

JOVAN A. JOVANOVIĆ

Faculty of Technology and  
Metallurgy, University of  
Belgrade, Yugoslavia

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## MODELS OF AN ASPHALTENE AGGREGATE AND A MICELLE OF THE PETROLEUM COLLOID SYSTEM

*Using recent proposals for the hypothetical structure of an average asphaltene molecule and the results of determining the dimensions of asphaltene molecules and aggregates, a model of the asphaltene aggregate (nucleus) was constructed. It contains three or more layers, each made up of four asphaltene molecules. The asphaltene nucleus is held together by van der Waals forces which act between numerous hydrogen atoms, the interaction of  $\pi$ - $\pi$  bonds of the planar parts of the asphaltene molecule, and hydrogen and ion-dipole bonds. The form of an irregular rectangular "brick" for the asphaltene molecule was used to build the model. It contains vertical cavities the dimensions of which enable the containment of metal ions and/or salt molecules. By assigning quasi rectangular forms to the resin molecule, a model of the petroleum colloid system micelle was constructed. In the model four asphaltene molecules which build a layer, are surrounded by seven resin molecules. The presentation of the asphaltene nucleus in the form of a brick building could make the three-dimensional computer analysis of possible structures much easier. 3- and 21-layer micelles have been constructed, and the possible positions of metal ions and salt molecules have been shown.*

It is generally accepted today, that petroleum represents a colloid system with oils as the dispersion medium and resins and asphaltenes as colloids which are in the form of a micelle with asphaltenes surrounded by resins [1-4]. The average content of oils, resins and asphaltenes in petroleum amounts to 81, 11 and 8 % wt., respectively [5].

The structure of asphaltenes has been investigated intensively since the beginning of their isolation, resulting in numerous proposals of the hypothetical structures of the average asphaltene molecule, one of which is shown in Fig. 1 [6]. The molar mass and the elemental analysis data, as well as the molecule dimensions, if the paraffinic chains are in the extended *trans*-conformation are also given in Fig. 1. The hypothetical asphaltene molecule is designated here by the dotted line located at the end of the projection of the hydrogen van der Waals diameters, being assigned the form of an irregular rectangular brick.

It has been established by low angle X-ray and neutron scattering techniques that the asphaltenes in the colloid system represent aggregates, consisting of several asphaltene molecules, in the form of a disk with a diameter of 8-20 nm and a thickness of up to 1 nm [7]. Molar mass measurements of asphaltenes at different temperatures and in different solvents have also shown, that the asphaltene particle consists of several asphaltene molecules [8]. Furthermore, it has been determined by X-ray diffraction that the asphaltene element of the aggregate has a length of 1.2 - 3.0 nm, which is approximately the length of the hypothetical structure shown in Fig. 1 (the paraffinic chains could have conformations that would shorten the molecule), and that the aggregates contain several layers with distances of 0.48 between the chain structural elements

and 0.35 nm between the planar structural elements of the layer [9]. Static and dynamic surface tension, small-angle neutron scattering, viscosity, dielectric relaxation, and conductivity measurements of asphaltenes in solutions have confirmed that asphaltene molecules exhibit a strong propensity for self-association [10,11]. Especially the latest results of conductivity measurements of asphaltene solutions have shown that asphaltene aggregate do not swell or redistribute [11]. It is more or less interlocked, and the energy required to unfold it and cause the swelling is too high. Also, there is a strict packing constraint, i.e. the asphaltene molecules in the aggregate are structurally matched. A recent study of colloidal dispersions of Athabasca asphaltenes in toluene by small angle X-ray scattering have shown that the colloidal particles are polydisperse spheres with an average diameter of 6.6 nm [12]. On the other hand, it has been shown by X-ray and neutron scattering methods that an asphaltene aggregate corresponds to a lamellar structural model [13].

A three layer asphaltene aggregate (nucleus) model was constructed in this study, by taking into account all of the mentioned experimental facts and by assigning the hypothetical asphaltene molecule the form of an irregular rectangular brick (Fig. 1). The "bricks" were combined by hand to match in aggregates with high values of the deliberated energy of the bonds acting between asphaltene molecules, taking into account that van der Waals bonds between hydrogen atoms and  $\pi$ - $\pi$  bonds between the planar structural elements contribute the most to the sum of the bond energies that hold the aggregate together. One layer of the asphaltene aggregate model is shown in Fig. 2. It consists of four bricks. The whole aggregate consists of three layers, as shown in Fig. 3, which represents the  $S_1 - S_1$  and  $S_2 - S_2$  cross-sections of the asphaltene aggregate model (Fig. 2). The saturated aliphatic structural elements of the top and bottom layer have a conformation (Fig. 3, down on the right) that results in a

Author address: J.A. Jovanović, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P.O. Box 3503, YU-11120 Belgrade, Yugoslavia  
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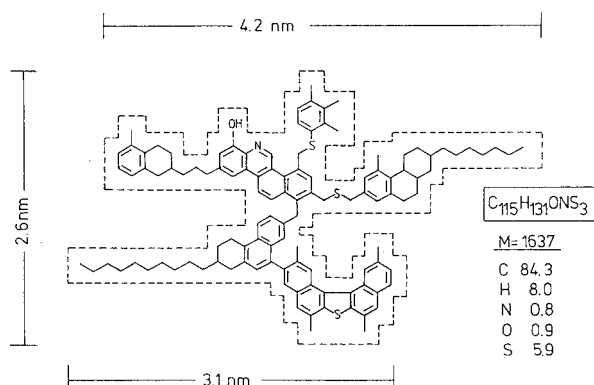


Figure 1. Hypothetical structure of the asphaltene molecule

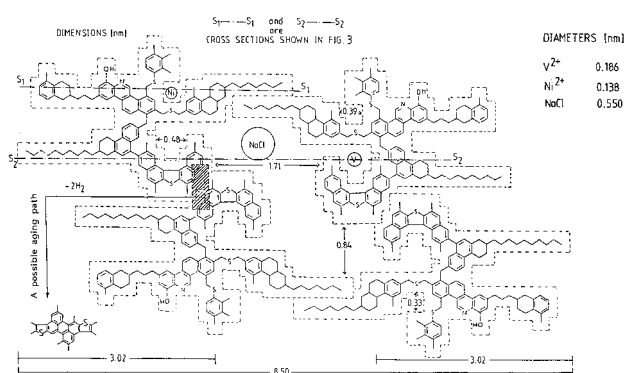


Figure 2. Model of a layer of the asphaltene aggregate (nucleus)

distance of 0.48 between the chains and naphthenic rings and 0.35 nm between the planar structural elements of the adjacent layers. The asphaltene aggregate contains vertical cavities, the dimensions of which enable the containment of metal ions or molecules of an inorganic salt (Figures 2 and 3). In the case when the asphaltene and ash contents in a vacuum-residue amount to 10.0 and 0.1 % wt., respectively, and taking into account that the molar

mass of the hypothetical three layer asphaltene aggregate amounts to 20000 and that the average molar mass of the ash compounds amounts to 83 (calculated on the basis of the composition of a typical ash sample and the molar mass of the compounds presented in it), it was calculated that there are 2.4 salt molecules and/or metal ions per one asphaltene aggregate in this particular case. Consequently, each asphaltene aggregate could contain salt molecules or metal ions, or both. The asphaltene aggregate model shows that there is enough space for this. Furthermore, it is easily understandable that the NaCl, V and Ni would readily remove themselves from the hostile hydrophobic, mostly paraffinic surroundings and to find a secure, more polar shelter[14].

The asphaltene aggregate is held together by van der Waals forces which act between numerous hydrogen atoms and by the interaction of the  $\pi$ - $\pi$  bonds of the planar parts of the asphaltene molecule. Metal ions and salt molecules "oscillating" in the vertical cavities could be a kind of junction of the adjacent layers, i.e. a kind of ion/dipole bond. The functional groups (phenolic OH) are located approximately evenly at the brim of the asphaltene aggregate (Fig. 2). They can build hydrogen bonds between layers, as in the model they are located above one another. The hydroxy groups could play an important role in the mechanism of asphaltene aggregate building, regulating the appropriate orientation of the asphaltene molecules. The sum of the energies of all these possible bonds of the three layer asphaltene aggregate model amounts to about 4300 kJ/mol. These statements can explain the fact that asphaltene self assemblies remain even in dilute solution and at higher temperatures [15]. A computer picture of the three layer asphaltene aggregate model is shown in Fig. 4. Its dimensions are similar to those of a model obtained by a very sophisticated calculation based upon newly developed software [16].

Compared to asphaltenes, resins have been investigated less intensively probably because of their higher chemical reactivity, and by more complicated

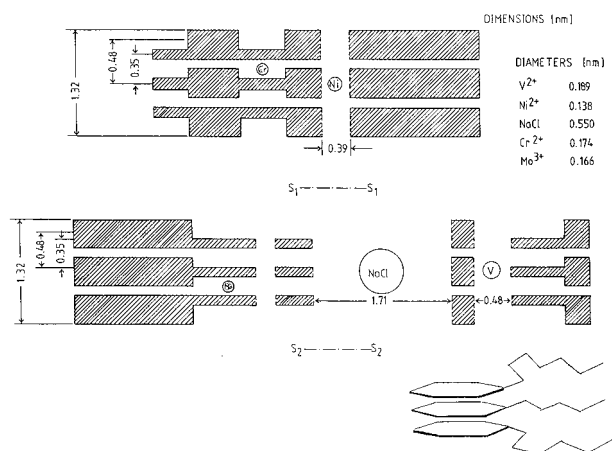


Figure 3. S<sub>1</sub> – S<sub>1</sub> and S<sub>2</sub> – S<sub>2</sub> cross-sections of the three layer asphaltene aggregate

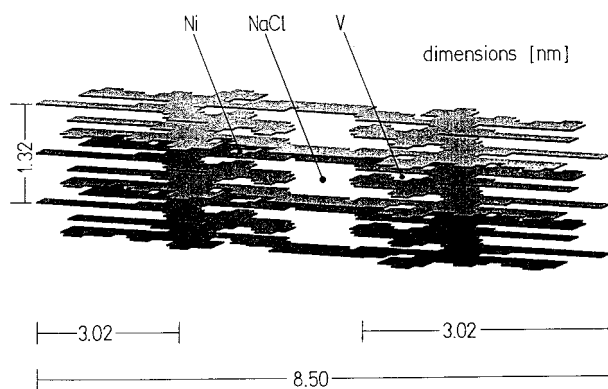


Figure 4. A computer picture of a three layer asphaltene aggregate model

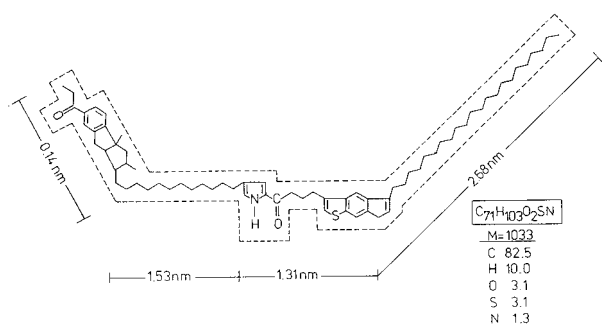


Figure 5. Hypothetical structure of the resin molecule

isolation paths, and because of the fact that asphaltenes have regularly been mentioned as the main trouble makers by refining, especially in the case of catalytic processes. Consequently, proposals of the structure of an average resin molecule are not numerous. A hypothetical structure of a resin molecule is shown in Fig. 5. It is based on the concept that resin molecules include the following structural elements [17]: long paraffinic chains, naphthenic rings, condensed aromatic-naphthenic systems, indene rings, a pyrrole N-H group, a carbonyl group and the usual sulphur containing structural elements. Fig. 5 also shows the molar mass, the elemental analysis data, and the empirical formula of the proposed molecule, as well as its dimensions, again calculated for the case that the paraffinic chains are in the extended *trans*-conformation, and taking into account the length of the projection of the hydrogen van der Waals diameters. The hypothetical resin molecule is designated by the dotted line located at the end of the projection of the hydrogen van der Waals diameters, being assigned a quasi rectangular form. Of course, other conformations than that shown in Fig. 5 are also possible.

By giving the resin molecule the form designated by the dotted line (Fig. 5) and by using for the long paraffinic chain, located at one end of the resin molecule, not only the extended conformation, but also other possible conformations and numbers of CH<sub>2</sub> - groups in the chain, which is presented by the shorter and wider parallelograms (Fig. 6), a model of the colloid system micelle was constructed, one layer of which is shown in Fig. 6. In this particular case a layer of the asphaltene nucleus (aggregate) is surrounded by seven resin molecules (it corresponds with the average mass ratio of resins toward asphaltenes in petroleum), four of which are connected to the asphaltene nucleus by hydrogen bonds. These bond are considerably weaker than the bonds that keep the asphaltene aggregate together, as shown by the well known experimental fact that asphaltenes are easily precipitated from the colloid system by *n*-pentane.

The chemical composition of the oil phase is of great importance for the stability of the petroleum colloid system. Fig. 6 contains structures of typical molecules of

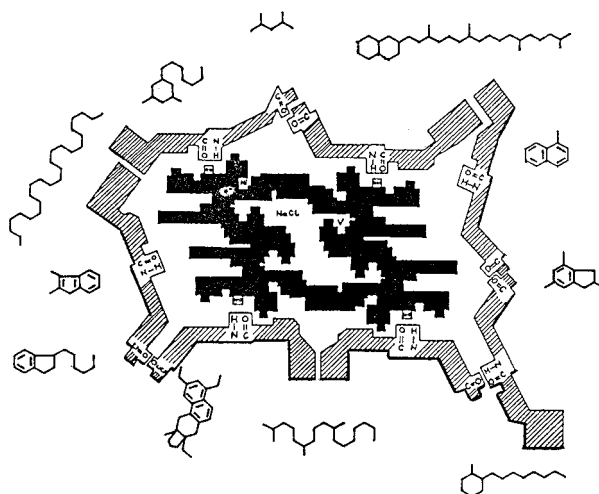


Figure 6. One layer of the colloid system micelle model

the oil phase. Previous experience indicates that the stability of the colloid system is higher if the oil phase contains more naphtheno-aromatic structural elements. Paraffinic molecules can destroy the system by precipitation of the asphaltenes.

As already said Fig. 6 represents one layer of the micelle. A complete picture of the micelle must include all three layers, and a computer picture of such a micelle is shown in Fig. 7. The length of 13.40 and thickness of 1.32 are in agreement with the literature data [7,9]. The position of Ni, V and NaCl could give a realistic impression of how difficult it could be to get rid of the salt molecules and metals. There is proof that the micelle of the petroleum colloid system is a sphere [11,12]. The three layer model (Fig. 7) is rather of a lamellar structure [13]. An irregular cube, that could represent a quasi-sphere, would be obtained if a micelle contains twenty-one layers. A computer picture of it is shown in Fig. 8. It is obvious that the twenty-one, as well as the three layer models are idealised and simplified pictures, with equal distances between layers. Analysis of the layers shows that if an unchanged distance of 0.48 nm exists between the paraffinic parts of the layers, the usual distance between the inner planar aromatic structures of 0.35 will amount to about 0.70 nm in every third layer. The model gives, however, an impression of

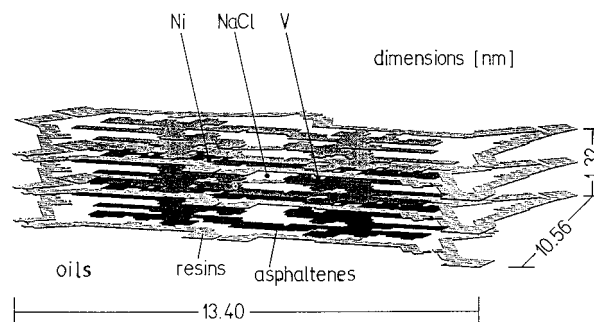


Figure 7. Three layer model of the colloid system micelle

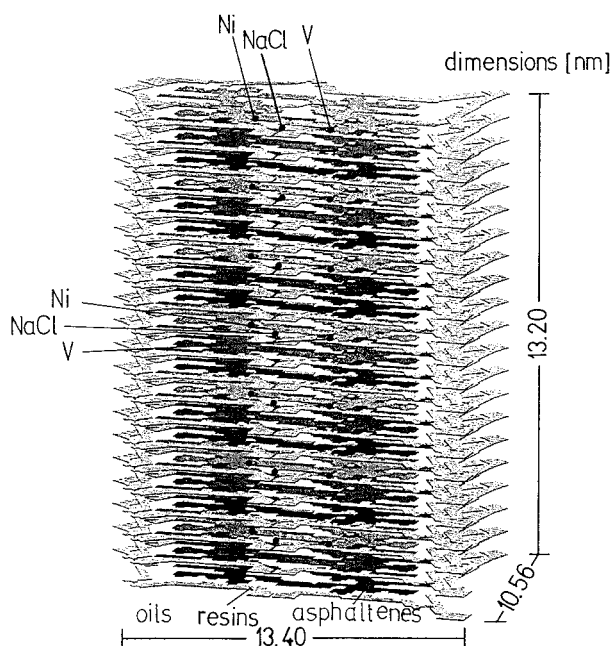


Figure 8. Twenty-one layer model of the colloid system micelle

spaces where salt molecules and metal ions, could safely be captured. The position of Ni and V given in the model is, however, just one possibility, as there is also enough space for locating metal ions between the planar structural elements (Fig. 3, positions of Cr and Mo) [18]. So the problem of the determination of non-porphyrin metal structures has still remained unsolved. The high sensitivity of the bis(arene)metal-complexes to the influence of air makes it especially difficult.

It is clear that the model does not take into account the polydispersity of asphaltenes and, hence, of the colloid system as a whole. It is hardly to be expected that the micelle is built from identical asphaltene molecules, as presented here, but the probability that it is made up of similar molecules is high, as asphaltenes, as well as resins could have the same precursors [19], for instance unsaturated fatty acids [20, 21, 22] and non-isoprenoid unsaturated long chain phenols [23]. Scanning tunneling microscopy images of asphaltenes showed that they are not heterogeneous, but form well-ordered structures in two dimensions [24]. The great number of possible combinations which arise by analysing the model indicates the complexity of the petroleum colloid system. Just one of many experimental results not considered here is the fact, that there are lower, medium and higher soluble asphaltene subfractions [25].

The model could be used as a basis for a more precise investigation of the mechanism of the ageing of petroleum residues, i.e., bitumen, not caused by light or air, as it shows some steric convenience for connecting the asphaltene molecules by condensation reactions ( $-2H_2$ ), as shown in Fig. 2. This aromatization process,

which enlarges the asphaltene molecules but not the asphaltene aggregate, is highly accelerated by temperature, especially in the presence of Ni, and could be one of the causes of the known uncertainties connected with the molar mass determination of asphaltenes [8]. It must have a great influence on the rheological properties of the colloid system, as the van der Waals bonds have been converted to covalent bonds. It could also explain why, on the basis of experience, bitumen producers and consumers prefer to use bitumen as fast as possible, not just to keep it at 150–180°C (storage and application temperatures).

By constructing the model this study did not take into account some other components of petroleum such as carboids, carbenes and porphyrins. There is very little information about carboids and carbenes and they are probably artefacts. They have usually been found in bitumen in a much less quantity compared to asphaltenes and resins. Nevertheless, the role of carboids and carbenes could be an important one, and a more developed model should consider them, too. Since the well known papers of Treibs [26], there has been intensive investigation of petroleum porphyrins [27]. Their presence in petroleum is less than that of asphaltenes, on average about 0.005–0.01 of the mass quantity of asphaltenes [28]. There are, however, only 2.5 to 5.0 three layer asphaltene aggregates (2.4 metal ions or salt molecules per one asphaltene aggregate – non-porphyrin metals) per one porphyrin molecule (one metal ion per molecule – porphyrin metals). Porphyrins are planar and the longest dimension is about 1 nm, so they could find a place in the cavities of the asphaltene aggregates (Fig. 2) and surely they can build  $\pi - \pi$  bonds. Porphyrins precipitate partly with asphaltenes when bitumen or petroleum are treated with n-pentane, n-hexane, n-heptane or other alkanes [27,29] and, hence they could be incorporated in the asphaltene aggregate model. On the other hand porphyrins could contribute to the peptisation of asphaltene aggregates, as the resin molecules do, but on average there are 50–100 resin molecules per one porphyrin molecule. Porphyrins, however, must be included in a more developed model of the petroleum colloid system micelle.

Of course, the model is built on the basis of a static description and the model structure dependence on temperature needs much more information and a dynamic description. The attractive forces (van der Waals,  $\pi - \pi$ , H-bridges, ion/dipole) depend differently not only on temperature, but also on the inter-atomic distances. As a result of that, at higher temperatures only those asphaltene aggregates that are built from the biggest and the most aromatic and polar molecules do not decompose. If the cooling process is slow, then a continuous association/dissociation equilibrium is dominated, producing stable asphaltene aggregates, that are able to associate with the more soluble resin like

molecules, giving micelles with a radial gradient of the content of hydrogen, that becomes higher going from the inner toward the outer region of the micelle, as is the case in the model introduced here. If the cooling process is fast, a continuous association/dissociation equilibrium can not be established and, consequently, metastable micelles have been built giving a product (bitumen) with the rheological properties changed in comparison to a unheated sample. This phenomenon is well known among bitumen producers and consumers.

The introduced model shows the usual sequence of a stable micelle: polar structural elements, even ions, near the centre of the micelle – medium polar structural elements in the contact region between the asphaltene nucleus and resin molecules – weakly polar structural elements in the outer space. The micelle stability could be changed, even at room temperature, by the influence of oxygen. Penetrating through the oil phase of the colloid system oxygen first contacts the outer region of the micelle and if oxidation has taken place, the usual sequence could become unusual, i.e. polar structural elements near the centre of the micelle – medium polar structural elements in the contact region between the asphaltene nucleus and resin molecules – polar structural elements in the outer space of the micelle. A reheating of such a bitumen oxidised (aged) at room temperature to 150–180°C and slow cooling should convert the unusual sequence to the usual one, i.e. oxygen containing structural elements would again be found in the inner or central part of the micelle, which is a well known experimental fact in the case of road bitumen aged by weathering, which was heated above 150°C before analysis.

The construction of every model, as well as this one, causes numerous justified and unjustified comments. The highest imprecision of the model is connected to the resin molecule structure and the need for an intensive investigation of this subject is obvious. Furthermore, the model of a petroleum colloid system micelle can hardly have a general character, but should rather be developed for each group of petroleum of similar precursors, and diagenesis and catagenesis routes.

However, the presentation of the asphaltene nucleus and the micelle of the petroleum colloid system in the form of a brick building could make the three-dimensional computer analysis of possible structures much easier, resulting in improved correlation between the micelle structure and the rheological properties of the colloid system, as well as in the better understanding of heavy oils production, transportation and refining problems.

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## IZVOD

### MODELI AGREGATA ASFALTENA I MICELE KOLOIDNOG SISTEMA NAFTE

(Naučni rad)

Jovan A. Jovanović  
Tehnološko–metalurški fakultet, Beograd

Koristeć i nove pretpostavke za hipotetičku strukturu prosečnog molekula asfaltena i rezultate određivanja dimenzija molekula asfaltena i njihovih agregata konstruisan je model asfaltenskog agregata, odnosno jezgra. Agregat (jezgro) sadrži tri ili više slojeva od kojih je svaki izgrađen od četiri molekula asfaltena. Asfaltenski agregat je relativno stabilan jer se drži pomoću van der Waals–ovih sila koje dejstvuju između brojnih vodonikovih atoma, zatim pomoću interakcije  $\pi - \pi$  veza planarnih delova molekula asfaltena i pomoću vodoničnih i jon–dipolnih veza. Da bi se izgradio model molekulu asfaltena je dat oblik nepravilne pravougaone "ciglice". Ona sadrži vertikalne šupljine čije dimenzije omogućavaju prihvatanje jona metala i/ili molekula soli. Dajući i molekulima smola kvazi–parvougaooni oblik konstruisan je model micidele koloidnog sistema nafte. Četiri molekula asfaltena, koji grade jedan sloj, okruženi su u modelu sa sedam molekula smola. Odnos četiri prema sedam je prosečan odnos broja molekula asfaltena prema broju molekula smola u nafti. Prikazivanje asfaltenskog jezgra u obliku građevine od cigala može da olakša trodimenzionalnu kompjutersku analizu mogućih struktura. Konstruisane su micidele sa 3 sloja i 21–nim slojem i prikazani su mogući položaji jona metala i molekula soli. Konstruisana micela ukazuje na mehanizam starenja bitumena preko reakcija kondenzacije cikličnih struktura. Ona, međutim, ukazuje i na mogućnost uklapanja u nju i molekula porfirina. Modeli asfaltenskog agregata i micidele jasno ukazuju na kompleksnost koloidnog sistema nafte. Modeli su napravljeni uklapanjem i spajanjem prosečnih molekula asfaltena i smola u strukture sa najvećim brojem mogućih sekundarnih hemijskih veza, vodeći računa o dimenzijama i međumolekulskim rastojanjima. Ovakvi modeli treba da se ograniče na grupe nafte sličnih prekursora i puteva diagenoze i katagenoze.

Ključne reči: asfalteni • micidele • koloidni sistem • model •  
Key words: Asphaltene • Micelle • Colloid system • Model •

