

Suggested “New Method for Determination of Dispersity in Petroleum Systems” Is Based on Trivial Experimental Artifacts

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A number of recent publications suggest a “new method for petroleum studies” based on circular dichroism (CD) spectra, which presumably feature a “characteristic CD band near 300 nm”. The authors ascribe this band to “resonance absorption of pure asphaltene, measured by a number of authors”. In fact, neither of supporting references deals with optical absorption of asphaltenes. Moreover, our experimental data as well as critical analysis of other publications on optical spectroscopy of asphaltenes show that the mythical “resonance absorption” is merely a solvent-related artifact. We conclude that the discussed “new method” is founded upon the same experimental artifacts and should be disregarded as basically erroneous.

Introduction

Despite decades of extensive research by a variety of experimental techniques, the available information on the properties of high-molecular-weight (MW) crude oil constituents (in particular, of asphaltenes) still remains highly controversial.¹ Hence, some petroleum scientists in their understandable efforts to improve this situation try to suggest “new” methods/techniques for “interrogation” of crude oils. However, frequently, they do not realize that the suggested methods either are not applicable to complex petroleum systems or are based on false information. A characteristic example is a series of recent publications,^{2–5} advertising circular dichroism (CD) spectrometry as “the new method for determination of dispersity in petroleum systems”. The authors should have been warned by the fact that research groups, for years specializing both in petroleum studies and in applications of the CD technique,⁶ never reported any noticeable CD activity in asphaltenes/crude oils. Moreover, as shown below, the major experimental evidence in support of the discussed “new method” most surely

is just an experimental artifact, while “resonance absorption of asphaltenes”, quoted as an underlying mechanism, is nonexistent.

Discussion

1. Some History of the “Resonance Absorption of Asphaltenes”. Over the past few years, a number of publications have reported UV absorption spectra for dilute solutions of crude oils and of petroleum- and coal-derived asphaltenes (all in toluene) with prominent peaks at 288–310 nm (4.3–4.0 eV). As an example, Figure 1 shows representative data (replotted from Figure 1 of ref 7) for solutions of Athabasca C7 asphaltenes with concentrations ranging (bottom to top) from 10 to 200 mg/L. The authors emphasize the presence of a common absorption maximum at 288 nm in most dilute solutions and recommend this wavelength as a standard one for calibration of optical measurements. For further discussion, it is important that they explain the apparent shift of this maximum to larger wavelengths (cf. the top curve in Figure 1) by that “the absorbance level exceeds the output range of the instrument” in more concentrated solutions.

Another example is the study of the Furrial and Hamaca asphaltenes.⁸ The authors present absorption spectra for toluene solutions with concentrations of 50 mg/L, both of which exhibit a maximum of absorbance around 310 nm. On the basis that “the spectral location of the absorption maximum varies considerably and almost continuously for the different crude oils”, they conclude that “the similarity of the absorption spectra of the asphaltenes studied provides evidence that the same type of chromophores is present in these fractions”. Another publication⁹ reports absorption spectra for toluene solutions of asphaltenes with concentrations below 100 ppm, which exhibit a common absorbance maximum at 305 nm. The authors conclude that the value of this wavelength “hints to the possibility of observing two-photon absorption”.

Even more far-reaching conclusions were formulated in a publication on “pattern recognition method” for discriminating

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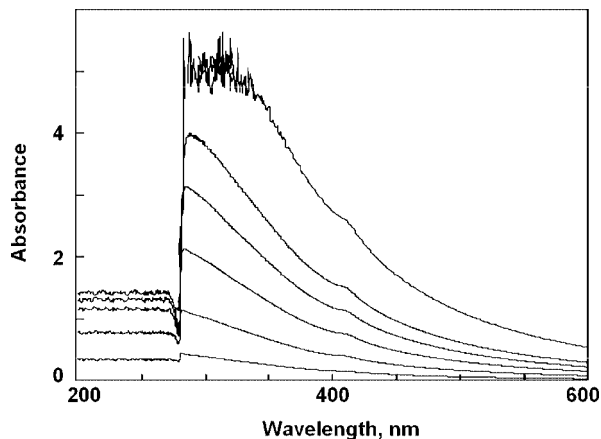


Figure 1. “Prominent resonance peak” in dilute toluene solutions of asphaltenes (after ref 7).

between crude oils belonging to different geographic origins.¹⁰ Each oil is represented by a circular profile (“fingerprint”) that consists of parameter axes that radiate from the center like spokes on a wheel. Two of the nine of these “individual” and “most representative” parameters are the intensity and the wavelength position of the discussed “characteristic absorbance maximum”.

Finally, a prominent absorbance maximum close to 300 nm has been reported for ppm (mg/L) solutions not only of crude oil asphaltenes but also of asphaltenes derived from coal.¹¹

In our first publication of preliminary data on crude oil absorbance below 315 nm, we also reported “a strong resonance band, peaked at ~ 285 nm” and even attempted to ascribe this feature to specific “ $\pi-\pi^*$ transitions in the conjugated aromatic chromophores of asphaltenes”.¹²

However, intercomparison of “resonance UV peaks” revealed a striking and a highly suspect coincidence of experimental data reported by different research groups for asphaltenes/crude oils of diverse origin.¹³ To emphasize coincidence, in Figure 2, the data from original publications are renormalized to equal absorbances at 350 nm. The numbers denote optical absorbance spectra for the following toluene solutions: (1) of a Tatarstan crude with 26 mg/L asphaltenes;¹³ (2) of coal asphaltenes, 34.8 mg/L;¹¹ (3) of asphaltenes from Athabasca bitumens, 100 mg/L;⁷ (4) of asphaltenes from a Hamaca crude, 50 mg/L.⁸ The thicker line represents the behavior of the “circular dichroism signal” for an oil solution with 11.2 mg/L asphaltenes,²⁻⁴ discussed below (cf. Figure 5).

Further investigation of the data like those in Figure 2 definitely revealed that “near 300 nm resonance absorption” not only can not be regarded as a “fingerprint attribute” of crude oils/asphaltenes but is nonexistent, being merely a trivial experimental artifact near the absorption edge of the solvent (toluene).^{13,14}

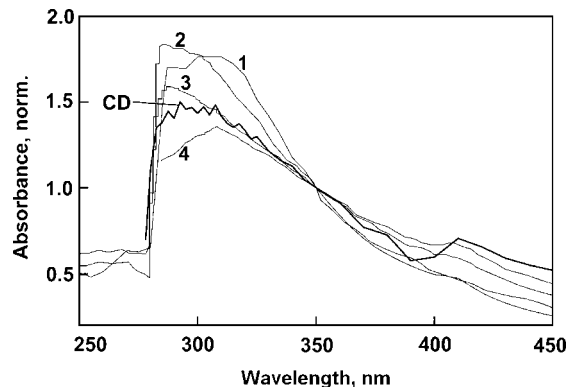


Figure 2. “Highly suspect coincidence” of absorbance spectra for crude oils and asphaltenes of diverse origin from various publications (lines 1–4). The thicker line “CD” shows replotted CD data from refs 2–4.

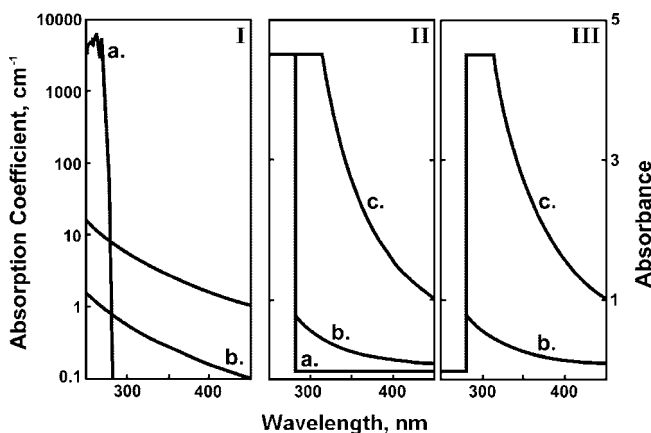


Figure 3. (I) Absorption coefficients for (a) 1 M toluene and (b and c) 1 and 10 ppm of asphaltenes, respectively. (II) Noncorrected absorbances for centimeter length cuvettes with (a) pure solvent (toluene) and (b and c) 1 and 10 ppm solutions of asphaltenes in toluene. Note the instrumental cutoff at high absorbances. (III) “Resonance absorption peak of asphaltenes”, an artifact of the solvent subtraction procedure.

2. Apparent Origin of “Resonance Absorption” Artifacts.

The spectroscopy specialists may regard the following arguments as being obvious; however, frequently, we found it difficult to convey to petroleum scientists and practitioners the nature of the discussed solvent-related artifacts. A common reaction is “can not be any solvent effects; these are accounted for in modern spectrometers”. A slightly more sophisticated response is “in spectrometers, the solvent absorption is properly subtracted from the sample’s signal”. In our recent book,¹⁴ we classified such attitude as a “syndrome of expensive equipment” when one finds it difficult to believe that the newly acquired expensive, modern, sophisticated, multifunctional, sensitive, automated, etc. spectrometer can provide questionable output. In fact, it can, mainly for the reasons that nowadays the details of signal processing and solvent subtraction are buried somewhere deep in the circuits of electronic blocs. Artifacts because of subtraction rarely appear in conventional fairly concentrated solutions with comparable solvent and solute absorption coefficients. However, studies of crude oil or asphaltene solutions present a special case. Because of extremely high UV–vis absorptivity of asphaltenes, acceptable absorbances ($A < 2-3$) in conventional (centimeter length) cuvettes may be achieved only in highly diluted ppm (mg/L) solutions. In this case, as illustrated in I of Figure 3, the ratio of solvent/solute absorption coefficients increases catastrophically in the immediate vicinity of the absorption edge of the solvent. For toluene (curve a), nonzero

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(14) Evdokimov, I. N.; Losev, A. P. *Potential of Optical Research Methods for Monitoring Oil Field Development*; Neft I Gas Publisher: Moscow, Russia, 2007 (in Russian).

absorption appears at wavelengths below 282 nm and 1 M absorption coefficient sharply rises to 6596 cm^{-1} at 261.75 nm.^{15,16} Precise quantitative evaluation of molecular/molar absorptivities of asphaltenes is impossible, owing to controversies regarding their molecular weights.¹ Hence, curves b and c in I of Figure 3 show order-of-magnitude (but sufficient for further discussion) estimates for 1 and 10 ppm concentrations in 1 M toluene. In these estimates, we employed experimental data for 315–750 nm asphaltene absorptivities¹⁷ and extrapolated these to shorter wavelengths via a frequently assumed exponential dependence of absorptivity on inverse wavelength.^{13,14}

II of Figure 3 shows estimated absorbances in centimeter length cuvettes filled with pure toluene (curve a) and 1 ppm (curve b) and 10 ppm (curve c) asphaltene solutions in toluene. Of crucial significance is that calculations predict absorbance values rising above 10^3 , while any real spectrometer possesses certain threshold sensitivity to low relative intensities of the light, transmitted by a cuvette I_T/I_0 (where I_0 is incident intensity) and, hence, threshold sensitivity to high absorbances $A = -\log(I_T/I_0)$. For many commercial spectrometers, I_T/I_0 thresholds are typically 10^{-4} – 10^{-6} ($A_{\text{max}} \approx 4$ – 6). Any transmitted intensity below the threshold is fed into the processing electronic block as a common “noise” signal, and consequently, the respective processed absorbances are regarded as being “saturated” at a common maximum level. In II of Figure 3, this “saturation” level corresponds to $A = 4.5$.

In the final “solvent subtraction” operation in an electronic block of a spectrometer, processed absorbances of the solvent (curve a in II of Figure 3) are numerically subtracted from absorbances of solutions (curves b and c in II of Figure 2). The result is provided as an output signal of a spectrometer, which in most situations, represents true absorption spectrum of the studied solute. However, in the vicinity of the absorption edge of the solvent, because of subtraction of equal (“saturated”) solution and solvent absorbances, the output signal sharply drops to (and remains at) close-to-zero level, an artifact absent in the properly measured absorption spectra. As illustrated in II of Figure 3, visually this artifact for toluene solutions may be classified as a sharp absorption maximum close to 300 nm and, evidently, is the persistent “resonance absorption peak of asphaltenes”, illustrated in Figures 1 and 2.

The direct experimental verification of the above conclusions was performed by studying absorption spectra of crude oil solutions in solvents with different absorption edges.^{13,14} As shown in Figure 4 (spectra 1 and 2), the “UV artifact” does follow the changes in an absorption edge of a solvent, ~ 282 – 285 nm for toluene and ~ 265 nm for carbon tetrachloride. The solvent-free absorbance spectrum of a neat crude oil (curve 3 in Figure 4) was obtained by a thin film technique.^{13,14} This spectrum practically coincides with reliable parts of the spectra of the solution and does not exhibit any “resonance absorption”.

Summarizing, we conclude that many of previously reported UV–vis absorption properties of asphaltenes/crude oils may have been noticeably distorted by experimental artifacts. The most notorious artifact is “resonance absorption close to 300 nm”.

3. Relevance of Absorption Artifacts to the Suggested “New Method for Determination of Dispersity in Petroleum

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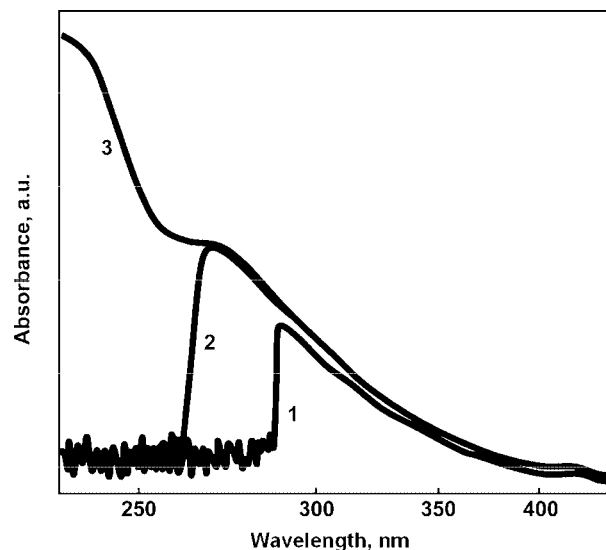


Figure 4. UV–vis absorption spectra of crude oil solutions (1) in toluene, (2) in CCl_4 , and (3) of a neat crude oil.

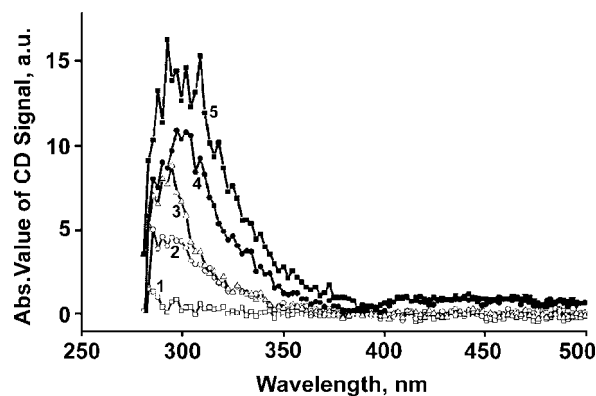


Figure 5. Absolute value of the “circular dichroism signal” in toluene solutions of a crude oil (1 cm cuvette) with asphaltene concentrations of 1–0.3, 2–0.6, 3–3.7, 4–5.6, and 5–11.2 mg/L (after refs 2–4).

Systems”. The authors of the discussed “new method” (cf. Introduction) in all publications^{2–4} present experimental CD spectra that exhibit “the short-wave band with a maximum near 300 nm”. Because their “CD signal” is negative, for ease of comparison with the above results, in Figure 5, we show the discussed spectra in terms of respective absolute values.

Immediately evident is close resemblance of CD data in Figure 5 to absorption data of Figures 1–4. Moreover, in the Discussion of their “300 nm CD maximum”, the authors directly state that² “there is a correlation between the CD band position of crude oil toluene solutions and resonance absorption of pure asphaltene toluene solutions measured by a number of authors^{10,14,15”}. Characteristically nonexistent “resonance absorption” they try to support by nonexistent references. The first one is a publication on “the critical micelle concentration of asphaltenes as measured by calorimetry”,¹⁸ while the second one is our paper on “excess density in oilfield water—crude oil dispersions”.¹⁹ Neither of publications provides any information on optical properties of asphaltenes/crude oils. The third publication is quoted as being in 2007 “in press”,²⁰ but it does not appear in either the 2007 or 2008 issues of the respective journal. Moreover, in an answer to our recent enquiry, an editor

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of this journal replied that “we do not have a paper from this author in press, neither do we have a submission from him under consideration”.

It so happens, however, that disregarding wrong referencing, the coincidence with absorption artifacts is indeed strong enough to conclude that the “300 nm CD maximum” is an artifact of the same nature. To illustrate this coincidence, in Figure 2, we compare CD spectrum 5 from Figure 5 with the above-discussed artifact “absorption peaks”. Furthermore, the obvious origin of CD artifacts is in instrumental “saturation” of processed absorbances, as discussed with respect to Figure 3. The only (nonprincipal) difference in CD measurements is that the output of a spectrometer is a difference of “saturation”-distorted signals not from nonpolarized light passing through a solvent and a solution but from left- and right-circularly polarized (CPL and CPR) light passing through the same solution. The inevitable result of measurements in the vicinity of the solvent (toluene) absorption edge is an artifact “maximum” of the type illustrated in III of Figure 3.

Suggestion of the discussed “new method” based on artifacts can not be excused by a certain lack of previous information inherent to novel techniques. Strong solvent interference in CD measurements is well-known and has been discussed in multiple publications.^{21–23} Moreover, in manuals for CD spectrometers,

(21) Snyder, P. A.; Vipond, P. M., Jr. *Biopolymers* **1973**, *12*, 975–992.

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it is emphasized²³ “that whilst CD is a measure of the absorbance difference for CPL and CPR, the conventional absorbance of the sample must also be considered as it can severely impair the transmission of the probe beam, particularly in the far UV, to the point where no meaningful measurement can be made. This not only applies to the sample, but to the solvent as well, and oversights in this regard probably account for many unsuccessful or erroneous CD measurements”. In the same manual, it is specifically stated that for successful applications of the CD technique “an understanding of the limitations caused by sample and solvent absorption and some knowledge of the theory of CD measurement is unavoidable”. The above-discussed artifacts in the suggested “new method” clearly reveal the lack of expected understanding and knowledge.

Conclusions

Following the style of a recent critique of other methods for “optical interrogation” of petroleum,¹ we may conclude that frequent publications of such artifact as “resonance absorption band of asphaltenes” has caused a measure of confusion that hopefully now has been resolved and this episode in asphaltene studies has been closed for good.

Accordingly, we conclude that the suggested “new method for determination of dispersity in petroleum systems”^{2–5} is also founded upon the same trivial experimental artifacts and should be disregarded as basically erroneous.

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