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Asphaltene nano-aggregates: structure, phase transitions and effect on petroleum systems

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Abstract. Data on the structure of oil asphaltene molecules and their aggregation routes is systematized. The possible phase transitions in asphaltene nano-aggregates and their influence on the properties of oil disperse systems are analyzed. The bibliography includes 204 references.

I. Introduction

Along with the major hydrocarbon components, crude oils contain polycyclic aromatic or naphthenoaromatic compounds with heteroatoms (O, N, S) and side chain substituents. Such compounds are called resin-asphaltene substances (RAS). The most polar and high-molecular fraction of RAS is called asphaltenes. There are several hypotheses on the origin of asphaltenes, the most popular is based on the similarity of the structure of oil asphaltenes, bitumen asphaltenes and kerogen and states that oil asphaltenes are in fact large soluble kerogen fragments, which underwent catagenetic transformations in the process of oil formation.[1] Another point of view exists stating that oil asphaltenes are of a secondary origin, *i.e.*, they are products of transformations of oil components in the process of its catagenetic transformation.[2] Kontorovich suggests[2] that both mechanisms can co-exist in nature.

Asphaltenes do not dominate as oil components: their content may vary from trace amounts in light crude oils to 16% – 20% in highly viscous oils. The interest in asphaltene chemistry is caused by their negative influence on the properties of oil systems. Thus, oils with high content of asphaltenes possess high viscosity, and so require costly processes for efficient production and transportation.[3 – 6] High asphaltene percentage leads to difficulties in oil refining, as they are catalyst poisons and decrease the yields of desired products.[7] Less viscous oils with lower amounts of asphaltenes are in most cases less stable with respect to asphaltene precipitation,[8, 9] which results in plugging of boreholes, surface equipment and pipelines causing additional finances to be spent on clean-up and maintenance. Morover, asphaltens have great influence on the wettability of formations[10] and stability of oil – water emulsions.[11, 12]

For investigations, asphaltenes are isolated from oils by precipitation upon the addition of lower molecular weight n-alkanes. With only a few exceptions,[13] elongation of the carbon chain length in the alkane causes the amount of asphaltene precipitate to diminish, while the content of high-molecular-mass, aromatic and lower H : C ratio components is increased.[14 – 16] The amount and composition of the asphaltene precipitate also depends on the oil : flocculant volumetric ratio.[14] Thus, the term asphaltenes, as noted by Gottlieb,[17] has as many definitions as there are methods for their isolation. To avoid disagreements in determination of asphaltene content and composition, standard procedures have been developed, which clearly describe the isolation of these compounds.[18, 19] Nevertheless, the problem of developing standard methods of asphaltene isolation is still topical, as it is influenced by many auxilary operations such as, time of contact with the flocculant, time of washing, drying temperature, *etc.*[16, 20 – 24]

High susceptibility of asphaltene molecules to aggregation has long hampered the determination of their molecular masses and sizes. Recent use of mass-spectrometric techniques, such as field ionization (FI-MS), electrospray ionization Fourier transform ion cyclotron resonance (ESI-FT-ICR-MS), atmospheric pressure photoionization (APPI-MS), field desorption and ionization (FD-FI-MS) and laser desorption (LDI-MS) mass-spectrometry, systematized in a review by Akbarzadeh *et al.*,[25] made it possible to estimate the molar mass of asphaltenes to be in the range of 300 – 1400 g mol^{-1} and in average it is 750 – 800 g mol^{-1}. Measuring molecular diffusion by time resolution fluorescence depolarization (TRFD)[26] and by

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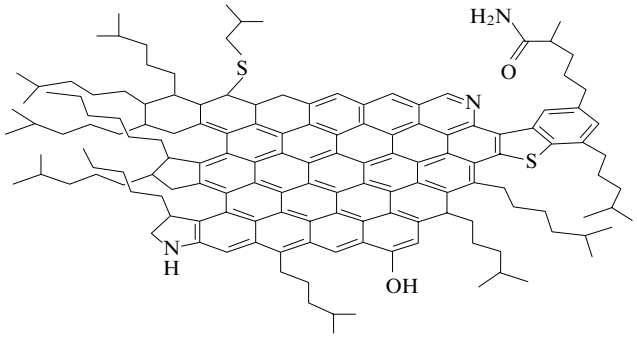
NMR spectroscopy (^{1}H – DOSY NMR)[27] was used to show the size of an asphaltene molecule to vary between 1.2 – 2.4 nm.

Analysis of the publications of the past 10 – 15 years demonstrates that data on asphaltene structure and influence on the important properties of oil fluids become more and more detailed. However, the mechanism of formation of supramolecular structures, their possible phase transitions and their influence on oil disperse systems are still debated. The present review is dedicated to systematization of recent (published mainly in the last 10 – 15 years) data on the structure and properties of asphaltene molecules and their aggregates and their influence on oil disperse systems as a whole.

II. Models of asphaltene molecules

Asphaltenes isolated from oils represent a mixture of molecules with various masses and structures. Is there any sense in determination of the 'average' asphaltene structure? Pokonova,[28] Safieva[7] and Kamyanov[29] consider that it is more correct to use structural parameters to describe the average asphaltene structures. However, the presence of structure – property relationship (as the Noble Prize winner Crick said,[30] if you want to understand a function, study the structure) defines the necessity to find an optimal model of an asphaltene molecule in order to model the behaviour of petroleum systems in various natural and industrial processes.

Modelling of asphaltene molecules is based on spectral data and elemental analysis, as well as on the average molecular mass. Thus, computer simulation of the molecular force field taking into account the average values of experimental parameters of asphaltenes from the oil residue with bp > 510 °C of a Venezuela crude[31, 32] resulted in the following presumable structures of asphaltene molecules; the spatial model is presented in Fig. 1.



It can be seen that model molecules consist of a fused aromatic core in the centre with a few saturated rings and short side substituents, and the authors[33] note that its shape is 'like your hand'. This model received the name 'continental' in the literature. Other methods were invoked to study the core of the model molecule, and its presumable size gradually decreased. Mullins[26] systematized his molecular diffusion studies by TRFD and fluorescence correlation spectroscopy (FCS), comparative analysis of absorption and fluorescence spectra of highly dilute benzene solutions of asphaltenes and model compounds, employing high resolution transmission electron microscopy (HRTEM) and X-ray combinational scattering (XRRS) to show that in most cases, the asphaltene molecule has one polyfused core consisting of 7 aromatic rings.

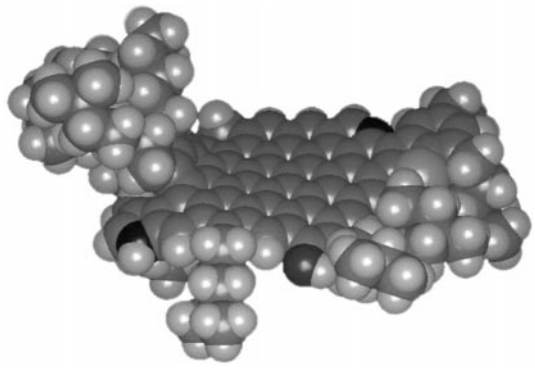


Figure 1. Spatial model of an asphaltene molecule suggested in pulications.[31, 32]

Another type of asphaltene molecules was suggested[34, 35] as the result of studies of asphaltenes precipitated with n-pentane from Atabasca bitumen (Canada). According to the authors, an asphaltene molecule consists of small aromatic clusters, linked by methylene, sulfide, ester and oxygen bridges. Peripheral substituents include non-branched and branched aliphatic groups, hydroxyl and carboxyl groups, *etc*. Such structure type received the name of 'archipelago'.

On the basis of experimental data[34] and the use of molecular mechanics, most energy-favourable (in vacuum) spatial model of an asphaltene molecule from Atabasca bitumen was proposed.[36] As it is seen from Fig. 2, this molecule has a structure of 3D globule with small inner cavities formed by polymethylene bridges, linking the aromatic areas. Such a distribution of side and bridging chains among the aromatic areas and/or saturated rings was deduced also for asphaltenes of paraffin-rich oils of Duri oil fields (Indonesia), sour crude oil of Boscan (Venezuela),[37] inmature heavy Jing Han sour oil (China),[38] and asphaltenes of vacuum distillation residue of arabian oil.[39]



Figure 2. Three-dimensional model of an asphaltene molecule isolated from Atabasca bitumen.[36]

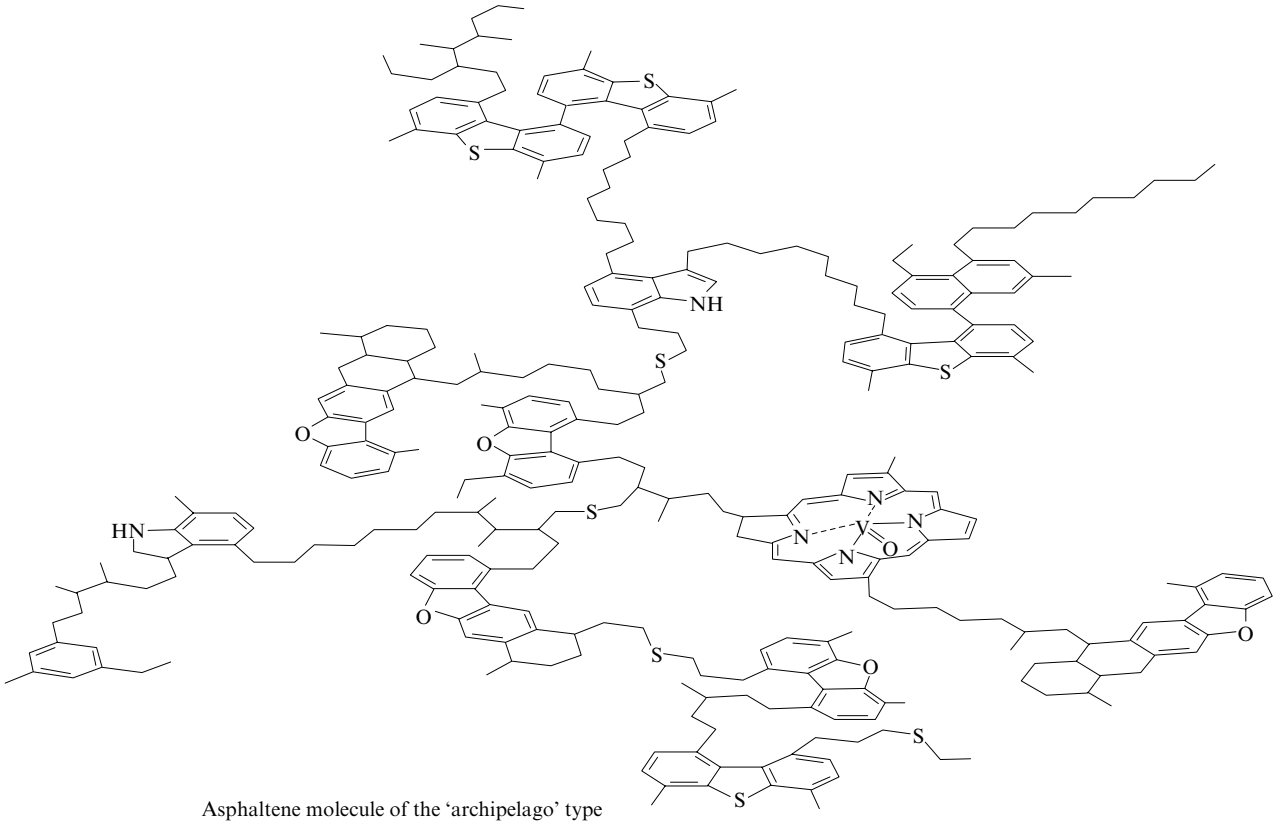
Data on the linking bridges were obtained by studying the products of selective ruthenium-catalyzed oxidation (RICO method), desulfurization with nickel boride, hydrolysis and thermolysis of asphaltenes by gas chromatography, gas chromatography/mass spectrometry, FTIR-spectroscopy, NMR spectroscopy, *etc.*[34, 37–40] The conclusion that the average asphaltene molecule represents isolated clusters of 5–7 fused rings linked by methylene and heteroatom bridges was also confirmed by spectral data (^{1}H and ^{13}C NMR, IR, EPR).[41]

Later, the 'archipelago' type structure for Atabasca bitumen asphaltenes was confirmed by single molecule force spectroscopy (SMFS).[42] It was shown that upon the action of an external force, asphaltene molecules behave like long-chain polymers.

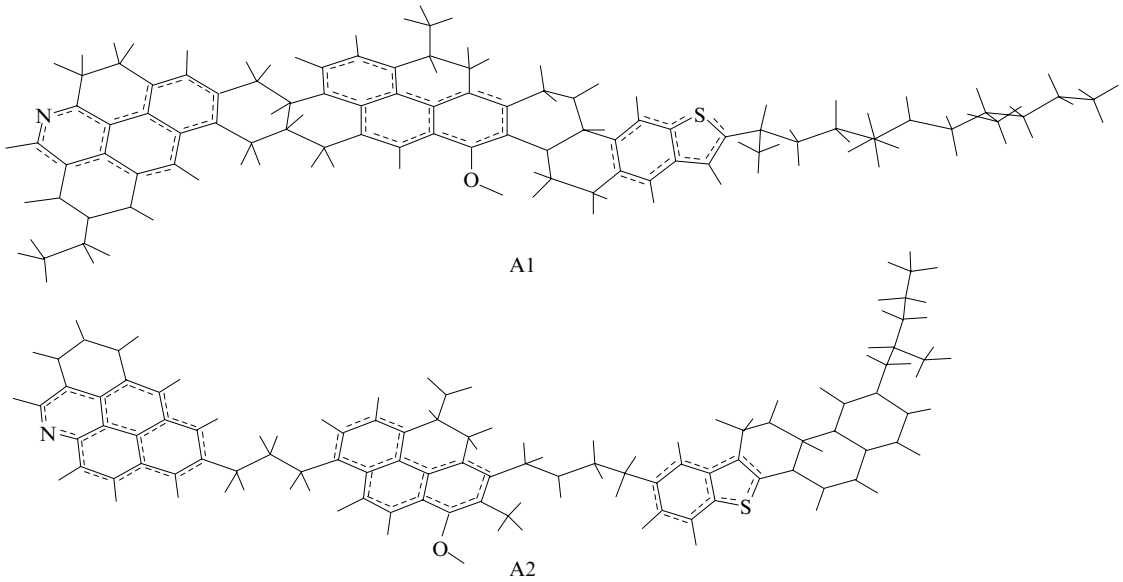
Integrated studies of asphaltenes and their fractions with different solubility allowed researchers to prove the coexistence of both the 'continental' and 'archipelago' type molecules. Asphaltenes can be divided into fractions using various ratios of components in binary solvent systems (toluene–n-heptane,[43, 44] toluene–n-pentane,[45] dichloromethane–n-pentane,[46, 47] acetone–n-heptane[48]), and aslo by the formation of complexes of asphaltenes with *p*-nitrophenol.[9] The fraction that precipitates from asphaltene solution upon the addition of minimum amount of n-alkane in the binary solvent or that precipitates upon the addition of *p*-nitrophenol is called in various publications heavy,[43] insoluble[9, 44, 45] and polar fraction.[46–48] In recent literature, it has been common to call this fraction A1, and the molecules that occur in this fraction are called type A1 molecules. The fraction that precipitates from solution with the maximum amount of n-alkane was called light, soluble, non-polar or A2 fraction, and its molecules were called A2 type molecules. According to research data,[9, 43–51] the A1 fraction, which represents dense shiny black particles, consists of highly fused aromatic compounds with high aromaticity and low H : C ratio. This fraction has most often high contents of metals (V, Ni, Fe), nitrogen and chlorine and low solubility in aromatic solvents (0.1 g litre^{-1} in toluene at ambient temperature). When the metals are removed, the solubility and dissolution rate greatly increase.[46, 47] Fraction A2 is a matted brown powder with low aromaticity factor and relatively high H : C ratio. The solubility of A2 fraction is comparable with the solubility of non-fractionated asphaltenes and amounts to 50–100 g litre^{-1} (Ref. 9).

It should be noted that a number of authors[50, 52] believe that the aromaticity factor is not the best criterion to characterize asphaltene fractions. According to a publication,[52] the pronounced difference between the solubilities of A1 and A2 fractions in toluene can be mainly related to the fusion mode of the polycyclic rings rather than to different molecular mass, aromaticity and heteroelement percentage. The authors suggest that the A1 type molecules have predominantly rigid structure, and the A2 type molecules consist of polycyclic rings connected by methylene chains. Such structures are flexible and are able to undergo conformational transformations, which stipulates their high solubility.

In contrast to the discussed publications which deal with fractionating of asphaltene concentrates, Fossen *et al.*[53] obtained asphaltene fractions by gradual addition of flocculants directly into crude oil. Comparative analysis of asphaltenes isolated from oil upon the addition of n-pentane in 1 : 3 ratio (the first fraction) and those precipitated from the filtrate upon secondary addition of the flocculant with the ratio oil : n-pentane = 1 : 18 (the second fraction) showed that the differences in properties of asphaltenes that



Asphaltene molecule of the 'archipelago' type



precipitate at minimum and maximum flocculant amounts are confirmed. It was found that a toluene solution of the first fraction has lower stability to precipitation and greater surface tension at toluene–water interface, which implies a higher amount of fused rings in the molecules of this fraction compared to the second one.

Domination of the 'continental' type molecules, which propagate aggregation in petroleum systems, or the 'archipelago' type molecules, which terminate aggregation, will certainly influence the properties of oil fluids. Indeed, it was found that asphaltenes from unstable oils (which show the tendency to precipitation of asphaltenes) have low H : C ratio and high aromaticity,[54] high degree of fusing of the aromatic rings,[8] high polar fraction percentages,[55] which is characteristic of the 'continental' type. Domination of A1 type asphaltenes in asphaltene deposits also confirms their lower resistance to precipitation.[54, 55] In asphaltenes derived from oxidized bitumen (the products of oxidation of residual oils from various Russian deposits), the content of A1 fractions reaches ~60%–80% and determines the colloid structure of the bitumen,[56] which is responsible for the physicochemical properties.

III. Self-organization of asphaltenes. Asphaltene nano-aggregates

1. Supramolecular structures of different levels

Asphaltene molecules in solutions tend to be aggregated even at low concentrations. Akhmetov[57] and Rogacheva[58] report asphaltenes to exist as separate molecules at concentrations of $< 1-2$ mg litre^{-1}; according to Evdokimov,[59] these concentrations are $< 5-10$ mg litre^{-1}. At higher concentrations, oligomers (dimers and dimer pairs) are formed.[60] Stable nano-aggregates consisting of 6–10 asphaltene macromolecules[25, 26] occur at the critical nano-aggregate concentration (CNAC) (the term was introduced by prof. J Sjöblom),[33] which varies from 50 to 200 mg litre^{-1} (Refs 26, 27, 33, 60–64). The aggregates themselves are 2–10 nm in size.[26] Further increase in the concentration leads to increase in the amount of nano-aggregates but not in their size. Clusters are formed when the concentration of asphaltenes reaches 2–5 g litre^{-1} (Fig. 3).[25, 26]

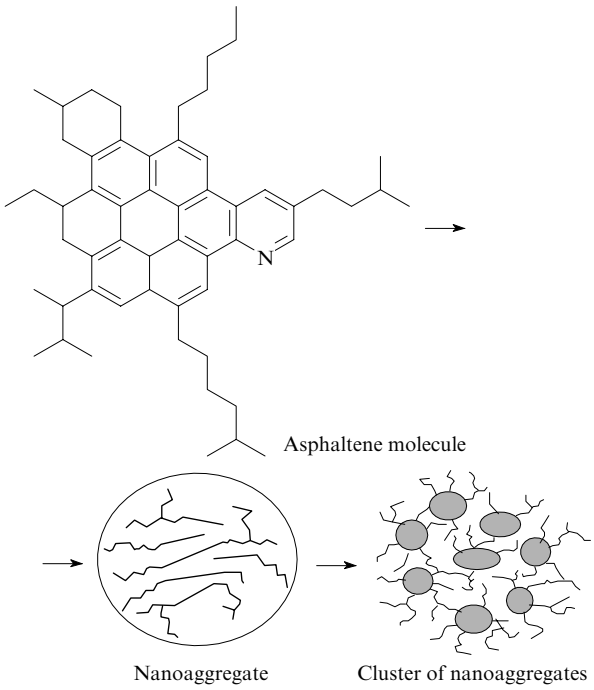


Figure 3. The hierarchical stages of asphaltene supramolecular organization.[26]

The clusters possess fractal structure[26] and consist of about 8–10 nano-aggregates.[26, 65] The cluster size of different asphaltenes can be from 6 nm[26] to 30 nm,[65] and some researchers report it to reach 100 nm.[25] Further increase of the concentration (> 5 g litre^{-1}) leads to the formation of flocculs[25, 26] or various nano-phases of flocculated nano-colloids (FNP),[66] which can exceed 100 nm in size;[25, 66, 67] the continued aggregation can lead to the loss of sedimentation stability by the solution.[25]

The growth of asphaltene aggregates, their flocculation and loss of sedimentation stability are also observed on addition of low-molecular n-alkanes (flocculants) to toluene (benzene) solutions of asphaltenes. In this case, the solution

is characterized not by CNAC but by the onset point, *i.e.*, the flocculant concentration which causes flocculation of asphaltenes and their precipitation from the solution. The data on stability of asphaltene aggregates formed on the addition of flocculants are quite discrepant. For example, it was reported [68–70] that asphaltene aggregates reach a stable state in the course of several days; during this period, the composition, structure and size repeatedly vary. Another research,[71] on the contrary, gives evidence for high stability of the forming aggregates in n-heptane – toluene mixtures at 20 °C for at least as long as the observation continued (about 7 days).

A dependence was deduced of the aggregation rate of asphaltenes of various sizes on the flocculant concentration (Fig. 4).[68] Yudin *et al.*[68] experimentally found the formation of asphaltene aggregates in heptane – toluene solutions to proceed according to two different kinetic laws, depending on the asphaltene concentration. At low concentrations of asphaltene, diffusion-limited aggregation takes place, while at high asphaltene concentration reaction-limited aggregation occurs. The kinetics of formation of asphaltene aggregates depends on the nature of oil from which they originate.[68,72] For the stable Boscan oil (Venezuela), fast growth of the aggregate size and decrease in the number of aggregates occur at the onset point. For the unstable Furrial oil (Venezuela), the number of aggregates is increasing, while their size is growing gradually.[72] Studies of asphaltene flocculant-induced aggregation dynamics in four different crude oils by dynamic light scattering (DLS) showed [68] that in unstable oils (with low aromatic HC : saturated HC ratio, HC are hydrocarbons), asphaltenes possess low aggregation rate. On the contrary, stable oils with high ratio of aromatic HC : saturated HC have a higher rate of asphaltene aggregation.

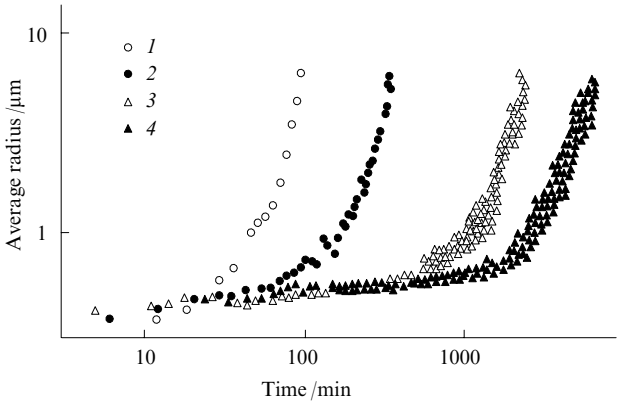


Figure 4. The average radius of asphaltene aggregates as time function for different flocculant concentrations.[68]
Amount of n-heptane (%): 25 (*1*), 18 (*2*), 9 (*3*), 5 (*4*).

Selectivity of asphaltene aggregation was reported. Spectral ^{1}H – DOSY NMR studies of the diffusion coefficient for toluene solutions of Buzurgan oil asphaltenes reveal a phase transition at ~3 mass %, which results in the formation of two aggregate types, with different sizes: microaggregates and nanoaggregates.[73] The formation of asphaltene aggregates of two sizes was also confirmed in the Blue Sky Energy company oil by DLS, upon addition of 44 vol.% of n-heptane.[68] A suggestion can be made that the selectivity of asphaltene aggregation can be due to the presence of two different types of the asphaltene molecules, namely, 'continental' and 'archipelago' types, which have different properties. The suggestion is confirmed by experimental data,[74] which show that in an aromatic solvent, only 75% of Maya oil asphaltenes (flocculated with heptane from the vacuum distillation residue) formed large colloid particles, it was just the fraction with high molecular mass typical of A1 type molecules. The remaining 25% did not undergo association and did not form asphaltene aggregates in the aromatic solvent.[74]

The outlined trends for the sizes of supramolecular structures and the rates of their formation depending on the concentrations of asphaltenes and flocculants and on thre ambient pressure [75] and temperature,[75,76] along with detection of asphaltenes in oils at temperatures as high as 100 – 200 °C (Refs 77 and 78) indicate that asphaltene aggregates are real and are not density fluctuations, as some researchers consider, *e.g.*, Sirota.[79,80]

It should be noted that in real oils CNAC and the onset point are determined not only by the concentration and nature of the asphaltenes and the flocculant, but also by the concentration and composition of other oil components. For instance, it is known that Carboniferous oils, though have a higher asphaltene content, are more resistant to asphaltene precipitation than Devonian oils, due to the nature of the other components.[81]

The data on the shape of asphaltene aggregates in solutions mainly come from small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) measurements. Thus, SAXS and SANS data were interpreted to deduce the shape of asphaltene aggregates to be spherical,[82] elongated cylindrical,[83] rod-like,[74,84] disk-like,[85] or elongated ellipsoids transforming into spheres at elevated temperatures.[86] The rheological studies of heavy oil residues [87] are well-interpreted to consider the aggregates to have disk-like shape. In highly concentrated asphaltene-containing systems — residual bitumen,[88–90] oxidized bitumen [51,56] and petroleum pitches [91] — 'bee-like' microscopic-size supramolecular structures were described (Fig. 5).

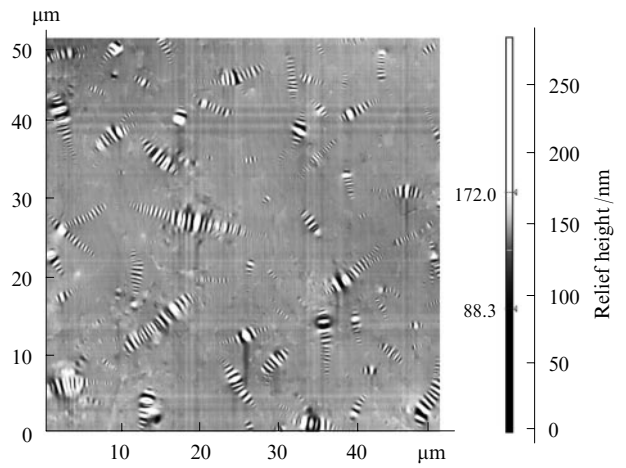


Figure 5. AFM imasge of the surface of oxidized bitumen.[51]

2. Intermolecular interactions leading to the formation of nano-aggregates

Colloid particles in petroleum systems are electrically charged.[92–95] However, regardless of a rather high electrostatic interaction energy (5–100 KJ mol^{-1}), aggregation of asphaltenes in solutions and oils is considered to proceed due to donor–acceptor interactions with the formation of various charge-transfer complexes (CTCs). An asphaltene molecule parts of which possess different ionization potentials (IPs) and electron affinities (EAs) acts simultaneously as a donor and as an acceptor, which promotes the formation of CTCs between the parts of a single molecule and between the parts of different molecules. High values of EA and low values of IP, determined by a special method of integral electronic spectroscopy of multicomponent mixtures,[96] show an extraordinary ability of asphaltenes to accept and give off electrons. Radicals form CTCs more easily than molecules due to higher electron affinity and lower ionization potential. Proceeding from Unger's suggestion[97] that the characteristic trait of asphaltenes is paramagnetism, exchange interactions of two stable radicals should be dominating. However, it was reported[28] that the total amount of free radicals in asphaltenes is comparatively low, so the major infuence in CTCs formation is believed to belong to aromatic and heteroaromatic π-orbitals and functional substituents. Moreover, a great contribution to the formation of supramolecular structures is made by van der Waals interactions.[7]

Rogel estimated[98,99] that increased number of aromatic rings and the fusing degree results in more molecules to form nano-aggregates due to π–π-interactions (stacking) and in decreased CNAC. Akbarzadeh *et al.*[100] showed the influence of functional groups on the formation of supramolecular structures. Thus, non-polar polyaromatic compounds, pyrene and dipyrenyldecane, do not form associates in *o*-dichlorobenzene. But when C=O and OH groups are introduced into their molecules, dimers are formed at 75 and 100 °C, respectively. The contribution of heteroelements to the self-association of asphaltenes was estimated,[101] showing methylation and silylation with blocking of free O, N and S atoms and only O atoms, respectively, to lower the hydrogen bond index (IR spectral data) and the association enthalpy (isothermal titration calorimetry data). If aliphatic substituents are removed and ring heteroatoms are replaced by carbon atoms, dissociation of asphaltene aggregates occurs at lower temperatures and to a higher degree than for the initial structure, which also attests to the influence of side substituents and heteroatoms on the complexation ability of asphaltenes.[102] Experiments on model 'continental' type asphaltenes [synthetic alkylated (C_6 and C_9) hexabenzocoronenes (HBC)] showed[103] that self-association of C_6-HBC occurs due to π–π-, and alkyl–alkyl interactions, and the tendency for association remains up to 400 °C.

The great role of hydrogen bonding in the formation of asphaltene aggregates is noted by many authors.[104] It was shown that the presence of water accelerates the association of asphaltenes. Researchers from China[105] used FTIR to study benzene solutions of asphaltenes derived from Chinese oil vacuum distillation residues and also pointed at hydrogen bonding as the driving force in the aggregation of asphaltenes.

Continental model of asphaltenes[26] suggests the formation of aggregates as packs of several (4–6) molecules with their aromatic systems parallel. Yen[106] called such molecular aggregates 'crystalites' and used X-ray diffraction studies to find out that in these stacked structures, fused polycyclic aromatic systems 0.9–1.7 nm in diameter are located at a distance of 0.36 nm from each other. Increased sizes of aromatic substructures lead to a higher ordered systems and to approximation of them to graphite, which has 0.334 nm intraplanar distance. Computer models using molecular dynamics of aggregation of 'continental' type asphaltenes in vacuum show that the aggregation occurs spontaneously with the formation of dimers, trimers and tetramers.[107] The most energy-favourable orientation of two asphaltene molecules in vacuum is face-to-face, the bonding energy of the molecules is then 12–15 kcal mol^{-1} (Ref. 108), the distance between the aromatic planes is 0.3844 nm.[109] The influence of the solvent on the structure and formation enthalpy of the aggregates was shown.[109–111] In solutions, the interplanar distance is ~0.36 nm in heptane and >0.5 nm in toluene. Increasing temperature from 323 to 573 K causes the distance between the molecules in the dimer to diminish.[108] Almost the same interplanar distances in dimers and trimers formed in toluene and heptane were obtained by other researchers[110] (0.5–1 nm). It was found that the aromatic planes are nearly parallel and that the free energy of dimer formation in toluene and heptane ranges from −6.6 to −12.1 KJ mol^{-1} (from −3 to −5.4 kT). Molecular modelling considering the solvent dielectric constant conducted by Ortega-Rodríguez *et al.*[111] showed that at 273 K in heptane and toluene, the bonding energy of asphaltene molecules calculated using the radial distribution function is from −4 kT to −5 kT, which is close to the bonding energy value obtained by other authors[110] and substantially lower than bonding energy in vacuum.[108]

Molecular modelling showed[107,108] that along with face-to-face disposition with domination of π–π interactions (most energy favourable), two additional orientations of polycyclic aromatic asphaltene rings are possible: T-shaped geometry formed due to π–σ interactions (with hydrogen bonding contribution) and displaced π-stacking due to σ–σ interactions (Fig. 6). There is evidence that polar functional groups at the periphery of asphaltene molecules can promote reversible association of asphaltenes into two-dimensional layers (porous membranes model[89]) and data of SAXS and viscosity measurements give evidence for the formation of asphaltene aggregates as hollow vesicles.[112]

The formation of 'archipelago' type asphaltene aggregates is a more complex process. For such molecules, fundamentally different supramolecular structures are typical. The presence of long bridge chains promotes conformational changes in individual macromolecules and leads to intermolecular tangling.[113] The process of tangling and disentangling can be rather slow, which can explain the long time required to achieve equilibrium when Athabasca oil asphaltenes are being dissolved in a suitable solvent.[114] In 'archipelago' type asphaltene aggregates, not all aromatic fragments are involved in the formation of the aggregate,[110] which, on one hand, makes the aggregates more fragile but, on the other hand, promotes the formation of inter-aggregate bonds. Limited staking with lateral intermolecular bonding is the reason for the formation of more or less planar aggregates in solutions of this type of asphaltenes.[115] The aromaticity of 'archipelago' type mole-

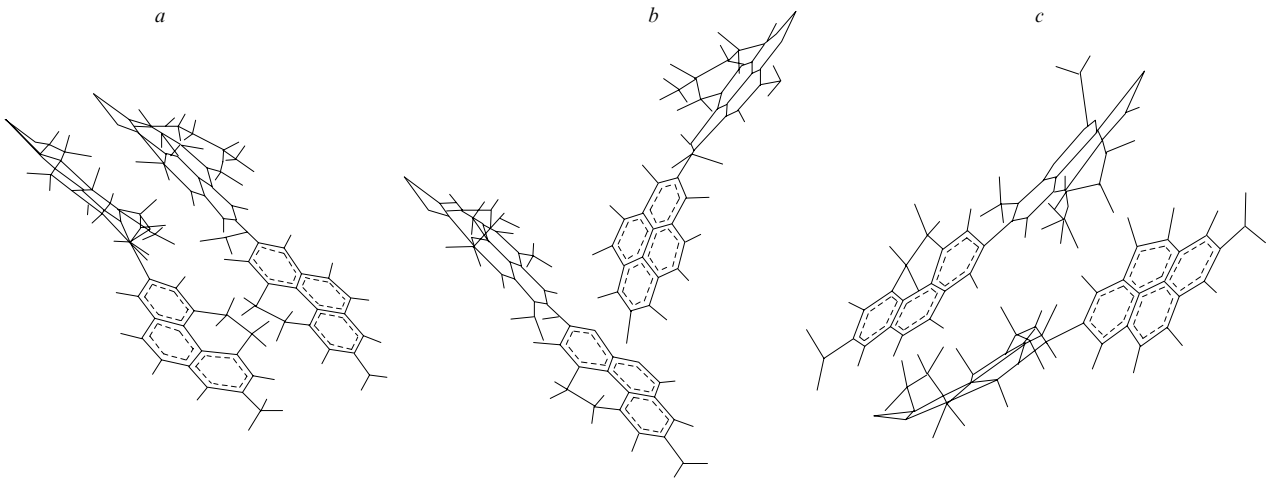
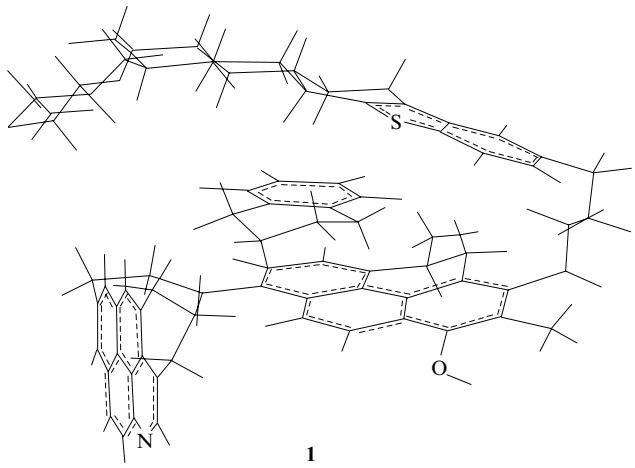


Figure 6. Possible types of mutual disposition of neighbouring asphaltene molecules that correspond to different predominant interaction types.
(*a*) Parallel (face-to-face) $\pi-\pi$-interactions; (*b*) T-like geometry (edge-on, edge-to-face), $\pi-\sigma$ interactions; (*c*) π-offset π-stacking, $\sigma-\sigma$ interactions.

cules is slightly lower, and other intermolecular forces, such as hydrogen bonding, compete with stacking. Athabasca and Cold-Lake oil asphaltenes (of the 'archipelago' type) were found to self-associate similarly to linear polymerization due to interaction of active sites at the periphery of the molecules (which are in fact functional groups).[42, 116]

Using PBP, which has two pyrene groups linked to a bipyridyl spacer, as a simplified model compound of the 'archipelago' type asphaltene, ^{1}H NMR, fluorescence spectroscopy and vapour phase osmometry were employed to determine that PBP undergoes self-assoctiation in $CHCl_3$ and forms dimers in toluene due to $\pi-\pi$ interactions of both pyrene and bipyridyl fragments and that aromatic fragments having up to 4 fused rings and linked by bridging bonds are able to form associates in solution.[117] The start of aggregation of the model molecules corresponds to the start of aggregation of asphaltene molecules with 500–700 g mol^{-1} molecular masses; however, the aggregation degree of the model compounds is considerably lower than that of asphaltenes, which is, as the authors suggest, due to the absence of intramolecular interactions and ability to form hydrogen bonds.

Molecular mechanics calculations show that 'folded' molecules of the 'archipelago' type are much more stable



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and must prevail over the 'non-folded' ones.[52] The ability of the 'archipelago' type molecules to undergo conformational changes[27, 52] determines the ability of formation of host–guest complexes (*e.g.* complex **1** with tetralin molecule as a 'guest').

Data on the involvement of side chain aliphatic groups in the formation of asphaltene agregates are quite contradictory and are mainly discussed in the aspect of the possible interaction of asphaltenes and saturated hydrocarbons. Such interactions were first detected back in 1968.[118] The influence of asphaltenes on cloud point and inhibition of alkane crystallization in waxy oils was shown. Further investigations[119–124] showed this influence to depend on the structure of asphaltenes, the degree of their aggregation and the alkanes : asphaltenes ratio. Depending on the aggregation degree, asphaltenes act either as crystallization centres for alkanes or as sufractants, preventing the crystallization by inserting their side aliphatic chains into the crystal structure of alkanes. It was shown that more alkylated asphaltenes lower the gelation temperature more appreciably than less alkylated ones.[120, 124] Studies show[125–127] the interaction of asphaltene side alkyl chains with high-molecular saturated hydrocarbons to result in the formation of paraffin–asphaltene aggregates which tend to precipitate out of the petroleum system. Indeed, in a number of publications, joint presence of paraffins and asphaltenes was detected in paraffin deposits.[128–134] The explanations of this are, however, quite discrepant. Some researchers[135] report asphaltenes found in oil and paraffin deposits to be similar, so the presence of asphaltenes in the deposit is explained by the authors by capture of oil components by paraffin hydrocarbons as they are deposited. Other scientists[136] state that asphaltenes from Hassi Messaoud oil paraffin deposits (70% paraffins, 6% asphaltenes) to be more alkylated and to contain more heteroatoms compared to asphaltenes remaining in the oil. Moreover, a correlation between the start of flocculation and the length of the side hydrocarbon chain of asphaltenes was found; this gives evidence for the selectivity of asphaltene precipitation or for the possibility of paraffin–asphaltene interaction. The properties of the composites formed

upon the interaction of asphaltenes with parafins differ from the properties of their components and are rather determined by the nature of the asphaltenes and not by the composition of the paraffins or the way of formation of the composite.[137,138] Differential scanning calorimetry was used to study paraffin–asphaltene composites and the low-molecular fraction of A2 type asphaltenes, and the formation of a mesophase with a destruction temperature of 100–130 °C was detected,[51] which, as the authors suggest, proves the possibility of interaction of asphaltene molecules with their side alkyl chains.

Due to their structure and composition, asphaltenes easily form coordination compounds with metal chlorides.[139] Complexation with titanium chloride is used to accelerate the precipitation of asphaltenes from oils.[140] Donor–acceptor interaction was detected between asphaltenes and halogen-substituted benzoquinones. When the donor nature of coal asphaltenes was studied and two isomeric chloranils were used as the acceptors, it was found[141] that the molecules of chloranil enter the cavities of asphaltene aggregates forming charge transfer complexes with one of the asphaltene molecules. Electronic absorption spectral data showed that at asphaltene concentrations of 102–800 mg litre^{-1} two isomeric chloranils form a donor–acceptor complex containing aggregated asphaltenes. At lower concentrations, a 1 : 1 complex containing monomeric asphaltenes is formed.[142] *p*-Bromanil forms a 1 : 2 complex with coal asphaltenes.[143] It was estimated, based on the calculated enthalpy and entropy of complexation, that in chloroform the molecules of bromanil enter the cavities of asphaltene structures and that the complexation degree is increased with increasing temperature, while usually it is the other way round.

Intermolecular interactions are characterized by relatively low energies (5–100 KJ mol^{-1} for electrostatic interaction, 1–50 kJ mol for $\pi-\pi$-stacking $^{-1}$, 8–40 kJ mol^{-1} for hydrogen bonding, 0.4–4 kJ mol^{-1} for van der Waals forces; the covalent C—C bond energy in the molecule of benzene is, for compairson, higher than 500 kJ mol^{-1}). However, according to molecular mechanics and molecular dynamics calculations for Hafji oil (Saudi Arabia) vacuum distillation residue asphaltenes, the hydrogen bonds between the asphaltene molecules are cleaved in vacuum at 523 K and interactions between the polyaromatic rings ($\pi-\pi$ interactions) remain stable until 673 K, *i.e.*, the temperature at which covalent bonds can undergo cleavage.[102] This implies that the aggregates based on the multitude of non-covalent interactions are quite strong. High thermal stability of asphaltene aggregates in solutions was confirmed in several publications.[144,145] Studies of 0.5% solutions of asphaltenes in deuterated decalin, 1-methylnaphthalene and quinoline by SANS[144] showed that on raising the temperature from 25 to 350 °C, the average size of asphaltene aggregates decreased only to a limiting value of 25 Å, and asphaltenes from Maya oil, which possesses high density, molecular mass and heteroatom and metal contents, form a fractal grid in decalin, which is stable even at 350 °C. Studies of 3% solutions of asphaltenes in resins in the temperature range from 25 to 250 °C showed[145] that in the course of heating, the numbers of particles with the greatest and smallest diameters decrease and increase, respectively, while the number of medium-size particles passes its maximum. This also gives evidence that conversion of medium particles into smaller and larger ones is hampered by a relatively high potential barrier.

High thermal stability of asphaltene aggregates is also confirmed by their presence in crude oil at 100–200 °C.[77,78]

Thus, taking into account the polydisperse composition of asphaltenes in petroleum systems and various intermolecular interactions, the following model of asphaltene nanoaggregates is proposed. The 'continental' type molecules (A1) form strong stacked aggregates stable up to 400 °C. In petroleum systems, these supramolecular assemblies are stabilized by the interaction with more soluble asphaltene molecules of the 'archipelago' type (A2), which are adsorbed on the stacked aggregates of A1 molecules and stretch out their aliphatic groups, forming a sterically stabilizing shell (crown) around the core of A1,[69,145–147] the shell being stable up to 200 °C.[148] A 'colloidal grid' is thus formed,[149] which captures oil components, such as metal porphyrins, free radicals, resins, *etc.*; this was reported in a number of publications.[133,134,150] The captured molecules are probably located at the periphery of the asphaltene aggregates between the molecules of types A1 and A2 (Fig. 7).[149]

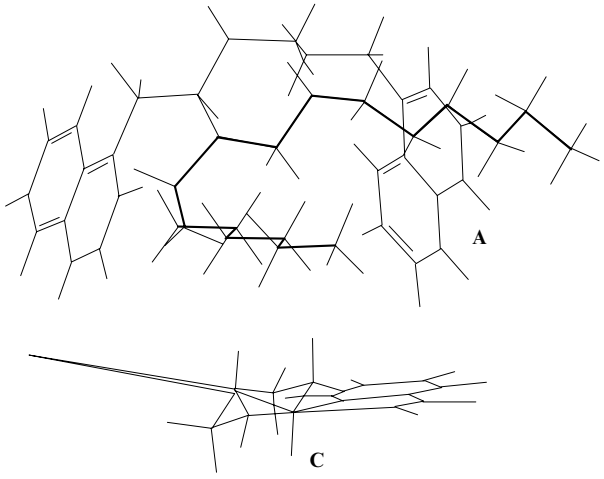


Figure 7. Molecular model showing the capture of hexadecane molecule by the collodial grid (see text).[149]
A is 'archipelago' type molecule; **C** is 'continental' type molecule. Bold lines show the carbon framework of heptadecane.

The formation of clusters and floccules is the next level of supramolecular organization of asphaltenes, it is driven by weak van der Waals interactions.[76,151]

It should be noted that some researchers prefer a fractal model,[152–156] according to which an asphaltene aggregate represents a paramagnetic framework of fractal geometry. Association takes place according to the 'particle–cluster' pattern for dilute systems and the 'cluster–cluster' pattern for condensed systems.[155] For densely packed particles the fractal dimension is the same as topological dimension, 3 in the case of three dimensions. If the cluster is loose, the fractal dimension can be fractional: <3 for three-dimensional objects. SAXS and SANS data are well interpreted if the aggregate fractal dimension is assumed to be 2.5.[156]

Particularly interesting are the structural features of asphaltene aggregates isolated from oils with high vanadium content. It is known that most of vanaduim is

concentrated in CAB. In oil residues and in high-viscosity oils and bitumen, the concentrations of vanadium can reach commercial amounts, which creates a need for processes for its most efficient extraction. From this standpoint, studies of vanadium forms in oils and its interaction with asphaltenes appear topical.

The data about vanadium involved in asphaltene aggregation processes are quite contradictory. Studies of Tagirzyanov *et al.*[157] show in relation to Tatarstan oils that increased vanadium content decreases the tendency of asphaltenes to form supramolecular structures. In other studies,[158,159] on the contrary, the authors show that increased amounts of vanadium raised the susceptibility of asphaltenes to aggregation and led to increased size of the particles. In a review[160] dedicated to investigation of different vanadium forms in heavy oils and bitumen, a vast array of experimental data (fine structure of near-edge X-ray adsorption spectra, electronic adsorption spectra, EPR spectra, mass spectra, *etc.*) has been colligated and the authors conclude that vanadium exists in oils in the form of vanadyl porphyrin complexes. There are currenty several points of view on the nature of interaction of vanadyl porphyrin complexes with asphaltene molecules. A suggestion[161] exists that the vanadyl porphyrin complex is a part of asphaltene structure and acts as a coordination centre in the aggregation process. Accodring to Dickie and Yen,[106] the vanadyl porphyrin complex is not a part of asphaltenes but serves as a link in the aggregation process. Inverse relationship of the contents of carbon radicals and vanadyl complexes in asphaltenes found using EPR gave the authors[162,163] a hint that planar vanadyl complex is attached to the plane of the polyaromatic asphaltene fragment where the unpaired electron of the paramagnetic centre is localized to form a diamagnetic complex with the enegry of intermolecular interaction estimated[164] to be 59.8 KJ mol^{-1}. However, Tagirzyanov considers[157] that the inverse relation is due to the changes in the ratio of polyaromatic to naphtheno-aliphatic fragments in the average molecular structure of asphaltenes from vanadium-enriched oils.

Finally, UV and fluorescence spectroscopy studies of vanadyl and nickel octaethylporphyrin complexes with model bridged (PBP) and fused (peri-hexa-n-dodecylhexabenzocoronene, HBC-C_{12}) aromatic compounds did not reveal[165] any interactions between porphyrins and aromatic condensed layers either in ground or in excited state. The authors conclude that association of most of the vanadyl and nickel porphyrins with the asphaltenes in oils occurs due to the side chain substituents and not due to $\pi-\pi$ interactions of the aromatic rings with the porphyrin rings.

According to a publication,[160] the major part of vanadyl porphyrins co-exists with the high-molecular asphaltene fraction (A1) with the help of multitude of intermolecular interactions (mostly interactions of functional groups and $\pi-\pi$ interactions). However, in the same review, a suggestion is made about the possible precipitation of vanadyl porphyrins together with the high-molecular asphaltenes, because they are also poorly soluble in low molecular weight n-alkanes.[166] The same authors studied diffusion of asphaltene solutions in toluene through 3–20 nm membranes and estimated that asphaltenes include free vanadyl porphyrins, which are only a small part of the total amount of vanadyl porphyrins and are linked to asphaltenes by noncovalent bonds or adsorption. There are also strongly bound vanadyl porphyrins that are bonded either covalently or through multiple intermolecular contacts ($\pi-\pi$ interactions, hydrogen bonds, *etc.*). Vanadyl porphyrins of such a type participate in asphaltene aggregation and are almost unseparable.

The question of the role of vanadium and vanadium porphyrin complexes in the processes of asphaltene aggregation and the possibility of their complete isolation from the oils has not been solved as yet and requires further investigations.

The contemporary model of an asphaltene aggregate according to which the core is formed by 'continental' type of asphaltenes and the periphery is composed of the 'archipelago' type molecules casts doubt concerning the necessity of solvatation by petroleum resins. Indeed, the latest data do not show any quantitative relationship between the resins and asphaltenes and support the lipophilic model of the oil disperse system.[167] Monte Carlo modelling in intermolecular interaction of asphaltenes and resins[168] showed an insignificant influence of the resins on the aggregation of asphaltenes. Homogenous distribution of resin molecules in the medium is caused by the fact that asphaltene–asphaltene interactions are much more energy-favourable than asphaltene–resin ones. However, there is a group of resins that is embedded in the asphaltene structure cavities. The authors consider[36] this embedding to be the result of structural correspondence (molecular recognition). León *et al.*[169] studied interactions of asphaltenes and native resins, and found that they penetrate into the microporous structure of asphaltenes and disintegrate it. The absence of asphaltene–resin relationship was also shown for natural oils. In papers[77,170] researchers found a gravitational gradient of asphaltenes in vertical 1000 m deepwater boreholes, while no gradient of resins was detected. Independent phase behaviour of asphaltenes and maltenes in 320–340 K temperature range with the DSC method was shown for Maya oil.[171] SARA-analysis (Saturated, Aromatic, Resin and Asphaltene fractions) of fractional composition of Atabasca bitumen and Maya oil using nano-filtration (20, 50, 100 and 200 nm pore size filters) at 473 K (without using solvents) also did not reveal any relation between asphaltene and other components. Moreover, it was shown that decreased filter pore size leads to a severalfold increase in the asphaltene residue on the filters (from 4.5% to 12.6% for bitumen, from 1.5% to 19.7% for oil), while the content of resins stays almost unchanged and is $\sim$20% for bitumen and 14% for oil.[78] The absence of a detectable influence of resins on the laws of stepwise aggregation of asphaltenes was also noted by Russian scientists.[57,60,172]

Thus, the structures of asphaltene molecules and the main types of intermolecular interactions responsible for the formation of supramolecular structures in petroleum systems have been thoroughly studied. Practical interest lies in determination of the relations of the structure of supramolecular assemblies and their properties and conditions such as pressure, temperature and concentration, as well as the study of the effect of asphaltene supramolecular organization on the macroscopic properties of petroleum systems.

IV. Phase transitions of asphaltene nano-aggregates

The phase state (the size and structure) of supramolecular assemblies has a significant influence on the physicochem-

ical properties of petroleum systems. This relationship was first taken into account by Syunaev,[173] who was the first to apply the phase transitions theory to oil disperse systems (ODS). He suggested a model of a particle of the disperse system as a complex structural unit (CSU) and made a suggestion that under the influence of external factors, the size of the asphaltene core and the CSU solvate layer thiclness vary in an antiparallel fashion. In an extreme state, anomalous sensitivity of the petroleum system to external factors appears, which should be considered in oil refining in order to manage the properties of the products. Thus, it was estimated that phase transition of asphaltenes in petroleum system has a predominant ifluence on coke formation [173–175] and the yield of light oil products.

Currently, the most interesting problem is the study of asphaltenes phase state and its influence on the properties of petroleum systems during transportation and storage, *i.e.*, under rather moderate conditions. The trends of asphaltene phase transitions depending on the concentration [25–27, 33, 60, 63] and composition [68, 176] of the disperse medium are quite well studied. Repeated abrupt changes in the physicochemical properties of the petroleum system at concentration limits corresponding to different degrees of asphaltene aggregation and also when flocculants are added to oil attest to reversible phase transitions which can be regulated, *e.g.*, by varying concentration and solvents.

Many research efforts are directed towards determination of the influence of other parameters on the phase state of supramolecular structures. The few data available is very contradictory and requires checking in most of the cases. Lowering of oil viscosity after exposure to magnetic field is explained in the literature both by increased [177] and by decreased [178, 179] sizes of supramolecular structures in magnetic field. Roux *et al.*[180] reported 'critical temperatures' of 8 and 20 °C at which dense micron-sized domains were formed in 0.3% – 10% solutions of asphaltenes in toluene. Studies of dielectric constants of Tatarstan heavy oils showed interesting results in the temperature range of 50 – 100 °C where the changes in the dielectric constant are due to the formation of spherical aggregares of asphaltene molecules.[181] It should be noted that such a phenomenon was not detected for vanadium-rich oils.

Evdokimov *et at.*[182–186] seem to be most consistent in investigation of asphaltene phase state. Along with concentrational dependence,[59, 66] they found a thermal relationship of the physicochemical properties of petroleum systems (viscosity, activation energy of viscous flow, pour point) at low temperatures. The authors explain abrupt changes of the properties of petroleum systems in 20 – 30 and 39 – 40 °C temperature ranges [182, 183] (or for long-term heating of oils at 30 – 42 °C) [184] by first order phase transition of asphaltene – resin components or change of the structure of asphaltene aggregates which leads to abrupt decrease in their surface energy. In another work,[185] the stepwise increase in the size of nanoparticles (Fig. 8) after heating above the critical temperature was explained by change of the nature of non-covalent interactions between the aggregating asphaltene molecules. Before thermal treatment, the loose and irregular structure of the nanoparticles is stipulated by the formation of edge-to-face structures with T-like geometry [187] with the help of hydrogen bonds. At temperatures higher than the critical temperature, hydrogen bonds are cleaved and compact π – π-structures of the face-to-face type are formed.

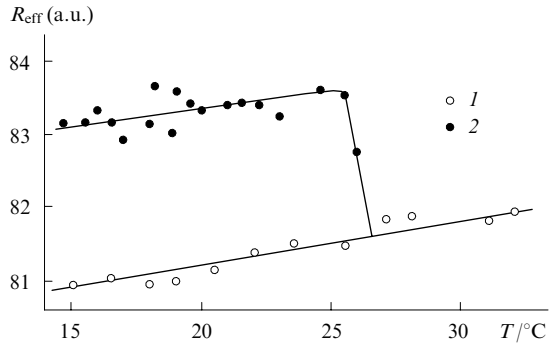


Figure 8. Temperature dependences of the effective radius of oil asphaltenes before (*1*) and after (*2*) the thermal pretreatment of oil at temperature exeeding the 'critical temperature' (27 °C).[185]

It is noted that paraffins can play a certain role in the change of physico-chemical parameters of oils in the studied temperature range (from 20 to 40 °C).[186] Depending on the state of paraffins in the oil (crystalline or dissolved state), asphaltene aggregates will either be adsorbed or act as crystallization centres, respectively. Then cooling the petroleum system can induce the formation of a firm finely crystalline structure, which will raise the efficient viscosity and pour point of the oil,[186] or the formation of large paraffin crystals, which has a positive influence on the rheological properties of the oil.

Molecular modelling has proved be useful in the study of intermolecular interactions of asphaltenes as functions of their structure and environment temperature.[188] It was shown that at high temperature (443.15 K) asphaltene molecules with long alkyl chains can be packed almost parallel to each other; at low temperature (238.15 K), the packing is almost orthogonal; at intermediate temperature (298.15 K), they are packed at 40° angle. Highly aromatic asphaltene molecules of the 'continental' type have a parallel orientation at low temperature and an orthogonal orientation at high temperature. The orientation of the neighbouring molecules depends also on the distance between the mass centres. Thus, calculations for model compounds (naphthalene, 1-methyl-, 2-methyl- and 1,7-dimethylnaphthalenes) showed [188] that when the distance between the mass centres is high, the aggregation is chaotic and when it is low, almost parallel structures are formed.

Conformational transformations of the asphaltene molecules can also lead to abrupt changes of their properties. Acevedo *et al.*[52] used the molecular mechanics method to show that properties of the 'archipelago' type molecules depend mainly on the spatial structure that is most favourable under the current conditions (Fig. 9, Table 1). In the folded state (see Fig. 9) the formation of dimers (aggregates) is hampered but the formation of host – guest complexes is possible. An unfolded 'archipelago' type molecule has properties similar to the 'continental' type.

^{1}H – DOSY NMR study of toluene solutions was used to confirm the conformational changes of asphaltene molecules, which precede the formation of molecular aggregates.[27]

Understanding the conditions and mechanism of asphaltene phase transitions in petroleum systems, especially in highly concentrated asphaltene systems (both natural and

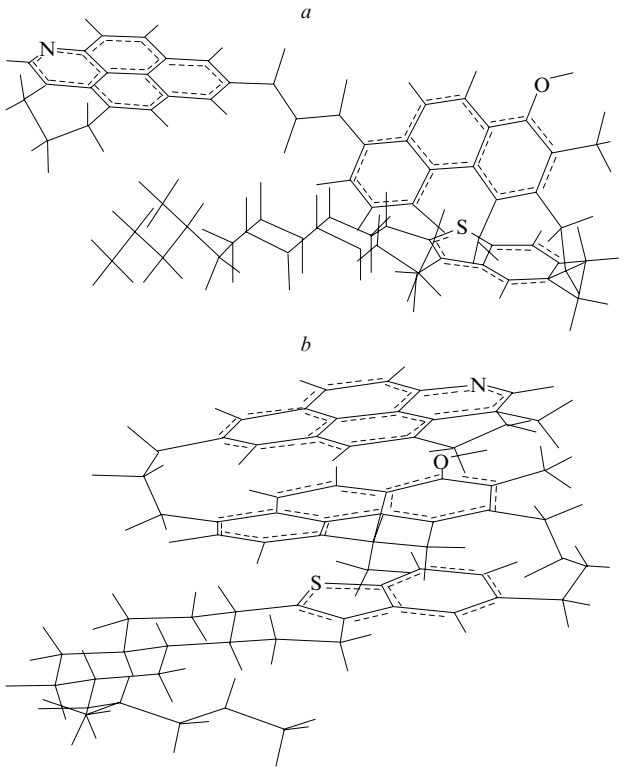


Figure 9. Different ways of folding the 'archipelago' type molecule (A2).[52]

Table 1. Calculated parameters of asphaltene molecules of types A1 and A2.[52]

Modelled molecule	$-\Delta E_D$ /J mol^{-1}	V/cm^3	Δ /MPa$^{0.5}$	ΔS_R
A1	203.649	933	14.77	0.00001
A2				
non-folded	204.569	949	14.68	0.00001
folded (Fig. 9 *a*)	141.284	949	12.2	0.036
folded (Fig. 9 *b*)	81.092	947	9.25	–

Note. ΔE_D is the energy of formation of dimers from two monomers calculated by MM+ molecular mechanics software; V is molecular volume; Δ is the solubility parameter; ΔS_R is the ratio of solubilities of 'continental' and 'archipelago' types.

technical bitumen, asphaltene deposits) can be promoted by studies of the structure of asphaltene concentrates and the temperatures of their structural transformations.

Employing SAXS, DSC and IR spectroscopy to analyze asphaltene concentrates isolated from Venezuela oil vacuum distillation residues, Rodriguez-Abreu *et al.*[189] concluded that asphaltenes consist of nano-structures with some (relatively low) degree of order. By transmission electron microscopy, it was found[67] that asphaltenes consist of agglomerates 350–550 nm in size, which are built up of ~50 nm particles, some of which tend to graphitize. Low-vacuum scanning electron microscopy shows[67] the surface of Maya oil residue asphaltenes to consist of fragments with different morphology. The surface quality (smooth or porous), as the authors consider, can depend on different content of heteroatoms on these areas.

One of the classic methods to study the phase composition of a compound is differential scanning calorimetry, but the results obtained with this method still give raise to disputes, in particular, the results dealing with the temperatures of phase transition of asphaltenes, and the nature of the transitions. As the DSC data is influenced by the conditions of asphaltene isolation, evaporation of solvents, thermal history of asphaltenes,[190] interpreting the experimental curves can prove to be very hard. The DSC curves show effects of various nature caused by thermal capacity changes, absorption or release of heat. Reversible stepwise changes of the DSC curve are attributed to vitrification. It was shown that the vitrification temperature of n-heptane precipitated asphaltenes from vacuum distillation residues of various oils when they are heated under nitrogen at a rate of 10 deg min^{-1} is 120–130 °C.[191] Vitrification temperatures of n-heptane asphaltenes isolated from residues of atmospheric pressure distillation of Turkish oils lie in 186–307 °C temperature range and depend on the heating rate.[192] Masson *et al.*[93] studied asphaltenes from residual bitumen and determined two vitrification temperatures (0 and 70 °C), which, as suggested by the authors, indicate the presence of two types of amorphous asphaltene domains formed by polar aliphatic and oligoaromatic fragments, respectively.

Canadian scientists[171,194–196] found two overlapping phase transitions (reversible and irreversible) by analyzing DSC curves of Maya oil asphaltenes and Atabasca bitumen in the range of 200–525 K. The transitions are accompanied by absorption and release of heat, respectively. Though the vitrification process is not always accompanied by a thermal effect, the authors[174,197–199] considering the low enthalpy value (~10 J g^{-1}) attribute the broad endotherm on the DSC curves in the range of 300–520 K to devitrification of asphaltenes, *i.e.*, partial transformation of asphaltenes from the solid amorphous state into the liquid state. Using additional study methods (SAXS[194] and rheometry[171]), the exothermal effect (~4 J g^{-1}) in the range of 400–450 K is explained by dissolution of some solid asphaltenes in the formed liquid melt at elevated tempetautres.

Tran[195] showed in his M.Sc. Thesis that in the range of 200–525 K the phase behaviour of Atabasca bitumen asphaltenes precipitated by n-alkanes (from pentane to decane) is almost the same. In publication,[196] the authors witnessed the formation of amorphous liquid crystal domains in n-heptane precipitated asphaltenes at 338–371 K (under nitrogen) and their subsequent disappearance at ~430 K. When the mixture was cooled and heated once more, the domains did not appear. The appearance and disappearance of the liquid crystal phase was also detected in the presence of toluene vapours at ambient temperature. Thus, Canadian researchers suggest asphaltenes to consist of at least two solid phases at low temperatures. When heated, they undergo a number of phase transitions: one of the solid phases turns into liquid at ambient conditions, the other turns into a liquid-crystalline phase. Further raising the temperature leads to exothermal dissolution of the liquid crystal phase in molten asphaltenes. The discovered trends of asphaltenes phase changes give evidence for the importance of thermal prehistory of oil for the formation of supramolecular structures in it.

Evdokimov *et al.*[197] analyzed the electrical conductivity of asphaltenes and concluded that a phase transition occurs at 35–40 °C. Below 40 °C the so-called 'cold' phase predominates in asphaltenes, in which the intermolecular interactions occur mainly with the help of polar side substituents. Above 40 °C, the 'cold' phase turns into the 'hot' one, where π–π interactions predominate. The authors stress the fact that on the surface of asphaltenes this phase transition occurs at lower temperatures (~20% lower).

A crystal-like phase was reported to be present in asphaltenes.[47, 97, 191] Masson *et al.*[193] studied residual bitumen asphaltenes and found a poorly ordered amorphous phase, which underwent isotropization (destruction) at 0 to 70 °C (most rapidly at 50 °C) and regenerates in about 14 days. Ganeeva *et al.*[51] also found reversible endotherms in the DSC curves in the range of 100–180 °C. Comparing the DSC curves of the initial asphaltene mixtures and their high- and low-molecular fractions allowed the authors to attribute the effect at 100–130 °C of the initial adphaltenes to the structural transformation of the low-molecular asphaltene fraction and the endothermal effect at 130–170 °C was attributed to the transformation of the high-molecular fraction.

Full transormation of asphaltenes into the liquid occurs at 220–240 °C under nitrogen.[191] Melting of thin films of the same asphaltenes under inert atmosphere at 16.5 deg s^{-1} heating rate is visually observed in the range of 214–311 °C.[198] It was found that the melting point of Maya oil asphaltenes is 294 °C, which is much higher than the melting point of Atabasca bitumen and Saudi Arabia oils asphaltenes (224–245 °C). This difference does not agree with the chemical and structural characteristics of the different asphaltenes. Pyrolysys of asphaltenes takes place at 350–550 °C.[192]

Evdokimov colligated his long-term research of oils and their fractions and asphaltene concentrates, as well as the results of other scientists to construct a phase diagram of nano-phases in the temperature–asphaltene content coordinates, the simplified version is shown in Fig. 10.[59, 66, 199] The diagram clearly shows the lines of critical concentrations and 'critical temperatures' (the lines of phase transitions), which divide the domains of existence of different nano-phases of asphaltenes.

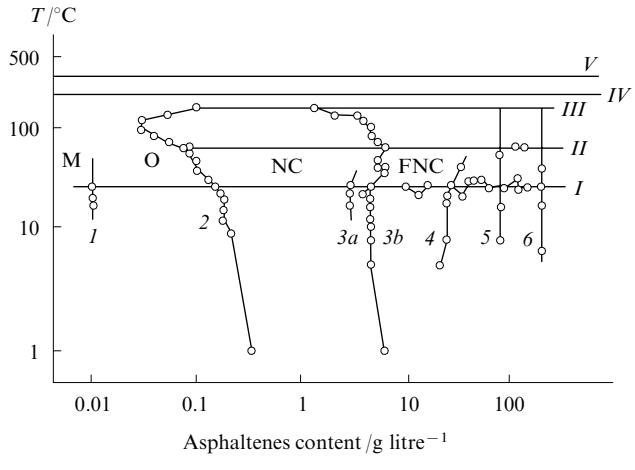


Figure 10. Nanophase state diagram for oil asphaltenes, logarithmic scale used.[59, 66, 199]
M are monomers, O are oligomers, NC are nano-colloids, FNC are flocculated nanocolloids, (*I*–*V*) are 'critical temperature' lines, (*1*–*6*) are critical concentration lines (see text).

Least studied are the processes for the lines of 'critical temperatures'. A suggestion was made that at temperatures below the phase boundary *I* (25–30 °C) the structure of all nano-phase particles is amorphous due to the interaction of asphaltene side alkyl chains. Crossing this boundary as the result of heating causes bonding between the aromatic fragments to predominate, the molecules and particles become more dense and decrease in size. Between the boundaries *II* and *III* (temperatures 100–180 °C) some nano-phases acquire some crystal-like order. Crystal-like formations begin to melt near the boundary *IV* (220–240 °C), and upon reaching the boundary *V* (350–400 °C), destruction of asphaltenes starts to give liquid crystalline meso-phases, preceding the formation of coke.

Lines *1*–*6* corresponding to the influence of concentration on the size of the aggregates are quite well studied. Before boundary *1*, corresponding to the concentration of 7–10 mg $litre^{-1}$, asphaltenes in oils exist as isolated molecules (monomers) (see Fig. 10, area M). When this concentration is exceeded, primary association of 2–4 molecules occurs and the phase of oligomers is formed (the O area). Between the boundaries *2* (0.1–0.15 g $litre^{-1}$) and *3a* (1–3 g $litre^{-1}$) asphaltene aggregates 2–10 nm in diameter are formed (the NC area). According to Evdokimov and Losev,[59] further boundaries *3b* (7–10 g $litre^{-1}$), *4* (20–35 g $litre^{-1}$), *5* (70–90 g $litre^{-1}$) and *6* (140–160 g $litre^{-1}$) separate the different states of flocculated nano-colloids (the FNC area). Thus, between the boundaries *3b* and *4* asphaltene aggregates about tens of nanometers in size are formed. Between the boundaries *4* and *5* these aggregates start interacting with the formation of loose fractal objects. The area between the boundaries *5* and *6* corresponds to the phase consisting of large (>0.1 μm) flocculated particles which can from ordered gel-like structures.

Evdokimov suggests employing the phase diagrams to mix different oils (nanotechnology of oil mixing),[200–202] heat them (nanotechnology of thermal impact in the processes of oil production, transportation and storage) and evaluate the quality of crude oil.[59] Such an approach requires revision of many traditional techniques and development of new ones that will take into account the phase state of asphaltenes.

V. Conclusion

The discussed material gives an introduction to the basic principles, mechanisms and driving forces of asphaltene aggregation. The formation of supramolecular structures, due to geometrical and chemical complementarity and multiplex intermolecular interactions allows one to classify them, as well as oil disperse systems as a whole, as objects of supramolecular chemistry,[203, 204] the basic principle of which is self-organization, and the main goal is to synthesize nanostructures with regulated morphology and properties. Though the data on many possible phase states of asphaltene nano-aggregates and the depenences of them on 'critical' system parameters (concentration, pressure, temperature) are not vast and sometimes contradictory, even now it is clear that such an approach to oil disperse systems is

very promising. Targeted changes of the interactions of asphaltene molecules and obtaining nano-aggregates with different structures and properties by the changes of external parameters will allow one to control the properties of petroleum systems and obtain oil processing products of the desired quality. Research in this sphere will also help to recover more efficiently vanadium and porphyrins, valued chemical resources, from oil and bitumen on an industrial scale. We should note, however, that the current knowledge base in this field is enough to make predictions but not enough yet to govern the phase behaviour of asphaltenes, and thus petroleum systems as a whole.

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