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

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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:

$$V_{ideal} = V_1 + V_2 \tag{1}$$

Consequently, the density of the ideal binary blend:

$$\rho_{ideal} = \rho_1 \phi_1 + \rho_2 \phi_2, \tag{2}$$

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":

$$S = \frac{V_{ideal} - V_{blend}}{V_{ideal}} \tag{3}$$

and "excess density":

$$\rho_{ex} = \frac{\rho_{blend} - \rho_{ideal}}{\rho_{ideal}} \tag{4}$$

where, by definition:

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

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):

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

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/m³	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 ± 0.5°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
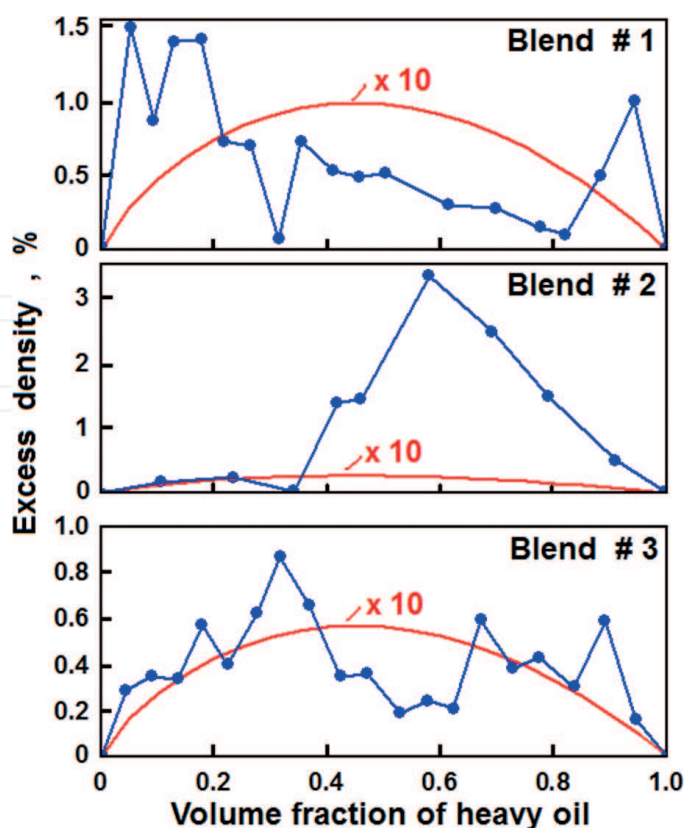
Figure 1. Filled circles connected by straight-line segments—experimental values of excess density in the studied crude oil blends. Continuous curves—excess densities (multiplied by 10) calculated according to the standard API model.

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 compo-
nents 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 dif-
ference 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 sp^2=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
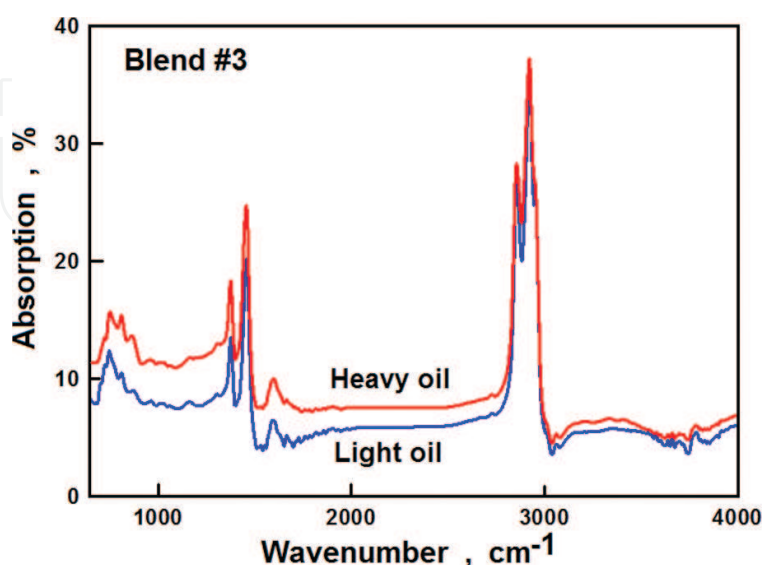the main absorption bands—cf. the lower part of **Figure 3**.

Figure 2. IR absorption spectra of the parent light and heavy oils, employed as components of Blend #3.
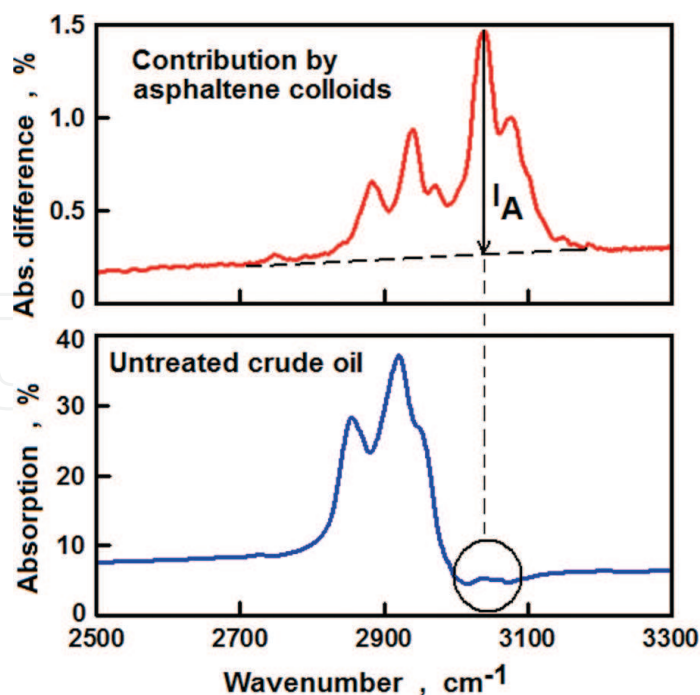
Figure 3. Above: specific contribution to IR absorption by asphaltene colloids (cf. text). Below: the same part of absorption spectrum for the parent heavy crude oil.

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.
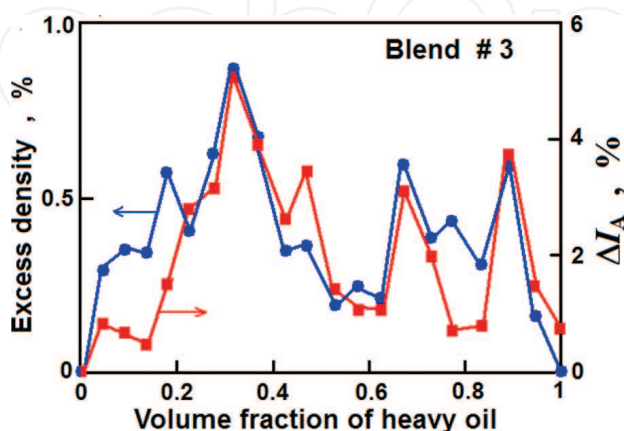

Figure 4. Close relationship of excess density variations in crude oil Blend #3 with content of colloidal-sized asphaltenes, characterized by intensity increments ΔI_A of the IR absorption peak at 3041 cm^{-1}.

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 $\Delta Log(C_A) = 0.05$ 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.
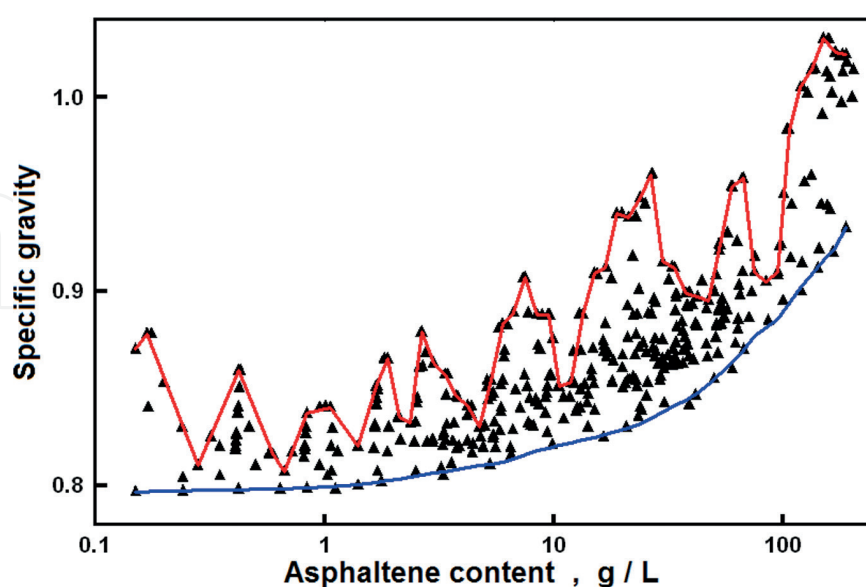

Figure 5. Data points: the scatter plot of specific gravity (density) in a database of world's native crude oils from a diversity of geographical/geological locations. Continuous lines: analysis of maximum and minimum values of specific gravity in this database. Note specific gravity peaking at some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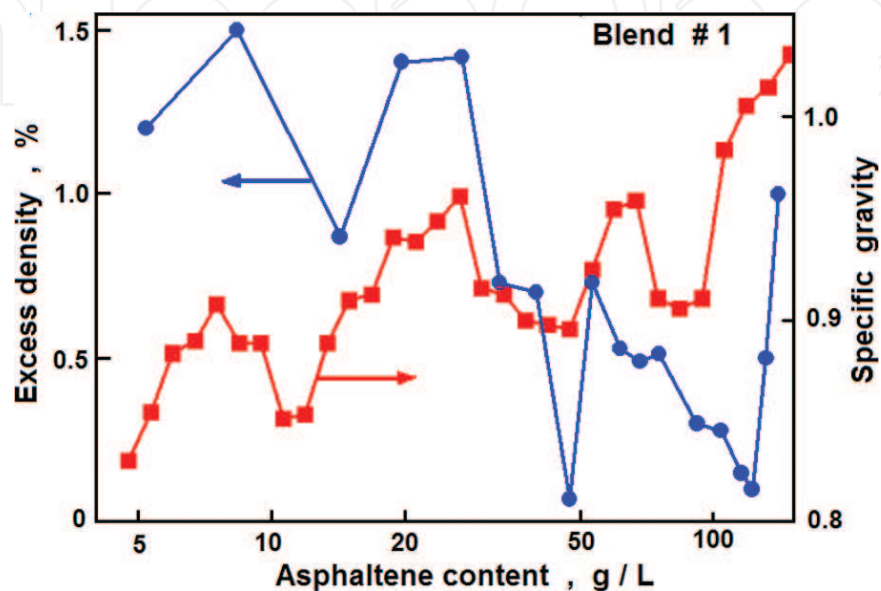

Figure 7. Comparison of the experimental excess density data for Blend #2 (filled circles) with the maximum values of specific gravity from a database of world's native crude oils (filled squares).

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).
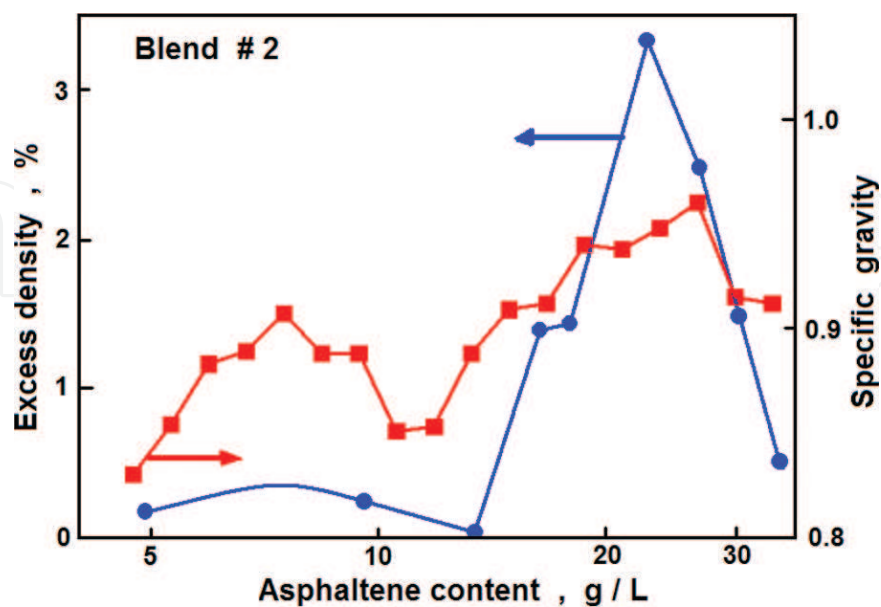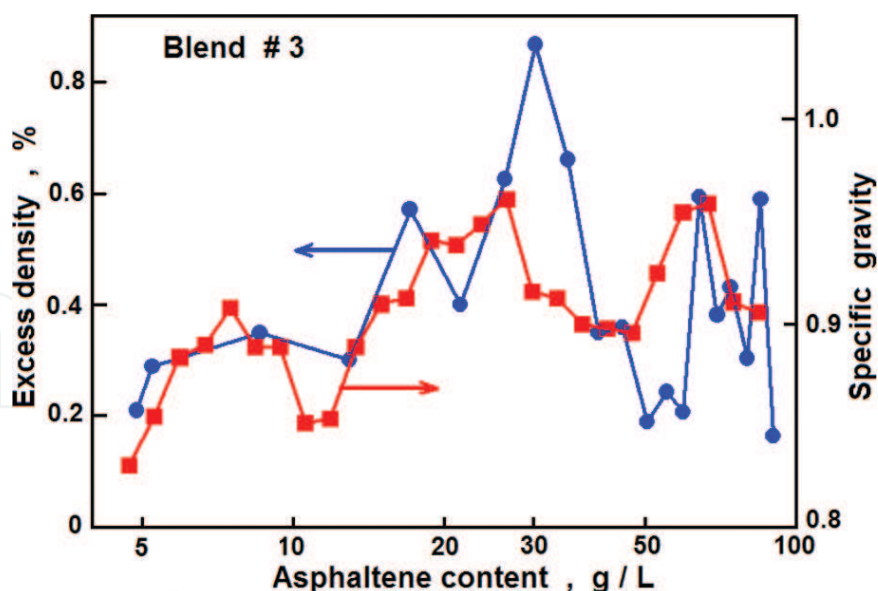
Summarizing, **Figures 6–8** indicate that the observed multiple nonideal anomalies in the properties of equilibrated crude oil blends (multiple peaks of excess density/volumetric shrinkage values) apparently result from step-like changes between several equilibrium structural phases of suspended asphaltene 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" ≈ 2–10 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" ≈ 100–200 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 "nano-aggregates" 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]:

$$\text{MOLECULE} \xrightarrow{CMC} \text{COLLOIDAL MICELLE}$$

- The current paradigm [41, 42]:

$$\text{MONOMER} \xrightarrow{CNAC} \text{COLLOIDAL NANOAGGREGATE}$$

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 $C \leq 0.5$–0.6 mg/L. Aggregation of basic asphaltene molecules commences at $C = 0.6$–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 $C \approx 100$–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.
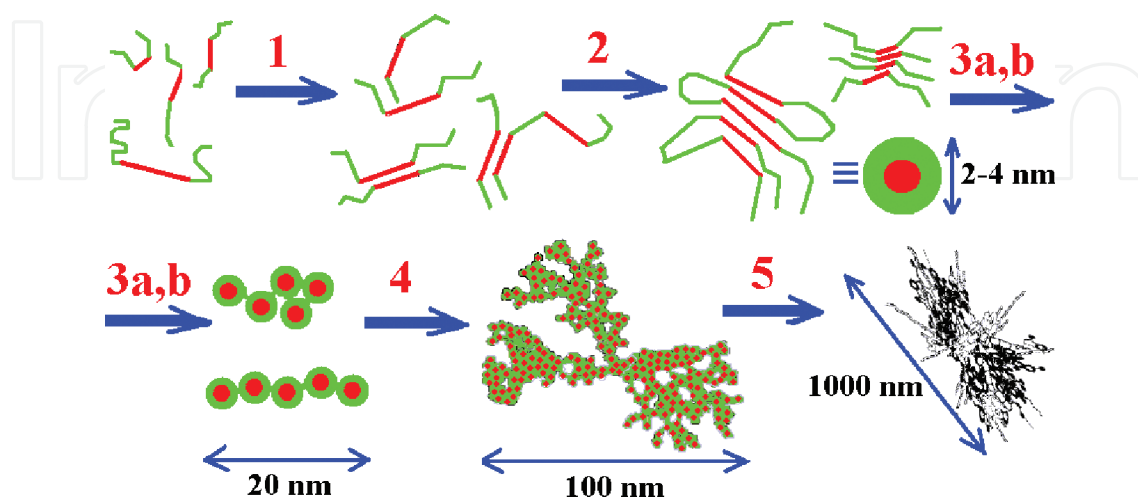

Figure 9. Plausible petructural phase transformations of asphaltenes at some characteristic asphaltene contents, numbered as in Ref. [23].

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 sp^2=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.

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