

## A TRANSITION FROM MONOMERIC TO ASSOCIATED ASPHALTENES IN CRUDE OIL SOLUTIONS

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**Abstract.** It is widely recognized that physicochemical properties of crude oil asphaltenes in processes of refining and processing (i.e. transfer rates in catalyst's porous networks) depend on their association state in a hydrocarbonated environment. For various industrial applications it is necessary to have a detailed knowledge of physico-chemical and structural properties of complex asphaltene colloids, in order to be able to master their behavior. We have studied optical and dielectric properties (molar absorptivity, refractive index, dielectric constant, dielectric loss) in dilute toluene solutions of Russian crude oils and of solid asphaltenes. Sharp inflections in measured concentration dependencies are indicative of changes in association states of asphaltenes. Apparently, asphaltenes may exist in a monomeric state only at concentrations below 1-2 mg/l, while at 60-90 mg/l there is a demixing transition to a colloidal system of asphaltene aggregates. By analysis of correlations between measured properties we expect to obtain quantitative information on dipole moments of asphaltene monomers.

**Keywords:** Crude Oil, Asphaltenes, Associated State.

### 1. Introduction

Properties of crude oil asphaltenes in refining and processing depend on their association state in a hydrocarbon environment. Increased association may result in lower transfer rates in catalyst's porous networks, in higher levels of entrapment of light fractions within asphaltene aggregates. For various industrial applications it is necessary to have a detailed knowledge of complex asphaltene colloids in order to be able to master their behavior. Refractive index (RI) represents various important properties of multicomponent crude oils 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) (Touba et al., 1997). Information obtained from RI measurements can be applied for various reservoir engineering calculations.

The RI of light crude oils is directly measured in conventional refractometers (Yang et al., 2002; Buckley and Wang, 2002; Buckley, 1999). However, direct measurements of the RI of heavy crudes are unattainable since these liquids are too opaque. In these cases RI is determined for a series of oil/solvent mixtures and the data are extrapolated (in an assumption of a certain mixing rule) to determine the RI of the crude oil (Yang et al., 2002; Goual and Firoozabadi, 2002; Taylor et al., 2001). It is usually assumed that a solution of a crude oil behaves as an ideal binary mixture of the components (Taylor et al., 2001; Buckley, 1999; Buckley et al., 1998).

It should be noted that there are no universally accepted mixing rules for interpreting the refractive indices of such presumably ideal mixtures. Most frequent are mixing rules based on the Lorentz-Lorenz additivity rule for specific polarizabilities/refractions of the components (Shoemaker et al., 1996). In notations of Buckley and Wang, 2002; Buckley et al., 1998 and Wattana et al., 2005 :

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

where  $\phi_{oil}$  is a volume fraction of a crude oil and  $F(RI) = (n^2 - 1) / (n^2 + 2)$ .

Obviously, the assumption of “an ideal mixture” is valid only provided there are no compositional changes in the complex petroleum “component”. Indeed, noticeable deviations from simple mixing rules have been observed when asphaltenes flocculate and commence to precipitate out of a crude oil solution (Taylor et al., 2001; Buckley, 1999; Buckley et al., 1998). However, presently there is no experimental evidence whether the RI may be sensitive to specific aggregation phenomena of asphaltenes which remain suspended in solution.

Conventionally, “critical micellisation concentrations” (“CMCs”) of asphaltenes in solutions were revealed by various experimental techniques (Sheu, 1996). The “CMC” values for asphaltenes in toluene range from  $\approx 2$  g/l (Castillo et al., 1998) to  $\approx 5$  g/l (Andersen and Christensen, 2000). Over the past years it became clear that conventional “CMCs” are not signatures of primary monomer-micelle transformations, but 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 (Evdokimov et al., 2003a,b,c) we have presented experimental data which indicate that aggregation of asphaltene monomers commences at concentrations as low as 2-5 mg/l, while massive formation of asphaltene “molecular nanoclusters” is observed at concentrations  $\approx 90$ -150 mg/l. Aggregation processes were no longer detected at asphaltene concentrations above 500-700 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 RI measurements in toluene solutions of a Tatarstan crude oil. Results for concentrated solutions (with asphaltenes in a “steady” aggregated state) are in agreement with ideal mixing rules. An “anomalous” behavior of RI 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. Results and Discussion

### 2.1. Samples and Equipment

The virgin crude oils were collected from well-heads at Romashkinskoye reservoir (Tatarstan). Crude #1, employed in RI experiments, had a density of 875.6 g/l, contained 3.6 wt. % asphaltenes. For comparative absorptivity measurements we used crude #2 (895 g/l, 3.5 wt. % asphaltenes) and solid n-heptane asphaltenes precipitated from a blend of Tatarstan crude oils. The samples were 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 on optical absorption have been studied in a spectrometer (Evdokimov et al., 2003a,b), equipped with a set of narrow-band light filters (KFK-2 Photocolorimeter). The

UV/Vis absorption spectra have been measured in a FLUORAT<sup>®</sup>-02-PANORAMA analyzer equipped with a high-pressure xenon arc lamp. All measurements were performed at 20°C and at ambient pressure.

## 2.2. Refractive Index in Concentrated Solutions

Figure 1 shows the results of RI measurements in oil/toluene solutions for a wide range of oil concentrations, from 0.011 to 50.25 vol. % of oil (note a log scale). For concentrated solutions ( $\geq 1$  vol. % oil) each data point was obtained with a new sample, prepared by mixing the required volume of the crude oil with  $\approx 10$  ml of toluene. No effects of the manner of mixing (e.g., introducing oil into toluene or vice versa) were observed. Owing to the dark and opaque nature of our crude oil, it was not possible to measure the RI of solutions with  $>50$  % of oil. In studies of such opaque crudes (or bitumen) there is a well-established technique for estimation of the  $RI_{oil}$  of a “pure crude” (Goual and Firoozabadi, 2002; Taylor et al., 2001; Buckley, 1999; Buckley et al., 1998). Namely,  $RI_{oil}$  is found by an extrapolation of the experimental data to a volume fraction of 100 %, in accordance with mixing rules. A best fit of Eq. (1) to our data points (coefficient of determination  $R^2 = 0.995$ ), shown by a solid line in Figure 1, provided a value of  $RI_{oil} = 1.4785$  for the studied crude. In a number of publications it has been stated that RI correlates with density and with an asphaltene content of a crude oil. We have compared the RI of our oil with RIs for 45 crudes of various origin (Yang et al., 2002; Buckley and Wang, 2002; Goual and Firoozabadi, 2002; Buckley et al., 1998). Our results appear to be in a reasonable agreement with previously published data. There is good overall correlation of RI with oil’s density ( $R^2 = 0.76$ ), though a correlation of RI with asphaltene content is much worse ( $R^2 = 0.29$ ).

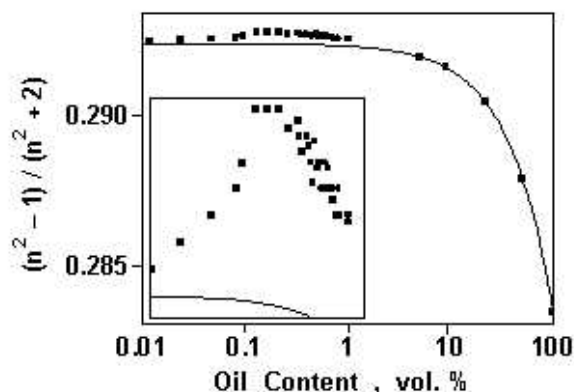


Fig. 1. Refractive index for a wide range of oil concentrations in toluene. Solid line - the ideal mixing rule (Eq. 1).

## 2.3. “History Effects” in Dilute Oil Solutions

Studies of solutions with oil content below  $\approx 1$  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 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 intervals, etc.

The most pronounced “history effects” were in solution with oil contents of  $\approx 0.2$ - $0.5$  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 “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 (Hammami et al., 2000; 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. 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 procedure of sample preparation used in our previous studies (Evdokimov et al., 2003a,b,c). 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 with dilute solutions a concentration of a single sample is increased step-wise, at equal time intervals (0.5 – 10 min.), by means of consecutive additions to toluene (100 ml) of calibrated oil drops ( $m_{drop}=10.3\pm 0.3$  mg). Hence, the concentration increments in solutions are 0.012 vol. % for the crude oil (3.7 mg/l for oil’s asphaltenes). At the beginning of each time interval a solution is gently stirred with a glass rod, at the end – RI measurements are performed. The results revealed consistent dependence on the rate of concentration increase above  $\approx 0.2$  vol. % of oil per hour. There were practically no time effects at slower rates, hence such data sets were considered to be representative of the “equilibrium” states of solutions. In particular, the RI results reported in this paper were obtained with a rate of concentration increase equal to 0.14 vol. % of oil per hour.

#### 2.4. Break-up of Ideal Mixing Rules in Dilute Solutions

It is clear from Figure 1 that in dilute solutions the data show “anomalous” deviations of RI from the simple ideal mixing rule (solid line in Fig. 1). Two most obvious “anomalies” are : 1) the “concentrated” approximation does not terminate at  $(n^2-1)/(n^2+2)$  for pure solvent; 2) the measured concentration dependencies are non-monotonous, with an extremum at oil content of about 0.2 vol. % and a sharp drop of RI at lower contents. Such “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., Goual and Firoozabadi, 2002 have measured RI vs. wt. % in toluene of a Hamaca heavy crude. By fitting a straight line to the respective graph, they found extrapolated RI of “pure crude”. However, in the graph they do not plot data for pure toluene, while extrapolations to zero concentrations result in inconsistency of extrapolated RI of toluene (1.4987). If the reference value of RI for toluene (1.4969) is included in the data set, the results of Goual and Firoozabadi, 2002 show an obvious “anomalous” drop of RI at oil concentrations below 1 wt. %, qualitatively similar to that observed in our experiments. Taking into account earlier evidence of peculiar behavior of other properties in dilute oil solutions (cf. Introduction), we ascribe the observed

“anomalies” of RI to phenomena of de-aggregation of oil asphaltenes. Hence, in the following we refer to the respective asphaltene concentrations in oil-toluene solutions.

Figure 2 presents a comparison of the “equilibrium” concentration dependence of RI (filled symbols) with linear dependencies (solid lines) based on the Lorentz-Lorenz ideal mixing rule (Eq. 1). Solid line “1” represents the RI behavior in 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 remaining in an aggregated state. Deviations of experimental data from “ideal” values (presumably due to a change of the crude’s properties caused by de-aggregation of asphaltenes) become noticeable at asphaltene concentrations of ~ 540-600 mg/l, i.e. in the range observed in our previous studies (cf. Introduction). “Non-ideality” of experimental results increases with dilution and an extrapolation of the experimental concentration dependence does not terminate at the F(RI) of pure toluene, as expected from Eq. (1). However, below asphaltene concentrations of ~63-79 mg/l experimental data again form an almost linear succession with the origin at the F(RI) of toluene. Hence, these solutions, at least formally, may be regarded as “binary”, where the oil component in a modified “steady state” (containing de-aggregated asphaltenes). Solid line “2” in Figure 2 is the best linear fit ( $R^2=0.980$ ) to the data for asphaltene concentrations <47 mg/l. On the basis of this linear fit it seemed reasonable to evaluate a modified  $RI_{oil} = 2.0121$ , close to the refractive indices of amorphous carbon and graphite (Silva, 2001).

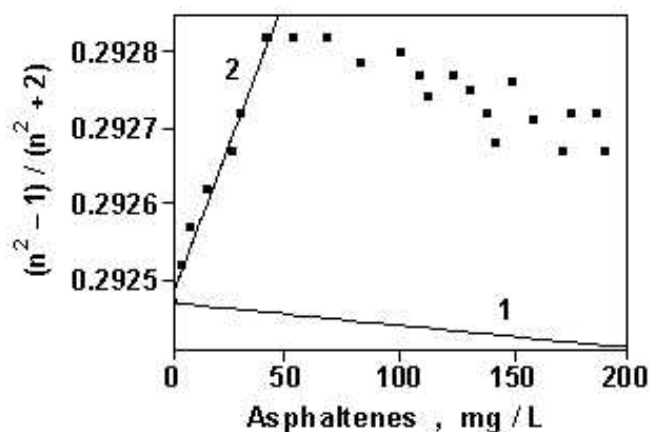


Fig. 2. RI behavior in dilute solutions. Solid lines – ideal mixing rule with different RIs of the crude..

## 2.5. Nature of Aggregation Effects on Refractive Index

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 variations of molar volumes / densities. RI of a fluid is assumed to be directly related to its density (Gray and Gubbins, 1984). If asphaltene de-aggregation is regarded as a dissolution, 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 in our experiments. On the other hand, some non-ideal solutions exhibit negative excess volume of mixing which may have been expected to be related to positive excess RI. In our experiments deviations of RI from ideal mixing rules are  $\sim 0.1\%$ , typical for excess RI in binary hydrocarbon mixtures (Fermeglia and Torriano, 1999; Resa et al., 2004). However, excess volume effects are the largest in solutions with volume fractions of  $\sim 0.5$ , while in our experiments maximum excess RI is at volume fraction of oil close to  $2 \cdot 10^{-3}$  (cf. Fig. 1). Moreover, a causative relationship between excess volume and excess RI never has been proven either theoretically or experimentally (cf. Fermeglia and Torriano, 1999 and of Resa et al., 2004).

For the above reasons, we conclude that density mechanisms are not responsible for the observed RI anomalies. Comparative studies of various properties of dilute solutions indicate that non-ideal RI behavior may be ascribed to optical dispersion effects, accounted for by Kramers–Kronig relations (Jackson, 1999). It should be noted that dispersion effects are neglected in simple RI mixing rules.

## 2.6. Correlation of RI with Optical Absorptivity

RI of dilute solutions is known (Gray and Gubbins, 1984) to be affected mainly by: 1) changes in molecular polarizability of a solute (due to variations in intermolecular interactions), 2) changes in the number of solute molecules per unit volume (solute concentration). A trivial concentration factor may be excluded by calculation of a “RI increment”  $dn/dc$ , which is directly proportional to the molecular polarizability  $\alpha$  :

$$\alpha = (M / 2\pi N_A)(dn/dc) \quad (2)$$

where  $M$  is the molar mass,  $N_A$  is the Avogadro number and  $c$  is the solute concentration.

The left part of Figure 4 shows the behavior of RI increment in the studied solutions. At higher concentrations  $dn/dc$  is fairly constant and negative (i.e. polarizability of asphaltenes is smaller than that of toluene). In more dilute solutions  $dn/dc$  becomes positive and at 2-8 mg/l of asphaltenes its absolute value increases by a factor of about 12. According to Eq. (2), this may have been interpreted as a 12-fold polarizability increase of asphaltene monomers as compared to molecules in asphaltene aggregates. However, there is strong theoretical and experimental evidence (Jensen et al., 2002) that electronic molecular polarizability (which determines a magnitude of RI for visible light wavelengths) is almost unchanged by the intermolecular association. On the other hand, the behavior of  $dn/dc$  appears to be qualitatively similar to the behavior of optical absorptivity at 670 nm (shown in the right part of the Figure).

As stated above, we attribute the observed changes of the optical properties to association/dissociation of asphaltene molecules in the crude oil. This attribution is further supported by virtual coincidence of characteristic concentrations in both graphs of Figure 3. Namely, both  $dn/dc$  and absorptivity exhibit a high peak at  $\sim 2-8$  mg/l of asphaltenes (and show a tendency of decreasing at lower concentrations). Two secondary maxima are observed at 25-30 and at 55-65 mg/l, while above 80-90 mg/l saturation levels are reached.

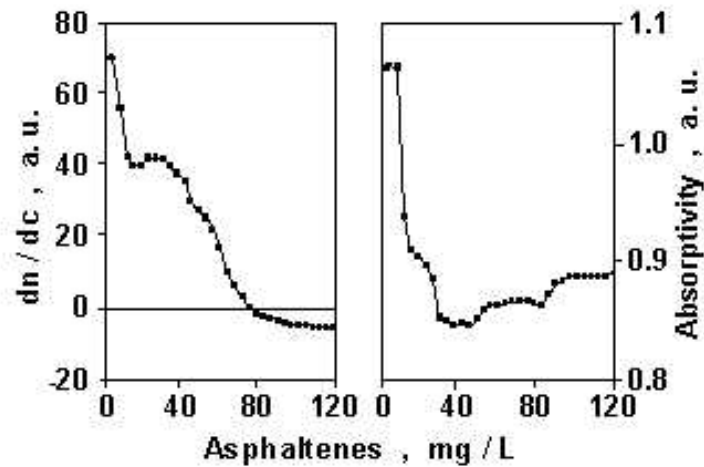


Fig. 3. RI increment (left) and optical absorptivity (right) in dilute solutions of crude #1.

Moreover, the above characteristic concentrations are close to those observed in our earlier studies of asphaltene-containing solutions. As an example, Figure 4 shows the behavior of absorptivity at 670 nm in toluene solutions of crude oil #2 (lower curve) and of solid asphaltenes (upper curve). The data are adapted from Evdokimov et al., 2003b.

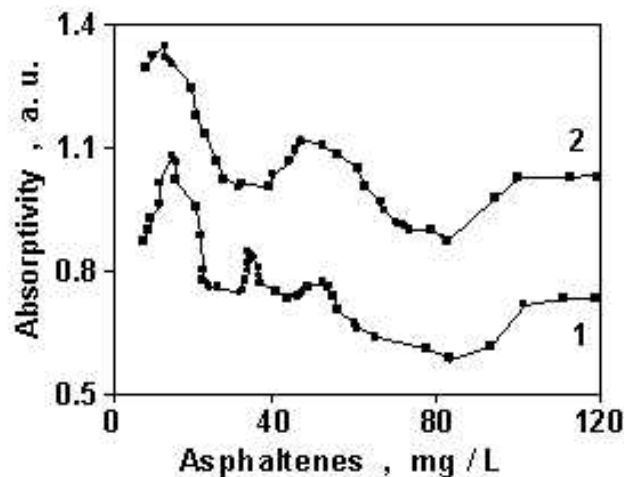


Fig. 4. Optical absorptivity in dilute solutions of crude #2 (1) and of solid asphaltenes (2).

Interrelationship between optical absorption and refractive index is implied in well-known Kramers-Kronig (K-K) equations. However, this interrelationship is not immediately proved by similarity of the dependencies in Figure 3, measured at fixed wavelengths. The exact K-K formula (Sheik-Bahae, 2004) requires the knowledge of absorptivity  $\kappa$  in the entire range of wave frequencies :



$$n(\omega) = 1 + \frac{c}{\pi} \int_0^{\infty} \frac{\kappa(\Omega)}{\Omega^2 - \omega^2} d\Omega \quad (3)$$

Figure 5 shows some preliminary experimental data on UV/Vis absorptivity spectra in solutions of crude oil #1, measured at asphaltene concentrations of 3.7 mg/l (curve 1) and > 320 mg/l (curve 2). It is clearly seen that a transition from associated to de-aggregated asphaltenes is accompanied by an emergence of a strong resonance band, peaked at ~285 nm.

UV/Vis absorptivity of crude oils is known to be governed by  $\pi$ - $\pi^*$  transitions in the conjugated aromatic chromophores of asphaltenes (cf. references in Evdokimov et al., 2003a,b). By analogy with other aromatic compounds (Birks, 1970) we may attribute a resonance band (285 nm) to the  $S_0(^1A_g) \rightarrow S_2(^1B_{3u})$  transition. The lower energy transition  $S_0(^1A_g) \rightarrow S_1(^1B_{1u})$  may be assigned to a low-intensity broad band centered at ~ 580-600 nm and clearly revealed only in derivative spectra.

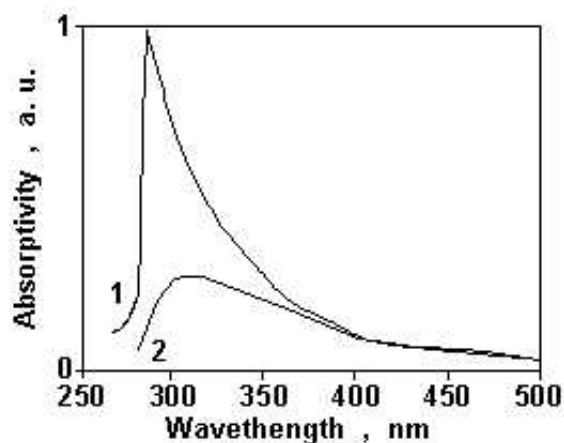


Fig. 5. UV/Vis absorptivity spectra in highly diluted (1) and more concentrated (2) oil solutions.

Numerical evaluation of K-K formula was performed for both spectra of Figure 4. Even if only this limited frequency range is considered, evaluation shows that K-K effects may account for a large increase of  $RI_{oil}$  - from  $\approx 1.47$  in concentrated solutions to  $\approx 1.72$  at high dilutions. It may be expected that with inclusion of short-UV and IR spectral ranges, K-K effects would be found fully responsible for a “surprisingly high” experimental value of  $RI_{oil} = 2.0121$  (cf. Section 2.4).

### 3. Conclusions

Dilute asphaltene-containing solutions in toluene (asphaltene concentrations below 150–200 mg/l) show peculiar non-ideal behavior of refractive index and UV/Vis absorptivity. Sharp inflections in experimental concentration dependencies are indicative of changes in association states of asphaltenes. Apparently, asphaltenes may exist in a monomeric state only at concentrations below 1-2 mg/l. A transition from monomeric to associated asphaltenes is accompanied by a notable increase of a resonant absorption band at ~285 nm. Since



the emerging absorption band is located in a wavelength region shorter than the probe wavelength for RI, it creates a positive refractive index change, according to the Kramers-Kronig relations. We believe that the present study may provide further insight into the formation, stability and optical properties of molecular aggregation in crude oils, as well as in other asphaltene-containing industrial fluids

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