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**Assembly of asphaltene molecular aggregates as studied by near-UV/visible spectroscopy I. Structure of the absorbance spectrum**

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**Abstract**

The aim of this paper is to provide new data on the properties of molecular aggregation in toluene solutions of crude oils and of solid asphaltenes. The shape of the optical absorption spectrum was found to be sensitive to the details of asphaltene aggregation processes. In dilute solutions, these processes are apparently determined by the net concentrations of asphaltenes; other oil constituents play a secondary role. Our experimental data indicate that molecular solutions of asphaltenes are possible only for concentrations below 1 mg/l. With increasing asphaltene content, more and more complex molecular aggregates are formed. In particular, asphaltene dimers evidently are the predominant species in the range of 5–15 mg/l, while stable “nanocrystallites” (dimer pairs) are predominant at concentrations ~90 mg/l. Aggregates at higher concentrations may be viewed as assemblies of such “crystallites”. The observed gradual aggregation process is distinct from conventional micellisation phenomena with step-like changes at critical micelle concentrations (CMCs).

Keywords: Petroleum fluids; Asphaltenes; Molecular aggregates; Colloidal suspensions

**1. Introduction**

Asphaltenes play a prominent role in the petroleum industry. The increase in viscosity of crudes with increased asphaltene content, stabilisation of oil–water emulsions and deposition of solid precipitates create significant difficulties in the production and transportation of crude oil. Despite the impact of asphaltenes in many technological and economic spheres, some of their fundamental molecular properties have remained unresolved. Studies of asphaltene solutions, particularly with aromatic solvents such as toluene, could give important information regarding the concentration at which the asphaltene aggregation begins and the manner of interaction of asphaltenes with other crude oil components such as resins and aromatics. The association of asphaltenes has been the subject of several studies, basically focusing on the apparent micellisation of asphaltenes in solutions.

A number of studies have been devoted to determination of the “critical micelle concentration” (CMC) of asphaltenes (for earlier publications, cf. Sheu, 1996 and references therein). The methods employed have been calorimetry (Andersen and Birdi, 1991; Andersen and Christensen, 2000), measurements of surface tension (Sheu, 1996; Leon et al., 2000), small-angle neutron scattering (Ravey et al., 1988; Deme, 2001), optical fluorescence (Syunyaev et al., 2000) and adsorption at solid surfaces (Castillo et al., 1998). The reported CMC values for asphaltenes range from 1.5–2 g/l (Castillo et al., 1998) and 3–5 g/l (Andersen and Christensen, 2000) in toluene to 5–18 g/l in CCl<sub>4</sub> (Leon et al., 2000; Syunyaev et al., 2000). At asphaltene concentrations of 7–9 g/l, maxima of viscous flow parameters were observed in toluene solutions of a petroleum vacuum residue (Evdokimov and Eliseev, 1999; Evdokimov et al., 2001). Quite recently, there were several new publications on “critical concentrations” in asphaltene solutions (Priyanto et al., 2001; Branco et al., 2001; Ramos et al., 2001). Despite of all the experimental evidence, the nature of these “critical concentrations” is still not well understood and it is still not clear whether one should consider asphaltenes below the measured CMC either as a true molecular solution or as a dispersion of stable molecular associates such as dimers, trimers, etc. (Sheu et al., 1992). It should also be noted that aggregation studies are conducted mostly not with oil samples, but with samples of

asphaltenes precipitated from original crudes. Some authors point out that the precipitation techniques may provide an excessively strong interference into the delicate molecular organisation of asphaltene associates, leading to their irreversible transformation. Consequently, supramolecular architecture in solutions of the precipitated material may be different from that in solutions of a native crude.

The object of this research was to determine the presence of asphaltene molecular aggregates below reported CMCs both in solutions of precipitated asphaltenes and in solutions of crude oils. As such measurements require the examination of highly diluted solutions, a sensitive and specific technique should be used. In this study, we measured the optical absorption in the near-UV/visible (NUV/V) range. It is known that NUV/V absorption spectra of crude oils and asphaltene solutions are monotonously decreasing with increasing wavelength (Bastow et al., 1997; Groenzin and Mullins, 2000) and thus have been largely ignored because of their apparently featureless character. But this very featurelessness is induced by the specific colour of asphaltenes, which is a part of their definition (Yen and Chilingarian, 1994; Sheu and Mullins, 1995). In solutions, the colour evidently depends on the concentration: in benzene, it is deep red, but a concentration as low as 0.0003% makes the solution distinctly yellowish (Mansoori, 1995). Thus, it seemed reasonable to look for some structural information on asphaltene molecular aggregates reflected in their apparently featureless absorption spectra.

## 2. Experimental

### 2.1. Samples

The solid asphaltenes and the crude oil have been provided by the ‘‘TATNEFT’’ oil production company and used as received. The asphaltenes have been precipitated from a mixture of Tatarstan virgin crude oils (Romashkinskoye reservoir) by the standard technique of dilution with 40 volumes of n-heptane at room temperature. The unprocessed crude oil was directly collected from a production well at Romashkinskoye reservoir and contained 3.5 wt.% asphaltenes, as determined by 40 volumes n-heptane precipitation. Both oil and asphaltene samples were stored in the dark, in air. As a solvent, we used ‘‘chemically pure’’ grade toluene. In optical studies, the crude oil was used directly for preparation of toluene solutions. Solid asphaltenes were predissolved in toluene to a concentration of 1.5 g/l and this ‘‘primary solution’’ was further diluted for preparation of the studied samples.

### 2.2. Apparatus and procedure

The optical absorption spectra in the NUV/V range (315–750 nm) have been studied using a spectrometer, routinely employed in Russian infield laboratories (Devlikamov et al., 1970), namely, a KFK-2 photocolimeter equipped with a set of narrow-band light filters. The sample and the reference (toluene) optical cuvetts had the path length of 5.07 mm. The reliably reproducible results were obtained with absorbances from  $\sim 5 \cdot 10^{-3}$  to  $\sim 1.9$ . Hence, the fixed path length determined the studied range of asphaltene concentrations: from 1.6 mg/l to 1.3 g/l for asphaltene samples, and from 5.1 mg/l to 1.3 g/l for crude oil samples. In all, about 150 asphaltene/toluene and about 110 oil/toluene samples were studied. Only freshly prepared samples were used in each experiment within 10–15 min.

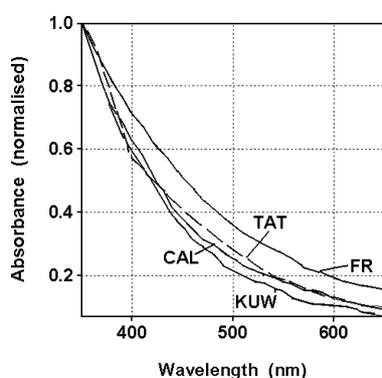
## 3. Results and discussion

### 3.1. Absorption spectra of asphaltene solutions

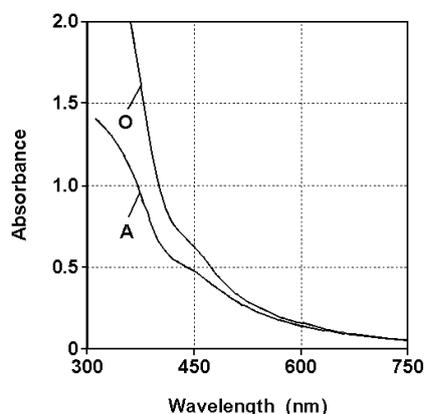
The solid lines in Fig. 1 present the normalized absorbance spectra (Groenzin and Mullins, 2000) for toluene solutions of solid asphaltenes from crudes of France, California and Kuwait, with asphaltene concentrations of  $C = 6\text{--}25$  mg/l. The dashed line in Fig. 1 shows our results in the same wavelength range for a toluene solution of Tatarstan asphaltenes ( $C = 12.6$  mg/l). In spite of large differences in geographical/geological origin of asphaltenes, there is a lot in common between the spectra of Fig. 1. In particular, all spectra may be approximated by a simple power law  $A \sim \lambda^{-m}$  with the powers ranging from  $m = 3.14$  (FR) to  $m = 4.33$  (KUW). The closest agreement is between our

TAT asphaltenes ( $m= 3.83$ ) and asphaltenes from California ( $m= 3.82$ ), with relatively smaller (compared to FR and KUW) molecular sizes/weights, as determined by fluorescence spectroscopy (Groenzin and Mullins, 2000). The fluorescence data also indicated that the CAL asphaltenes contain relatively more porphyrin-like chromophores responsible for a Soret absorption band (an intense absorption band due to higher energy  $\pi\text{-}\pi^*$  type electronic transitions) at  $\lambda\sim 400\text{--}440$  nm (Phillips, 1963), which may be resolved by calculating the derivatives of  $A(\lambda)$ .

The complete absorbance spectrum of TAT asphaltenes in toluene ( $C = 66$  mg/l) is shown by curve ‘‘A’’ in Fig. 2. The porphyrin Soret band is seen as a low ‘‘hump’’ at  $\lambda\sim 440$  nm. The most intense feature is a broad absorption band in the near-UV range, which shows a tendency of going through a maximum just below  $300\text{--}320$  nm. It may be interpreted as a Soret band ( $\pi\text{-}\pi^*$  transitions) of aromatic chromophores, red-shifted due to a high degree of conjugation in aromatic systems of asphaltene molecules (Lambert et al., 1997; Workman, 2000). The degree of the red shift indicates that the number of fused rings in asphaltene molecules is higher than five. This is consistent with the estimates of 4–10 rings made in earlier studies by various techniques (Groenzin and Mullins, 2000 and references therein).



**Fig. 1.** The absorption spectra for toluene solutions of solid asphaltenes from: Tatarstan (TAT) crude oils (our data, dashed line); crudes from France (FR), California (CAL) and Kuwait (KUW) (Groenzin and Mullins, 2000, solid lines). All asphaltene concentrations are below 25 mg/l.



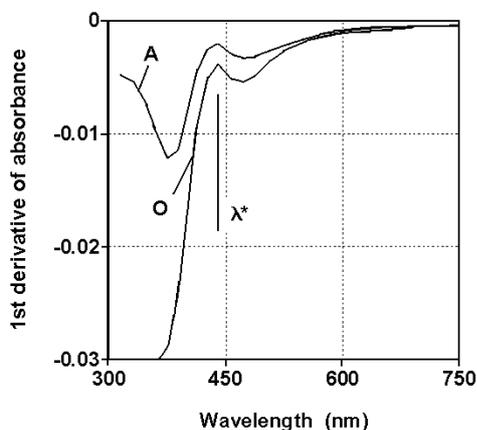
**Fig. 2.** The absorption spectra for toluene solutions of Tatarstan solid asphaltenes (A) and of a Tatarstan crude oil (O). Both asphaltene concentrations are close to 66 mg/l.

### 3.2. Absorption spectra of crude oil solutions

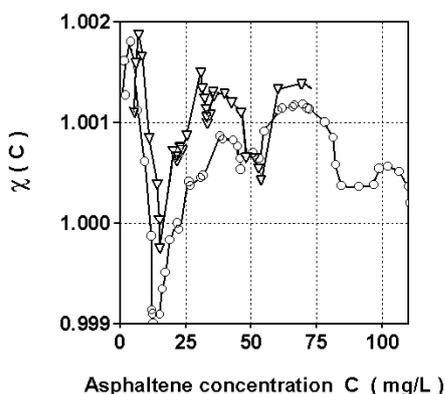
Curve ‘‘O’’ in Fig. 2 presents the measured absorbances for a toluene solution of the crude oil. Asphaltene concentration ( $\sim 66$  mg/l) is the same as in the asphaltene/toluene solution (curve ‘‘A’’). Both spectra practically coincide at  $\lambda = 700\text{--}750$  nm but, compared with the asphaltene spectrum, oil absorbance increases more sharply with decreasing  $\lambda$ . The power law approximation for the oil sample give the power of  $m= 4.80$ , notably larger than  $m= 3.83$  for the asphaltene solution. The difference is due to the increased intensity of the near-UV absorption band in oil solutions. The results of Fig. 2 show also that the maximum of this band is well outside the studied  $\lambda$  range, i.e., it is shifted to shorter wavelengths compared to the corresponding band for asphaltene solutions. These observations may be explained by the presence in oil samples of heavy aromatics and resins, which provide additional UV absorbance. Finally, in the oil solutions, the porphyrin Soret band just below 450 nm is no more prominent than in the asphaltene samples, indicating that this feature is determined primarily by asphaltenes and not by other oil constituents.

### 3.3. Derivatives of absorption spectra

Fig. 3 presents the first derivatives of the spectra in Fig. 2. In the wavelength range of 350–650 nm, the shapes of our derivative spectra resemble the derivative spectra obtained by Groenzin and Mullins (2000) for asphaltenes from Kuwait and California. Namely, the characteristic feature in all derivative spectra is the curve peak at a wavelength  $\lambda^*$  below 450 nm. According to Groenzin and Mullins (2000), this characteristic wavelength corresponds to the Soret band of porphyrin-type chromophore in asphaltene molecules. In our studies, the process of asphaltene aggregation in solutions was monitored by measuring the changes of  $\lambda^*$ .



**Fig. 3.** The first derivatives of the absorption spectra from Fig. 2. The characteristic wavelength  $\lambda^*$  was used as the convenient indicator of asphaltene aggregation phenomena (cf. Fig. 4).



**Fig. 4.** The “excess” nonmonotonic factor  $\chi(C)$  in the overall “blue shift” of the characteristic wavelength  $\lambda^*$  with increasing asphaltene concentration in toluene solutions. The well-resolved minima are interpreted as concentration ranges with the relative predominance of different types of coexisting asphaltene aggregates.

### 3.4. Dependence of characteristic wavelength $\lambda^*$ on concentration of asphaltenes in solutions

Due to limitations imposed on the values of reliably measured absorbances (cf. Section 2.2), it was possible to register variations of  $\lambda^*$  at asphaltene concentrations, not exceeding 130 mg/l. Asphaltene aggregation at higher concentrations was studied by computing extinction coefficients for a wide range of wavelengths and these results will be reported in a separate paper.

The main effect, observed in all samples, was a gradual shift of the porphyrin-type Soret band to shorter wavelengths (a so-called “blue shift”) with increasing asphaltene concentration  $C$ . In solutions of precipitated asphaltenes, the measured values of  $\lambda^*$  decreased from  $\approx 445$  nm for  $C = 1.6$  mg/l to  $\approx 436$  nm for  $C = 130$  mg/l. In molecular spectroscopy, a blue shift of the Soret band is often regarded as a consequence of formation of the face-to-face (H-type) molecular aggregates via specific  $\pi$ -interactions, i.e., via the so-called  $\pi$ - $\pi$  stacking (Shanker and Applequist, 1996; Voigtle, 1996; Yang et al., 2000). In asphaltene solutions,  $\pi$ -stacking may be facilitated by a charge transfer through propagation of Wannier excitons within and among polynuclear  $\pi$ - $\pi$  systems of asphaltenes (Yen and Young, 1973; Yen and Chilingarian, 1994; Wong and Yen, 2000).

Hence, the observed blue shift of the Soret band was regarded as indicative of the formation of face-to-face asphaltene aggregates. This type of molecular aggregation has been extensively investigated for porphyrin-type compounds and organic dyes (Purrello et al., 1998; Zhao and Malinowski, 1999; Carroll et al., 1999). The concentration dependencies of optical absorption

were often nonmonotonic and exhibited multiple extrema due to the processes of consecutive formation of molecular dimers, trimers, etc. (Carroll et al., 1999).

The comparatively weak nonmonotonic details of our measured  $\lambda^*(C)$  dependencies were revealed as follows. The original  $\lambda^*(C)$  data sets were smoothed (with a five-point data window) and then approximated by smooth functions  $F(C) = \alpha - \beta \cdot \log C$  (the best fits were obtained with  $a = 442$ ;  $b = 2.75$  for asphaltene samples and  $a = 445$ ;  $b = 4.43$  for crude oil samples). Finally, the measured concentration dependencies were regarded as the products of two factors:  $\lambda^*(C) = \chi(C)F(C)$ , where  $\chi(C)$  is an “excess” nonmonotonic contribution to the overall “blue shift”  $F(C)$ . This procedure resulted in the well-structured 275  $\chi(C)$  curves shown in Fig. 4, with easily observed minima, obviously related to consecutive stages of asphaltene aggregation. Circles denote the results for solutions of precipitated asphaltenes. Triangles are the data for oil solutions (3.5 wt.% asphaltenes in the original crude).

The remarkable feature of Fig. 4 is the virtual coincidence of  $\chi(C)$  dependencies for solutions of solid asphaltenes and for solutions of the crude oil. This coincidence indicates that crude oil constituents other than asphaltenes may provide a noticeable influence on the adsorption properties (Fig. 2) but variations of the studied Soret band (induced by aggregation) are determined only by the asphaltene content. Specifically, at these strong dilutions, there appears to be no “stabilising effect” frequently associated with the presence of resin molecules in oil media (Dickie and Yen, 1967; Mansoori, 1995; Escobedo and Mansoori, 1997).

There are several distinct minima of  $\chi(C)$  in Fig. 4, which may be considered as the first experimental evidence of multiple aggregation stages in asphaltene solutions with concentrations as low as several milligram per litre (i.e., three orders of magnitude lower than the routinely measured CMCs of several grams per litre). A literature analysis, made shortly after the completion of the above experiments (August 2001), has revealed only three previous observations of aggregation below the frequently quoted CMCs:

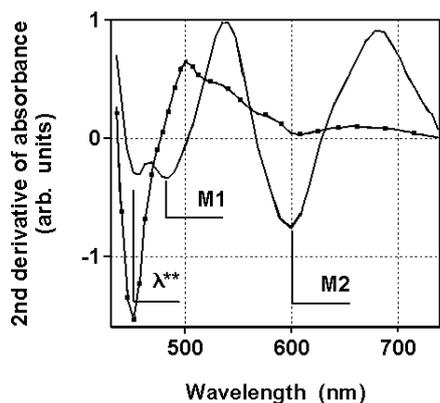
(1) Thermo-optical studies of toluene solutions of asphaltenes have shown a deep minimum near 50 mg/l (Acevedo et al., 1999), in an agreement with one of our minima in Fig. 4. The concentration range in this publication extended down to  $10^{-4}$  mg/l, but no data were presented for the interval from 0.1 to 20–30 mg/l, so our minimum at ~10–15 mg/l would also fit into their data set.

(2) In a discussion of the above thermo-optical results, Groenzin and Mullins (2000) interpreted their earlier fluorescence data. They stated that at asphaltene concentrations in toluene  $\geq 60$  mg/l, fluorescence anisotropy curves begin to exhibit a second exponential decay, which may be due to molecular complex formation.

(3) In a Russian book on asphaltenes (Sergienko et al., 1979, p. 214), there is a reference to earlier studies of fluorescence intensity in asphaltene/ $\text{CHCl}_3$  solutions. A resolved minimum of intensity was observed at asphaltene concentrations of 10–15 mg/l and a shallow one, near 60 mg/l, both in agreement with the data of Fig. 4.

### 3.5. Other aggregation-sensitive features of the absorption spectra

Besides variations of the specific wavelength  $\lambda^*$  at longer wavelengths (450–700 nm), there are concentration-related changes of some less pronounced features, revealed in the higher derivative spectra. The second derivatives of  $A(\lambda)$  for solutions of solid asphaltenes are shown in Fig. 5. The minimum at  $\lambda^{**}$  is related to the same absorption band as characterised above by  $\lambda^*$  (Fig. 3). In dilute solutions (the solid curve in Fig. 5,  $C = 1.6$  mg/l), this minimum is strongly suppressed and the dominant features are the absorption bands defined by the minima M1 and M2 (at about 480 and 600 nm). At concentrations  $\geq 3$ –6 mg/l, these minima abruptly collapse to shallow features, observed at all higher concentrations (cf. the dotted curve in Fig. 5, for  $C = 99$  mg/l). We could not attribute weak bands M1 and M2 to any specific electron transitions, but they are evidently characteristic of the smallest asphaltene species, presumably of asphaltene monomers.



**Fig. 5.** The second derivative spectra for toluene solutions of solid asphaltenes with concentrations 1.6 (solid curve) and 99 mg/l (dotted curve). The absorption bands M1 and M2 are attributed to the presence of asphaltene monomers.

### 3.6. Attribution of the observed aggregation stages

There are several arguments in favour of identifying the above “smallest asphaltene species” as single asphaltene molecules (monomers). Firstly, there are abrupt changes in the derivative spectra at low asphaltene concentrations. Massive suppression of some absorption bands and enhancement of the others may be interpreted as the well-known “solvation effect” due to interactions of the solvent molecules with the absorbing chromophores (Rao, 1975). Evidently, all chromophores are accessible to solvent only in monomers, while at larger concentrations, they may be buried inside molecular aggregates and shielded by other asphaltene molecules. Another argument is the fluorescence study of asphaltene/toluene solutions (Groenzin and Mullins, 2000) where, at concentration of  $\sim 6$  mg/l, the predominant solute species were shown to be flat asphaltene monomers (with diameters of  $\sim 1.5$ – $2.5$  nm).

The concentration dependence of the solvation effect indicates that chromophores assume “interior positions” already in the smallest aggregates, presumably dimers. In turn, this is possible only if the two faces of an asphaltene molecule are not equivalent and its “front face” (F) should be distinguished from the “rear face” (R), so that an asphaltene monomer may be denoted as [FR] (or [RF]). Effective chromophore shielding may occur if the chromophore-carrying F-face is more active in the process of face-to-face  $\pi$ -stacking (Section 3.4), so that stacked asphaltene dimers are predominantly of the type [RF–FR], while the structures [RF–RF] or [FR–RF] seem to be energetically less favourable.

Under the above assumptions, a trimer (dimer + monomer) may be expected to be a comparatively weakly bound aggregate. The direct F–F interactions are excluded in its possible stacked types [(RF–FR)FR] or [(RF–FR)RF]. Moreover, asphaltene dimers may acquire new properties (as compared to monomers), which may facilitate further aggregation not by formation of trimers, but by dimer–dimer association. Namely, some models interpret  $\pi$ -stacking of asphaltene monomers as being due to a charge transfer among aromatic ring systems (Yen and Young, 1973; Yen and Chilingarian, 1994). The concept of a charge transfer implies redistribution of electron density, so that the resulting dimers may be expected to carry an additional electric dipole moment, parallel to the axis of the flat aromatic systems. In addition, formation of  $\pi$ -aggregates may involve free radicals possessing unpaired electrons (Wong and Yen, 2000) so that an asphaltene dimer may exhibit paramagnetic properties with an axial magnetic dipole moment. Hence, a system of two dimers may be expected to assume the least energy- stacked configuration with mutual cancellation of antiparallel dipole moments, which makes addition of further dimers less effective. The aggregate of two stacked dimers (four asphaltene molecules) may be energetically favoured also due to its low surface-to-volume (S/V) ratio, which minimises solute–solvent interactions. The “thickness” of an aromatic subsystem of a flat asphaltene monomer may be evaluated as  $\geq 0.35$ – $0.36$  nm (van der Waals diameter of a carbon atom), so that the “height” of a four-membered  $\pi$ -stack is  $\sim 1.4$ – $1.45$  nm. The height of a dimer pair should be somewhat larger (i.e.,  $1.5$ – $2$  nm) allowing for the flexible side chains. This coincides with the above-cited estimate of a monomer’s diameter, which makes a dimer pair a quasi-spherical microparticle with a low S/V ratio.

For the first time, the structural preference of asphaltene nano-sized aggregates (“crystallites”) containing four to six flat ring systems has been pointed by Dickie and Yen (1967). There is multiple indirect evidence of such “crystallites” (Dickie and Yen, 1967; Yen et al., 1984; Wong and Yen, 2000 and references therein) and they have been directly observed in electron micrographs as “polyhedral-shaped particles possessing an average diameter of 2–3 nm” (Dickie et al., 1969). To our knowledge, the processes of assembly of Yen’s “crystallites” from more simple units have never been detected previously.

Owing to the expected stability of nano-crystallites (dimer pairs), asphaltene molecular assemblies may be divided into two main families—those of “primary” and of “secondary” aggregates. “Primary” species are assembled by consecutive additions of asphaltene monomers, the most stable aggregates being dimers and dimer pairs. More complex stacked oligomers with the odd number of molecules may be regarded as transient unstable aggregates for the same reasons as in case of a trimer. The complex stacked structures with even numbers of molecules are unfavourable as they have much higher S/V ratios as compared to a nano-crystallite (with the only probable exception of a stacked 6-mer). In the “secondary” family of aggregates, the basic structural units are not asphaltene molecules, but the quasi-spherical nanocrystallites. Comparatively loosely bound assemblies of such crystallites may be viewed as precursors of flocks and precipitates.

On the basis of the above discussion, we may attribute the specific minima of  $\chi(C)$  in Fig. 4 to the consecutive stages of molecular aggregation. However, as pointed out in Section 3.4, the nonmonotonic features of the “blue shift” are comparatively weak, implying that an aggregation process is gradual and formation of larger aggregates is not accompanied by a step-like disappearance of smaller ones, so that at any studied asphaltene concentration, there is a coexistence of various oligomers in a solution. Hence, the positions of minima in Fig. 4 should not be interpreted as some “critical concentrations”. Sooner, these minima define the transient states with the relatively stronger predominance of one type of aggregate (monomers, dimers, etc.). So, at asphaltene concentrations ~5–15 mg/l, we assign the first minimum in Fig. 4 to predominance of asphaltene dimers. Consequently, we may conclude that the properties of asphaltene monomers should be studied in solutions with asphaltene concentrations not exceeding 1–2 mg/l. The small minimum at ~45–55 mg/l in Fig. 4 might be assigned to a transient predominance of trimers. The wider minimum at ~80–95 mg/l is most likely due to massive formation of dimer pairs (“nano-crystallites”), which, at higher concentrations, may form complex “secondary” aggregates.

Finally, the observed gradual buildup of more and more complex asphaltene aggregates is quite distinct from a conventional model of “micellisation”—a sharp transition from monomers to large micelles at a specific critical concentration (CMC). On the other hand, the gradual, stage-by-stage, aggregation behaviour of molecular species has been frequently observed in hydrocarbon solvents, where the notions of “micellisation” and of CMC were regarded as inapplicable (Mittal, 1977, Chapter 12).

#### 4. Conclusions

Variations of the near-UV/visible absorption spectra reflect the common features of asphaltene aggregation phenomena in toluene solutions of pre-precipitated asphaltenes and in toluene solutions of crude oils. In dilute solutions, the aggregation stages are evidently determined by the net concentrations of asphaltenes, while the presence of other crude oil constituents (e.g. resins) is not a determining factor. In all solutions, monomers are predominant species only at asphaltene concentrations below 1–2 mg/l. The most stable species are apparently asphaltene dimers (predominant in the range of 5–15 mg/l) and dimer pairs (most effectively formed at concentrations close to 90 mg/l). The latter stable aggregates may be described as quasi-spherical nano-crystallites with diameters of about 2 nm. Gradual increase of average complexity in an ensemble of coexisting asphaltene molecular aggregates is incompatible with the notions of “critical concentrations”. In particular, this type of aggregation is quite distinct from conventional micellisation processes with step-like changes at CMCs.

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