МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РЕСПУБЛИКИ ТАТАРСТАН
АЛЬМЕТЬЕВСКИЙ ГОСУДАРСТВЕННЫЙ НЕФТЯНОЙ ИНСТИТУТ

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ДОСТИЖЕНИЯ, ПРОБЛЕМЫ И ПЕРСПЕКТИВЫ РАЗВИТИЯ НЕФТЕГАЗОВОЙ ОТРАСЛИ

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TRUE SIZE OF ASPHALTENE MONOMERS

ИСТИННЫЙ РАЗМЕР МОНОМЕРОВ АСФАЛЬТЕНОВ

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The size and structure of aggregating asphaltene molecules has been a controversy for several decades. In recent years, advocates of the so-called "Modified Yen Model" (MYM) describe the smallest asphaltene molecules as species with fairly large aromatic chromophores, typically with 7–10 fused rings, aggregating by π-π stacking. Our new experimental results clearly show that the MYM description of the smallest asphaltenes is fundamentally wrong. Their experiments were misinterpreted because of the assumption that asphaltenes do not aggregate at concentrations of 10-25 mg/L, while our new data indicate that asphaltenes form primary aggregates at concentrations as low as ca. 0.7 mg/L. In contrast to the popular MYD description, our new experiments show that aggregating asphaltenes appear to be much smaller molecular species, typically with 1-3 ring aromatic chromophores, while typical primary asphaltene aggregates may be described as head-to-tail hydrogen-bonded complexes of basic asphaltene molecules.

Key word: asphaltene, aggregation, SSFE.
Ключевые слова: асфальтены, агрегация, спектры флуоресценции

For many years, the dominant conceptual model for aggregation of asphaltenes in native petroleum and in solutions has been based on compact clusters ("nanoaggregates") formed by assembly of some basic molecules, conventionally referred to as "asphaltene monomers". [1] Presumably, the distinctive structural units of these "monomers" are fairly large sheets of 7-10 condensed aromatic rings which facilitate aggregation into parallel stacks via π-π interactions at asphaltene contents only above a specific "critical nanoaggregate concentration" (CNAC) of ca. 100 mg/L. [1] However, recent steady state fluorescence emission (SSFE) experiments demonstrated that asphaltene "monomers" appear to be much smaller molecular species (predominantly containing 1-3 ring aromatic fluorophores, with a possible presence of some most compact 4-ring fluorophores) aggregating into head-to-tail manner predominantly via hydrogen bonding. [2,3] Moreover, these experiments demonstrated primary asphaltene aggregates are formed at concentrations as low as 0.05-0.5 mg/L even in "good" solvents (benzene, toluene, etc.).

Our SSFE measurements were made using a Cary Eclipse fluorescence spectrophotometer with classic 90° geometry and 10 mm quartz sample cuvettes. Excitation wavelength was set at 265 nm, SSFE spectra were recorded with 5 nm excitation and emission slits in a 270-540 nm wavelength range with 1 nm intervals, and a scan rate of 120 nm/min. The measured spectra were corrected for "inner filter" effects by the standard absorbance-based method [2,3] and the solvent (toluene) backgrounds were subtracted.

In this study we used two samples of toluene solutions with asphaltene concentrations C=0.34 mg/L and C=4.01 mg/L, i.e. smaller and larger than the initial conditions for observation of primary asphaltene aggregates.[2.3]

The graph in the lower part of Fig. 1 shows the corrected SSFE spectrum for C=0.34 mg/L with asphaltene emission maxima in the wavelength range characteristic for individual small aromatic molecules (monomers). For comparison, the upper part of Figure 1 shows standard SSFE spectra for the following excited monomers with 1-4 aromatic rings: 1 - 1,4-dicyanobenzene; 1A – styrene; 2 – naphthalene; 3 – anthracene; 4 – pyrene (for references to original publications with these spectra cf. our papers [2,3]).

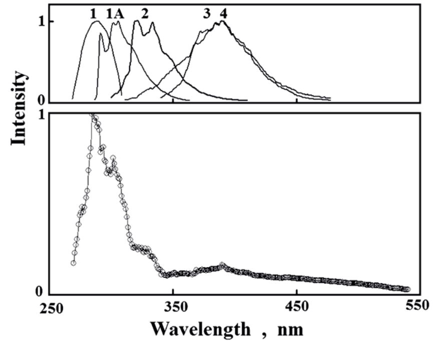

Figure 1 - Bottom—fluorescence emission spectrum from a solution with asphaltene monomers. Top—characteristic spectra for monomers of molecules with 1–4 aromatic rings (cf. text)

The graph in the lower part of Figure 2 shows that in solution with C=4.01 mg/L fluorescence emission from asphaltene monomers is strongly suppressed (virtually non-existent). Emission maxima of the newly-formed asphaltene species (primary molecular aggregates) are notably shifted to much larger wavelengths. By analysis of experimental results, obtained for chemically pure substances, these maxima may be reliably attributed to emission from excited head-to-tail aggregates of molecules with 1-4 aromatic rings. In support, the upper part of Figure 2 shows SSFE spectra for excited aggregates of the following molecules: 1 – of 1,4-dicyanobenzene; 1A – of styrene; 2 – of naphthalene; 3 – of anthracene; 4 – of pyrene (for references to original publications with these spectra cf. our papers [2,3]). Note that purely hydrocarbon single ring molecules, like styrene, form dimers and more complex aggregates by comparatively weak van der Waals and π-π interactions (cf. references in [2,3]). The characteristic emission peaks of these aggregates are outside the SSFE wavelengths range, observed in the asphaltene solution with C=4.01 mg/L – cf. spectrum 1A in Figure 2. On the other hand, the maximum of asphaltene emission in this solution coincides with the SSFE peak for dimers of single-ring 1,4-dicyanobenzene – a molecule with heteroatoms of nitrogen, which facilitate much stronger hydrogen bonding, known to be important in primary self-association of asphaltenes [4].

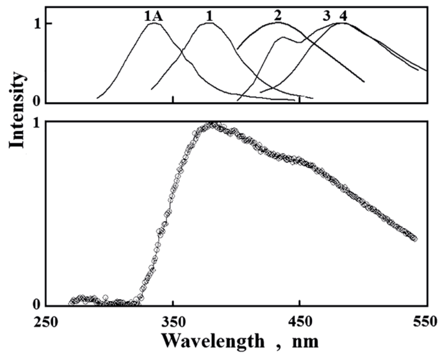

Figure 2 – Bottom—fluorescence emission spectrum from a solution with asphaltene primary aggregates. Top – characteristic spectra for head-to-tail aggregates of molecules with 1–4 aromatic rings (cf. text)

Summarizing, the principal result of this study is that individual asphaltene molecules, prone to aggregation at higher concentration, are relatively small species with predominant 1-3 aromatic ring chromophores, in contrast to the widely publicized erroneous assumptions of the "Modified Yen Model" [1] about much larger 7-10 ring "monomers" – Figure 3.

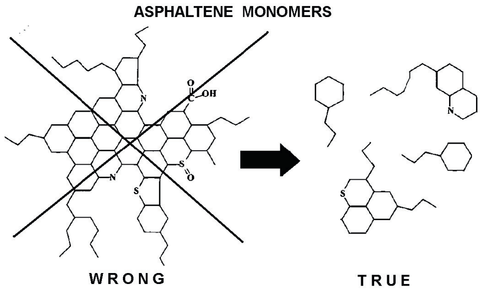

Figure 3 – Wrong and true descriptions of the structure of asphaltene monomers.

Furthermore, our results show that primary asphaltene aggregates are predominantly formed not by π-π stacking [1], but by head-to-tail hydrogen bonding [2,3] – Figure 4.

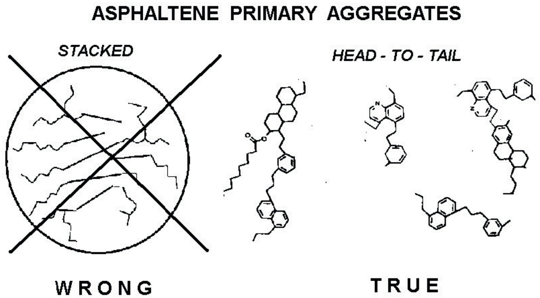

Figure 4 – Wrong and true descriptions of the structure of asphaltene primary aggregates

The erroneous "Modified Yen Model" [1] appears to originate in multiple publications of this prolific research group evidently aimed at designing a simplified "effective" structural description of asphaltenes, immediately suitable for spectacular practical applications in Flory-Huggins equations of state, in interpretations of the data on "reservoir compartmentalization, connectivity, baffling, tar mat and heavy oil formation, disequilibrium gradients, diffusive gradients in reservoirs, biodegradation, reservoir fluid geodynamics" (*https://www.linkedin.com/in/oliver-mullins-a7229810*). In a quest for such effective description these researchers decided to consider molecular species observed at concentrations up to 10-25 mg/L as individual asphaltene molecules, ignoring multiple experimental evidence by other research groups that asphaltenes remain aggregated at these and at much lower concentrations, down to 5 mg/L, or even below 1 mg/L. Moreover "experimental proofs" of the 7-10 ring model appear to be erroneous. In particular, fluorescence emission spectra have not been corrected for "inner filter effects". Also, there were multiple flaws in the fluorescence depolarization-rotational correlation time experiments, as was convincingly demonstrated in ref. [5], with the conclusion that the 7-10 ring results "*are egregiously wrong*" and the "*inferences postulated with respect to the molecular architecture of asphaltene … should in their entirety be disregarded*".

While the fallacy of the "Modified Yen Model" is evident to a fairly limited number of experts

in fundamental science of physicochemical properties of petroleum (the critical ref. [5] is cited in ca. 9 publications annually), the simplicity of this model is still appealing to much larger audience of scientists in various aspects of applied research and to oilfield practitioners (the respective ref. [1] is annually cited in ca. 60 papers). Hence, we hope that the above experiments will add new arguments for disregarding the long-standing misconceptions about the size of predominant asphaltene molecules in most dilute solutions and, hence, about the plausible structures of asphaltene aggregates in concentrated solutions and in native petroleum.

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МАТЕМАТИЧЕСКАЯ МОДЕЛЬ СТАТИСТИЧЕСКОГО АНАЛИЗА ПОКАЗАТЕЛЕЙ РАБОТЫ СКВАЖИН

MATHEMATICAL MODEL OF THE STATISTICAL ANALYSIS OF THE WELLS PERFORMANCE

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В данной работе представлен практико-ориентированный опыт в создании математической модели статистического анализа показателей работы скважин.

The paper reveals the practice-focused experience in creating a mathematical model of the statistical analysis of the wells performance.

Ключевые слова: математическое моделирование; практико-ориентированный подход.
Key words: mathematic modelling; practice-focused approach.

Использование математического моделирования при проектировании высокозатратных геолого-технических мероприятий при разработке месторождений получило широкое распространение как в России и за рубежом и является одним из перспективных направлений практико-ориентированного подхода в математической практике. Задачей использования математической модели статистических методов анализа промысловых исследований в рамках проекта являлось построение алгоритма выявления закономерностей изменения одних параметров исследования относительно других, а именно дебитов жидкости скважин с изменением давления выше и ниже давления насыщения.

Оценка влияния забойного давления ниже и выше давления насыщения на дебиты жидкости скважин проводилась на основе анализа и интерпретации статистического материала по исследованию скважин, представленного фонда. Кроме того, проводились исследования с применением компьютерного моделирования.

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ЧАСТЬ I

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