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## **On the Nature of UV/Vis Absorption Spectra of Asphaltenes**

[*a shortened version of the title: UV/Vis Absorption Spectra of Asphaltenes*]

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### **ABSTRACT**

New experimental data show that previously reported UV/vis spectra of asphaltenes/crude oils may have been strongly distorted by artifacts, affecting not only quantitative parameters (spectra's slopes), but also qualitative features (a presence of strong UV peaks). In a popular revised "amorphous semiconductor" (AS) model, the properties of UV/vis spectra are defined by population distribution of higher aromatics. This interpretation is obviously incompatible with the newly observed concentration effects in toluene solutions. Some specific features of UV/vis absorbance in asphaltenes/crude oils may be better described by the traditional AS model, taking into account the distribution of defects in chromophore carriers, e.g. nanosized carbonaceous species of the graphene family.

## INTRODUCTION

Methods of optical absorption spectroscopy are increasingly being used for the analysis of crude oils because they offer high speed, low cost, non-contact, and non-destructive testing options, desirable for environmental protection, process control, or oil exploration purposes (Andrews et al., 2001). The absorption behavior of petroleum oils strongly depends on the wavelength range employed. In particular, UV/vis absorption of crude oils is due to the presence of a wide range of cyclic aromatic compounds, including asphaltenes, with the intensity and the spectral properties of this absorption being directly related to chemical composition (Mullins, 1999). It has been emphasized (Speight, 1998) that of all of the methods applied to determining the types (and degree of condensation) of aromatic ring systems in petroleum asphaltenes, one with considerable potential is ultraviolet spectroscopy.

We have been investigating the UV/vis absorption behavior of crude oils and asphaltenes in toluene solutions with a view to developing a sensitive and reliable method for analysis of asphaltene aggregation phenomena (Evdokimov et al., 2003). In these previous works, we have monitored concentration effects on absorptivities at fixed wavelengths. It has been observed, that in dilute solutions aggregation stages are determined by the net concentrations of asphaltenes, while the role of other oil constituents is negligible. As an example, Fig. 1 shows absorptivities at 670 nm vs asphaltene content in solutions of solid asphaltenes (filled symbols) and of a crude oil (open symbols). For further discussion, the most important is the primary aggregation stage (attributed to formation of asphaltene dimers) at 10-15 mg/l.

In this work we describe the effects of asphaltene aggregation on optical absorbance over a wide range of UV/vis wavelengths, and possible impacts on the reliability of “*optical interrogation of ...crude oils and asphaltenes*” (Mullins, 1999).

## **EXPERIMENTAL**

### **Samples and Apparatus**

The virgin crude oil was collected from a well-head at Romashkinskoye reservoir (Tatarstan), had a density of 875.6 g/l, contained 3.6 wt. % asphaltenes. Oil samples were stored in the dark, in air. As a solvent, a “chemically pure” grade toluene was used.

The concentration effects on UV/Vis absorption spectra in toluene solutions have been studied in a Shimadzu UV-2201 UV/VIS double-beam spectrophotometer. Spectra in other solvents as well as spectra of the neat crude oil (Figure 6) were measured in a Specord UV VIS spectrometer. Quartz optical cuvettes had the path lengths of 5 and 10 mm. All measurements were performed at 20°C and at ambient pressure.

### **Preparation of Dilute Solutions**

Our previous studies of dilute asphaltene solutions have revealed strong effects of the “history of asphaltene/oil dissolution in toluene”. Namely, the results have shown poorly controlled dependencies on such factors as the manner of introducing one component into the other, the manner of stirring the mixture, experimental time intervals (between mixing, stirring and measurements), thermal history of a sample during these time intervals, etc. The most pronounced “history effects” were registered in solution with concentrations below  $\approx 200$  mg/l where the main aggregation stages were observed (cf. Figure 1). Hence, these effects were attributed to the complex kinetics of asphaltene dissolution which is known to vary significantly depending on the physical state of the system (Cosultchi et al., 2003). We agree with Cosultchi

et al., 2003, that the differences between the reported data for crude oil and asphaltene solutions may be often related to non-standard times and procedures of dissolution, while in most publications the time to reach the dissolution of the solid matrix of aggregated asphaltenes and the equilibrium of the solution is mentioned only as a minor factor.

To obtain consistent concentration dependencies of UV/vis spectra, we have employed a procedure of sample preparation developed in our previous studies (Evdokimov et al., 2003). Operationally, this technique is “titration of toluene with oil”. Crude oil is introduced into a large volume of toluene by minute quantities, to facilitate quick redistribution of maltenes over the sample, so that asphaltene aggregates are almost immediately subjected to the environment of solvent molecules. In each experiment a concentration of a single sample was increased step-wise, at equal time intervals  $\Delta t$ , by consecutive additions to toluene (100 ml) of calibrated oil drops ( $m_{drop}=10.3\pm 0.3$  mg), which corresponds to asphaltene concentration increments  $\Delta C\approx 3.7$  mg/l. At the beginning of each time interval a solution was gently stirred with a glass rod, at the end optical measurements were performed. The results revealed consistent time dependence for the rates of concentration increase above  $\Delta C/\Delta t \approx 60$  mg/l per hour, and practically no time effects for slower rates, considered to be representative of the “equilibrium” states of solutions. In the presents experiments we have employed rates  $\Delta C/\Delta t \leq 40$  mg/l per hour.

## **RESULTS AND DISCUSSION**

### **Concentration-Dependent Slopes of UV/Vis Spectra**

Effects of asphaltene aggregation on optical absorption were investigated within a wavelength range 315-700 nm, to ensure direct comparison with our previous experiments.

Figure 2 shows absorptivity spectra for toluene solutions with asphaltene contents ranging from 2.2 mg/l (highest curve) to 59.2 mg/l (lowest curve). In concord with the current practice (Mullins, 1999), absorptivity is plotted on a logarithm scale against photon energy. All spectra are virtually featureless, apart from two weak maxima, denoted by arrows, at  $\sim 2.16$  eV (573 nm) and at  $\sim 3.02$  eV (410 nm), usually ascribed to petroleum porphyrins (Miller et al., 1999).

Sufficiently far from these maxima all spectra exhibit expected (Mullins, 1999) exponential dependencies of absorptivity  $\varepsilon$  on photon energy  $h\nu$ :  $\varepsilon = \varepsilon_0 \exp(h\nu/E_i)$  where  $E_i$  is a characteristic energy for a particular wavelength range (a slope of a corresponding straight line in Fig. 2). The discussed peaks naturally subdivide the spectra of Fig. 2 into three intervals: 1)  $1.77 < h\nu < 2.11$  eV ( $584 < \lambda < 700$  nm) 2)  $2.23 < h\nu < 2.85$  eV ( $434 < \lambda < 555$  nm); 3)  $3.34 < h\nu < 3.9$  eV ( $315 < \lambda < 371$  nm). The corresponding characteristic energies (slopes)  $E_1$ ,  $E_2$  and  $E_3$  for various asphaltene concentrations were obtained by fitting straight lines to the experimental data ( $r^2=1.000$  in 68 % of fits,  $r^2=0.999$  in 17 % and  $r^2=0.998$  and  $0.997$  in the remaining cases).

Figure 3 shows that asphaltene aggregation affects all characteristic energies, but with different degrees. The most pronounced effect was observed for  $E_1$ , characteristic for a longest wavelengths range, which sharply increases below  $\sim 10$  mg/l (i.e. with transition to non-aggregated asphaltenes – cf. Introduction). Sensitivity of  $E_1$  to aggregation phenomena was verified by studying thermal effects in solutions with fixed concentrations. Figure 4 shows a maximum of  $E_1$  at specific temperatures of a structural phase transition in asphaltene colloids, earlier revealed by viscosity measurements (Evdokimov et al., 2001).

It should be emphasized, that a widely employed experimental procedure is to obtain “representative” UV/vis absorption spectra of crude oils/asphaltenes by splicing spectra for solutions of different crude oil/asphaltene concentrations (cf. extensive review by Mullins,

1999). The observed concentration/thermal sensitivity of spectra's slopes implies that a spectrum, constructed by splicing (and without a proper temperature control) may appear to be an artificial "chimera" which does not belong to any real substance.

Moreover, UV/vis spectrum's slope is the basic subject in current theoretical interpretations of optical properties of crude oils/asphaltenes. These interpretations utilize a revised "amorphous semiconductor" (AS) model of optical properties, originally relating spectrum's slope to a distribution of states (density of states) in similar chromophores (molecules). With respect to petroleum, now it is stated that the slopes of "*optical absorption spectra of crude oils give the population distributions of chromophores*" (distributions of aromatic molecules) and that "*all crude oils, from the heaviest tar to the lightest gas condensate...exhibit the same slope*", the reason for similarities of distributions/slopes being "*the underlying similarities of the geophysical and geochemical processes which give rise to different crude oils*" (all quotes from Mullins, 1999).

Obviously, our experimental results do not fit into the revised AS model, as population distribution of chemical species in a given oil is not expected to be changed merely by dilutions or mild temperature variations. Even if asphaltene aggregates are regarded as appearing "heavy species", the revised AS model predicts *an increase* of the spectra's slopes at higher asphaltene concentrations, contrarily to *the decrease*, observed experimentally (cf. Figure 3). As an alternative, we tried to employ a non-revised AS model for interpretation of the obtained data.

### **Relevance of a Traditional "Amorphous Semiconductor" (AS) Model**

The name of AS model sounds restrictive and may be misleading. In fact this model is applicable to description of optical properties of a wide range of solid, liquid or even gaseous

molecular systems. The only requirements are the absence of a long-range (crystalline) order, and the presence of some degree of a short-range order. The latter requirement makes it possible to employ concepts of “densities of states” and of “energy bands”. The main electronic transition, responsible for UV/vis absorbance of AS systems are the following (Adachi, 1999; Singh and Shimakawa, 2003).

1. *Tauc region*. Band-to-band transitions for photon energies in excess of the band gap  $E_0$ . In this strong absorption region absorptivity  $\epsilon$  can be described by the Tauc relation  $\epsilon h\nu \sim (h\nu - E_0)^2$ . Apparently, this region is beyond our experimental range of Figure 2.

2. *Urbach region*. Transitions involving disorder-related exponential band tails with  $\epsilon \sim \exp(h\nu/E_U)$ , where “Urbach energy”  $E_U$  indicates the width of the band tails of localized states. We suggest, that this region corresponds to the ranges of our absorbance spectra, characterized by practically equal and constant energies  $E_3$  and  $E_2$  (cf. Figure 3).

3. *Low absorption region*. Transitions involving defect states (e.g. dangling bond states) within the band gap determine another exponential dependence  $\epsilon \sim \exp(h\nu/E_d)$ , where the width of the defect states  $E_d$  usually is larger than  $E_U$ . It is established that this region (contrary to the Urbach one) is rather sensitive to structural properties of materials. We suggest, that this region corresponds to the longer-wavelength range of our absorbance spectra, characterized by the energy  $E_1$ , which exhibits high structural sensitivity to phenomena of asphaltene aggregation (cf. Figures 3,4). An increase of  $E_1$  at high dilutions signifies an appearance of some dangling bonds in non-associated asphaltene monomers, which explains their high propensity to aggregation.

An expected counterargument to the above attributions is that Urbach energy  $E_U$  should increase linearly with temperature (Mullins, 1999) which is not observed in petroleum systems. Indeed, this strong temperature dependence was predicted by earlier theories which took into



account only thermally-activated disorder (phonon-assisted transitions). However, based on more recent experimental results, the current stage of thinking is that in many AS systems the Urbach tails are caused by frozen-in static disorders with weak temperature effects on  $E_U$  (Adachi, 1999; Singh and Shimakawa, 2003).

### **Probable Molecular Carriers of AS Optical Properties in Petroleum**

Literature analysis shows that among the molecules with well-proven AS-type absorption features (e.g., continuous UV/vis absorption spectra), most closely related to asphaltenes are species of the graphene family. According to the current IUPAC definitions, *graphene* is the name given to a large single planar sheet of  $sp^2$  bonded carbon atoms densely packed into an aromatic benzene-ring structure. Graphene can be considered part of a structural continuum, with the smaller size part represented by pericondensed PAHs, which, in turn, are regarded to be structurally similar to UV/vis - absorbing aromatic chromophores in asphaltenes (Bergmann et al., 2004).

AS optical features of graphene are widely used to describe common optical properties of many carbon-based nanomaterials, including fullerenes, carbon nanotubes, soot etc. (Dresselhaus et al., 1996). Some of these properties are close to those observed in our experiments with respect not only to qualitative features (extended continuous spectra) but to some quantitative parameters. For example, Czerw et al., 2001 report absorbance spectra for concentrated solutions of carbon nanotubes in chloroform, which may be characterized by the following slopes in the above discussed wavelength ranges:  $E_2=0.50$  eV,  $E_1=0.36$  eV, close to the respective values for our concentrated solutions in Figure 3:  $E_2=0.52$  eV,  $E_1=0.43$  eV.

However, the crucial test for the presence of graphene-related absorbing species would have been observation of their characteristic non-AS properties, e.g. intense UV peaks in 4-6 eV range due to collective  $\pi$  plasmon excitations (Murakami et al., 2005).

### **Experimental Verification of Expected UV Peaking of Absorbance in Crude Oil Solutions**

Recently, several publications have reported UV spectra for solutions of petroleum and coal asphaltenes (all in toluene) with prominent peaks at 288-310 nm (4.3 – 4.0 eV). In our preliminary experiments with crude oil solutions at the wavelength range below 315 nm we have registered spectra in perfect coincidence with the results of other authors, as illustrated in Figure 5. In order to emphasize coincidence, original data were re-normalized to equal absorbances at 350 nm. The numbers denote the spectra for the following toluene solutions: (1) of our Tatarstan crude with 26 mg/l asphaltenes; (2) of coal asphaltenes, 34.8 mg/l (Guin and Geelen, 1996); (3) of asphaltenes from Athabasca bitumens, 100 mg/l (Alboudwarej et al., 2004); (4) of asphaltenes from a Hamaca crude, 50 mg/l (Goncalves et al., 2004).

Further investigation has shown, however, that apparently all UV peaks in Figure 5 are just experimental artifacts near the absorption edge of the solvent (toluene) at 285 nm (Lambert et al., 1976). The effect is trivial, though easily neglected. In routine double-beam experiments absorbance spectra of solvents most frequently are not registered, once there is a perfect “zero line”. However, below the absorption edge this line corresponds to negligible transmittance, which cannot be further affected by the solute.

The above conclusions were verified by studying crude oil spectra in solvents with different absorption edges: chloroform (254 nm), benzene (280 nm) and carbontetrachloride

(265 nm). For technical reasons, we employed a Specord UV VIS spectrometer, with a graphical output and a non-linear wavelength scale. As shown in Figure 6 (spectra 1 and 2), the “UV artefact” does follow the changes in an absorption edge of a solvent. Hence, it appears that UV absorbance features of neat asphaltenes can not be fully investigated in experiments with conventional transmittance-type spectrometers: asphaltene solvents (e.g. aromatics,  $\text{CCl}_4$ ) possess absorption edges in the wavelengths range of interest, while substances which do not absorb above 200 nm (e.g. pentane, hexane) are asphaltene precipitants. The alternative is to investigate asphaltene absorption in natural environments – undiluted heavy crudes/bitumens. Our tests have shown that high absorptivity of the studied heavy crude makes impossible the use of standard quartz cuvettes (with path lengths down to 1 mm). Hence, preliminary information on UV absorbance features of a neat crude oil was obtained with samples “of undefined path length”, by smearing a thin film of the heavy crude oil onto a wall of one of a pair of empty quartz cuvettes (no evaporation effects were registered). The respective spectrum (curve 3 in Figure 6) practically coincides with reliable parts of solution’s spectra and exhibits a number of well-resolved peaks. Peak (A) at 410 nm (3.02 eV) is associated with porphyrins (cf. spectra in Figure 2). The existence of peak (D) at ~218 nm (5.69 eV) currently is questionable, as it is close to the range of spectrometer’s nonlinearity (indicated by a dashed line). With respect to the above discussed graphene hypothesis, the most important are peak (B) at ~275 nm (4.51 eV) and peak (C) at ~244 nm (5.08 eV). These practically coincide with a characteristic structure at 4.5 eV and 5.25 eV observed in absorbance spectra of carbon nanotubes and attributed to anisotropic electronic properties of graphene sheets (Murakami et al., 2005).

## CONCLUSIONS

Newly obtained experimental evidence shows that, in spite of large amount of published data, current knowledge/understanding of UV/vis absorption of asphaltenes still is far from being satisfactory. Previously reported UV/vis properties of asphaltenes/crude oils may have been noticeably distorted by experimental artifacts. Verification of suitable absorption models requires measurements at UV wavelengths, apparently inaccessible in asphaltene solutions, due to strong solvent interference. Hopefully, some relevant information may be obtained by studying UV absorbance in thin films of natural (undisturbed by dilution) asphaltene-containing media. Preliminary experiments with films of Tatarstan heavy crude oil indicate a possible existence of UV peaks, frequently observed in absorbance spectra of nanosized carbonaceous species of the graphene family.

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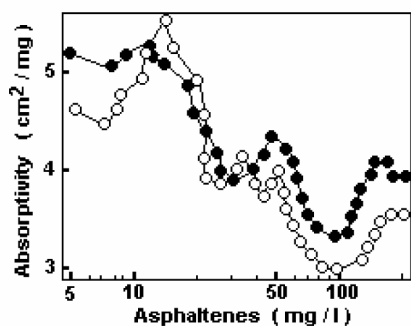
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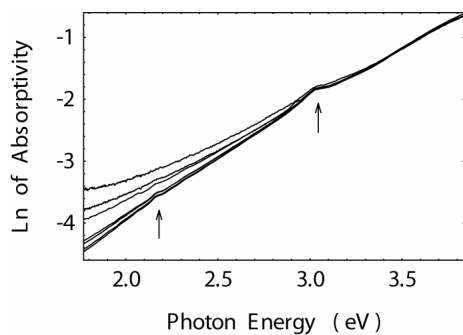
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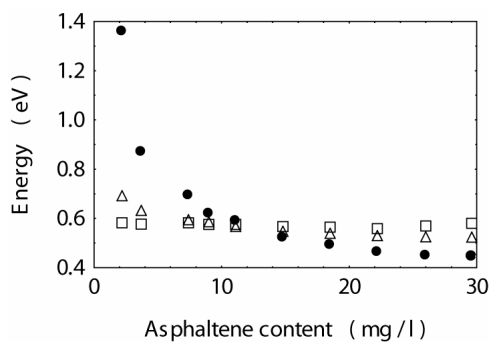
## FIGURES



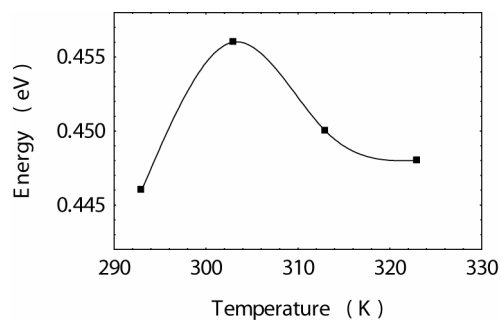
**Figure 1.** Effects of asphaltene aggregation on absorptivities in toluene solutions of solid asphaltenes (filled symbols) and of a crude oil (open symbols) (Evdokimov et al., 2003).



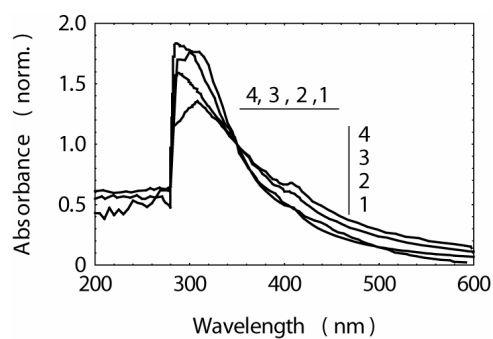
**Figure 2.** Effects of asphaltene aggregation in toluene solutions on the slopes of UV/vis absorptivity spectra.



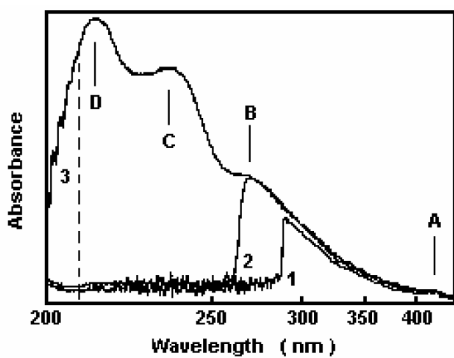
**Figure 3.** Characteristic slope energies of UV/vis spectra vs asphaltene content in toluene solutions.



**Figure 4** . Temperature dependence of a characteristic energy  $E_1$  in a toluene solution with  $\sim 150$  mg/l asphaltenes.



**Figure 5** . Apparent coincidence of UV peaks in toluene solutions of a crude oil (1) of coal asphaltenes (2) and of petroleum asphaltenes (3,4).



**Figure 6** . UV/vis absorption spectra of crude oil solutions in toluene (1), in  $\text{CCl}_4$  (2) and of a neat crude oil (3).



## FIGURE CAPTIONS

**Figure 1.** Effects of asphaltene aggregation on absorptivities in toluene solutions of solid asphaltenes (filled symbols) and of a crude oil (open symbols) (Evdokimov et al., 2003).

**Figure 2.** Effects of asphaltene aggregation in toluene solutions on the slopes of UV/vis absorptivity spectra.

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