

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Density Anomalies in Crude Oil Blends Reflect Multiple Equilibrium States of Asphaltene Colloidal Aggregates

Igor N. Evdokimov, Aleksey A. Fesan and
Aleksandr P. Losev

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.71813>

Abstract

Density measurements revealed anomalies of nonideality (maxima of excess density) at some compositions in binary blends of light and heavy crude oils from diverse origins. By IR absorption measurements, density anomalies were attributed to increased contents of suspended asphaltene colloidal-sized particles/aggregates in the blends. By comparison with a database of world's native crude oils, it was concluded that density anomalies may correspond to different equilibrium structural states of asphaltene colloids that occur at several specific asphaltene contents, apparently common for petroleum media of any origin.

Keywords: crude oil blends, nonideality, excess density, volumetric shrinkage, asphaltene aggregates, structural transformations

1. Introduction

A common approach frequently used in the petroleum industry for either transportation or refining purposes is blending of heavy crude oils with lighter ones [1–5]. Therefore, studying the effect of blending on the physical and chemical properties of produced petroleum fluids has become increasingly important. It was soon realized that blends of multicomponent crude oils are nonideal systems, for which ideal “mixing rules” developed for binary mixtures of pure chemical substances [6–8] are not applicable. For example, in ideal mixtures, both mass and volume are additive parameters and the total volume of the binary blend V_{ideal} is equal to the sum of the volumes of the components:

$$V_{ideal} = V_1 + V_2 \quad (1)$$

Consequently, the density of the ideal binary blend:

$$\rho_{ideal} = \rho_1 \phi_1 + \rho_2 \phi_2, \quad (2)$$

where ϕ_1 and ϕ_2 are volume fractions of the components.

In binary blends of crude oils, deviations of the measured volume V_{blend} and density ρ_{blend} from the above ideal mixing rules are usually characterized [9–14] by such interrelated dimensionless quantities as “volumetric shrinkage”:

$$S = \frac{V_{ideal} - V_{blend}}{V_{ideal}} \quad (3)$$

and “excess density”:

$$\rho_{ex} = \frac{\rho_{blend} - \rho_{ideal}}{\rho_{ideal}} \quad (4)$$

where, by definition:

$$\rho_{ex} = S/(1 - S) \quad (5)$$

Empirical testing of crude oil blends by a number of major oil companies has produced vast amounts of volumetric shrinkage and excess density data [10]. An API Measurement Committee correlated the data collected over several decades and in 1996 released equations, published in the API Manual of Petroleum Measurement Standards [15], which served as the accepted industry standard for over 20 years. In particular, the standard equation for volumetric shrinkage (in % units):

$$S = 2.69 \times 10^4 C (100 - C)^{0.819} \left(\frac{1}{dL} - \frac{1}{dH} \right)^{2.28} \quad (6)$$

where C is the concentration, in liquid volume % of the lighter oil in the blend (i.e., $C = 100 \phi$); dL and dH are the densities (in kg/m^3) of lighter and heavier oil, respectively.

The authors of Eq. (6) made no attempts to account for the presence of any specific molecular fractions in the blended oils. Consequently, for all blends, the $S(C)$ dependencies are similar dome-shaped functions peaked at $C \approx 55\%$, while the densities of particular oils affect only the magnitude of this peak. In spite of its over-simplified nature, Eq. (6) is still frequently employed by various research groups for approximating experimental data [9, 14, 16, 17].

More recent tendencies in discussing the measured nonideal properties of crude oil blends are attempts to reveal specific molecular substances responsible for nonideality. The most discussed nonideal petroleum constituents in crude oil blends are asphaltenes [18–27]. In particular, it was suggested that volumetric shrinkage/excess density may result from an increase in the equilibrium content of asphaltene colloidal aggregates dispersed in the blend, which occur at some specific asphaltene contents [23–27].

In this work, we describe a study of the nonideality phenomena in three blends of native crude oils of diverse origin by experimental density measurements. This study is supplemented by IR optical absorption experiments, which provide the direct proof of the crucial role of asphaltene aggregation.

2. Diversity of studied native crude oils: preparation of oil blends

To ensure that the observed nonideal effects are not specific for particular crude oils, in the described series of experiments, we employed blends of light and heavy native crude oils collected from the well heads at several Russian oilfields geographically separated by thousands of kilometers (cf. **Table 1**).

| | Heavy oil | Light oil |
|----------------------------------|------------------------|------------------------|
| Blend #1 | | |
| Region | Samara | Volgograd |
| Oilfield; well # | Kalmayursk.; 238 | Korobkovsk.; n/a |
| Location | 53°12'10"N; 50°08'27"E | 50°19'00"N; 44°48'00"E |
| Density, 20°C, kg/m ³ | 963.9 | 820.3 |
| Viscosity, 20°C, cSt | 3732 | 4.6 |
| Asphaltenes, wt% | 15.48 | 0.064 |
| Resins, wt% | 35.91 | 16.00 |
| Paraffins, wt% | 1.53 | 9.00 |
| Sulfur, wt% | 2.5 | 0.3 |
| Metals (V + Ni), wt% | 0.175 | n/a |
| Solids, wt% | 0.587 | 0.06 |
| Blend #2 | | |
| Region | Tatarstan | Yugra |
| Oilfield; well # | Aznakayevsk.; 24,534 | Pogranichn.; 43P |
| Location | 54°32'16"N; 52°47'54"E | 63°11'57"N; 75°27'02"E |
| Density, 20°C, kg/m ³ | 893.2 | 818.3 |
| Viscosity, 20°C, cSt | 39.3 | 2.94 |
| Asphaltenes, wt% | 4.19 | 0.14 |
| Resins, wt% | 20.57 | 3.82 |
| Paraffins, wt% | 0.89 | 2.59 |
| Sulfur, wt% | 2.28 | 0.28 |
| Metals (V + Ni), wt% | 0.076 | 0.018 |
| Solids, wt% | 0.07 | 0.006 |

| | Heavy oil | Light oil |
|----------------------------------|------------------------|------------------------|
| Blend #3 | | |
| Region | Komi | Yugra |
| Oilfield; well # | Usinsk.; n/a | Potochn.; 401 |
| Location | 66°10'38"N; 57°21'14"E | 61°15'15"N; 75°12'44"E |
| Density, 20°C, kg/m ³ | 955.3 | 840.8 |
| Viscosity, 20°C, cSt | 962.7 | 7.37 |
| Asphaltenes, wt% | 10.87 | 0.46 |
| Resins, wt% | 9.45 | 2.34 |
| Paraffins, wt% | 5.45 | 5.21 |
| Sulfur, wt% | 1.09 | 0.56 |
| Metals (V + Ni), wt% | 0.0111 | 0.0137 |
| Solids, wt% | 0.46 | 0.04 |

Table 1. The diverse properties of native crude oils employed in the studied blends.

Samples of blends with various oil volume fractions ϕ (determined with an accuracy $\Delta\phi \leq 0.01$) were prepared in 100 ml dark glass vessels. Each prepared sample was intermixed manually with a glass rod and was aged at room temperature over a standard period of 3 days for equilibration. Before density measurements, samples were again homogenized by stirring with a glass rod for 2 minutes.

3. Density measurements reveal multiple “excess density” peaking in crude oil blends of varying compositions

Densities of all samples of Blend #1 were determined using a standard 10 ml pycnometer. In the studied density range of 818–964 kg/m³ (cf. **Table 1**), an accuracy of density measurement was ≤ 1 kg/m³. For samples of Blend #2 and Blend #3 measurements were performed in an oscillating U-tube densitometer (model VIP-2M, produced by TERMEX, Tomsk, Russia) with an accuracy of ± 0.3 kg/m³. All measurements were performed at $24 \pm 0.5^\circ\text{C}$.

Experimental values of “excess density” ρ_{ex} were calculated according to Eq. (4) on the basis of the measured densities of the parent crude oils and of samples of oil blends with various compositions. These experimental values are shown in the graphs of **Figure 1** by filled circles connected by straight-line segments. For comparison, continuous curves in **Figure 1** illustrate the predictions of the standard API model in Eq. (6) converted to ρ_{ex} units by Eq. (5).

Immediately evident is a strong quantitative disagreement of model predictions with experimental data (note that in **Figure 1**, all model data are multiplied by the factor of 10). A fundamental

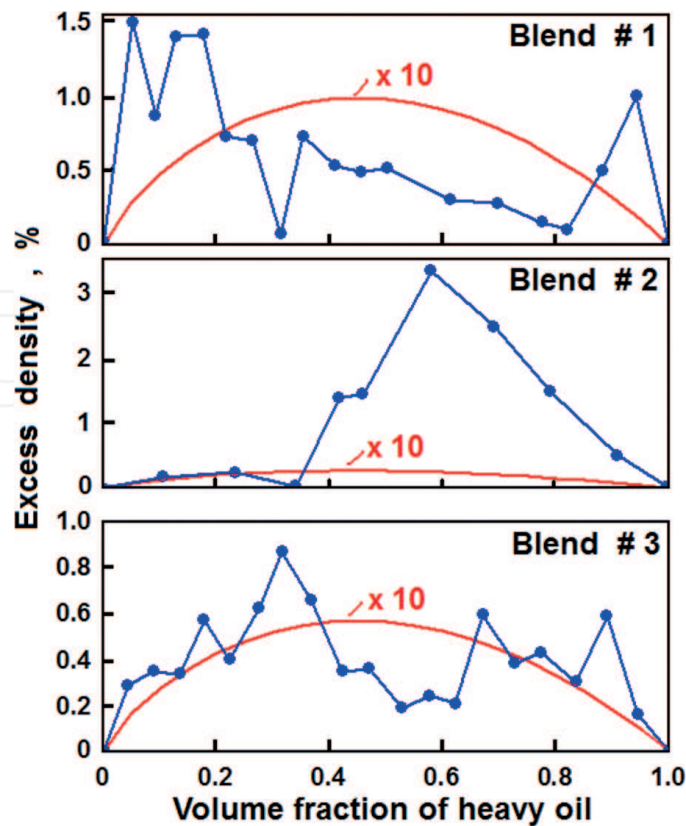


Figure 1. Filled circles connected by straight-line segments—experimental values of excess density in the studied crude oil blends. Continuous curves—excess densities (multiplied by 10) calculated according to the standard API model.

qualitative difference of the model with experimental results appears even more significant. Namely, as noted in Introduction, the API model predicts a single maximum of ρ_{ex} roughly at equal contents of light and heavy oil in any blend. In contrast, experimental data in **Figure 1** reveal multiple peaks of the measured excess density for all studied blends with diverse properties of the parent light and heavy oils.

In accordance with previous publications [23–27], we suggest that the main mechanism behind the observed multiple extrema of ρ_{ex} not accounted for by the standard API model, is an increase in the equilibrium content of asphaltene colloidal aggregates dispersed in the blend, which occur at some specific asphaltene contents. A direct experimental verification of this assumption by IR absorption measurements is described in the following section.

4. IR absorption experiments confirm close relationship of excess density with the content of asphaltene colloidal aggregates in crude oil blends

Infrared optical absorption spectra were measured in the 650–4000 cm^{-1} range with 2 cm^{-1} increment using a model FT-801 FTIR Spectrometer (Simex, Novosibirsk, Russia). For convenience of presentation/discussion, the values of “transmittance” T output of the instrument (in %) were converted to the values of “absorption” (in %) calculated as $(100 - T)$.

Figure 2 show experimental IR absorption spectra for the parent light and heavy oil components of Blend #3 (cf. **Table 1**). By literature analysis, we could not reliably distinguish in these complex spectra any characteristic peaks representative of asphaltene colloidal aggregates.

To solve this problem, we utilized a well-known method of changing the aggregation state of asphaltenes by dilution of crude oils with *n*-heptane [28–30]. At strong dilutions (e.g., at the ratio of 1/40 v/v, as in the standard ASTM D 6560 method [28]), asphaltenes precipitate, flocculate, and fall out of a solution as solid deposits. At small dilutions, the precipitated asphaltenes form a conglomeration of colloidal species suspended in solution, but no solid deposits may be formed even in course of lengthy experiments [29, 30]. In our studies, we diluted the parent heavy oil, employed as a component in Blend #3, with *n*-heptane at the ratio of 1/4 (v/v). The diluted oil was stored for 2 days in quiescent conditions to ensure gravitational spatial segregation of asphaltene colloidal particles (no solid deposits were registered even at the end of this period). Samples from the lower and the upper layers of diluted crude oil (enriched and deficient in asphaltene colloidal particles) were then extracted with syringe, and the respective IR absorption spectra were measured. Specific contribution of asphaltene colloids to IR absorption was revealed by calculating the difference between both spectra and smoothing the difference spectrum by 11-point sliding data window. In the difference spectrum, as illustrated at the upper part of **Figure 3**, the most prominent group of absorption peaks above a continuous background (dashed line) was registered in the range of 2800–3200 cm^{-1} , with the main absorption peak of intensity I_A at 3041 cm^{-1} . By literature analysis [31, 32], absorption at 3040–3050 cm^{-1} may be ascribed to excitation of the aromatic $\text{sp}^2\text{=C-H}$ stretching vibrations. Note that in various previous experiments, this =C-H absorption band was regarded as one of the principal structural parameters of asphaltenes [33–36]. Note also that in the IR spectra of the original crude oils and of their blends, the discussed peak at 3041 cm^{-1} has a very small intensity compared to the main absorption bands—cf. the lower part of **Figure 3**.

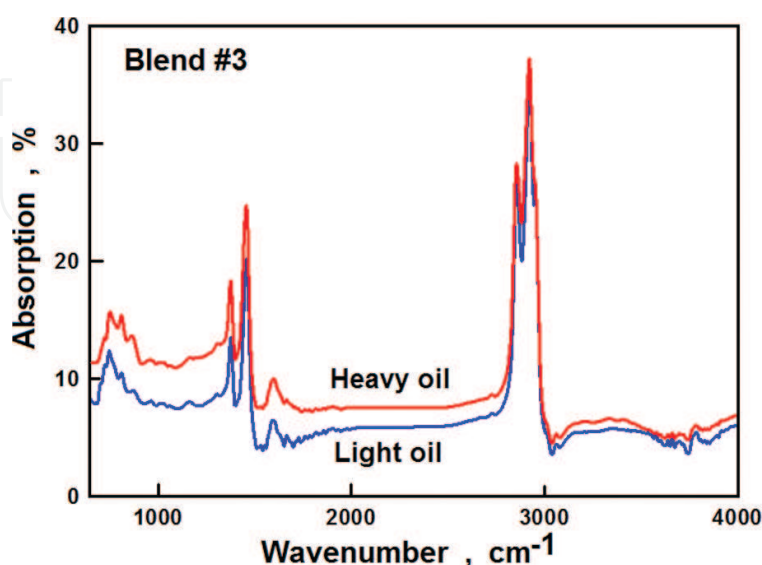


Figure 2. IR absorption spectra of the parent light and heavy oils, employed as components of Blend #3.

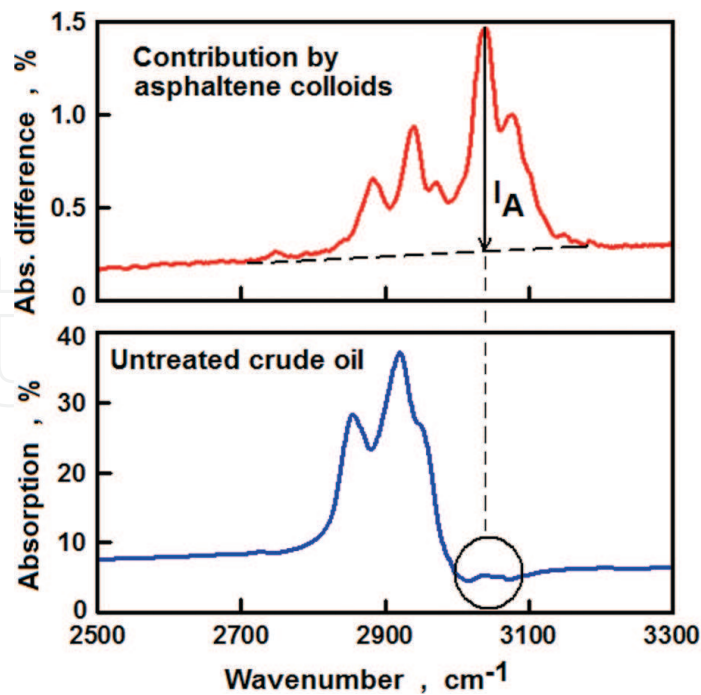


Figure 3. Above: specific contribution to IR absorption by asphaltene colloids (cf. text). Below: the same part of absorption spectrum for the parent heavy crude oil.

On the basis of the above arguments, we concluded that changes in the content of colloidal-sized asphaltenes in crude oil blends with varying compositions may be characterized by intensity increments of the 3041 cm^{-1} absorption peak ΔI_A (measured with respect to the I_A value in the lighter crude oil). **Figure 4** shows a good correspondence of ΔI_A variations in Blend #3 with the measured excess density variations from **Figure 1**. Hence, IR experiments confirm the above suggestion that peaking of ρ_{ex} is caused by the growth of the equilibrium contents of asphaltene colloidal aggregates suspended in crude oil blends. Moreover, as shown in the following section, maxima of excess density apparently occur at some specific asphaltene contents in all blends, independent of the origin of the blended crude oils.

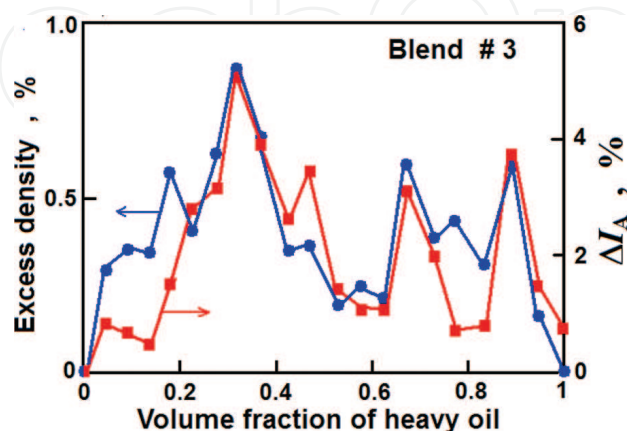


Figure 4. Close relationship of excess density variations in crude oil Blend #3 with content of colloidal-sized asphaltenes, characterized by intensity increments ΔI_A of the IR absorption peak at 3041 cm^{-1} .

5. Density maxima in the studied crude oil blends and in the database of world's native crude oils are observed at the same special asphaltene contents in petroleum media

Previously, we have analyzed distributions of density/specific gravity in a database of several hundreds world's native crude oils from a diversity of geographical/geological locations [23]. **Figure 5** shows the scatter plot of specific gravity (SG) versus Log of asphaltene content (C_A) in this database (filled triangles). The analysis of these data revealed that (1) minimum values of SG are randomly distributed along some smooth curve and (2) distribution of maximum SG values is not random, and these tend to concentrate near certain asphaltene contents. To highlight these points, maximum and minimum values of SG in the scatter plot were evaluated in consecutive equal intervals of $\Delta \text{Log}(C_A) = 0.05$ and the results were connected by continuous lines, as illustrated in **Figure 5**. It is clearly seen that anomalous peaking of specific gravity/density is observed in native crude oils with some particular asphaltene contents C_A^* listed in **Table 2**. In Ref. [23], these anomalies were attributed to different structural states (structural phases) of asphaltene colloids suspended in crude oils and the reliability of the values of respective asphaltene contents C_A^* was demonstrated by the analysis of databases from other publications [37–39].

Additional analysis of excess density measurements from **Figure 1** in terms of asphaltene content has shown that in all blends peaking of ρ_{ex} apparently occurs at the same characteristic asphaltene contents C_A^* revealed in native crude oils. The results of this analysis are illustrated in **Figures 6–8**. The experimental excess density values from **Figure 1** are denoted by filled circles. Filled squares denote maximum values of specific gravity from a database of world's native crude oils (**Figure 5**). A fairly good qualitative coincidence of both data sets is observed in all cases.

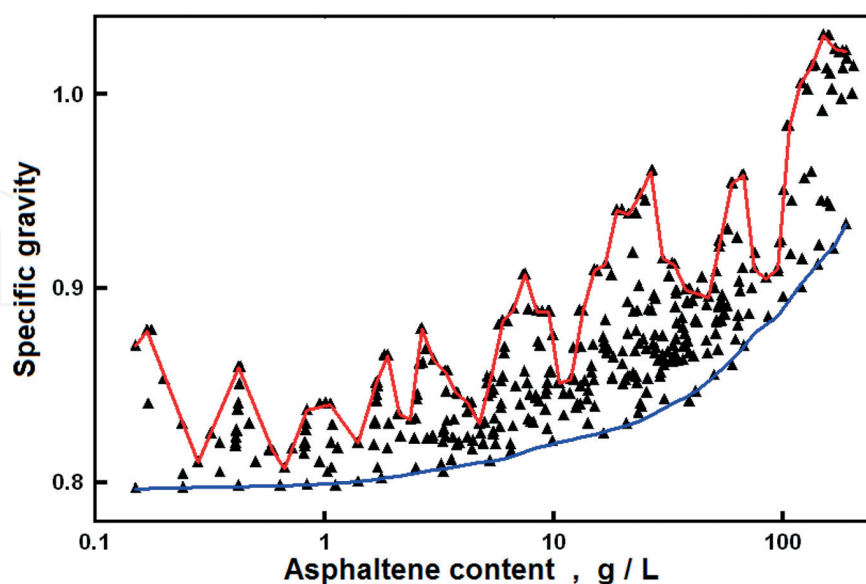


Figure 5. Data points: the scatter plot of specific gravity (density) in a database of world's native crude oils from a diversity of geographical/geological locations. Continuous lines: analysis of maximum and minimum values of specific gravity in this database. Note specific gravity peaking at some characteristic asphaltene contents.

| No. | 3a | 3a | 3b | 4 | 5 | 6 |
|---------------|------|------|------|------|------|-------|
| C_A^* , g/L | 1.88 | 2.66 | 7.50 | 26.6 | 66.8 | 149.6 |

Table 2. Characteristic asphaltene contents C_A^* (numbered as in Ref. [23]) at which maximum density anomalies are observed in native crude oils (cf. Figure 5).

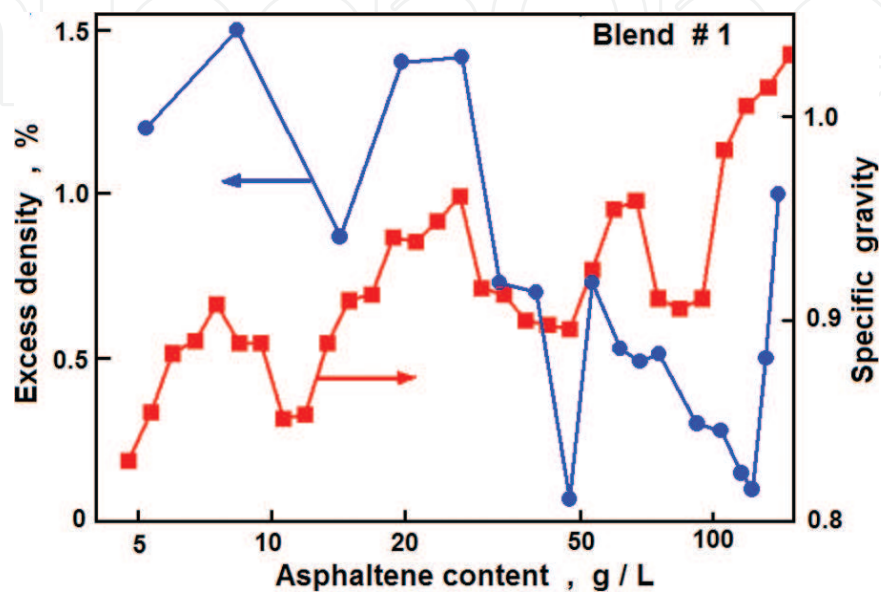


Figure 6. Comparison of the experimental excess density data for Blend #1 (filled circles) with the maximum values of specific gravity from a database of world's native crude oils (filled squares).

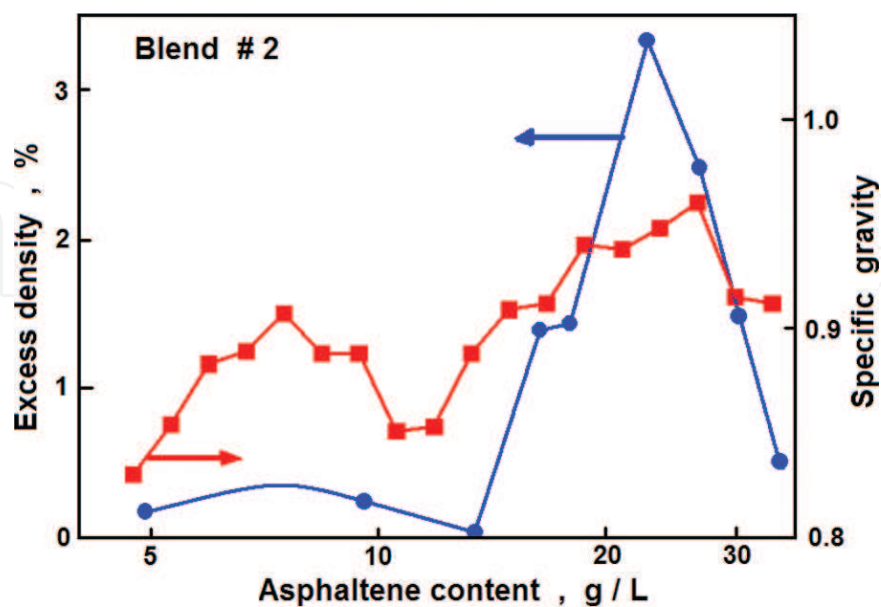


Figure 7. Comparison of the experimental excess density data for Blend #2 (filled circles) with the maximum values of specific gravity from a database of world's native crude oils (filled squares).

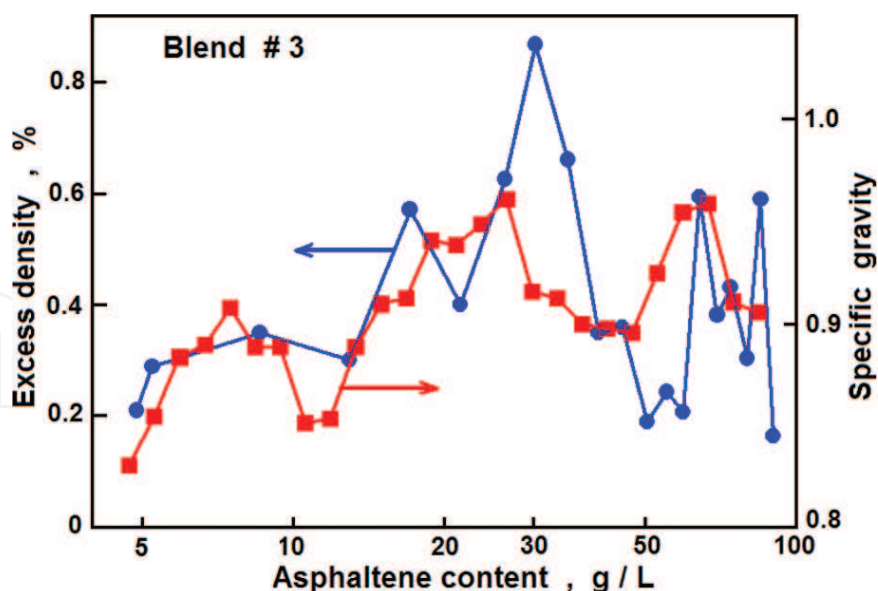


Figure 8. Comparison of the experimental excess density data for Blend #3 (filled circles) with the maximum values of specific gravity from a database of world's native crude oils (filled squares).

Summarizing, **Figures 6–8** indicate that the observed multiple nonideal anomalies in the properties of equilibrated crude oil blends (multiple peaks of excess density/volumetric shrinkage values) apparently result from step-like changes between several equilibrium structural phases of suspended asphaltene colloids, which are observed between several particular asphaltene contents, apparently common for petroleum media of any origin.

6. Plausible constitution of multiple structural phases of asphaltenes.

Apparent resemblance of asphaltene transformations to those of block copolymers

In spite of intensive experimental and theoretical studies, association and aggregation mechanisms of asphaltene colloids are still not well characterized and are subjects of ongoing debate [22–25, 29, 30]. In particular, for decades, the prevailing aggregation paradigm (now dismissed as erroneous) has been that at a “critical micelle concentration” (“CMC” $\approx 2\text{--}10\text{ g/L}$) of asphaltenes in native petroleum, or in “good” solvents, such as toluene, there is a *one-step* transition from a structural phase of single asphaltene molecules to a structural phase colloidal asphaltene “micelles” of 4–6 molecules [40]. The development of more accurate experimental techniques provided substantial evidence of asphaltene aggregation at concentrations much lower than previously quoted “CMC.” Hence, the aggregation paradigm has been changed quantitatively, though not qualitatively. The most popular current model is that at a “critical nanoaggregate concentration” (“CNAC” $\approx 100\text{--}200\text{ mg/L}$) of asphaltenes in native crude oils, or in “good” solvents, there is a *one-step* transition from a phase of individual asphaltene monomers to a phase of colloidal “nanoaggregates” of 4–6 monomers (further clustering of primary aggregates is usually regarded as a dynamic random process and is not discussed in terms of a phase transformations) [41, 42].

- The dismissed paradigm [40]:



- The current paradigm [41, 42]:



Apparently, due to their simplicity, the above *one-step* (two-phase) paradigms have been and still are the ones, almost exclusively employed for description of asphaltene aggregation phenomena and for interpretation of experimental data. Regardless of the difference in suggested molecular mechanisms, the above paradigm closely resembles the idealized model of one-step aggregation (“micellization”) with just two indigenous solute phases developed for solutions of primitive amphiphilic surfactants like sodium dodecyl sulfate (SDS) [43]. It is now well known that much more common in nature are complex self-organizing amphiphilic species, e.g., block copolymers, which possess a wide array of indigenous colloidal phases in solutions [44].

However, all evidence for the close resemblance of petroleum asphaltenes to block copolymers, both in their molecular structure and in their propensity for self-assembly into wide array of nano-sized and micro-sized structures, still remains virtually unnoticed. In fact, the existence of several aggregation stages below and above CNAC has been repeatedly demonstrated by various experiments (cf. a review in Ref. [45]). It appears that the corresponding characteristic concentrations C_A^* only marginally depend on the geographical/geological origin of asphaltenes or on the type of solvents/crude oils.

Historically, asphaltenes are defined not as members of some particular family of chemical species, but as a fraction of petroleum, which is soluble in toluene (“good solvent”), and resemblance of asphaltene molecular architecture to that of block copolymers for the first time was suggested in 1994 by I.A. Wiehe [46], whereas in 2002, W. Loh noticed a parallel between some aggregation processes for block copolymers and asphaltenes [47]. Various molecular models of asphaltenes have been developed [22, 29, 30, 41]; all these models agree that asphaltene molecules contain the following principal “building blocks” [46]: (1) rigid flat condensed systems of aromatic rings with an affinity for “good solvents” and (2) flexible linear alkyl side chains, which may contain some heteroatoms, and have an affinity for “nonsolvents.” In the “continental-type” models, aromatic regions are large, whereas in “archipelago-type” models, aromatic blocks are much smaller. Aggregation of such “multiblock” molecules may proceed via π - π stacking and H- π bonding, involving aromatic blocks, as well as via polar and hydrogen-bonding interactions between side-chain blocks. By virtue of these noncovalent interactions, asphaltenes in solutions as well as in native petroleum apparently exhibit multiple structural phases—a well-known property of block copolymers [44].

Recently, it was experimentally proven [48–52] that basic asphaltene molecules (unimers, monomers) typically include very small, 1–3 ring, aromatic systems, in contrast to the popular notions about the predominance of large multiring fused systems [41, 42]. These basic molecules become predominant equilibrium species only after dissolution of solid asphaltenes in “good”

solvents (benzene, toluene, etc.) to asphaltene concentrations $C \leq 0.5\text{--}0.6$ mg/L. Aggregation of basic asphaltene molecules commences at $C = 0.6\text{--}0.7$ mg/L, much smaller than the above-discussed CNAC, and the predominant equilibrium species become polydisperse “primary” asphaltene aggregates, which may contain up to 10–12 basic molecules associated mainly in a head-to-tail manner by noncovalent interactions. On the basis of these experimental results, it concluded that the adequate structural description of primary asphaltene aggregates may be that suggested in Ref. [53]. The authors of this publication described that such aggregates as supramolecular assemblies of molecules, combining cooperative binding by Brønsted acid-base interactions, hydrogen bonding, metal coordination complexes, and interactions between cycloalkyl and alkyl groups to form hydrophobic pockets, in addition to aromatic π - π stacking. They suggested a range of aggregate architectures, which almost certainly occur simultaneously, including porous networks and host-guest complexes. The latter may include organic clathrates, in which occluded guest molecules stabilize the assembly of a cage, as methane does in gas hydrates [53]. With increasing asphaltene concentration (still below CNAC), several structural phases of soft, voluminous, primary aggregates are observed in solutions, which may be accompanied by a release of some occluded “guests” [51]. Finally, at $C \approx 100\text{--}130$ mg/L, primary aggregates shrink and may be described as “solid-like” asphaltene colloidal nanoparticles [52]. Interpretations of some structural asphaltene phases above CNAC by various authors were reviewed in Refs [23–25, 45, 54].

Plausible types of some of the multiple structural transformations of asphaltenes are schematically illustrated in **Figure 9**.

In **Figure 9**, characteristic asphaltene contents C_A^* are numbered as in Ref. [23] (cf. also **Table 2**):

1. At asphaltene contents of 0.6–0.7 mg/L, apparently there is a transition from a solution of small asphaltene basic molecules to a solution of voluminous primary aggregates.
2. At concentrations of 100–130 mg/L, soft primary aggregates are transformed to solid-like “nanocolloids” with individual nanoparticles 2–4 nm in diameter.

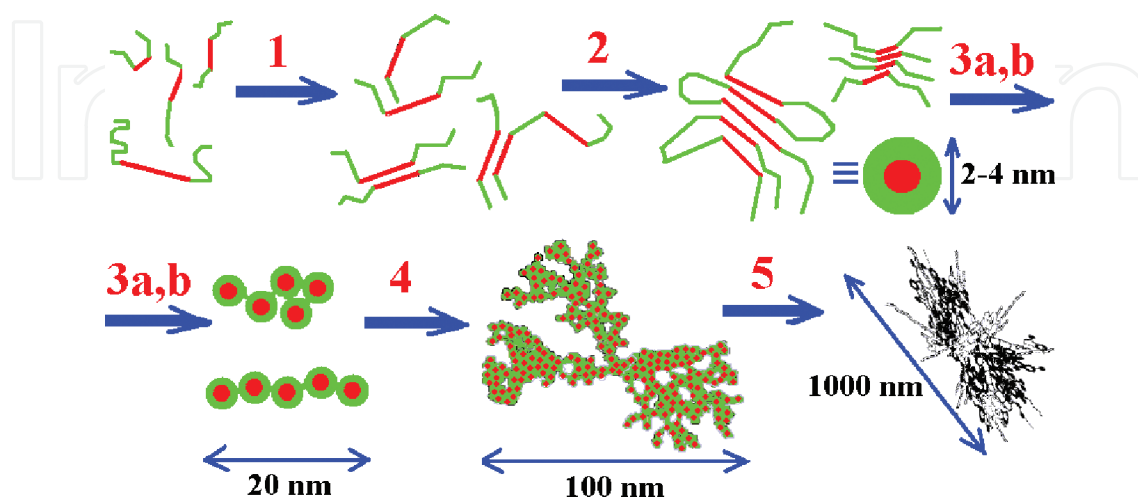


Figure 9. Plausible structural phase transformations of asphaltenes at some characteristic asphaltene contents, numbered as in Ref. [23].

3. This group of two close characteristic concentrations (3a,b) in the range of 1.7–8 g/L (cf. **Table 2**) may reflect the appearance of elongated colloidal clusters of solid-like nanoparticles, 15–20 nm in length.
4. At concentrations of 25–30 g/L, elongated clusters presumably form fractal aggregates ≥ 100 nm in size.
5. At 55–70 g/L, there start to appear micron-sized asphaltene flocs still suspended in the liquid media.

To conclude this section, it should be emphasized that revealing multiple asphaltene structural phases in solutions and in native petroleum was largely facilitated by a seemingly trivial but a crucial improvement in analysis of experimental data. Namely, previously overlooked details of analyzed correlations become perceptually well separated only at data plots with log concentration scales, common in surfactant chemistry, while in conventional petroleum studies, linear-scale plots are still employed [29, 30, 41].

7. Conclusion

In contrast to the predictions of the standard API model, the described density measurements revealed multiple anomalies of excess density at several compositions in all studied blends of light and heavy crude oils from diverse origins. It was suggested that density anomalies are caused by increased contents of suspended asphaltene colloidal-sized particles/aggregates in the blends. In IR absorption experiments, the most intense absorption peak representative of asphaltene colloids appeared to be that at 3041 cm^{-1} , by literature analysis, ascribed to excitation of the aromatic $\text{sp}^2\text{C-H}$ stretching vibrations. Intensity variations of this peak correlated with variations of excess density, supporting the conclusion of the governing role of asphaltene colloids in the observed density anomalies. By comparison with an extended database of world's native crude oils, it was further concluded that different density anomalies may correspond to different equilibrium structural states of asphaltene colloids, which occur at several specific asphaltene contents, apparently common for petroleum media of any origin.

It is hoped that the insight gained into the nonideal behavior of the densities of crude oils, upon mixing and the explanations proposed, will assist in a better scientific understanding of the mechanism of the changes that may occur in mixtures. This should help oil producers and refiners in a better utilization of the existing oil resources, i.e., crude oils and petroleum products.

Acknowledgements

We acknowledge the support from the Nedra-Test Research and Testing Establishment, LLC, Moscow, Russia, in purchasing the experimental equipment.

Author details

Igor N. Evdokimov*, Aleksey A. Fesan and Aleksandr P. Losev

*Address all correspondence to: physexp@gubkin.ru

Department of Physics, Gubkin Russian State University of Oil and Gas, Moscow, Russia

References

- [1] Gateau P, Hénaut I, Barré L, Argillier JF. Heavy oil dilution. Oil & gas Science and technology - rev. IFP. 2004;**59**(5):503-509. DOI: 10.2516/ogst:2004035
- [2] Todd CM. Downstream planning and innovation for heavy oil development - a producer's perspective. Journal of Canadian Petroleum Technology. 1988;**27**(1):79-86
- [3] Martínez-Palou R, Mosqueira ML, Zapata-Rendón B, Mar-Juárez E, Bernal-Huicochea C, Clavel-López JC, Aburto J. Transportation of heavy and extra-heavy crude oil by pipeline: A review. Journal of Petroleum Science and Engineering. 2011;**75**(3-4):274-282. DOI: 10.1016/j.petrol.2010.11.020
- [4] Gary JH, Handwerk GE, Kaiser MJ. Petroleum Refining Technology and Economics. 5th ed. Boca Raton, FL: CRC Press; 2007
- [5] Al-Besharah JM. The Effect of Blending on Selected Physical Properties of Crude Oils and their Products [PhD Thesis]. Birmingham, UK: The University of Aston in Birmingham; 1989
- [6] Reid RC, Prausnitz JM, Sherwood TK. The Properties of Gases and Liquids. 3rd ed. New York: McGraw-Hill, Inc.; 1977
- [7] Benson SW, Cruickshank FR, Golden DM, Haugen GR, O'Neal HE, Rodgers AS, Shaw R, Walsh R. Additivity rules for the estimation of thermochemical properties. Chemical Reviews. 1969;**69**(3):279-324. DOI: 10.1021/cr60259a002
- [8] Nielsen LE. Predicting the Properties of Mixtures: Mixture Rules in Science and Engineering. New York: Marcel Dekker, Inc.; 1978
- [9] Arenas FG, Garcia CA, Orozco LM. Models for Estimating the Shrinkage Factor in the Mixtures of Diluents with Colombian Heavy Crude Oils. Paper SPE-153554-MS. Presented at the SPE Latin America and Caribbean Petroleum Engineering Conference. Mexico: Mexico City; 2012. DOI: 10.2118/153554-MS
- [10] James JH. Shrinkage losses resulting from liquid hydrocarbon blending. In: Proceedings of the 87th Annual International School of Hydrocarbon Measurement. Vol. 1. Oklahoma City, Oklahoma, USA: Curran Associates, Inc.; 2012. pp. 452-458
- [11] Ashcroft SJ, Booker DR, Turner JCR. Volumetric behavior of mixtures of crude oils and light hydrocarbons. Journal of the Institute of Energy. 1992;**65**(464):131-136

- [12] Shanshool J, Talib E. Fitted shrinkage formula of spiked crude oil. *Petroleum Science and Technology*. 2002;**20**(3-4):435-439. DOI: 10.1081/LFT-120002111
- [13] Saryazdi F. Density Prediction for Mixtures of Heavy Oil and Solvents [MSci Thesis]. Calgary, Alberta, Canada: University of Calgary; 2012
- [14] Shanshool J, Habobi N, Kareem S. Volumetric behavior of mixtures of different oil stocks. *Petroleum & Coal*. 2011;**53**(3):223-228
- [15] API Manual of petroleum measurement standards (MPMS). Chapter 12. Calculation of petroleum quantities. In: Section. Vol. 3. Volumetric shrinkage resulting from blending light hydrocarbons with crude oil. Washington, D.C.: American Petroleum Institute; 1996
- [16] Nengkoda A. The Role of Crude Oil Shrinkage in Heavy Mix Light Crude in Main Oil Pipeline: Case Study Oman. Paper SPE 148925. Presented at the SPE Heavy Oil Conference and Exhibition. Kuwait: Kuwait City; 2011. DOI: 10.2118/148925-MS
- [17] Slaiman EN, Al-Qamaje HM, Atta SZ. Composition and temperature dependence of excess volume of heavy oil-stocks mixtures + (gas oil or toluene or reformat). *Al-Khwarizmi. Engineering Journal*. 2011;**7**(3):59-67
- [18] Rodríguez S, Ancheyta J, Guzmán R, Trejo F. Experimental setups for studying the compatibility of crude oil blends under dynamic conditions. *Energy & Fuels*. 2016;**30**(10):8216-8225. DOI: 10.1021/acs.energyfuels.6b01698
- [19] Bassane JFP, Sad CMS, Neto DMC, Santos FD, Silva M, Tozzi FC, Filgueiras PR, de Castro EVR, Romão W, Santos MFP, da Silva JOR, Lacerda Jr V. Study of the effect of temperature and gas condensate addition on the viscosity of heavy oils. *Journal of Petroleum Science and Engineering*. 2016;**142**:163-169. DOI: 10.1016/j.petrol.2016.02.006
- [20] Gabrienko AA, Martyanov ON, Kazarian SG. Effect of temperature and composition on the stability of crude oil blends studied with chemical imaging in situ. *Energy & Fuels*. 2015;**29**(11):7114-7123. DOI: 10.1021/acs.energyfuels.5b01880
- [21] Weihe IA, Kennedy RJ. The oil compatibility model and crude oil incompatibility. *Energy & Fuels*. 2000;**14**(1):56-59. DOI: 10.1021/ef990133+
- [22] Wiehe IA. Asphaltene solubility and fluid compatibility. *Energy & Fuels*. 2012;**26**(7):4004-4016. DOI: 10.1021/ef300276x
- [23] Evdokimov IN. The importance of asphaltene content in petroleum - the revision of some persistent stereotypes. *Petroleum Science and Technology*. 2010;**28**(7):756-763. DOI: 10.1080/10916460902804739
- [24] Evdokimov IN. The importance of asphaltene content in petroleum II - multi - peak viscosity correlations. *Petroleum Science and Technology*. 2010;**28**(9):920-924. DOI: 10.1080/10916460902937018
- [25] Evdokimov IN. The importance of asphaltene content in petroleum III - new criteria for prediction of incompatibility in crude oil blends. *Petroleum Science and Technology*. 2010;**28**(13):1351-1357. DOI: 10.1080/10916460903096731

- [26] Wang Z, Liu H, Sun X, Ji S, Guo A, Chen K. Compatibility of heavy blends evaluated by fouling and its relationship with colloidal stability. *Petroleum Science and Technology*. 2015;**33**(6):686-693. DOI: 10.1080/10916466.2015.1007380
- [27] de la Cruz JLM, Cedillo-Ramírez JC, Aguirre-Gutiérrez AJ, García-Sánchez F, Aquino-Olivos MA. Incompatibility determination of crude oil blends from experimental viscosity and density data. *Energy & Fuels*. 2015;**29**(2):480-487. DOI: 10.1021/ef501512b
- [28] ASTM. D6560-00; IP 143/01: Standard Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products. West Conshohocken, PA: American Society for Testing and Materials; 2000
- [29] Andersen SI, Speight JG. Asphaltene precipitation and incipient flocculation in mixed solvents. Preprints – Division of fuel chemistry. American Chemical Society. 1992;**37**(3): 1335-1341
- [30] Speight JG. Petroleum asphaltenes - Part 1: Asphaltenes, resins and the structure of petroleum. *Oil & gas Science and technology - Rev. IFP*. 2004;**59**(5):467-477. DOI: 10.2516/ogst:2004032
- [31] Bellamy LJ. *The Infra-Red Spectra of Complex Molecules*. New York: John Wiley & Sons; 1957
- [32] Silverstein RM, Webster FX. *Spectrometric Identification of Organic Compounds*. 6th ed. New York: John Wiley & Sons; 1998
- [33] Almusallam AS, Shaaban M, Nettem K, Fahim MA. Delayed aggregation of asphaltenes in the presence of alcohols by dynamic light scattering. *Journal of Dispersion Science and Technology*. 2013;**34**(6):809-817. DOI: 10.1080/01932691.2012.704737
- [34] Guillen MD, Iglesias MJ, Domingues A, Blanco CG. Semi quantitative FTIR analysis of a coal tar pitch and its extracts and residues in several organic solvents. *Energy & Fuels*. 1992;**6**(4):518-525. DOI: 10.1021/ef00034a025
- [35] Apicella B, Alfè M, Barbella R, Tregrossi A, Ciajolo A. Aromatic structures of carbonaceous materials and soot inferred by spectroscopic analysis. *Carbon*. 2004;**42**(8-9):1583-1589. DOI: 10.1016/j.carbon.2004.02.010
- [36] Santamaria A, Yang N, Eddings E, Mondragon F. Chemical and morphological characterization of soot and soot precursors generated in an inverse diffusion flame with aromatic and aliphatic fuels. *Combustion and Flame*. 2010;**157**(1):33-42. DOI: 10.1016/j.combustflame.2009.09.016
- [37] Katz BJ, Robison VD. Oil quality in deep-water settings: Concerns, perceptions, observations, and reality. *AAPG Bulletin*. 2006;**90**(6):909-920. DOI: 10.1306/01250605128
- [38] Mansoori GA. Asphaltene Deposition and its Control [Internet Publication]. 1995. Available from: http://tiger.uic.edu/~mansoori/Asphaltene.Deposition.and.Its.Control_.html [Accessed 2017-08-15]

- [39] Alboudwarej H, Felix J, Taylor S, Badry R, Bremner C, Brough B, Skeates C, Baker A, Palmer D, Pattison K, Beshry M, Krawchuk P, Brown G, Calvo R, Triana JAC, Hathcock R, Koerner K, Hughes T, Kundu D, de Cardenas JL, West, C. Highlighting heavy oil. *Oilfield Review*. 2006;**18**(2):34-53
- [40] Sheu EY. Physics of asphaltene micelles and microemulsions - Theory and experiment. *Journal of Physics: Condensed Matter*. 1996;**8**(25A):A125-A141. DOI: 10.1088/0953-8984/8/25A/009
- [41] Lisitza NV, Freed DE, Sen PN, Song Y-Q. Study of asphaltene nanoaggregation by nuclear magnetic resonance (NMR). *Energy & Fuels*. 2009;**23**(3):1189-1193. DOI: 10.1021/ef800631a
- [42] Rane JP, Harbottle D, Pauchard V, Couzis A, Banerjee S. Adsorption kinetics of asphaltenes at the oil-water interface and nanoaggregation in the bulk. *Langmuir*. 2012; **28**(26):9986-9995. DOI: 10.1021/la301423c
- [43] Hartley GS. Aqueous Solutions of Paraffin Chain Salts. A Study in Micelle Formation. Hermann et Cie: Paris, France; 1936
- [44] Hadjichristidis N, Pispas S, Floudas G. Block Copolymers: Synthetic Strategies, Physical Properties, and Applications. Hoboken, NJ, USA: John Wiley & Sons, Inc.; 2003
- [45] Evdokimov IN. Characterization of asphaltenes and crude oils by near-UV/visible absorption spectroscopy. In: Duncan JA, editor. Asphaltenes: Characterization, Properties and Applications. New York: Nova Science Publishers, Inc.; 2010. pp. 1-46
- [46] Wiehe IA. The pendant-core building block model of petroleum residua. *Energy & Fuels*. 1994;**8**(3):536-544. DOI: 10.1021/ef00045a003
- [47] Loh W. Block copolymer micelles. In: Hubbard A, editor. Encyclopedia of Colloid and Surface Science. New York, USA: Marcel Dekker Inc.; 2002. pp. 802-813
- [48] Evdokimov IN, Fesan AA. Multi-step formation of asphaltene colloids in dilute solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2016;**492**:170-180. DOI: 10.1016/j.colsurfa.2015.11.072
- [49] Evdokimov IN, Fesan AA, Losev AP. New answers to the optical interrogation of asphaltenes. Monomers and primary aggregates from steady state fluorescence studies. *Energy & Fuels*. 2016;**30**(6):4494-4503. DOI: 10.1021/acs.energyfuels.6b00027
- [50] Evdokimov IN, Fesan AA, Losev AP. New answers to the optical interrogation of asphaltenes. Complex states of primary aggregates from steady state fluorescence studies. *Energy & Fuels*. 2016;**30**(10):8226-8235. DOI: 10.1021/acs.energyfuels.6b01943
- [51] Evdokimov IN, Fesan AA, Losev AP. Occlusion of foreign molecules in primary asphaltene aggregates from near-UV-visible absorption studies. *Energy & Fuels*. 2017; **31**(1):1370-1375. DOI: 10.1021/acs.energyfuels.6b02826

- [52] Evdokimov IN, Fesan AA, Losev AP. Asphaltenes: Absorbers and scatterers at near-ultraviolet-visible-near-infrared wavelengths. *Energy & Fuels*. 2017;**31**(4):3878–3884. DOI: 10.1021/acs.energyfuels.7b00114
- [53] Gray MR, Tykwinski RR, Stryker JM, Tan X. Supramolecular assembly model for aggregation of petroleum asphaltenes. *Energy & Fuels*. 2011;**25**(7):3125-3134. DOI: 10.1021/ef200654p
- [54] Evdokimov IN. “Fine phase transformations” in petroleum - the basis for emerging nanotechnologies. In: Montclair KL, editor. *Petroleum Science Research Progress*. New York, USA: Nova Science Publ; 2008. pp. 235-260

IntechOpen