Fig. 5). In studies of “CMC” by viscosity measurements<sup>44</sup> additional strong effects were observed at  $\sim 20\text{--}35$  g/l (line 4 in Fig. 5) and were ascribed to a “second aggregation concentration”. As a result of detailed SANS studies, phase behavior in the highest-concentration range was interpreted as follows.<sup>38</sup> In the “dilute regime” (between boundaries 3 and 4 in Fig. 5) asphaltene aggregates are independent entities with radii of a few nanometers. In the “semidilute regime” (above boundary 4 in Fig. 5) the internal structure of aggregates remains unchanged, but these aggregates interpenetrate and form soft fractal objects, imparting high fluid viscosities. The “concentrated regime”, apparently above  $\sim 70\text{--}90$  g/l (boundary 5 in Fig. 5), 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” (gel-like structures) and sedimentation of this phase may also occur. Hence, in simpler fluids, boundary 5 may be regarded as a “free-flowing” limit. Higher asphaltene concentrations apparently are encountered only in multicomponent highly viscous/gelled systems (bitumen).

### **Temperature-Defined Phase Boundaries**

The majority of experimental data on “specific temperatures” has been obtained for asphaltene-rich bitumen and for corresponding neat (solid) asphaltene fractions.<sup>35,45-47</sup> In short, these experiments revealed the presence of several temperature-controlled phases of aggregated asphaltenes (cf. the right-hand part of Fig. 5). At freezing temperatures (not shown in Fig. 5) asphaltenes exhibit a heat



capacity consistent with that of an ordered solid, while at ca.  $-30^{\circ}\text{C}$  they undergo a phase transition to an amorphous (glassy) phase, structurally controlled by interactions between polar alkane side chains, and dominant up to  $25\text{--}30^{\circ}\text{C}$  (denoted as  $\alpha$ -phase in Fig. 5). In a following phase transition asphaltenes acquire more dense structures, which are fairly stable up to ca.  $100^{\circ}\text{C}$ , and are controlled by bonding to pericondensed aromatic segments, ( $\beta$ -phase in Fig. 5). In  $100\text{--}180^{\circ}\text{C}$  temperature range there appear yet another asphaltene phase with some crystalline order ( $\gamma$ -phase in Fig. 5). At higher temperatures, amorphous asphaltenes soften and liquefy, while crystalline domains melt at  $\sim 220\text{--}240^{\circ}\text{C}$ . Finally, above ca.  $350^{\circ}\text{C}$ , asphaltenes decompose and form liquid crystalline mesophase, precursor of coke.

For asphaltene-containing free-flowing fluids, including native crudes, the best documented specific temperatures fall onto **the  $\alpha$ - $\beta$  phase boundary** in the range of  $25\text{--}35^{\circ}\text{C}$  (line A in Fig. 5). E.g., a transition to a more dense ( $\beta$ ) phase was manifested by noticeable shrinking of complex asphaltene aggregates,<sup>38</sup> by a decrease of surface tension<sup>44</sup> and by an increase of deposition from asphaltene solutions.<sup>14</sup> In support of the above discussed demixing phenomena, this boundary has been interpreted as “upper critical solution temperature” (UCST) both in bitumen<sup>45</sup> and in asphaltene solutions.<sup>48</sup> Comparatively less investigated are the  **$\beta$ - $\gamma$  phase boundary** (line B in Fig. 5) and the **upper  $\gamma$ -phase boundary** (line C in Fig. 5). At the “closed loop” domain the latter boundary may be identified with “lower critical solution temperature” (LCST).

The data of Fig. 5 show that temperature-driven transitions between  $\alpha$ ,  $\beta$  and  $\gamma$  phases are observed at all asphaltene concentrations above the demixing boundary (line 2). Hence, apparently, these phases are inherent already to the primary asphaltene nanoparticles and, most probably, their inner structures are controlled by different types of possible bonding of asphaltene monomers, as discussed above. In view of thermally-induced variations of structural order, earlier proposed models of primary aggregates

may be more closely related, than conventionally believed. Among these models are “asphaltene crystallite” with some degree of order,<sup>49</sup> more disordered “hairy tennis ball”<sup>50</sup> and “polymer structure”<sup>51</sup>, a liquid-like “glassy droplet”.<sup>52</sup>

### **Immediate Relevance to the Properties of Native Petroleum**

We are aware that some skeptical reservoir engineers may wonder: “who needs these scientific speculations and nice pictures obtained in laboratory exercises with artificially designed formulations; most probably all this is just one more showoff in the fashionable subject of “NANO” with little relevance to honest reservoir fluids?” It is true that at the moment we can not make any suggestion about the details of nanocolloid phases in “**live**” petroleum – this will need much more complicated and costly experiments. However, a detailed inspection of available information on the properties of world’s “**dead**” (recovered) petroleum fluids show surprisingly strong effects which may originate in the phase diagram of asphaltene nanocolloids of Fig. 5. In particular, we have compiled a database for several hundreds of recovered world’s crudes with various asphaltene contents. Previously published analysis of this database<sup>53</sup> did not take into account the newly obtained information on asphaltene phase diagram, which now highlights some of the previously overlooked features.

As an example, Fig.6 shows a log-log plot of viscosity vs asphaltene content for ca. 200 crudes of various geographical/geological origin. The solid line in Fig. 6 has no special significance and is drawn just to emphasize the apparent viscosity extrema.

For quantitative interpretation of underlying mechanisms, the statistics has to be improved, especially in the range of low asphaltene contents; nevertheless even the “raw” data of Fig. 6 clearly demonstrate a striking coincidence of sharp viscosity anomalies with **all** (but one) phase boundaries of asphaltene nanocolloids in Fig. 5.

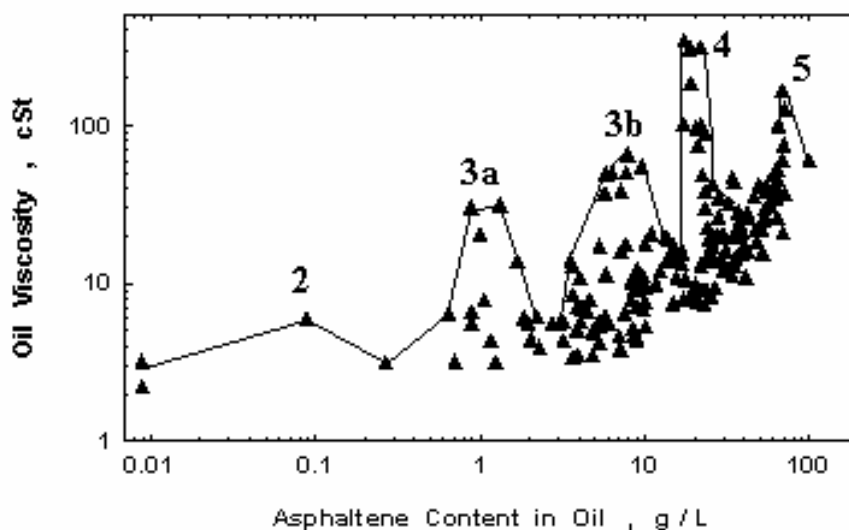


Fig. 6. Complex variations of viscosity with asphaltene content for world's (dead) crudes. Apparent extrema are numbered in accordance with asphaltene phase boundaries in Fig. 5.

Phase boundary 1 corresponds to oil's asphaltene content of ca. 0.001 wt% while most current databases classify all values below 0.01 wt% as “zero asphaltene content”. Note that Fig. 6 shows a virtual absence of native free-flowing crude oils with asphaltene contents above the phase boundary 5 which, as discussed above, may be a natural “solubility limit” of asphaltenes in native crudes.

There is a well-known interdependence of viscosities and of specific gravities (densities) in crude oils. Indeed, our database reveals noticeable peaking of specific gravities at asphaltene phase boundaries, as shown in Fig. 7. In fact, “asphaltene nanophase” effects are so persistent, that once one starts searching for them, they emerge even in very limited data collections. E. g., a Web site on asphaltene deposition presents a table with “Resin and Asphaltene Content of various Crude Oils”.<sup>54</sup> The table contains properties of just ca. 20 crudes with non-zero asphaltene content from diverse locations (Canada, Venezuela, Mexico, USA, Russia, Brazil, Iraq, France, Algeria).

A plot of specific gravity vs. asphaltene content for this collection of oils is shown in Fig. 8. In the absence of the above discussed

data, the peculiar behavior of data points would be regarded merely as an extensive scatter. However, comparison with the larger database of Figs. 6 and 7 allows attributing peaks of specific gravity to the same asphaltene phase boundaries (boundary 3b is not reproduced due to the lack of data points in the respective concentration range).

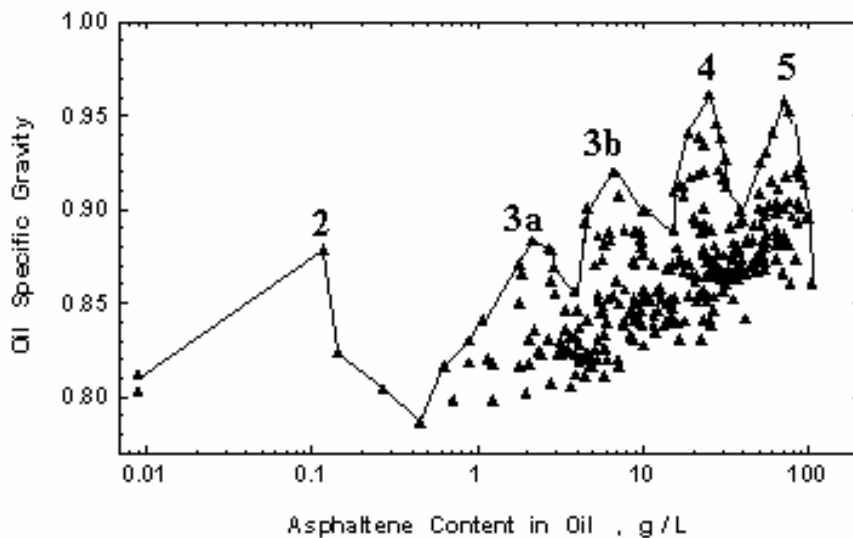


Fig. 7. Complex variations of specific gravity with asphaltene content for world's (dead) crudes. Apparent extrema are numbered in accordance with asphaltene phase boundaries in Fig. 5.

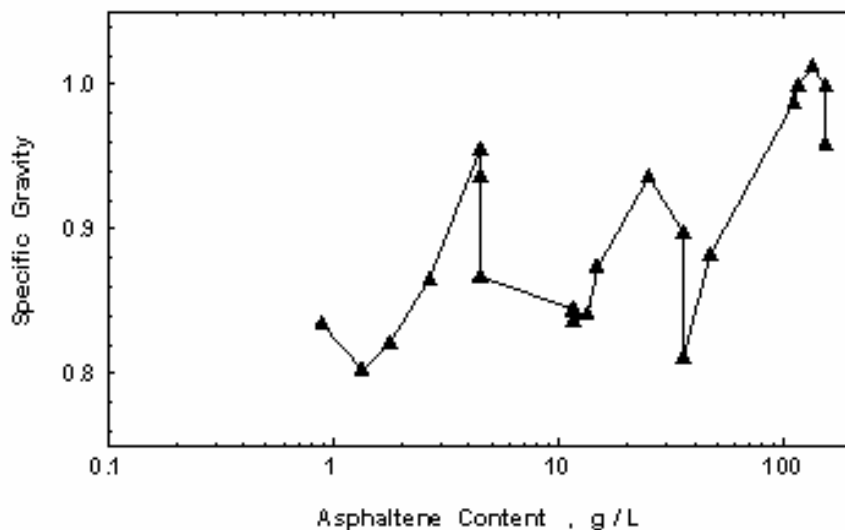


Fig. 8. Complex variations of specific gravity with asphaltene content in the limited collection of world's (dead) crudes.

Our experiments revealed noticeable transformations of the macroscopic properties of native crudes at the temperature-defined nanophase boundary “A” in Fig. 5. The left-hand part of Fig. 9 shows variations of the pour point of a Tatarstan crude after 1 hour thermal pre-treatments at temperatures close to the discussed phase boundary.<sup>55</sup> The crude had a density of 895 g/l, contained ~3.5 wt. % asphaltenes, ~20 wt. % resins, ~0.3 wt. % waxes. First deviations of the pour point became noticeable after pre-treatment at ca. 30°C, while the most dramatic increase, from -16.2 to +11.2°C, was registered after pre-treatment at temperature of 37.5°C.

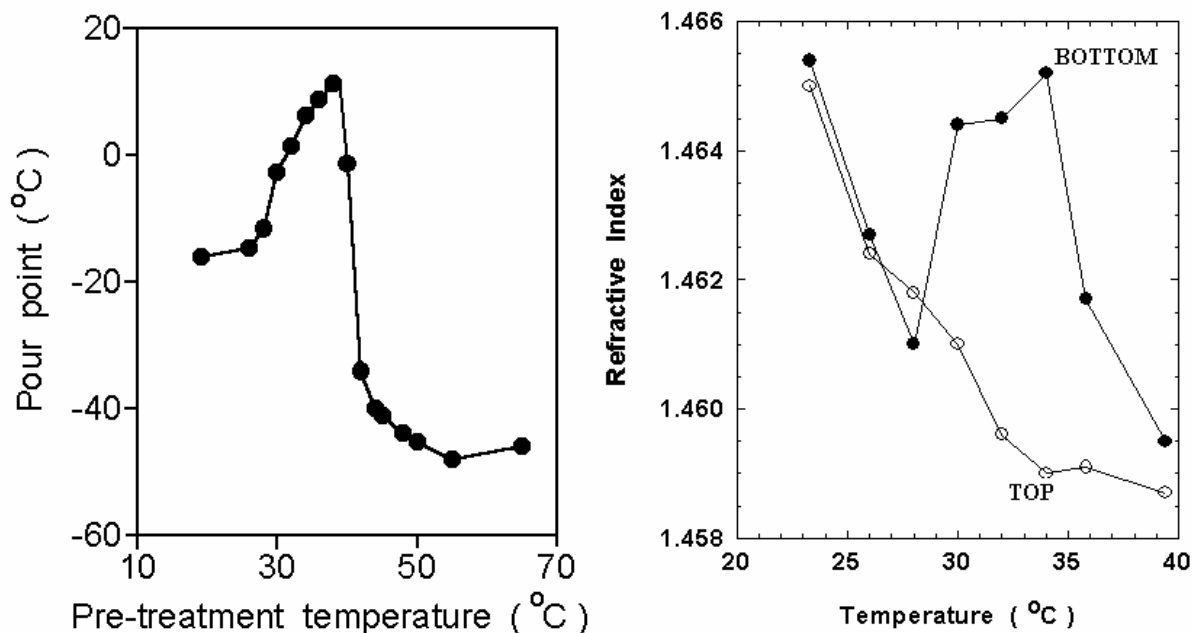


Fig. 9. Strong variation of native crude oil properties at asphaltene nanophase boundary “A” in Fig. 5.

The right-hand part of Fig. 9 shows dramatic density stratification near the discussed asphaltene nanophase boundary “A” in 10 cm-high samples of a Yamal native crude (West Siberia), stored at various temperatures. Density variations were evaluated via refractive index (RI) measurements in the minute quantities of oil extracted from the top and from the bottom of the sample. In the absence of “phase boundary” phenomena, an expected effect is a

gradual decrease of RI due to thermal expansion, with the density at the top being only marginally smaller than at the bottom. Indeed this behavior was observed below ca. 28°C and, once again, above ca. 37°C. At intermediate temperatures, in the vicinity of asphaltene nanophase boundary, there was a strong transient stratification of density and, presumably of composition of the oil. Some of the effects induced at the nanophase boundary “A” may be very long-lived, apparently governed not by thermodynamic but by kinetic control.<sup>14</sup> E.g., pour point changes, illustrated in Fig. 9, persisted for as long as four months.<sup>55</sup>

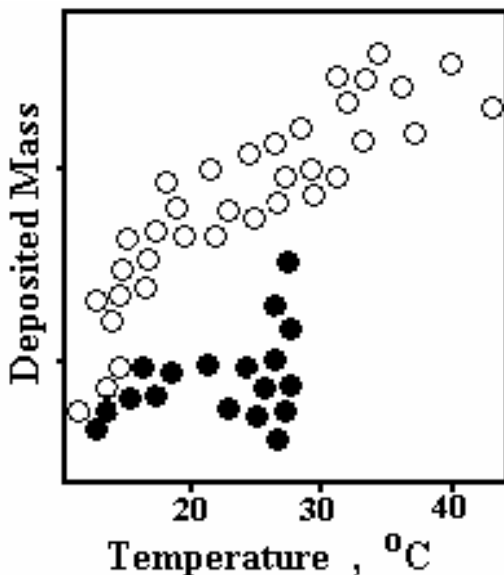


Fig. 10. Kinetically controlled long-lived increase in the mass of deposits from petroleum media, induced at asphaltene nanophase boundary “A” (adapted from Ref. 14).

Another example of long-lived effects is from our recent study of deposits at steel surfaces from petroleum fluids with high asphaltene content (12.3 g/l).<sup>14</sup> Filled symbols in Fig. 10 show deposits from a fluid which in its “thermal history” never has crossed the phase boundary “A”. Open symbols show deposits from a fluid at least once heated above 28–29°C. After that, the increase of deposition, characteristic to higher-temperature nanophase, persisted below the phase boundary (at 12–29°C) for at least one month.

## Nanophase-Resembling Phenomena in Brine-Petroleum Dispersions

The output of a production oil well consists typically of a dispersion of formation water (brine) in a crude oil. Detailed knowledge of the properties of these dispersions is necessary if the behavior and characteristics of multiphase flows are to be predicted correctly.<sup>56</sup> Certainly, reservoir water/oil mixtures are not “nanosystems”. However it appears that from the practical point of view, their properties may resemble those of the above discussed nanocolloids in a sense that morphological behavior of water-in-oil dispersions is characterized by well-structured “phase diagrams”. Moreover, w/o dispersion morphology is known to be controlled by oil’s “indigenous surfactants” including nanocolloidal asphaltenes.<sup>57</sup>

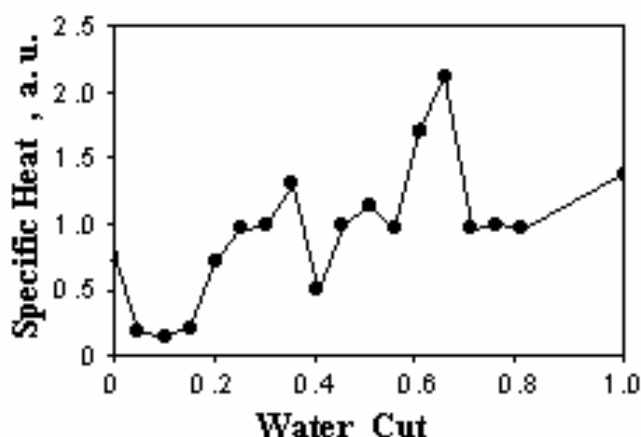


Fig. 11. Specific heat variations due to “*nano-resembling*” changes in phase morphology of native w/o dispersions.

As an example, Fig.11 shows complex variations of an effective specific heat of freshly prepared w/o emulsions at 20–25°C, subjected to microwave heating. The native crude oil was collected a well-head at Korobkovskoye reservoir (Russia), had a density of 832 g/L, contained ca. 1 wt. % asphaltenes, 8 wt. % resins, 2 wt. % waxes; the water was a double distillate with pH≈5.5. Sharp variations of specific heat were attributed to abrupt changes of dispersion’s morphology/phase state, strongly resembling those observed

in model nanoemulsion/microemulsion systems.<sup>58</sup> In particular, “percolation threshold” obviously occurs at water cuts close to 0.2, phenomena at water cuts close to 0.4 most probable are due to emergence of “bicontinuous morphology” while “close packed” phases emerge at water cuts above 0.6.

A complex “*nano-resembling*” phase behavior may be a fairly common property of native brine/oil emulsions, as indicated by our density measurements for mixtures of 12 native (dead) crude oils with their respective oilfield brines.<sup>59</sup>

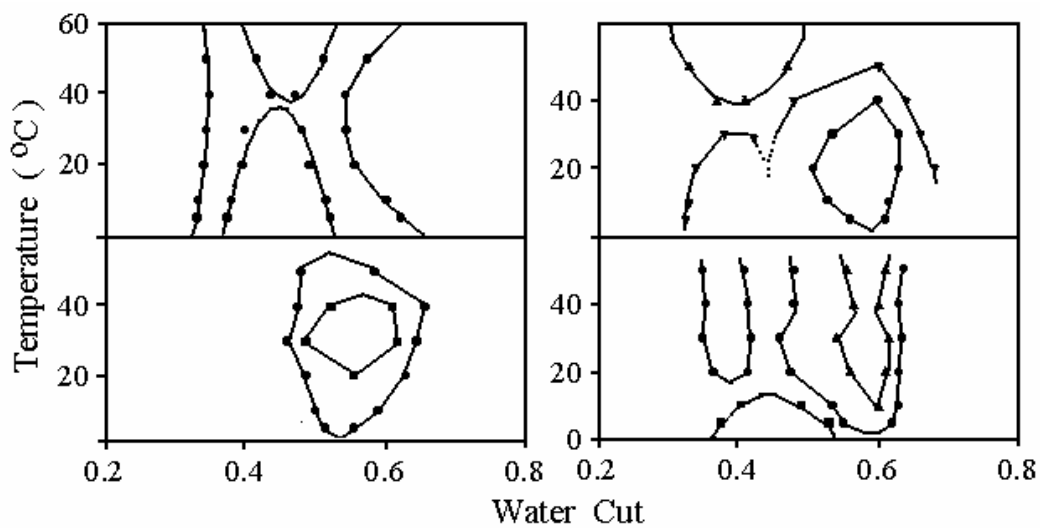


Fig. 12. The complex morphology/phase behavior of native brine/oil dispersions, as revealed by density measurements. (Adapted from Ref. 59).

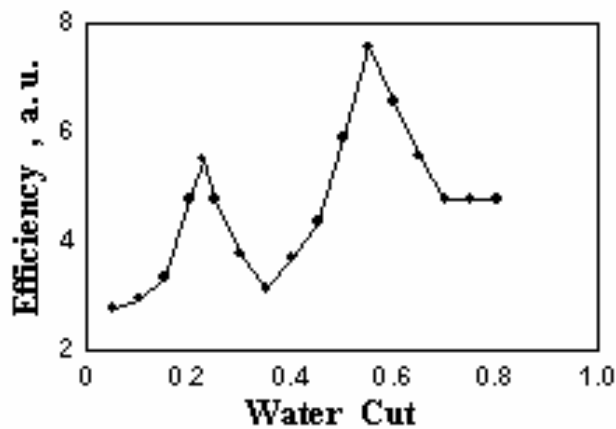


Fig. 13. Efficiency of microwave demulsification of water emulsions in a native crude oil.



Easily detectable nonzero excess (non-ideal) densities for water cuts from 0.4 to 0.6 were regarded as indicative of formation of a dense asphaltene-mediated “middle phase” with an apparent bicontinuous morphology. Fig. 12 shows T–C contours of equal excess (non-ideal) density for four representative w/o dispersions. The shapes of excess density “phase domains” strongly resemble bicontinuous domains of T–C phase diagram for association nanocolloids in Fig. 3.

Of an immediate practical importance is a substantial increase of de-emulsification efficiency (inverse time of the onset of free phase separation) in w/o emulsions with “nanoresembling” morphologies. Fig. 13 shows improved microwave demulsification at specific water cuts attributed to “percolation” and “bicontinuous” phenomena (cf. Fig. 10).

### **What May be Regarded as a Petroleum-Oriented Nanotechnology for Reservoir Engineering?**

Our opinion is that the term “nanotechnology” may be used for any industrial operations which are designed and performed with an understanding of importance of the above discussed complex nanophase diagrams of petroleum fluids. Such technology should include specifically designed processes (employ specifically selected parameters) to purposely avoid/instigate particular phase transformations in petroleum nanocolloids in order to improve (or, at least, not to ruin) the practically important bulk properties of petroleum.

E. g., any lengthy operations in the vicinity of the temperature-defined phase boundary “A” (cf. Fig. 5) should be avoided in view of undesirable increase of viscosity and pour point (cf. Fig. 9), as well as of deposition (cf. Fig. 10) at lower temperatures. On the other hand, intentional storage of petroleum at this phase boundary may be employed to facilitate increased stratification of petroleum light/heavy components (cf. Fig. 9). Hypothetically, mechanical removal of some strata may constitute a low-cost method of improving oil quality.

Approaching a concentration-defined nanophase boundary by blending of crude oils may be the cause of some severe compatibility problems like noticeable viscosity and density peaking (cf. Figs. 6, 7). Alternatively, blending of viscous/dense crudes with native asphaltenes at critical concentration boundaries (e.g. ca. 8 and ca. 20 wt. %) will provide a product (containing ca. 14 wt. % asphaltenes) with greatly improved properties as follows from the data of Fig. 6 and of Fig. 7.

With respect to immediate practical applications, it should be emphasized once more that the above discussed T–C diagrams contain only “the most obvious” nanophase boundaries, reflect our *current knowledge* of structural transformations in petroleum and should be subjected to further investigation.

## Conclusions

At present, practical/commercial examples of “nanotechnology” are almost exclusively from such industrial domains as electronic microchip fabrication, construction of new materials, pharmacology/cosmetics and biomedical sciences. In petroleum industry, “nanotechnologies” still are not considered to be important enough for widespread practical applications, with only exception being refinery processes. In upstream applications, most attention is currently devoted to research in development of new nanostructured “smart fluids” for EOR/IOR and drilling operations.

However, our research shows that now there is enough factual evidence to consider native crude oils themselves 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 underinvestigated) 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”).

Moreover, it appears that such optimization may be required also with respect to handling some macroscopic disperse systems like reservoir water/crude oil dispersions which are “nano-resembling” in a sense that their behavior may be characterized by well-structured morphological/phase diagrams.

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## A TRANSITION FROM MONOMERIC TO ASSOCIATED ASPHALTENES IN CRUDE OIL SOLUTIONS

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### Abstract

It is widely recognized that physicochemical properties of crude oil asphaltenes in processes of refining and processing (i.e. transfer rates in catalyst's porous networks) depend on their association state in a hydrocarbonated environment. For various industrial applications it is necessary to have a detailed knowledge of physico-chemical and structural properties of complex asphaltene colloids, in order to be able to master their behavior. We have studied optical and dielectric properties (molar absorptivity, refractive index, dielectric constant, dielectric loss) in dilute toluene solutions of Russian crude oils and of solid asphaltenes. Sharp inflections in measured concentration dependencies are indicative of changes in association states of asphaltenes. Apparently, asphaltenes may exist in a monomeric state only at concentrations below 1–2 mg/l, while at 60–90 mg/l there is a demixing transition to a colloidal system of asphaltene aggregates. By analysis of correlations between measured properties we expect to obtain quantitative information on dipole moments of asphaltene monomers.

**Keywords:** Crude Oil, Asphaltenes, Associated State.



## 1. Introduction

Properties of crude oil asphaltenes in refining and processing depend on their association state in a hydrocarbon environment. Increased association may result in lower transfer rates in catalyst's porous networks, in higher levels of entrapment of light fractions within asphaltene aggregates. For various industrial applications it is necessary to have a detailed knowledge of complex asphaltene colloids in order to be able to master their behavior. Refractive index ( $RI$ ) represents various important properties of multicomponent crude oils as well of the respective components. Values of  $RI$  can be measured very accurately and are used to correlate density, parachor, and other properties of hydrocarbons with high reliability) (Touba et al., 1997). Information obtained from  $RI$  measurements can be applied for various reservoir engineering calculations.

The  $RI$  of light crude oils is directly measured in conventional refractometers (Yang et al., 2002; Buckley and Wang, 2002; Buckley, 1999). However, direct measurements of the  $RI$  of heavy crudes are unattainable since these liquids are too opaque. In these cases  $RI$  is determined for a series of oil/solvent mixtures and the data are extrapolated (in an assumption of a certain mixing rule) to determine the  $RI$  of the crude oil (Yang et al., 2002; Goual and Firoozabadi, 2002; Taylor et al., 2001). It is usually assumed that a solution of a crude oil behaves as an ideal binary mixture of the components (Taylor et al., 2001; Buckley, 1999; Buckley et al., 1998).

It should be noted that there are no universally accepted mixing rules for interpreting the refractive indices of such presumably ideal mixtures. Most frequent are mixing rules based on the Lorentz–Lorenz additivity rule for specific polarizabilities/refractions of the components (Shoemaker et al., 1996). In notations of Buckley and Wang, 2002; Buckley et al., 1998 and Wattana et al., 2005 :

$$F(RI)_{\text{mixture}} = F(RI)_{\text{oil}}\phi_{\text{oil}} + F(RI)_{\text{solvent}}(1 - \phi_{\text{oil}}) \quad (1)$$

where  $F(RI) = (n^2 - 1)/(n^2 + 2)$  and  $\phi_{oil}$  is a volume fraction of a crude oil.

Obviously, the assumption of “an ideal mixture” is valid only provided there are no compositional changes in the complex petroleum “component”. Indeed, noticeable deviations from simple mixing rules have been observed when asphaltenes flocculate and commence to precipitate out of a crude oil solution (Taylor et al., 2001; Buckley, 1999; Buckley et al., 1998). However, presently there is no experimental evidence whether the  $RI$  may be sensitive to specific aggregation phenomena of asphaltenes which remain suspended in solution.

Conventionally, “critical micellisation concentrations” (“CMCs”) of asphaltenes in solutions were revealed by various experimental techniques (Sheu, 1996). The “CMC” values for asphaltenes in toluene range from  $\approx 2$  g/l (Castillo et al., 1998) to  $\approx 5$  g/l (Andersen and Christensen, 2000). Over the past years it became clear that conventional “CMCs” are not signatures of primary monomer-micelle transformations, but reflect some secondary processes of aggregation into complex colloid structures. Indeed, it has been experimentally proven that distinct aggregation stages of asphaltenes are observed at concentrations well below the conventionally reported “CMCs”. E.g., in our previous publications (Evdokimov et al., 2003a,b,c) we have presented experimental data which indicate that aggregation of asphaltene monomers commences at concentrations as low as 2–5 mg/l, while massive formation of asphaltene “molecular nanoclusters” is observed at concentrations  $\approx 90$ –150 mg/l. Aggregation processes were no longer detected at asphaltene concentrations above 500–700 mg/l, indicative of some “steady” state of asphaltene aggregates in more concentrated solutions (up to 1.6 g/l).

In this paper, we report  $RI$  measurements in toluene solutions of a Tatarstan crude oil. Results for concentrated solutions (with asphaltenes in a “steady” aggregated state) are in agreement with ideal mixing rules. An “anomalous” behavior of  $RI$  in dilute solutions is attributed to de-aggregation of asphaltenes. The  $RI$  data

are supplemented by some new results on optical absorptivity in dilute crude oil solutions.

## 2. Results and Discussion

### 2.1. Samples and Equipment

The virgin crude oils were collected from well-heads at Romashkinskoye reservoir (Tatarstan). Crude #1, employed in *RI* experiments, had a density of 875.6 g/l, contained 3.6 wt. % asphaltenes. For comparative absorptivity measurements we used crude #2 (895 g/l, 3.5 wt. % asphaltenes) and solid n-heptane asphaltenes precipitated from a blend of Tatarstan crude oils. The samples were stored in the dark, in air. As a solvent, a “chemically pure” grade toluene was used.

The *RI* measurements were performed in an Abbe-type refractometer IRF-454-B2M (KOMZ, Kazan, Russia). For toluene at 20°C the measured *RI* was 1.4967, close to the value of 1.4969 quoted by the producer. The effects of crude oil concentration in toluene on optical absorption have been studied in a spectrometer (Evdokimov et al., 2003a,b), equipped with a set of narrow-band light filters (KFK-2 Photocolorimeter). The UV/Vis absorption spectra have been measured in a FLUORAT®-02-PANORAMA analyzer equipped with a high-pressure xenon arc lamp. All measurements were performed at 20°C and at ambient pressure.

### 2.2. Refractive Index in Concentrated Solutions

Figure 1 shows the results of *RI* measurements in oil/toluene solutions for a wide range of oil concentrations, from 0.011 to 50.25 vol. % of oil (note a log scale). For concentrated solutions ( $\geq 1$  vol. % oil) each data point was obtained with a new sample, prepared by mixing the required volume of the crude oil with  $\approx 10$  ml of toluene. No effects of the manner of mixing (e.g., introducing oil into toluene or vice versa) were observed. Owing to the dark and opaque nature of our crude oil, it was not possible to measure the *RI* of solutions with  $>50$  % of oil. In studies of such opaque crudes (or bitumen) there is a well-established technique for estimation of

the  $RI_{oil}$  of a “pure crude” (Goual and Firoozabadi, 2002; Taylor et al., 2001; Buckley, 1999; Buckley et al., 1998). Namely,  $RI_{oil}$  is found by an extrapolation of the experimental data to a volume fraction of 100 %, in accordance with mixing rules. A best fit of Eq. (1) to our data points (coefficient of determination  $R^2 = 0.995$ ), shown by a solid line in Figure 1, provided a value of  $RI_{oil} = 1.4785$  for the studied crude. In a number of publications it has been stated that  $RI$  correlates with density and with an asphaltene content of a crude oil. We have compared the  $RI$  of our oil with  $RI$ s for 45 crudes of various origin (Yang et al., 2002; Buckley and Wang, 2002; Goual and Firoozabadi, 2002; Buckley et al., 1998). Our results appear to be in a reasonable agreement with previously published data. There is good overall correlation of  $RI$  with oil’s density ( $R^2 = 0.76$ ), though a correlation of  $RI$  with asphaltene content is much worse ( $R^2 = 0.29$ ).

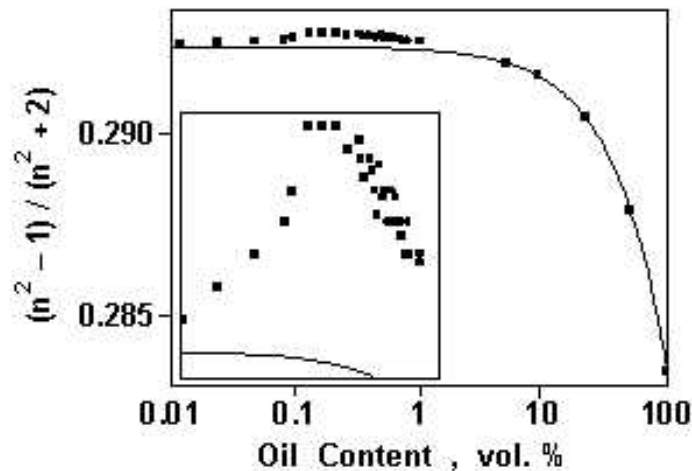


Fig. 1. Refractive index for a wide range of oil concentrations in toluene. Solid line - the ideal mixing rule (Eq. 1).

### 2.3. “History Effects” in Dilute Oil Solutions

Studies of solutions with oil content below  $\approx 1$  vol. % revealed strong effects of the “history of oil dissolution in toluene”. When the above technique of sample preparation was employed, the results have shown poorly controlled dependencies on such factors as

the manner of introducing one component into the other (e.g. from a vial or from a pipette), the manner of stirring the mixture (by hand, in a mechanical stirrer), experimental time intervals (between mixing, stirring and measurements), thermal history of a sample during these intervals, etc. The most pronounced “history effects” were in solution with oil contents of  $\approx 0.2\text{--}0.5$  vol. %. The respective asphaltene concentrations of about 60–150 mg/l correspond to conditions of the expected phenomena of de-aggregation of asphaltenes (cf. Introduction). Hence, the “history effects” may be attributed to the complex kinetics of asphaltene dissolution which is known to vary significantly depending on the physical state of the system (Hammami et al., 2000; Cosultchi et al., 2003). We agree with Cosultchi et al., 2003 that the differences between the reported data for crude oil and asphaltene solutions may be often related to non-standard times and procedures of dissolution. In most of the experimental procedures, the time to reach the dissolution of the solid matrix of aggregated asphaltenes and the equilibrium of the solution is mentioned only as a minor factor.

To obtain consistent concentration dependencies of  $RI$  and to reduce the scatter of results, we have employed a procedure of sample preparation used in our previous studies (Evdokimov et al., 2003a,b,c). Operationally, this technique is “titration of toluene with oil”. Crude oil is introduced into a large volume of toluene by minute quantities, to facilitate quick redistribution of maltenes over the sample so that asphaltene aggregates are almost immediately subjected to the environment of solvent molecules. In each experiment with dilute solutions a concentration of a single sample is increased step-wise, at equal time intervals (0.5–10 min.), by means of consecutive additions to toluene (100 ml) of calibrated oil drops ( $m_{drop}=10.3\pm 0.3$  mg). Hence, the concentration increments in solutions are 0.012 vol. % for the crude oil (3.7 mg/l for oil’s asphaltenes). At the beginning of each time interval a solution is gently stirred with a glass rod, at the end –  $RI$  measurements are performed. The results revealed consistent dependence on the rate of concentration increase above  $\approx 0.2$  vol. % of oil per hour. There were

practically no time effects at slower rates, hence such data sets were considered to be representative of the “equilibrium” states of solutions. In particular, the *RI* results reported in this paper were obtained with a rate of concentration increase equal to 0.14 vol. % of oil per hour.

#### **2.4. Break-up of Ideal Mixing Rules in Dilute Solutions**

It is clear from Figure 1 that in dilute solutions the data show “anomalous” deviations of *RI* from the simple ideal mixing rule (solid line in Fig. 1). Two most obvious “anomalies” are: 1) the “concentrated” approximation does not terminate at  $(n^2-1)/(n^2+2)$  for pure solvent; 2) the measured concentration dependencies are non-monotonous, with an extremum at oil content of about 0.2 vol. % and a sharp drop of *RI* at lower contents. Such “anomalous” behavior of *RI* may seem highly unusual. However, a literature survey reveals a number of publications, containing experimental results which, subjected to a proper analysis, show specific features which may be attributed to the above mentioned “anomalies”. Apparently these features have not been noticed by the authors. E.g., Goual and Firoozabadi, 2002 have measured *RI* vs. wt. % in toluene of a Hamaca heavy crude. By fitting a straight line to the respective graph, they found extrapolated *RI* of “pure crude”. However, in the graph they do not plot data for pure toluene, while extrapolations to zero concentrations result in inconsistency of extrapolated *RI* of toluene (1.4987). If the reference value of *RI* for toluene (1.4969) is included in the data set, the results of Goual and Firoozabadi, 2002 show an obvious “anomalous” drop of *RI* at oil concentrations below 1 wt. %, qualitatively similar to that observed in our experiments. Taking into account earlier evidence of peculiar behavior of other properties in dilute oil solutions (cf. Introduction), we ascribe the observed “anomalies” of *RI* to phenomena of de-aggregation of oil asphaltenes. Hence, in the following we refer to the respective asphaltene concentrations in oil-toluene solutions.

Figure 2 presents a comparison of the “equilibrium” concentration dependence of  $RI$  (filled symbols) with linear dependencies (solid lines) based on the Lorentz–Lorenz ideal mixing rule (Eq. 1). Solid line “1” represents the  $RI$  behavior in an ideal binary mixture of toluene ( $RI=1.4969$ ) with the “steady state” crude characterized by a constant  $RI_{oil} = 1.4785$ , the value estimated in concentrated solutions, with asphaltenes remaining in an aggregated state.

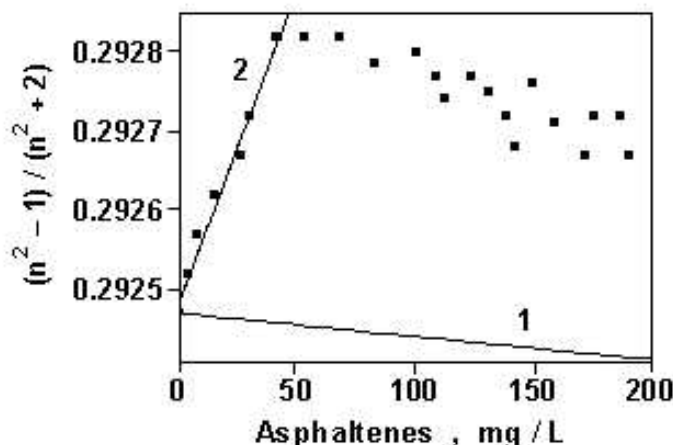


Fig. 2.  $RI$  behavior in dilute solutions. Solid lines – ideal mixing rule with different  $RI$ s of the crude.

Deviations of experimental data from “ideal” values (presumably due to a change of the crude’s properties caused by de-aggregation of asphaltenes) become noticeable at asphaltene concentrations of  $\sim 540\text{--}600$  mg/l, i.e. in the range observed in our previous studies (cf. Introduction). “Non-ideality” of experimental results increases with dilution and an extrapolation of the experimental concentration dependence does not terminate at the  $F(RI)$  of pure toluene, as expected from Eq. (1). However, below asphaltene concentrations of  $\sim 63\text{--}79$  mg/l experimental data again form an almost linear succession with the origin at the  $F(RI)$  of toluene. Hence, these solutions, at least formally, may be regarded as “binary”, where the oil component in a modified “steady state” (containing de-aggregated asphaltenes). Solid line “2” in Figure 2 is the best linear fit ( $R^2=0.980$ ) to the data for asphaltene concentrations

<47 mg/l. On the basis of this linear fit it seemed reasonable to evaluate a modified  $RI_{oil}$  from a binary mixing rule (Eq. 1). Surprisingly, such evaluation resulted in a very high value of  $RI_{oil} = 2.0121$ , close to the refractive indices of amorphous carbon and graphite (Silva, 2001).

## **2.5. Nature of Aggregation Effects on Refractive Index**

Literature analysis shows that, previously, aggregation effects on  $RI$  of non-precipitating petroleum fluids have never been registered experimentally, and even the possibility of such effects has never been discussed. Hence, a nature of the observed  $RI$  anomalies requires an explanation. Studies of simple binary mixtures have shown that  $RI$  may be affected by variations of molar volumes/densities.  $RI$  of a fluid is assumed to be directly related to its density (Gray and Gubbins, 1984). If asphaltene de-aggregation is regarded as a dissolution, one may expect a smaller density of a crude with de-aggregated asphaltenes and a decrease of  $RI$  in dilute solutions, i.e. the effect qualitatively opposite to that in our experiments. On the other hand, some non-ideal solutions exhibit negative excess volume of mixing which may have been expected to be related to positive excess  $RI$ . In our experiments deviations of  $RI$  from ideal mixing rules are  $\sim 0.1\%$ , typical for excess  $RI$  in binary hydrocarbon mixtures (Fermeglia and Torriano, 1999; Resa et al., 2004). However, excess volume effects are the largest in solutions with volume fractions of  $\sim 0.5$ , while in our experiments maximum excess  $RI$  is at volume fraction of oil close to  $2 \cdot 10^{-3}$  (cf. Fig. 1). Moreover, a causative relationship between excess volume and excess  $RI$  never has been proven either theoretically or experimentally (cf. Fermeglia and Torriano, 1999 and of Resa et al., 2004).

For the above reasons, we conclude that density mechanisms are not responsible for the observed  $RI$  anomalies. Comparative studies of various properties of dilute solutions indicate that non-ideal  $RI$  behavior may be ascribed to optical dispersion effects, ac-



counted for by Kramers–Kronig relations (Jackson, 1999). It should be noted that dispersion effects are neglected in simple *RI* mixing rules.

## 2.6. Correlation of *RI* with Optical Absorptivity

*RI* of dilute solutions is known (Gray and Gubbins, 1984) to be affected mainly by: 1) changes in molecular polarizability of a solute (due to variations in intermolecular interactions), 2) changes in the number of solute molecules per unit volume (solute concentration). A trivial concentration factor may be excluded by calculation of a “*RI* increment”  $dn/dc$ , which is directly proportional to the molecular polarizability  $\alpha$  :

$$\alpha = (M / 2\pi N_A)(dn/dc) \quad (2)$$

where  $M$  is the molar mass,  $N_A$  is the Avogadro number and  $c$  is the solute concentration.

The left part of Figure 3 shows the behavior of *RI* increment in the studied solutions. At higher concentrations  $dn/dc$  is fairly constant and negative (i.e. polarizability of asphaltenes is smaller than that of toluene). In more dilute solutions  $dn/dc$  becomes positive and at 2–8 mg/l of asphaltenes its absolute value increases by a factor of about 12. According to Eq. (2), this may have been interpreted as a 12-fold polarizability increase of asphaltene monomers as compared to molecules in asphaltene aggregates. However, there is strong theoretical and experimental evidence (Jensen et al., 2002) that electronic molecular polarizability (which determines a magnitude of *RI* for visible light wavelengths) is almost unchanged by the intermolecular association. On the other hand, the behavior of  $dn/dc$  appears to be qualitatively similar to the behavior of optical absorptivity at 670 nm (shown in the right part of the Figure).

As stated above, we attribute the observed changes of the optical properties to association/dissociation of asphaltene molecules in the crude oil. This attribution is further supported by virtual co-

incidence of characteristic concentrations in both graphs of Figure 3. Namely, both  $dn/dc$  and absorptivity exhibit a high peak at  $\sim 2\text{--}8$  mg/l of asphaltenes (and show a tendency of decreasing at lower concentrations). Two secondary maxima are observed at  $25\text{--}30$  and at  $55\text{--}65$  mg/l, while above  $80\text{--}90$  mg/l saturation levels are reached.

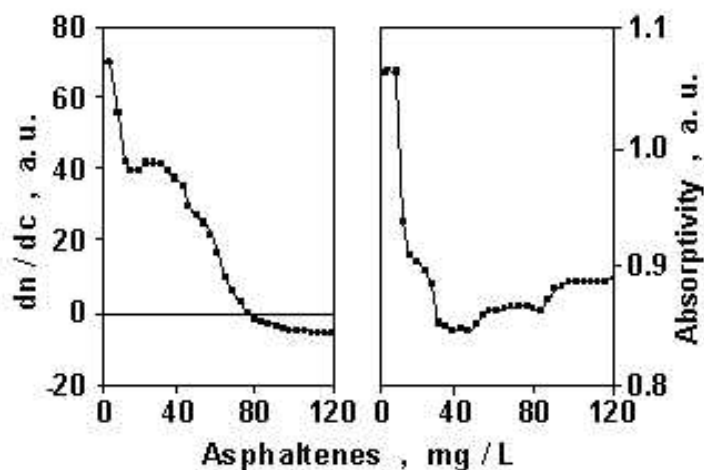


Fig. 3.  $Rl$  increment (*left*) and optical absorptivity (*right*) in dilute solutions of crude #1.

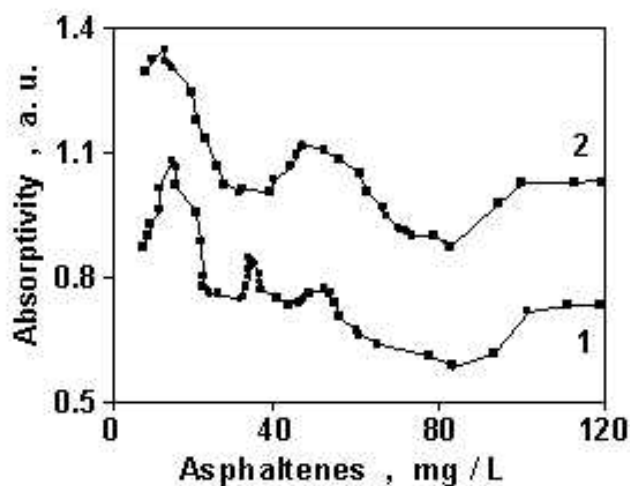


Fig. 4. Optical absorptivity in dilute solutions of crude #2 (1) and of solid asphaltenes (2).

Moreover, the above characteristic concentrations are close to those observed in our earlier studies of asphaltene-containing solu-

tions. As an example, Figure 4 shows the behavior of absorptivity at 670 nm in toluene solutions of crude oil #2 (lower curve) and of solid asphaltenes (upper curve). The data are adapted from Evdokimov et al., 2003b.

Interrelationship between optical absorption and refractive index is implied in well-known Kramers–Kronig (K–K) equations. However, this interrelationship is not immediately proved by similarity of the dependencies in Figure 3, measured at fixed wavelengths. The exact K–K formula (Sheik-Bahae, 2004) requires the knowledge of absorptivity  $\kappa$  in the entire range of wave frequencies :

$$n(\omega) = 1 + \frac{c}{\pi} \int_0^{\infty} \frac{\kappa(\Omega)}{\Omega^2 - \omega^2} d\Omega \quad (3)$$

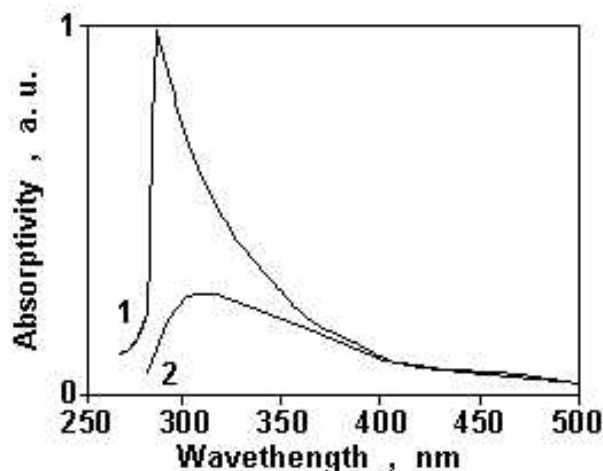


Fig. 5. UV/Vis absorptivity spectra in highly diluted (1) and more concentrated (2) oil solutions.

Figure 5 shows some preliminary experimental data on UV/Vis absorptivity spectra in solutions of crude oil #1, measured at asphaltene concentrations of 3.7 mg/l (curve 1) and >320 mg/l (curve 2). It is clearly seen that a transition from associated to deaggregated asphaltenes is accompanied by an emergence of a strong resonance band, peaked at ~285 nm.

UV/Vis absorptivity of crude oils is known to be governed by  $\pi$ - $\pi^*$  transitions in the conjugated aromatic chromophores of asphaltenes (cf. references in Evdokimov et al., 2003a,b). By analogy with other aromatic compounds (Birks, 1970) we may attribute a resonance band (285 nm) to the  $S_0(1A_g) \rightarrow S_2(1B_{3u})$  transition. The lower energy transition  $S_0(1A_g) \rightarrow S_1(1B_{1u})$  may be assigned to a low-intensity broad band centered at  $\sim 580$ – $600$  nm and clearly revealed only in derivative spectra.

Numerical evaluation of K–K formula was performed for both spectra of Figure 4. Even if only this limited frequency range is considered, evaluation shows that K–K effects may account for a large increase of  $RI_{oil}$  – from  $\approx 1.47$  in concentrated solutions to  $\approx 1.72$  at high dilutions. It may be expected that with inclusion of short-UV and IR spectral ranges, K–K effects would be found fully responsible for a “surprisingly high” experimental value of  $RI_{oil} = 2.0121$  (cf. Section 2.4).

### 3. Conclusions

Dilute asphaltene-containing solutions in toluene (asphaltene concentrations below 150–200 mg/l) show peculiar non-ideal behavior of refractive index and UV/Vis absorptivity. Sharp inflections in experimental concentration dependencies are indicative of changes in association states of asphaltenes.

Apparently, asphaltenes may exist in a monomeric state only at concentrations below 1–2 mg/l. A transition from monomeric to associated asphaltenes is accompanied by a notable increase of a resonant absorption band at  $\sim 285$  nm. Since the emerging absorption band is located in a wavelength region shorter than the probe wavelength for  $RI$ , it creates a positive refractive index change, according to the Kramers–Kronig relations.

We believe that the present study may provide further insight into the formation, stability and optical properties of molecular aggregation in crude oils, as well as in other asphaltene-containing industrial fluids.

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## Glossary of Some Technical Terms

### A

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Abbe-type refractometer	рефрактометр типа Аббе, оптическая схема которого основана на принципе полного внутреннего отражения
abrupt	[q' brApt] <i>прил.</i> внезапный, резкий
absorption	[qb' z0:pS(q)n] <i>сущ.</i> поглощение
absorption band	[qb' z0:pS(q)n bXnd] полоса поглощения
absorptivity	["x bz0:p' tlvltl] <i>сущ.</i> коэффициент поглощения, коэффициент экстинкции; molar~ молярный коэффициент экстинкции
acquire	[q' kwalq] <i>гл.</i> приобретать
AFM	<i>аббр.</i> atomic force microscope – атомный силовой микроскоп
aggregated state	['x grlgeltqd] агрегированное состояние; “steady”~ стабильное, равновесное состояние агрегирующей системы
alteration	["Lltq' relS(q)n] <i>сущ.</i> изменение, перемена
apparently	[q' pXrqntll] <i>нареч.</i> очевидно, явно
association colloids	[q"sqVsl' elS(q)n] ассоциативные коллоиды
association state	ассоциированное состояние
assumption	[q' sAmpS(q)n] <i>сущ.</i> предположение

### B

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bicontinuous	[blkqn' tlnjVqs] <i>прил.</i> биконтинуальный
binder	['balndq] <i>сущ.</i> крепитель, связующее вещество, пескоукрепитель
blending	['blendIN] <i>сущ.</i> смешивание
blood clot	[blAd klot] тромб, сгусток крови
boundary	['baVnd(q)rl] <i>сущ.</i> граница, контур
brine	[braIn] <i>сущ.</i> рассол, пластовая минерализованная вода
bulk	[bAlk] <i>прил.</i> объемный
buoyancy	['b0lqnsI] <i>сущ.</i> плавучесть

**C**

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СМС	<i>аббр.</i> critical micellization concentration – критическая концентрация мицеллообразования, ККМ
coincidence	[kqV'lnsld(q)ns] <i>сущ.</i> совпадение
compatibility	[kqm"pxtq'bliltl] <i>сущ.</i> совместимость
consecutive	[kqn'sqkjvtlv] <i>прил.</i> последующий
consistent	[kqn'slst(q)nt] <i>прил.</i> сообразный, соответствующий, подходящий

**D**

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dead crude	[ded krHd] «мертвая», «сырая» дегазированная нефть
decisive	[dl'salslv] <i>прил.</i> имеющий решающее значение
demixing systems	несмешивающиеся, расслаивающиеся системы
derivative	[dl'rlvqtlv] <i>сущ.</i> производная (функции); ~spectrum спектр производной
determination	[dl"tE:ml'eIS(q)n] <i>сущ.</i> установление (границ и т.п.), определенность; coefficient of~ коэффициент множественной регрессии
dielectric loss	["dall'lektrik los] диэлектрические потери
dilute	["dal'lj)u:t] <i>гл.</i> растворять, разбавлять; <i>прил.</i> разбавленный
distinct	[dls'tIN(k)t] <i>прил.</i> отличающийся, отчетливый, различный
drag reduction	[drxg rI'dAKS(q)n] снижение сил трения

**E**

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emphasize	['emfqsalz] <i>гл.</i> выделять, особо обращать внимание, подчеркивать
entrapment	[In'trxpmqnt] <i>сущ.</i> ловушка, захватывание, улавливание; ~of light fractions захватывание и удержание легких фракций нефти



EOR	<i>аббр.</i> enhanced oil recovery – методы увеличения нефтеотдачи, МУН
evidence	[ˈeɪd(ə)ns] <i>сущ.</i> основание, факт, свидетельство, очевидность
evolve	[ɪˈvɒlʋ] <i>гл.</i> развиваться, эволюционировать, развертываться (о теории)
excess volume	[ˈɛksɛs ˈvɒljʊ:m] избыточный объем

## F

facilitate	[fəˈsɪlɪteɪt] <i>гл.</i> облегчать, способствовать, оказывать содействие
fluorescence	[flʋ(ə)ˈres(ə)ns] <i>сущ.</i> флюоресценция
foreseeable	[fɔːˈsi:jəb(ə)l] <i>прил.</i> предвидимый заранее, предсказуемый, обозримый (в будущем)
forthcoming	[ˈfɔːtɪˈkʌmɪŋ] <i>прил.</i> предстоящий, грядущий, ожидаемый

## G

gyration	[Gaɪˈreɪʃ(ə)n] <i>сущ.</i> вращение
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## H

heat capacity	[hi:t kəˈpæsɪtɪ] теплоемкость
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## I

immiscibility	[ɪˈmɪsɪˈbɪlɪtɪ] <i>сущ.</i> расслоение (фаз), не-смешиваемость
increment	[ɪˈnkrɪmənt] <i>сущ.</i> приращение, прирост, прибавляемая величина
indigenous	[ɪnˈdɪʒ(ə)nəs] <i>прил.</i> местный, туземный, собственный
inflection	[ɪnˈflekʃ(ə)n] <i>сущ.</i> перегиб (кривой), изгиб, излом
inherent	[ɪnˈhɪ(ə)rənt] <i>прил.</i> внутренний (о свойстве), присущий, свойственный
inner	[ˈɪnə] <i>прил.</i> внутренний
instigate	[ɪˈnstɪgeɪt] <i>гл.</i> побуждать, провоцировать, инициировать

intentional	[In'tenS(q)nql] <i>прил.</i> преднамеренный, умышленный
interchangeably	['Intq'tSelnGqblI] <i>нареч.</i> взаимозаменяемо
interpenetrate	['Intq'penItrelt] <i>гл.</i> взаимно проникать, наполнять собою
intrinsic	[In'trInslk] <i>прил.</i> подлинный, присущий
IOR	<i>аббр.</i> improved oil recovery – увеличение нефтеотдачи
IR	<i>аббр.</i> infrared – инфракрасный

## L

log–log plot	график в двойных логарифмических координатах
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## M

mechanosynthesis	[ml'kxnq'sInTIsIs] <i>сущ.</i> механосинтез
merely	['mlqII] <i>нареч.</i> только, попросту, всего лишь, всего-навсего
micellization	[ml'selal'zelS(q)n] <i>сущ.</i> мицеллообразование

## N

narrow-band	['nXrqV bXnd] <i>прил.</i> узкополосный; ~light filters узкополосные светофильтры
neglect	[nl'glekt] <i>гл.</i> пренебрегать, игнорировать, не учитывать
NMR	<i>аббр.</i> nuclear magnetic resonance – ядерный магнитный резонанс, ЯМР
NMR relaxation	['rIIXk'selS(q)n] ЯМР-релаксация, времена релаксации сигнала ЯМР
nonionic	['nOnal'OnIk] <i>прил.</i> неионогенный

## O

opaque	[qV'pqIk] <i>прил.</i> непрозрачный, мутный
overlook	['qVvq'IVk] <i>гл.</i> игнорировать, пренебрегать, пропускать, просматривать

**P**

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parachor	["pʰrɔq'k0:(r)] <i>сущ.</i> парахор (от пара... и <i>греч.</i> chōros – пространство), эмпирическая величина, отражающая некоторые физические свойства индивидуального вещества (главным образом неассоциированных органических жидкостей)
peculiar	[pɪ'kʲɪHɪɪq] <i>прил.</i> особенный, особый, специфический
percolation threshold	["pɛ:kq'leɪs(q)n 'TɾeS(h)qVɪd] порог перколяции
phase behavior	[felz bl'helvjɔ] фазовое поведение; rich~ богатое фазовое многообразие
polarizability	["pɔvlqɾalɔq'blɪɪtɪ] <i>сущ.</i> поляризуемость
polymorphism	["p0ɪɪ'm0:flzm] <i>сущ.</i> полиморфизм
pour point	[p0: p0ɪnt] температура застывания
precipitation	[prɪ'sɪplɪteɪs(q)n] <i>сущ.</i> выделение, образование твердой фазы в среде жидкой фазы; <i>ср.</i> deposition – выпадение, отложение
precise	[prɪ'sals] <i>прил.</i> определенный, прецизионный, точный
precursor	[prɪ'kɛ:sq] <i>сущ.</i> предшественник, исходное вещество (материал, реагент)
predominantly	[prɪ'd0mɪnɔntɪɪ] <i>нареч.</i> главным образом, преимущественно
preliminary	[prɪ'ɪɪmɪn(q)rɪ] <i>прил.</i> предварительный
preserve	[prɪ'zq:v] <i>гл.</i> сохранять, предохранять
presumable	[prɪ'zju:mɔb(q)ɪ] <i>прил.</i> возможный, предполагаемый

**R**

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reentrant	[rɪ'entrɔnt] <i>прил.</i> возвратный (о фазовом переходе)
refraction	[rɪ'frɔks(q)n] <i>сущ.</i> рефракция
refractive index	[rɪ'frɔktɪv 'ɪndeks] показатель преломления

resemble	[rɪ'zemb(q)l] <i>гл.</i> Походить, иметь сходство, напоминать
reveal	[rɪ'vɛl] <i>гл.</i> выявлять, обнаруживать
RT	<i>аббр.</i> room temperature – комнатная температура

## S

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SANS	<i>аббр.</i> small-angle neutron scattering – малоугловое рассеяние нейтронов
saturation	['sætʃə'reɪʃ(q)ən] <i>сущ.</i> насыщение
scatter	['skætə] <i>гл.</i> разбрасывать, рассеивать, рассеиваться
shrinking	['ʃrɪŋkɪŋ] <i>сущ.</i> усадка, сжатие, сокращение объема
solidify	['sɒlɪfaɪ] <i>гл.</i> застывать, затвердевать, кристаллизоваться
solubility limit	['sɒljə'bɪlɪtɪ 'lɪmɪt] предел растворимости
stirred	['stɪəd] <i>прил.</i> взбалмученный, перемешанный
STM	<i>аббр.</i> scanning tunneling microscope – сканирующий туннельный микроскоп
subtle	['sʌtl] <i>прил.</i> тонкий, нежный, трудноуловимый
substantial	[sqb'stʃʌnʃ(q)l] <i>прил.</i> значительный, крепкий, прочный, существенный
succession	[sqk'seʃ(q)ən] <i>сущ.</i> последовательность, преемственность, ряд
supramolecular chemistry	['s(j)ʌprəmq'lekjəlkə 'kɛmɪstrɪ] супрамолекулярная химия
surfactant	[sɛ:'fʌkt(q)ənt] <i>сущ.</i> поверхностно-активное вещество, ПАВ

## T

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terminate	['tɛ:mɪneɪt] <i>гл.</i> завершать(ся), истекать
tiny	['taɪnɪ] <i>прил.</i> очень маленький, крошечный, миниатюрный

transfer rate	['trʌnsfE: reIt] <i>хим.</i> скорость массообмена, коэффициент массообмена; ~in catalysts porous networks скорость массообмена в пористых катализаторах
transient	['trʌnzIqnt] <i>прил.</i> переменный, переходный, нестационарный
<b>U</b>	
unattainable	['ʌnq'telInqʌ(q)I] <i>прил.</i> недостижимый, неосуществимый
unfavorable	[ʌn'felv(q)rʌbl] <i>прил.</i> неблагоприятный, отрицательный
UV	<i>аббр.</i> ultra violet – ультрафиолетовый, УФ; short~ ближний УФ, коротковолновый УФ
<b>V</b>	
vial	[v'ail] <i>сущ.</i> склянка, чаша
vice versa	['vals(I)'vE:sq] <i>нареч.</i> наоборот, обратно
vicinity	[vI'sIntI] <i>сущ.</i> близость, соседство, окружающее пространство
Vis	<i>аббр.</i> visible – видимый
<b>W</b>	
wettability	['wetq'bIItI] <i>сущ.</i> смачиваемость
<b>Z</b>	
zeolite	['zJqvlait] <i>сущ.</i> цеолит

*Учебное пособие*

**ЕВДОКИМОВ Игорь Николаевич  
ЛОСЕВ Александр Павлович**

Комплект учебных пособий  
по программе магистерской подготовки  
**«НЕФТЕГАЗОВЫЕ НАНОТЕХНОЛОГИИ ДЛЯ  
РАЗРАБОТКИ И ЭКСПЛУАТАЦИИ МЕСТОРОЖДЕНИЙ»**

**ЧАСТЬ 2**

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