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Effects of molecular de-aggregation on refractive indices of petroleum-based fluids

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Abstract

It is conventionally assumed that refractive index (RI) for a crude oil, a processed fuel or any petroleum-based solution may be evaluated in an assumption of an ideal binary mixture of non-precipitating components. However, new experimental data reveal strong non-ideality of RI in dilute oil solutions, which we attribute to de-aggregation of asphaltenes.

Keywords: Refractive index; Crude oil; Asphaltenes; Aggregation;

1. Introduction

Refractive index (RI) has been shown to represent various important properties of multicomponent native petroleum, processed fuels, as well of the respective components. Values of RI can be measured very accurately and are used to correlate density, parachor, and other properties of hydrocarbons with high reliability [1]. Information obtained from RI measurements can be applied for various reservoir engineering calculations. The examples are PVT behavior and surface tension of reservoir fluids [1], wetting alterations in reservoirs [2,3], asphaltene precipitation [4-6]. The refractive index of light crude oils can be directly measured using conventional refractometers [2,3,5]. However, direct measurements of the refractive index of many crudes, natural bitumen and heavy fuels are unattainable since these liquids are too opaque. In these cases RI is determined for a series of oil/solvent mixtures and the results are extrapolated (in an assumption of a certain mixing rule) to determine the value for the crude oil [2,4,7]. It is usually assumed that a solution of a crude oil (bitumen) behaves as an ideal binary mixture of the components [4-6].

It should be noted that there are no universally accepted mixing rules for interpreting the refractive indices of such presumably ideal mixtures. In some studies of crude oil solutions [8] refractive index of a mixture was regarded as a linear combination of the *constant* refractive indices n of the individual components:

$$n_{mixture} = n_{oil}\phi_{oil} + n_{solvent}(1-\phi_{oil}) \quad (1)$$

where ϕ_{oil} is a volume fraction of a crude oil.

More frequent are mixing rules based on the Lorentz-Lorenz additivity rule for *constant* specific polarizabilities/refractions of the components [9]. In notations of Refs. 3,6,10 :

$$F(RI)_{mixture} = F(RI)_{oil}\phi_{oil} + F(RI)_{solvent}(1-\phi_{oil}) \quad (2)$$

where

$$F(RI) = (n^2 - 1) / (n^2 + 2) \quad (3)$$

Obviously, the assumption of “an ideal mixture” is valid only provided there are no appreciable compositional changes in the complex petroleum subsystem of a solution. Indeed, noticeable negative deviations from simple mixing rules have been observed in cases when asphaltenes flocculate and commence to precipitate out of a crude oil solution [4-6]. However, presently there is no experimental evidence whether the refractive index measurements may be sensitive to specific aggregation phenomena of asphaltenes which remain suspended in solution. Conventionally, “critical micellization concentrations” (“CMCs”) of asphaltenes in solutions were revealed by various experimental techniques, e.g. calorimetry [11,12], measurements of surface tension [13,14], small-angle neutron scattering [15], photothermal displacement spectroscopy [16], etc. The “CMC” values for asphaltenes in toluene typically range from ≈ 2 g/l [16] to ≈ 5 g/l [12]. Over the past several years it became clear that conventional “CMCs” are not signatures of primary monomer-micelle transformations, but evidently reflect some secondary processes of aggregation into complex colloid structures. Indeed, it has been experimentally proven that distinct aggregation stages of asphaltenes are observed at concentrations well below the conventionally reported “CMCs”. E.g., in our previous publications [17-19] we have presented experimental data on optical absorptivity, viscosity and NMR relaxation, which indicate that aggregation of asphaltene monomers may commence at concentrations as low as 2-5 mg/l, while massive formation of tightly bound asphaltene “molecular nanoclusters” is observed at concentrations ≈ 90 -150 mg/l. Aggregation processes were no longer detected at higher asphaltene concentrations (above ~ 500 mg/l), indicative of some “steady” state of asphaltene aggregates in more concentrated solutions, up to 1.6 g/l.

In this paper, we report refractive index measurements in toluene solutions of a Tatarstan crude oil. Results for concentrated solutions (with asphaltenes in a “steady” aggregated state) are in agreement with conventionally observed ideal mixing rules. An “anomalous” behavior of refractive index in dilute solutions is attributed to de-aggregation of asphaltenes. The RI data are supplemented by some new results on optical absorptivity in dilute crude oil solutions.

2. Experimental

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

The RI measurements were performed in an Abbe-type refractometer IRF-454-B2M (KOMZ, Kazan, Russia). For toluene at 20°C the measured RI was 1.4967, close to the value of 1.4969 quoted by the producer. The effects of crude oil concentration in toluene solutions on optical absorption at 670 nm have been studied in a spectrometer, equipped with a set of narrow-band light filters (KFK-2 Photocolorimeter [17,18]). The UV/Vis absorption spectra have been measured in a Shimadzu UV-2201 UV/VIS double-beam spectrophotometer. All measurements were performed at 20°C and at ambient pressure.

3. Results and discussion

3.1. “Conventional” behavior of RI in concentrated solutions, RI of the crude oil

Figure 1 shows the results of refractive index measurements in concentrated oil-toluene solutions (≥ 1 vol. % oil). $F(RI)$ is the function defined by Eq. 1. Each data point was obtained with a new sample, prepared by mixing the required volume of the crude oil with ≈ 10 ml of toluene. No significant effect of the manner of mixing (e.g., introducing oil into toluene or vice versa) was observed for concentrated solutions. Owing to the dark and opaque nature of our unprocessed crude oil, it was not possible to measure the RI of solutions with oil volume fractions in excess of about 50%. In studies of such opaque crudes (or bitumen) there is a well-established “conventional” technique for estimation of the refractive index of a “pure crude oil” RI_{oil} [4-7]. Namely, the value of RI_{oil} is found by a linear extrapolation of the experimental data to a volume fraction of 100 %, the procedure apparently justified by commonly employed mixing rules (cf. Eqs. 1,2). A best linear fit to our data points (coefficient of determination $r^2 = 0.995$), shown by a solid line in Fig. 1, gives a value of $RI_{oil} = 1.4785$ for the studied crude.

In a number of publications it has been stated that RI apparently correlates with density (API gravity) and with an asphaltene content of a crude oil. In Figures 2,3 we compare the RI of our oil (open symbols, indicated by arrows) with RIs for 45 crudes of various origin from Refs. 2,3,6,7 (filled symbols). It can be seen that our results are in a reasonable agreement with previously published data. Fig.2 shows a good overall correlation of RI with oil's density ($r^2 = 0.76$). Fig. 3 demonstrates that a correlation of RI with asphaltene content in crude oils is much worse ($r^2 = 0.29$).

3.2. Reproducibility of concentration dependencies in dilute solutions

Studies of solutions with oil content below ≈ 1 vol.% revealed strong effects of the “history of oil dissolution in toluene”. When the above technique of sample preparation was employed, the results have shown poorly controlled (virtually random) dependencies on such

factors as the manner of introducing one component into the other (e.g. from a vial or from a pipette), the manner of stirring the mixture (by hand, in a mechanical stirrer), 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 oil contents of ≈ 0.2 - 0.5 vol.%. The respective asphaltene concentrations of about 60-150 mg/l correspond to conditions of the expected phenomena of de-aggregation of asphaltenes (cf. Introduction). Hence, the observed “history effects” may be attributed to the complex kinetics of asphaltene dissolution which is known to vary significantly depending on the physical state of the system [20,21]. We agree with the authors of Ref. 21 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. In most of the experimental procedures, 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 RI and to reduce the scatter of results, we have employed a standard procedure of sample preparation used in our previous studies [17-19]. 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 (0.5 – 10 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. At the beginning of each time interval a solution was gently stirred with a glass rod, at the end – RI measurements were performed. The results revealed consistent time dependence for the rates of concentration increase above ≈ 0.2 vol.% of oil per hour, and practically no time effects for

slower rates. In Fig. 4 open and filled circles denote data sets with two rates of concentration increase, respectively 0.71 and 0.14 vol. % of oil per hour. The latter data set was considered to be representative of the “equilibrium” states of solutions and was employed for further analysis. For comparison, an open square in Fig. 4 shows RI for a solution in which the respective concentration was achieved by one-step addition of oil to toluene (i.e. for a very high rate of concentration increase).

3.3. Break-up of ideal mixing rules in dilute oil solutions

It is clear that irrespective of different individual “histories” of the samples, all data show “anomalous” deviations of RI from the simple linear dependence on the oil content in concentrated solutions (solid line in Fig. 4). Two most obvious “anomalies” are: 1) the “concentrated” approximation does not terminate at $F(RI)$ for pure solvent; 2) the measured concentration dependencies are non-monotonic, with an extremum at oil content of about 0.13-0.15 vol.% and a sharp drop of RI at lower contents.

Taking into account earlier evidence of peculiar behavior of other physico-chemical properties in dilute oil solutions (cf. Introduction), we may ascribe the observed “anomalies” of RI to phenomena of de-aggregation of oil asphaltenes. Hence, in an additional axis at the top of Fig. 4 we indicate the respective asphaltene concentrations (units of mg/l) in oil-toluene solutions.

Dashed line in Fig. 4 shows the RI behavior predicted by the Lorentz-Lorenz ideal mixing rule (Eq. 2) for an ideal binary mixture of toluene ($RI=1.4969$) with the “steady state” crude characterized by a constant $RI_{oil} = 1.4785$, the value estimated in concentrated solutions (with asphaltenes presumably remaining in an aggregated state). At sufficiently high oil/asphaltene concentrations, this “ideal” linear behavior is practically indistinguishable from “the best linear fit” of Fig. 1. It should be noted that recent experiments with oil solutions [22]

have shown that linear Lorentz-Lorenz correlations are perfectly applicable at asphaltene concentrations above some hundreds mg/L.

Deviations of our experimental data from “ideal” values (presumably due to a change of the crude’s properties caused by de-aggregation of asphaltenes) became detectable at oil contents below ca. 1.6 vol.% . The respective asphaltene concentrations of ~ 510 mg/l are close to those observed in our previous studies [17-19] (cf. Introduction). “Non-ideality” of experimental results gradually increased with dilution and was the highest at ~ 0.13 vol.% of oil (asphaltene concentrations ~ 40 mg/l).

The observed “anomalous” behavior of RI may seem highly unusual. However, a literature survey reveals a number of publications, containing experimental results which, subjected to a proper analysis, show specific features which may be attributed to the above mentioned “anomalies”. Apparently these features have not been noticed by the authors. E.g., the authors of Ref. 7 have measured RI vs. wt.% in toluene of a Hamaca heavy crude and of its separated resins and asphaltenes. By fitting straight lines to the respective graphs, they found extrapolated RIs of pure solutes (e.g. 1.527 for the crude). However, in the graphs they never plot data points for pure toluene. Close inspection of their data shows that extrapolations to zero concentrations result in inconsistency of extrapolated RIs of toluene (1.4987, 1.4957 and 1.4973 in data sets for crude oil, resins and asphaltenes, respectively). The discrepancies are notably higher than the scatter of their data points (cf. Fig.5) and than the accuracy of their RI measurements (± 0.0003). In Fig. 5 we reproduce the respective data for solution of a Hamaca crude with an addition of the reference value of RI for toluene (1.4969). Solid line is a linear approximation employed in Ref. 7 to estimate a RI of the crude. Dashed line is drawn to emphasize an obvious “anomalous” drop of RI at oil concentrations below 1 wt. %. Note that application of the ideal mixing rule from Ref. 7 (Eq. 1) to this apparent behavior of RI in dilute oil solutions results in an extremely high value of $RI_{oil} > 1.8$.

3.4. Possible mechanisms of aggregation effects on RI

Literature analysis shows that, previously, aggregation effects on RI of non-precipitating petroleum fluids have never been registered experimentally, and even the possibility of such effects has never been discussed. Hence, a nature of the observed RI anomalies requires an explanation.

Studies of simple binary mixtures have shown that RI may be affected by changes in intermolecular interactions through variations of molar volumes/densities of a solution and of respective components. Firstly, it has been repeatedly demonstrated that linear relationships may be fitted to experimental correlations of refractive indices with fluids' densities [22,23]. Hence, RI measurements are used to monitor phase densities of hydrocarbon mixtures at high pressures [24], density anomalies in the vicinity of critical points and phase transitions [25]. If asphaltene de-aggregation is regarded as a solid-liquid transition, one may expect a smaller density of a crude with de-aggregated asphaltenes and a decrease of RI in dilute solutions, i.e. the effect qualitatively opposite to that observed in our experiments. Secondly, some non-ideal solutions/mixtures exhibit a negative excess volume of mixing, which may be expected to be related to a positive excess RI. Indeed, in our experiments, relative deviations of the mixture's RI from ideal mixing rules are up to 0.1%, typical for excess RI observed in binary hydrocarbon mixtures with excess volumes [26,27]. However, a causative relationship between an excess volume and an excess RI never has been proven experimentally. Moreover, contrary to our experiments, maximum excess deviations in binary mixtures are always observed at volume fractions close to 0.5, not at strong dilutions.

Another effect may be alteration of polarizability, induced by molecular aggregation [7]. However, aggregation mainly alters an orientational molecular polarizability (hence, a

static dielectric constant), while an electronic molecular polarizability (which determines a magnitude of RI for visible light wavelengths) is known to remain virtually unchanged [28].

We suggest that a probable explanation of experimentally observed aggregation effects follows from the well-known Kramers-Krönig relations [29], which show an interdependence of real and imaginary parts of a complex refractive index $n_c = n + i\varepsilon$, where n is a (real) RI obtained by refractometer measurements and ε is an absorption coefficient (absorptivity).

3.5. Apparent correlation of RI and absorptivity in crude oil solutions

Open symbols in Figure 6 show a dependence of absorptivity ε at 670 nm on oil/asphaltene content in toluene solutions, prepared by a “titration” technique described in section 3.2. As the solvent (toluene) does not absorb at these wavelengths, the observed variations of ε are determined solely by the solute (crude oil) molecules. Hence, for a “Kramers-Krönig” comparison one requires a concentration dependence of a refractive index of “the crude oil component”. The latter parameter can not be measured directly, although under certain assumptions it may be evaluated from experimental $F(RI)$ of solutions. Namely, we assumed that Eqs. (2) and (3) are fulfilled not only for a *constant*, but also for a *variable* refractive index of a solute. Accordingly, from experimental $F(RI)_{mixture}$ (filled symbols in Figure 4) we evaluated a concentration–dependent “effective RI of oil”, as shown by filled symbols in Figure 6. As can be seen, there is a strong qualitative coincidence between the dependencies of refractive index and absorptivity on oil/asphaltene concentration. In particular, both parameters are fairly constant (slowly varying) above ~0.13 vol. % of oil (~40 mg/l asphaltenes). In dilute solutions, both refractive index and absorptivity exhibit a sharp increase at 0.04-0.05 vol. % of oil (~12-15 mg/l asphaltenes) which may be attributed to an appearance of asphaltene monomers (cf. Introduction). Hence, the data of provide a

qualitative argument in favor of suggested absorptivity-governed effects on RI. Very high absolute values of the “effective RI” in dilute solutions with de-aggregated (monomeric) asphaltenes indicate that for quantitative evaluation, a linear Eq. (2) should be modified by inclusion of some non-linear terms to account for apparent solute-solvent interactions. Presently there is virtually no experimental data on interaction properties of asphaltene monomers, hence any suggestions of non-linear terms would be merely speculative.

An expected argument may have been that interdependence of RI and absorptivity reveals merely a *mechanism* of the experimentally observed effects, while the question about the *nature* of strong absorptivity variations remains unanswered. Some required information has been obtained by studying UV/vis absorption spectra in highly diluted oil solutions. In the following section we present some of the relevant results, the details of these experiments will be reported elsewhere.

3.6. Specific electronic absorption of de-aggregated asphaltenes

Figure 7 shows absorptivity spectra for toluene solutions with asphaltene contents of 2.2 mg/l (higher curve) and 40.7 mg/l (lower curve). In accordance with the current practice [30], absorptivity is plotted on a logarithm scale against photon energy. The spectra are virtually featureless, apart from a maximum ~ 3.02 eV (410 nm), characteristic of vanadyl petroporphyrins [31]. On both sides of this maximum the spectra exhibit exponential dependencies of absorptivity ε 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 linear slope in Fig. 7). Literature analysis of electronic absorption mechanisms in disordered systems [32,33] shows that the shorter wavelength exponent may be attributed to electron transitions involving energy band tails, related to intrinsic (frozen-in) disorder in chromophores. The corresponding “Urbach energy” E_U indicates the width of the band tails of localized states and is virtually independent

on asphaltene concentration, as shown by open symbols in Figure 8. The longer wavelengths range with the corresponding characteristic energy E_1 may be interpreted as the “low absorption region” of disordered systems [32,33], with additional transitions arising from defect states within the optical band gap. Filled symbols in Figure 8 show that the width of additional states E_1 - E_U sharply increases at asphaltene concentrations below ca. 10-12 mg/l (i.e. with transition to non-aggregated asphaltenes – cf. Introduction). As suggested in our recent publication [34], the additional defect states at high dilutions may be attributed to an appearance of some dangling bonds in asphaltene monomers, which, in turn, may be responsible for their high propensity to aggregation.

4. Conclusions

Knowledge of RI is important for various engineering applications in fossil fuel industry. Direct measurements of RI for many native crudes, natural bitumen and heavy fuels are unattainable since these liquids are too opaque. Hence, RI is determined for a series of oil/solvent mixtures and the results are extrapolated to crude oil RI in an assumption of an ideal binary mixture of the components. However, new experimental data show that this assumption is valid only at sufficiently high oil concentrations. In dilute oil solutions, a strong non-ideality of RI is observed, presumably due to de-aggregation of asphaltenes. An onset of non-ideal features of RI correlates with a step-wise increase of optical absorptivity, earlier ascribed to an appearance of non-associated asphaltene monomers in solutions.

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Figures

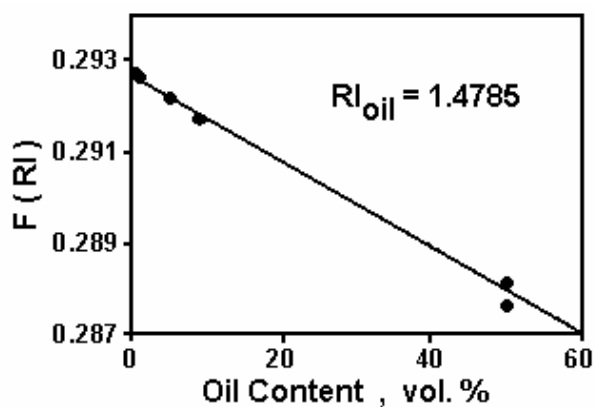


Fig. 1. Refractive index in concentrated oil/toluene solutions. Solid line is the best linear fit to experimental data points, providing a refractive index RI_{oil} of the neat crude.

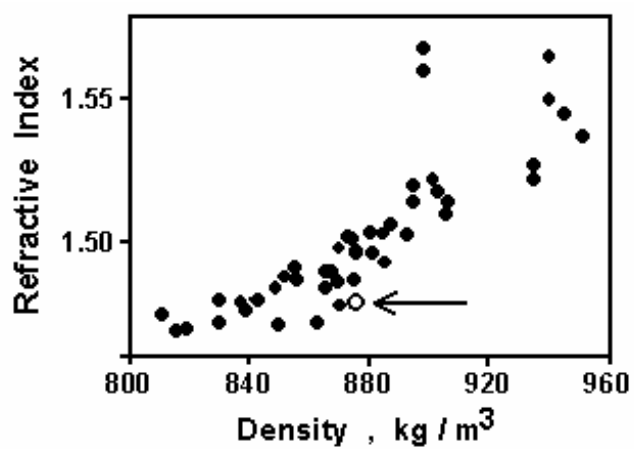


Fig. 2. Refractive index vs. density for 45 crude oils of various origin [2,3,6,7] (filled symbols). The open symbol – extrapolated RI_{oil} of our crude.

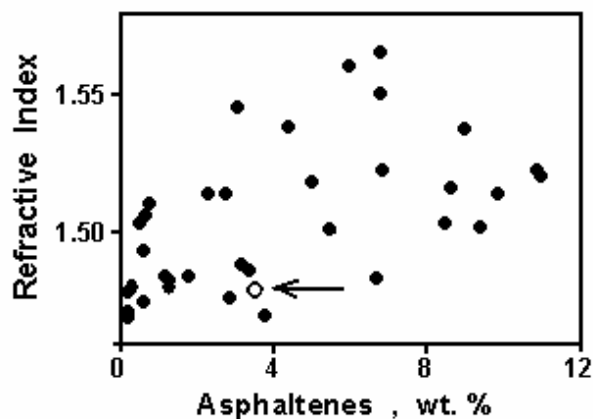


Fig. 3. Refractive index vs. asphaltene content for 45 crude oils of various origin [2,3,6,7] (filled symbols). The open symbol – extrapolated RI_{oil} of our crude.

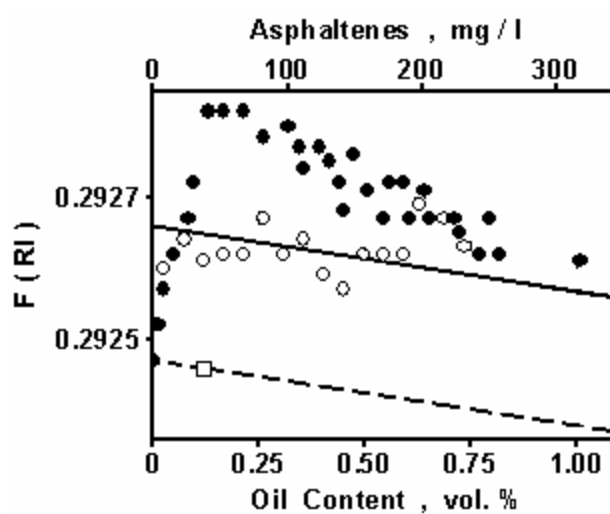


Fig. 4. Refractive index in dilute oil/toluene solutions. Filled and open symbols denote, respectively, data for “equilibrated” samples and for samples with strong “history effects” (cf. text). Solid line is “the best linear fit” from Figure 1, dashed line – an ideal binary mixing rule.

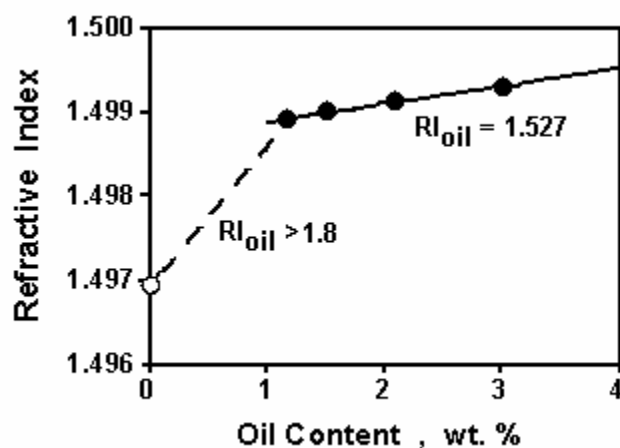


Fig. 5. Filled symbols - refractive indices for toluene solutions of a Hamaca heavy crude oil (from Ref. 7). Open symbol – a reference RI of toluene. Solid line – a linear fit employed in Ref. 7 to evaluate RI of the neat crude. Dashed line is drawn to indicate an apparent anomalous behavior of RI at high dilutions.

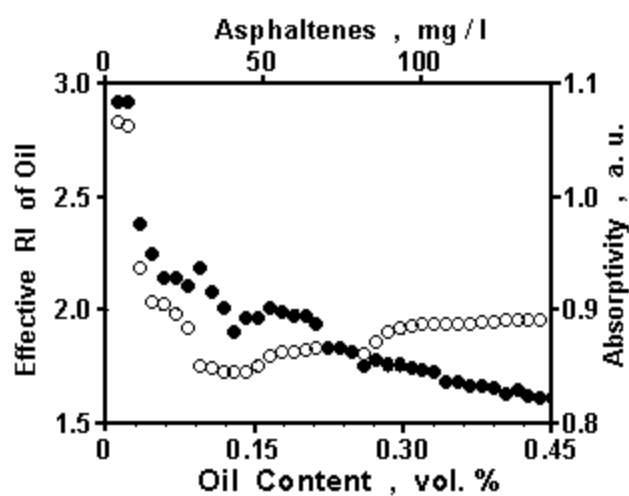


Fig. 6. Correlation of RI (filled symbols) and absorptivity at 670 nm (open symbols) of the “crude oil component” in toluene solutions.

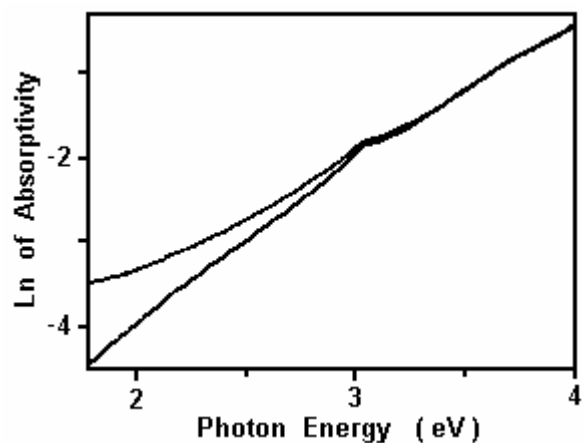


Fig. 7. Electronic absorption spectra for oil/toluene solutions with asphaltene contents of 2.2 mg/l (above) and 40.7 mg/l (below).

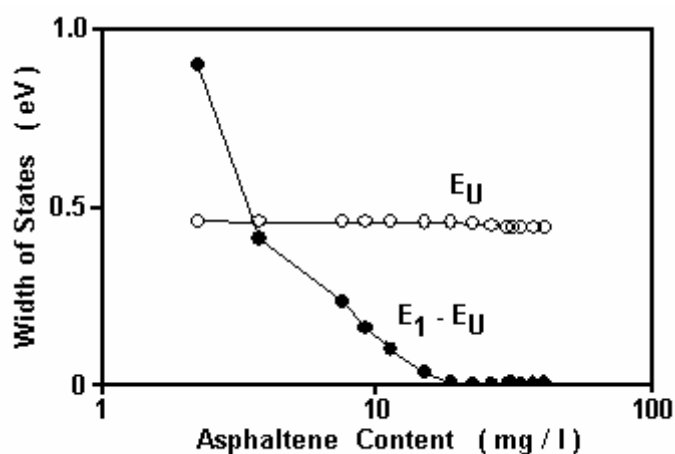


Fig. 8. Widths of electronic states in asphaltene chromophores arising from intrinsic static defects (open symbols) and from dangling bond defects in de-aggregated asphaltenes (filled symbols).