

POTENTIAL OF UV-VISIBLE ABSORPTION SPECTROSCOPY FOR CHARACTERIZING CRUDE PETROLEUM OILS

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New experimental data as well as analysis of published databases show that the potential of UV-Visible absorption (UVVA) spectroscopy for classification/evaluation of petroleum may be strongly underestimated. Even the simplest “coloration” approach, when monotonous UVVA spectra are characterized by a single numerical parameter, allows distinguishing various types of crude oils. Subjected to proper processing, apparently “featureless” UVVA spectrum shows a multiple peak structure superimposed on a general monotonous background providing a basis for UVVA employment for compositional analysis of crude oils. The main practical problem is that generally crude oils are opaque and have to be diluted for UVVA analysis. Our experiments show that oil dilution may strongly affect the measured UVVA spectra apparently due to de-aggregation of asphaltenes in a solution. Further development of UVVA techniques requires better understanding of the nature/composition of asphaltenes. A useful approach may be consideration of “molecular diversity” models, being developed for other systems with continuous UVVA spectra, in particular for humic acids and melanins

Introduction

The accurate determination of crude oil physical and chemical properties is critical not only to characterize and produce a reservoir, but also to design well completions, subsea tiebacks and topside facilities. To measure these properties, reservoir crude oil samples are frequently evaluated by UV/visible absorption (UVVA) spectroscopy [1]. This technique is increasingly employed for in-field applications [2-5], for laboratory studies of crude oils and petroleum asphaltenes [6-13]. In spite of a growing number of applications, some important problems of UVVA spectroscopy remain unresolved. E.g., while the absorption of many pure chemicals can be easily determined with conventional spectrophotometers, complex mixtures like crude oils, have very high absorption coefficients, typically of ca. $1 \mu\text{m}^{-1}$ [14]. Sophisticated methods have been developed to measure the absorption coefficients of these highly absorbing liquids directly [14, 15]. In conventional practice, oil samples are diluted in an organic solvent down to a concentration level which ensures transmission of light over distances of a few millimeters. In this way the use of complicated optical setups is avoided and UVVA measurements are performed with standard cuvettes and laboratory photometers. However, such experiments are conducted without taking into account a possible sensitivity of UVVA spectra to dilution due to de-aggregation of chromophore-

bearing molecules, first of all of asphaltenes [6-12]. This approach stems, mainly, from a widely publicized over-simplistic descriptions of UVVA spectra's shapes/profiles [1-5]. In particular, these descriptions employ a concept of "coloration", obviously based on traditional color scales (ASTM, Saybolt, etc.) widely employed for grading products in the petroleum refining industry [16, 17]. Such scales, originally based on sets of standard light filters, are essentially one-dimensional, i.e. it is implied that "color" UVVA spectra may be described by smooth single-parameter (maximum two-parameter) functions. With respect to UVVA spectra of crude oils, it is usually assumed that *"Despite the differences in optical absorption of various reservoir oils caused by composition, there is a common behavior. Electronic absorption decay...can be characterized by a single parameter, which can be thought of as the color of the oil"* [3]. The behavior of absorptivity ε (or optical density) is modeled by a universal wavelength-dependent exponential term $\varepsilon(\lambda) = Ce^{(\kappa/\lambda)}$, hence on a plot of $\ln\varepsilon$ vs photon energy all spectra should be featureless and linear over the entire range of UV/vis wavelengths:

$$\ln(\varepsilon) = \ln C + \kappa/\lambda = \ln C + hv/U \quad (1)$$

where κ and U are characteristic slope and energy¹ and C is a coloration coefficient [4]. In a "coloration" approach, these parameters are assumed to be unique signatures of a native crude oil, unaffected by measurement procedures, in particular by above mentioned dilution of original samples. Although such assumptions have not been properly verified, either experimentally or theoretically, they are implicitly employed in various correlation/evaluation studies, aimed on obtaining some "universal regularities" in world's petroleum rescors. E.g., a detailed and informative study on *"optical interrogation of ...crude oils and asphaltenes"* [1] is based on "experimental" crude oil UVVA spectra constructed from a number of spliced intervals obtained for samples with unspecified degrees of dilution. However in case of concentration-dependent UV/vis absorption, such spliced spectrum may appear to be an artificial "chimera" which does not belong to any real substance.

In this paper, we investigate the concept of "featureless" UVVA spectra of crude oils, analyze a possibility of one-dimensional UVVA characterization for fingerprinting of various types of crude oils and describe some effects of crude oil dilution on optical absorbance.

Experimental

UVVA properties have been investigated with a Shimadzu UV-2201 UV/VIS double-beam recording spectrophotometer (1 nm resolution). Quartz optical cuvettes had path lengths of 5 and 10 mm. All measurements were performed at 20°C and at ambient pressure. The UVVA data were collected with 1 nm wavelength increment and automatically stored. Obtained data sets were computer-processed according to the below described procedures.

The studied virgin crude oil was collected directly from an oil-producing well in Tatarstan, Russia. Original oil had a density of 875.6 g/l, contained 3.6 wt. % asphaltenes, 1.8 wt. % sulphur, ~6 wt. % paraffins/waxes. Samples for optical studies were prepared by dilution of the crude oil with “chemically pure” grade toluene.

Our previous studies of dilute oil solutions have revealed strong effects of the “history of oil dissolution in toluene” [9, 12, 18], attributed to complex kinetics of dissolution of asphaltene colloids [19, 20]. Hence, to obtain reproducible UVVA data, we employed a specific procedure of oil dilution, described in detail below.

Results and Discussion

One-dimensional (single-parameter) characterization of UVVA spectra.

Figure 1 shows a conventional (absorptivity vs. wavelength) spectrum for a diluted oil sample ($1.2 \cdot 10^{-4}$ v/v in toluene). Vertical lines denote two standard wavelengths widely employed for one-dimensional UVVA characterization of humic matter via a co-called E4/E6 ratio of absorptivities measured at 465 and 665 nm [21, 22].

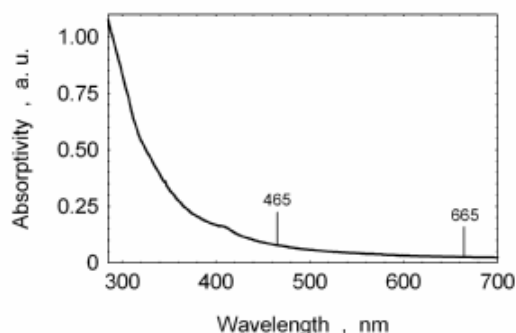


Figure 1. A conventional plot of the UVVA spectrum of diluted Tatarstan crude ($1.2 \cdot 10^{-4}$ v/v in toluene). The wavelengths indicated in the figure are those employed for evaluation of E4/E6 ratios

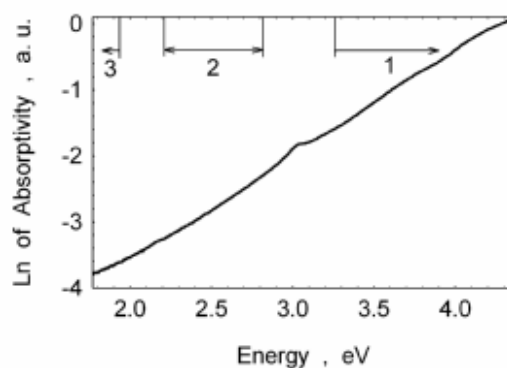


Figure 2. A plot of the spectrum from Figure 1, more appropriate for “coloration” analysis. The indicated ranges of photon energies are those employed for evaluation of characteristic energies U_1 , U_2 and U_3

A well-defined peak at 410 nm and a smaller, barely visible one at 573 nm are due to vanadyl etioporphyrins in the crude oil [23], as discussed in more detail below. For classification of “general spectra profiles” the appearance of these peaks is important because they interfere with the above discussed “universal” exponential approximation. Moreover, as illustrated in Fig. 2, porphyrin peaks naturally subdivide a plot of \ln of absorptivity vs. photon energy into three apparently linear intervals: 1) $h\nu > 3.26$ eV ($\lambda < 380$ nm); 2) $2.82 > h\nu > 2.21$ eV ($440 < \lambda < 560$ nm); 3) $1.94 > h\nu > 1.77$ eV ($640 < \lambda < 700$ nm). Contrary to “coloration” assumptions, characteristic energies (cf. Eq.1) for these intervals appear to be significantly *different*. In particular, for the data in Figures 1 and 2: $U_1 = 0.62$ eV, $U_2 = 0.64$ eV and $U_3 = 1.13$ eV. Further analysis revealed that U_1/U_3 ratio is sensitive to oil’s type/composition and may be recommended as a new parameter for one-dimensional UVVA characterization of crude oils.

To support this recommendation we analyzed UVVA data from a recently published catalogue of optical spectra of oils [24]. The spectra in this catalogue were obtained with the Kontron UVIKON 810 Spectrophotometer using quartz cuvettes with a 1 cm optical path length. To cover the entire wavelength range (250-700 nm), oil samples were highly diluted with cyclohexane down to concentrations that yielded data within the dynamical range of the instrument.

Some representative results of catalogue analysis are presented in Table 1. It is clear that the values of U_1/U_3 or E_4/E_6 ratios are markedly different in “Light Sweet” and “Heavy Sour” oils. In particular, in “light” oils $U_1/U_3 \approx 1.1-1.8$ ($E_4/E_6 \approx 3.4-4.8$),

while in “heavy” ones $U1/U3 \approx 0.5-0.7$ ($E4/E6 \approx 2.3-2.5$). Further analysis revealed strong linear correlation between the two ratios, namely: $U1/U3 = 0.51 \cdot E4/E6 - 0.67$ ($r^2=0.998$), indicating that these UVVA parameters may be employed interchangeably. Table 1 also shows that a simple “coloration” model with perfectly exponential UVVA spectra and a single characteristic energy U (i.e. with $U1/U3=1$) may be applied only to some “medium” oils. Furthermore, the above correlation between $U1/U3$ and $E4/E6$ shows that in case of “coloration”, the characteristic energy assumes a value of $U \approx 0.67$ eV, common for all types of “medium” oils. Certainly, the universality of this value should be related to some common properties of all “average” crudes. However, at the current state of experimental/theoretical data, any detailed discussion of these common features would be merely speculative.

Table 1

Differentiation of oil types by one-dimensional parameters of UVVA spectra

Oil Type/Name	ρ (g/cm ³)	S (wt.%)	ϵ_{460} (1/ μ m)	U_3 (eV)	E4/E6	U1/U3
Sweet Light/Medium						
Ekofisk	0.829	0.17	0.030	0.37	4.29	1.56
Brent Blend	0.833	0.40	0.043	0.60	3.37	1.07
Oman	0.851	0.94	0.076	0.32	4.75	1.81
Ninian Blend	0.846	0.43	0.071	0.31	4.73	1.78
Sour Heavy/Medium						
Basra Medium	0.871	2.58	0.137	1.21	2.32	0.50
Romashkino(Urals)	0.857	1.80	0.224	1.05	2.49	0.61
Arabian Medium	0.883	2.85	0.238	0.97	2.53	0.70
Arabian Heavy	0.891	2.80	0.263	1.19	2.39	0.58
Our Crude	0.876	1.80				
Concentr. Solution			-	0.44	5.15	1.41
Dilute Solution			-	1.79	2.50	0.36

To conclude this section, it should be noted that the straightforward relation of $U1/U3$ and $E4/E6$ to crude oil types apparently holds only for “sufficiently diluted” samples of crude oils. E.g., two bottom lines in Table 1 show these ratios for our Tatarstan crude in two states of dilution. By its density (0.876 g/cm³) and sulphur content (1.8 wt.%) this crude belongs to a type of “Sour Heavy” oils. Indeed, in a “dilute solution” ($1.2 \cdot 10^{-4}$ v/v in toluene) the values of $E4/E6=2.50$ and $U1/U3=0.36$ are typical for other oils of this type. On the other hand, in a “concentrated solution” ($1.4 \cdot 10^{-3}$ v/v in toluene), with UV optical density close to the instrumental cut-off, the values

of $E4/E6=5.15$ and $U1/U3=1.41$ become close to those observed in “Sweet Light” oils. In more detail, concentration effects will be discussed with respect to Figs. 7-10.

Revealing complex peak structures in presumably featureless UVVA spectra.

As mentioned above, some characteristic peaks (at ca. 410 and 570 nm) may be detected in the original (zero order) spectra of Figures 1 and 2. Less obvious absorption peaks usually are enhanced by computing higher order derivative spectra [25]. However, application of derivative spectroscopy is not without problems: derivative spectra, although enhancing peak resolution, show more noise and require greater care in their interpretation (cf. Ref. 26 and references therein). As an example, the lower curve in Figure 3 shows a first derivative of the zero order spectrum from Figure 1. In this noisy curve the presence of 410 nm peak is emphasized, but the only new feature which appears is some structure close to 300 nm. To reveal this structure, the derivative spectrum had to be further processed, namely it was smoothed 3 times with a sliding 3-point data window. The smoothed derivative is shown by the upper curve in Figure 3, shafted along Y-axis for clarity of presentation. Note that no peak structure is apparent above 420 nm. Due to noise problems, calculation of higher order derivatives proved to be no more informative.

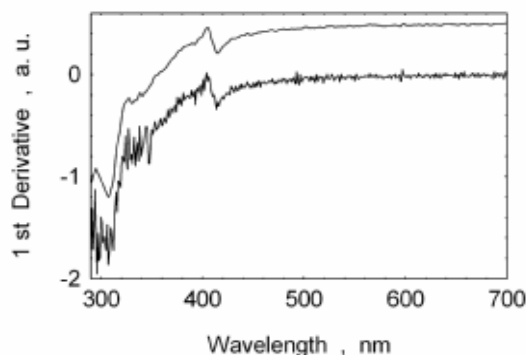


Figure 3. A limited power of derivative spectroscopy for revealing fine structure in UVVA spectra:
Below – a “noisy” first derivative of the original spectrum from Figure 1
Above – the derivative subjected to repeated smoothing

However, the overall smooth nature of zero order UVVA spectra allowed employing a non-derivative procedure of “continuum removal by division” [27], which is much less sensitive to data noise and usually reveals well-reproducible peak

structures. It is outside the scope of this paper to discuss/prove a possible nature of a continuum in UVVA spectra of crude oils, though some preliminary comments are presented in the concluding sections. Possible analytical approximations of this continuum have been tested with respect to “almost linear” plots of \ln of UVVA vs photon energy (cf. Figure 2). In the studied energy range of $h\nu=1.77-4.35$ eV, the simplest functions with coefficients of determination $r^2=1.00$ appeared to be 4-th order polynomials. In the continuum-removal procedure, the measured UVVA spectra were re-scaled via dividing them by the respective smooth approximations. The obtained re-scaled spectra clearly revealed a presence of reproducible peak structures virtually insensitive to a magnitude of optical density (degree of oil dilution) and, hence, evidently representative of a studied crude oil. As an example, Figure 4 shows re-scaled UVVA spectra for our Tatarstan crude at two different dilutions in toluene: $\sim 1 \times 10^{-4}$ v/v (lower curve) and $\sim 5 \times 10^{-4}$ v/v (upper curve). With respect to major peak positions both spectra are virtually identical.

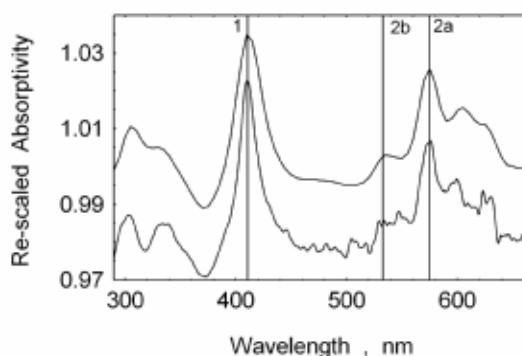


Figure 4. Multiple peak structures in UVVA spectra subjected to re-scaling via continuum removal by division. Vertical lines indicate absorption peaks of vanadyl petroporphyrins

One group of peaks in Figure 4 may be reliably ascribed to a specific type of petroporphyrins. Namely, according to a previous spectroscopic investigation of purified porphyrin fractions [23], peak 1 at 410 nm corresponds to the Soret band of vanadyl porphyrins, while peak 2a at 573 nm and peak 2b at 533 nm correspond, respectively, to the so-called Q_α and Q_β bands. Moreover, a clear predominance of Q_α peak allows classifying the discussed species more specifically as vanadyl Etio-porphyrins with a molecular composition of $C_{32}H_{36}N_4OV$ [23, 28]. Furthermore, a

double-peak structure just above 600 nm most probably also is due to the presence of porphyrins. In particular, UVVA spectra of metalloporphyrins feature just two Q bands, while in free base porphyrins (in which the central metal is replaced by two hydrogen atoms), the characteristic feature is splitting of the Q band into four components due to the loss of square symmetry [29].

There are two other prominent (and evidently multicomponent) UVVA bands in Figure 4, peaking at ~304 nm and at ~335 nm. We could not reliably attribute these bands, apparently present in various types of oils (cf. Figures 4-6), but they closely resemble double band structures in absorption spectra of some medium-sized polycyclic aromatics, e.g. pyrene (C₁₆H₁₀) [30], or quinine (C₂₀H₂₄N₂O₂) [31].

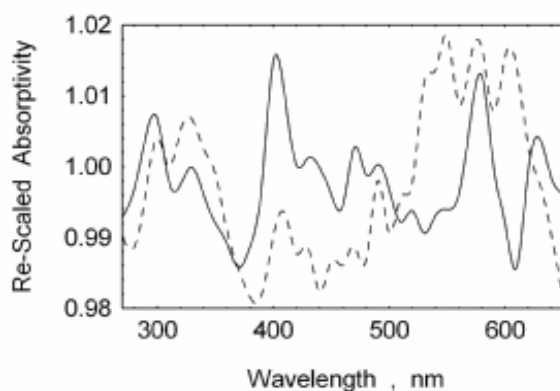


Figure 5. Peak structures in continuum-removed spectra for crude oils of the same “Sour Heavy” type, though with different vanadium contents: ≤ 30 ppm (dashed line) and ~ 700 ppm (solid line).

The usefulness and the reliability of the above re-scaling procedure was further supported by revealing a fine structure in seemingly featureless UVVA spectra from the Oldenburg Catalogue [24]. It should be noted that while our UVVA data in Figures 1-4 have been collected with a wavelength increment of 1 nm, those in Oldenburg Catalogue are tabulated with much larger increment of 10 nm. Nevertheless, as shown in Figures 5 and 6, all re-scaled spectra reveal a consistent peak structure closely related to that in our crude (Figure 4) and obviously dependent on the individual properties of a particular crude oil. In particular, Figure 5 shows re-scaled data for two crudes which belong to the same type of “Sour Heavy” oils (cf. Table 1) though are significantly different with respect to vanadium content. In Basra crudes (dashed line) vanadium does not exceed 30 ppm [32], while Romashkino(Urals) crudes (solid line) contain up to 700

ppm vanadium [33]. Accordingly, the Romashkino re-scaled spectrum exhibits well-defined and intense peaks of vanadyl porphyrins at ~ 408 nm and at ~ 575 nm (cf. the above discussion of Figure 4).

Furthermore, even in the “low-resolution” case (10 nm data increment) some characteristic features of re-scaled spectra allow to distinguish “Sour Heavy” oils from “Sweet Light” ones (cf. Table 1). As an example, Figure 6 shows a significant increase of re-scaled UVVA above ca. 450 nm apparently typical for all considered “Sweet Light” crudes, in particular for Brent Blend oil (solid line). For comparison, the dashed line shows a “Sour Heavy” spectrum for Basra crude from Figure 5.

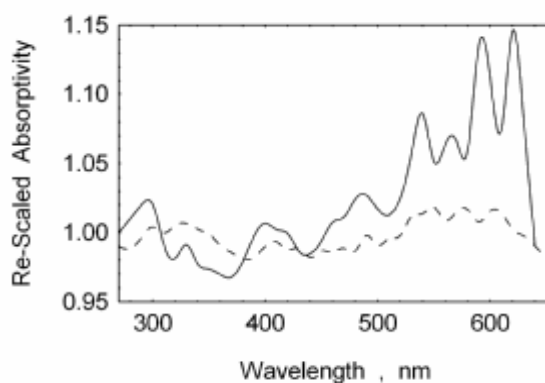


Figure 6. Peak structures in continuum-removed spectra for crude oils of the “Sour Heavy” type (dashed line) and of the “Sweet Light” type (solid line).

Effects of crude oil dilution on UVVA spectra.

As mentioned in Introduction, UVVA features of crude oils are defined by heavier oil constituents, first of all by asphaltenes [1, 5-13], which in native crudes and in solutions are known to exist in various states of aggregation. It has been experimentally demonstrated, that asphaltene aggregation phenomena may notably affect UVVA properties of crude oil solutions (in toluene), while the “control parameter” is not an oil/solvent ratio but a net asphaltene concentration in a studied sample [9, 10]. Hence, in the following discussion we will characterise toluene-diluted oil samples not by the oil contents (in v/v units), but by the respective asphaltene concentrations (in mg/L units).

It should be noted that our previous studies of dilute oil solutions have revealed strong effects of the “history of oil dissolution in toluene” [9, 12, 18]. The observed “history effects” we attributed to the complex kinetics of dissolution of asphaltene

colloids. This kinetics is known to vary significantly depending on the physical state of the system [19, 20], hence the differences between reported data for crude oil and asphaltene solutions may be often related to non-standard times and procedures of dissolution [20]. In most publications, the time to reach the dissolution of aggregated asphaltenes and the equilibrium of the solution is mentioned only as a minor factor.

To obtain consistent concentration dependencies of UVVA spectra, we employed a standard procedure of sample preparation used in our previous studies [9, 12, 18]. 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 present experiment with dilute solutions a concentration of a single sample was increased step-wise, at equal time intervals (~ 5 minutes), by means of consecutive additions to pure toluene (100 ml) of calibrated oil drops ($m_{drop}=10.3\pm 0.3$ mg). Hence, the concentration increments in solutions were 0.012 vol.% for the crude oil and, respectively, 3.7 mg/L for oil’s asphaltenes (some intermediate concentrations were obtained with toluene volumes other than 100 ml). At the beginning of each time interval a solution was gently stirred with a glass rod, at the end – UVVA measurements were performed.

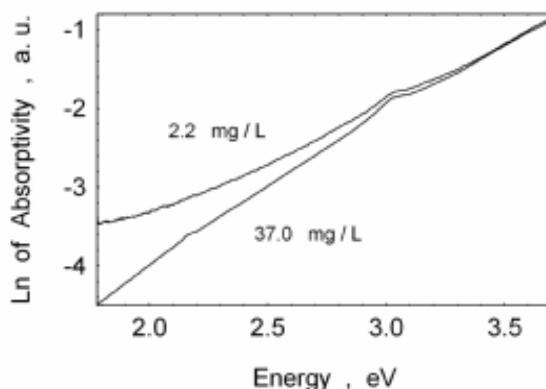


Figure 7. Effects of oil dilution by toluene on the shapes of UVVA spectra. Indicated in the figure are the net asphaltene concentrations in respective solutions

As indicated in Table 1, UVVA spectra of “dilute” and “concentrated” solutions appear markedly different with respect to one-dimensional (single-parameter) characterization. Figure 7 shows that the origin of this difference is in significant

variations of the spectrum's shape, most noticeable at photon energies below (at wavelengths above) the porphyrin Soret peak at 3.02 eV (410 nm). As discussed above, "natural" parameters for quantitative description of spectra's shapes are characteristic energies U1, U2 and U3. Figure 8 shows the measured dependencies of these energies on asphaltene concentration in toluene-diluted samples of Tatarstan oil. Note that at all studied dilutions the value of U1 (characteristic of a spectrum's shape at energies *above* the Soret peak) is virtually constant (0.617 ± 0.005 eV). On the other hand, the energy U3, characteristic of spectra's behavior at energies *below* the porphyrin Q_α peak at 2.16 eV (573 nm), may be regarded as constant (0.446 ± 0.008 eV) only in less diluted solutions with asphaltene concentration above 22-24 mg/L. A systematic increase of U3 starts at asphaltene concentrations somewhat below 16-18 mg/L and a rate of this increase become much larger at concentrations below ca. 5 mg/L. As indicated above, these U3 variations may be attributed to de-aggregation phenomena of asphaltenes [9, 10] which result in a change of one-dimensional parameter U1/U3 in dilute solutions listed in Table 1. Moreover, as shown in Figure 9, an analogous aggregation-dependent behavior is inherent to the other one-dimensional parameter – E4/E6 ratio.

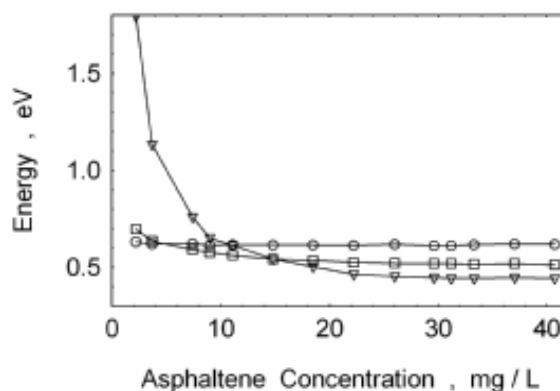


Figure 8. Effects of oil dilution by toluene on UVVA characteristic energies U1 (circles), U2 (squares) and U3 (triangles)

It should be noted that in our previous 2002 paper³⁴ and in 2003 publication [9, 10] the observed UVVA peculiarities at concentrations of 2-5 mg/L and 15-20 mg/L we interpreted as "the first experimental observations" of primary asphaltene aggregation stages. Recently, this interpretation has been confirmed by other research groups (cf. discussion in refs 35-37). However, new literature analysis has revealed an unduly

“forgotten” 1986 publication on UVVA of asphaltenes at high dilutions [6]. This paper contains (apparently the first) evidence of strong concentration effects on UVVA spectra of asphaltenes due to asphaltene aggregation commencing at concentrations above 5 mg/L.

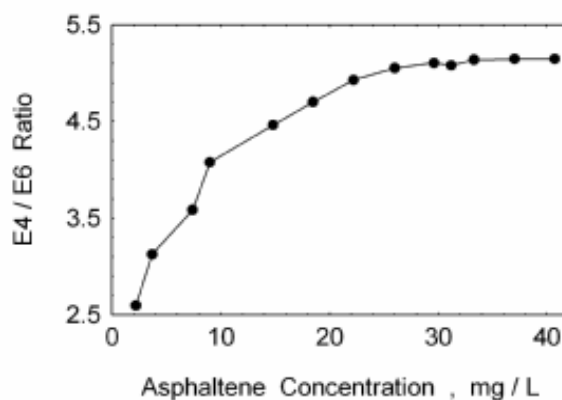


Figure 9. Effects of oil dilution by toluene on UVVA “coloration” parameter E4/E6

In more detail, concentration effects on the UVVA spectra were revealed by employing the technique of “difference absorption spectroscopy”(DAS) [38]. In particular, “conventional” absorption spectra in double-beam spectrometers (e.g. the one shown in Figure 1) are generated by subtracting signals from a studied solution and from a reference cuvette filled with pure solvent. In this technique, comparatively subtle UVVA changes, induced by aggregation, may seem to be negligible compared to the steeply falling “coloration” background. In the DAS technique these subtle changes are enhanced by replacing a reference solvent spectrum with a “representative” solution spectrum in a concentration range where aggregation effects are not present yet. Figures 8 and 9 show that in our experiments such representative concentration may be the highest one studied, namely 40.7 mg/L asphaltenes ($2 \cdot 10^{-3}$ v/v oil in toluene). The corresponding difference spectra for smaller concentrations are shown in Figure 10. A common rise at smallest wavelengths may be due to instrumental cut-off. The behavior of difference spectra at higher wavelengths is consistent with the data of Figures 7-9 and once again demonstrates the importance of asphaltene aggregation at concentrations of 15-20 and 5-6 mg/L. In particular, for asphaltene contents above 26-28 mg/L, UVVA spectra are virtually indistinguishable with difference absorptivities close to zero in the entire wavelength range shown. At concentration below ~ 20 mg/L a new wide

absorption band appears in the difference spectra. This band is virtually featureless, though with suggestions of some red-shifting peaks (e.g. at ~435 and ~480 nm for 14.8 mg/L asphaltenes).

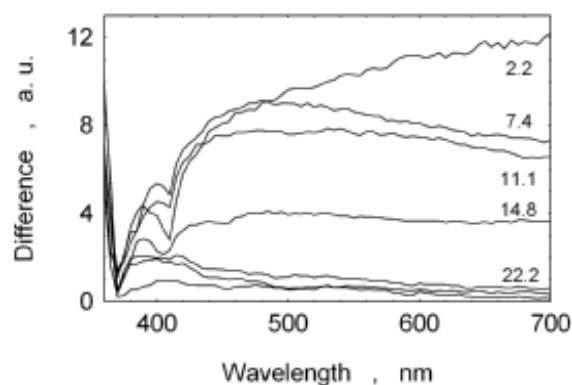


Figure 10. Difference spectra of oil samples with respect to solution with 40.7 mg/L asphaltenes. Indicated in the figure are net asphaltene concentrations in more dilute solutions.

At asphaltene contents of 10-11 mg/L this band “fully develops” (saturates) into an asymmetrical shape with a maximum at ca. 475-480 nm and a slowly decreasing tail at higher wavelength. Note that “a well-resolved peak” at 380-400 nm is most surely an artifact due to a presence of a “porphyrin dip” in difference spectra at 410 nm (cf. below). The transition to a new aggregation state of asphaltenes at concentrations below ~5 mg/L is accompanied by a build-up of an additional absorption band above ~500 nm apparently peaked outside the studied wavelength range, in the NIR region. The nature of the above absorption bands is not clear yet, but they resemble charge-transfer bands (intermolecular and intramolecular ones) frequently observed in aggregating aromatic donor-acceptor systems [39, 40].

It should be specially noted that difference spectra indicate that, apparently, molecular species with porphyrin chromophores only marginally (or not at all) are involved in asphaltene aggregation processes in the studied concentration range. Firstly, the intensity of a prominent Soret peak at 410 nm is virtually independent of asphaltene concentration as indicated by a minimum in difference spectra of Figure 10 and by a stable peak shape in re-scaled spectra of Figure 4. Secondly, concentration-induced aggregation of porphyrin molecules is known to be accompanied by large shifts of their Soret bands, namely by ~55 nm red shift in edge-to-edge J-aggregates or by ~15 nm

blue shift in stacked H-aggregates [41]. In our experiments, the position of porphyrin Soret band remained constant (410 ± 0.5 nm) within the studied concentration range. The above conclusions seem to contradict a recent observation that “*interactions of metalloporphyrins appeared to play a key role in the asphaltene aggregation mechanism*” [42]. However, our studies at high dilutions do not exclude a possibility of porphyrin aggregation at asphaltene concentrations above 40-50 mg/L. In fact, it has been experimentally demonstrated that the sharp Soret band of vanadyl porphyrins is characteristic only of the lowest MW asphaltene fraction [6], which may have a very high solubility in toluene, up to 59 g/L [43, 44]. On the other hand, aggregation stages in the mg/L concentration range were attributed [42] to the highest MW asphaltene fraction, with a solubility limit not exceeding 93 mg/L [43].

A possible nature of “continuum” in UVVA spectra.

As follows from the above experimental data and discussion, the most apparent feature in UVVA spectra of all crude oils is a smooth “continuum”, while characteristic molecular peaks are revealed only by applying proper processing procedures. In spite of many suggestions/models (cf. Introduction) a precise nature of continuous UVVA spectra of crude oils and asphaltenes still remains a mystery. For further research, it may be useful to consider other (few) molecular systems with virtually continuous UV/vis absorption.

a) Molecular 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. A typical graphene sheet is a $C_{62}H_{20}$ molecule which can be considered a part of a structural continuum, with the smaller size members represented by pericondensed PAHs, which, in turn, are regarded to be structurally similar to UV/vis - absorbing asphaltene chromophores [45]. Virtually continuous UVVA spectra of graphene are characteristic also to other related carbon-based nanomaterials, including fullerenes, carbon nanotubes, soot etc. [46] Some UVVA properties of graphene family are very close to those observed in crude oils. E.g., published absorbance spectra for concentrated solutions of carbon nanotubes in chloroform [47] may be characterized by values of U3

= 0.37 eV, $E_4/E_6 = 6.5$ and $U_1/U_3 = 1.78$, close to the respective parameters for our concentrated solutions listed in Table 1.

UVVA properties of graphene-type solutions are well-understood [46] and may be described by the so-called “amorphous semiconductor” (AS) model [48], which relates characteristic energies of continuous spectra to common distribution of states in all individual chromophores, irrespective of size or MW distributions of molecular species in solution. Previously, we have exploited a possibility of using the AS model for description of UVVA spectra of crude oils [12]. However, recent publications [49] show that the original AS model can not be directly applied to smaller members of the graphene family (apparently including asphaltenes).

b) Humic matter. Exponentially falling continuous UVVA spectra are well-known characteristic attributes of *humic acids* (HA) and of their mixtures: *chromophoric dissolved organic matter* (CDOM) [21, 22, 50]. One-dimensional parameters of these spectra are fairly close to those characteristic for crude oils (cf. Table 1), e.g. for a “typical” UVVA spectrum of Newport CDOM in Fig. 4 of Ref. 50: $U_3=0.30$ eV, $E_4/E_6=7.4$ and $U_1/U_3=2.2$. This proximity of UVVA features may appear to be due to some fundamental relationship, considering that HA are regarded as important precursors or components of kerogen, bitumen, petroleum, and coal [51]. Moreover, like asphaltenes, HA usually are operationally defined as species soluble in some solvents and insoluble in others. Experimentally, UVVA spectra of humic matter have been more extensively studied than spectra of crude oils. E_4/E_6 ratios were tabulated for a variety of substances and some “apparent” empirical correlations were proposed. E. g., usually it is assumed that lower E_4/E_6 ratios always are indicative of higher contents of high-MW species (or molecular aggregates) in studied substances. Our experimental results in Figure 9 show a decrease of E_4/E_6 in solutions with deaggregated asphaltenes, indicating that the above assumption may not be true. In studies of some size fractionated natural humic substances the larger molecular size fraction also showed an unusual high E_4/E_6 ratio, contrary to the empirical rules [52]. In view of a limited value of empirical models, more sophisticated theoretical treatments of UVVA in humic matter are being developed, taking in account possible molecular aggregation into polymeric or colloidal structures [22, 50, 53].

c) *Melanins*. The nature of continuous UVVA spectra of these biological molecular species has been an enigma for some decades, especially as melanin monomers are fairly small double-ring molecular species (MW~200-300) structurally similar to some subunits of more complex humic acids [54]. Due to their reactive nature, melanin monomers were expected to form extended heteropolymers with high electron mobility, hence for interpretation of melanin continuous UVVA spectra the above described AS model has been widely employed [55]. More recently, a prevailing view became that melanin monomers aggregate into a diverse variety of smaller compact oligomers which, in turn, may form complex nanocolloidal structures [56]. Hence, the latest models developed for melanins (and suggested for humic acids) regard a continuous UVAA spectrum as a specific property of a diverse ensemble of different monomers and oligomers [57], the approach that may appear fruitful for theoretical analysis of UVVA properties of crude oils/asphaltenes. The idea that some “chemical substance” with specific functional properties should be defined by molecular structure principally based upon diversity/disorder may seem controversial. Nonetheless, the notion of a structure based on disorder does not necessarily break with the structure-property-function paradigm of chemistry, though lately this paradigm has been questioned by the numerous experiences [58].

At first glance, the “diversity” UVVA models may resemble earlier interpretations of UV/vis spectra of humic acids [21] and of crude oils and asphaltenes [1], which also considered absorption by a multitude of different chromophores. It should be emphasised, that this resemblance is superficial – in earlier models magnitudes of absorption at smaller/larger wavelengths have been directly related to populations of lower/higher-MW molecules. Moreover, it has been stated that the shape of UVVA spectrum “directly gives the population distribution” [1]. As indicated above, these simplified models are not valid for description of our experimental results (cf. Figure 9). On the other hand, in the emerging “diversity” models a wide population/MW distribution is not necessarily assumed. A wide UVVA spectrum may result from a fairly narrow random distribution of comparatively low-MW molecules, as has been experimentally demonstrated for a complex coal pitch extract [59]. This system, a mixture of about 150 aromatic molecules, had an almost Gaussian MW

distribution, centered at ~240-250 amu (FWHM ~80 amu) and exhibited a virtually continuous UVVA spectrum in the range of 250-500 nm.

Conclusions

On the basis of newly obtained experimental evidence and of re-evaluation of existing databases we conclude that, in spite of large amount of published data, the potential of UVVA spectroscopy for crude oil analysis may be strongly underestimated. In fact, various types of crudes may be UVVA-differentiated even by the simplest “coloration” technique, when an entire UVVA spectrum is characterized by a single numerical parameter. Moreover, multiple absorption peaks may be “extracted” from a general continuous background by processing the measured spectra. One group of peaks may be reliably attributed to vanadyl Etio-porphyrins. Proper attribution of other peaks to individual oil components requires further studies. The main practical problem of UVVA spectroscopy is the opaque nature of crude oils which have to be diluted for analysis. Our experiments data show that at oil concentrations below a certain critical limit (equivalent to 30-40 mg/l net concentration of asphaltenes) crude oil UVVA spectra become appreciably affected by de-aggregation of asphaltenes in solutions. In particular, at high dilutions we observed an increase of absorptivities at larger wavelength. These dilution effects can not be accounted for by existing models of UVVA processes in crude oils and asphaltenes. Hence, further development of UVVA techniques requires better understanding of the nature/composition of asphaltenes. A useful approach may be consideration of “structural diversity” in chemical substances defined by specific functions, as in models being developed for other systems with continuous UVVA spectra, in particular for humic acids and melanins.

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