Changes in Asphaltene Microenvironments Evidenced by Fluorescence Solvatochromism

Gabriella-Maria Pietraru and David T. Cramb*
Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB, Canada T2N 1N4

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This work presents a novel and sensitive procedure to study the behavior of asphaltene solutions in toluene and o-dichlorobenzène. Fluorescence solvatochromism was used to observe changes in asphaltene microenvironments with the increase in asphaltene concentration. The environmentally sensitive molecular probe PRODAN (6-propionyl-2-(N,N-dimethylamino)naphthalene) was selected as the reporter molecule to provide clues as to the polarizability in the vicinity of asphaltene molecules. PRODAN displays substantial polarizability-induced shifting of its maximum fluorescence intensity, a feature that was exploited to characterize the various microenvironments found in asphaltene systems. A preaggregation model was developed to explain the experimental solvatochromic observations, and a definition for the critical aggregation concentration was proposed.

Introduction

The aggregation and precipitation of asphaltene is a constant problem in the production, transportation, processing, and refining of heavy crude oils rich in asphaltene. However, asphaltene deposits may form even in oils with fairly low asphaltene content. The capacity of asphaltenes to self-assemble influences the primary step in the formation of asphaltene particles that will agglomerate and eventually precipitate, forming undesirable deposits that could lead to interruptions of the oil flow. To avoid the costly consequences on crude oil production, it has become very important to understand asphaltene aggregation and its causes. Depending on the solvent properties of the oil, asphaltenes can be stable or very close to precipitation. Also, the precipitation of asphaltenes differs from field to field and from area to area. This makes it difficult to have a generally efficient method for the prevention of asphaltene aggregation.

Aggregation modifies the asphaltene structure on a colloidal scale and influences the behavior of asphaltene in solution. Substantial research on asphaltene properties has been taking place over the past century. However, due to the chemical complexity of the asphaltene fraction, the causes of asphaltene deposition are still controversial and there is no universal agreement as to what the mechanism for asphaltene precipitation is.

The asphaltene class is the most refractory, most polar, and heaviest component of oil, composed of thousands of molecules with high polydispersity. As it is generally accepted that this fraction of petroleum cannot be identified chemically, asphaltenes are typically defined by their solubility in n-alkanes (e.g. n-pentane and n-heptane). In the present work, the term “asphaltene” refers to the material that precipitates within and separates from bitumen by the addition of a low-boiling hydrocarbon. According to this definition, the precipitated asphaltenes may contain some resins (the peptizing agent of asphaltene) adsorbed on their surface.

Many authors have considered the self-association of asphaltene equivalent to the formation of surfactant reverse micelles. Thus, the small asphaltene aggregates/particles are sometimes referred to as “micelles” in the literature. It is important to point out that the asphaltene micelles may not be the traditional micelles that are usually formed by the surface-active amphiphatic molecules. Micellization is the phenomenon describing the self-association of surfactants in aqueous solution, initiated by the hydrophobic–hydrophilic imbalance. When the concentration of the surface-active materials reaches the critical micelle concentration (CMC), these molecules begin to self-aggregate to lower their free energy for better suspension in the solution. In a micelle formed in nonaqueous media, amphiphatic molecules would cluster with their hydrophilic heads together in the micellar core and their hydrophobic tails in the organic phase. The similarity between asphaltene and surfactant molecules was suggested by researchers who observed sharp transitions in some measurable physical properties of asphaltene (such as viscosity, surface tension or by calorimetry), similar to those observed as micelles are formed in surfactant solutions. Still, recent interfacial tension measurements indicated that the aggregates found in asphaltene solutions are not micelles. Hence, the term “micelle” found in the literature might be used arbitrarily to describe the self-aggregation phenomenon of asphaltene. Since there is no solid proof of asphaltene micelles and the literature reports are still contradictory, the term “aggregate” will be used in this paper to refer to the asphaltene entities formed by the self-association of asphaltene molecules.

The changes in asphaltene characteristics due to aggregation may be readily observable and measurable experimentally. Various methods were proposed to...
fluorescence spectroscopy can be a useful tool to study the chemical environment in the immediate surroundings of an asphaltene entity.

Fluorescence techniques have lately become increasingly popular for examining the microenvironment of solvent sensitive media. Generally, one wishes to use the solvent sensitivity of the fluorophore to infer the polarity of its surroundings. The method involves the use of a probe molecule that exhibits different characteristics depending upon the properties of the solubilizing media. The appearance of new spectral bands, shifts in emission wavelengths, or changes in fluorescence intensities provide valuable information regarding the probe’s local environment. Taken together, these phenomena are known as solvatochromism.

According to the literature, asphaltenes associate even at very low concentrations. Therefore examining a range of dilute to semi-concentrated asphaltene solutions (concentration regime not available with some of the other techniques) would provide the best opportunity to obtain additional information about aggregation in these systems. The present work offers a novel method of looking at asphaltene solutions, because, to our knowledge, it represents the first attempt to study asphaltene interactions using a fluorescence reporter molecule. This technique might be more sensitive to the onset of aggregation than other methods because it allows measurements at low asphaltene concentrations. As indicated by other studies, even slight changes in the character of the solvent have a significant effect on the asphaltene in solution. Consequently, small changes in solution characteristics can lead to large shifts in the fluorescence maximum.

To characterize the microenvironment of asphaltene, a probe molecule is needed that exhibits different fluorescence characteristics depending on the properties of the surrounding media. These characteristics are usually observed for molecules possessing large excited-state dipole moments. Additionally, the probe molecule to be used in this project would need to be amphiphilic, a feature that increases its solubility in all the microenvironments within an asphaltene solution. Thus, the environmentally sensitive fluorophore 6-propionyl-2-(N,N-dimethylamino)naphthalene (PRODAN) was chosen as the best reporter molecule.

PRODAN is one of the most solvatochromic fluorescent probes. Since its first synthesis and characterization, many publications on its spectroscopic properties and applications have appeared. Lately, it has been widely used in biological systems to determine the surface hydrophobicity of proteins, to investigate membrane dynamics, and to monitor ATPase reactions. In addition to its spectral sensitivity, this fluorophore is capable of displaying significant fluorescence in both polar and nonpolar solvents. The solubility of PRODAN in a broad range of media made it a successful and powerful molecular probe to characterize different microenvironments in aqueous and nonaqueous solutions, including microscopic polarities in micelles and membranes. It

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(20) Fenistein, D.; Barre, L. Fuel 2001, 80, 283.
(26) Rogel, E. Energy Fuels 2000, 14, 566.
was demonstrated\textsuperscript{28} that PRODAN partitions both from aqueous solution into more hydrophobic environments and from nonaqueous solution into more hydrophilic environments under appropriate conditions.

PRODAN exhibits large solvatochromic fluorescence shifts due to the charge-transfer character of its emitting electronic state. We have demonstrated the utility of PRODAN to detect micelle-like changes in aqueous and nonaqueous solutions.\textsuperscript{28}

In this article, we present the use of PRODAN as a reporter molecule for the proposed critical aggregation concentration (CAC) of asphaltene. To account for the effect of asphaltene behavior on PRODAN fluorescence properties, a model based on changes in refractive index was developed. The results presented here will further our knowledge of the complex structure of asphaltene systems and will help in the development of new methods for preventing the formation of asphaltene deposits.

Experimental Methods

Materials. Cold Lake dewatered bitumen (10° API, with 4.5 wt % sulfur, 500 Pa s viscosity at room temperature) and Cold Lake propane asphalt (fraction recovered from deasphalting Cold Lake bitumen with propane at 325 °C; solvent-to-oil ratio used, 13.3:1; DAO yield, 55.5 wt % asphaltene softening point, 94 °C) were used to extract asphaltene using n-pentane (98%, BDH) as the precipitant. These asphaltenes are referred to as C5-asphaltene. Cold Lake dewatered and desanded bitumen (10.7° API, 4.1 wt % sulfur, 65 Pa s viscosity at room temperature) recovered from an underground reservoir by cyclic steam injection was used to precipitate asphaltene by n-heptane. These asphaltenes donated by Dr. H. W. Yarranton (Department of Chemical and Petroleum Engineering, University of Calgary) were purified by soxhlet extraction and are referred to as C7-asphaltene. It is likely that the C5-asphaltene contain some resinous material. Asphaltene solutions were prepared using toluene (99.99% purity, OmniSolv) and o-dichlorobenzene (99% HPLC grade, Sigma-Aldrich). The fluorescent probe PRODAN was obtained from Molecular Probes and used as purchased.

Procedure to Prepare Solutions. Preparation of Stock Asphaltene Solutions. Asphaltene solutions were obtained using 360 nm light and using the solvents (toluene or o-dichlorobenzene). The stock solution was further diluted when added to the series of asphaltene solutions. All PRODAN stock solutions were kept in glass vials, covered with aluminum foil, and stored in the dark until used.

Preparation of Asphaltene–PRODAN Solutions. Asphaltene–PRODAN mixtures were prepared by diluting the respective stock solutions with the solvent. A constant volume of PRODAN stock was pipetted into each glass vial. A variable amount of asphaltene stock was added into the vials. The solution was further diluted to obtain a series of asphaltene concentrations. To get the desired set of solutions, the materials were mixed such that in each mixture the concentration of PRODAN was 4 × 10\textsuperscript{-5} M and the concentration of asphaltenes was the same as in the mixtures without PRODAN. Each solution was sonicated for 10 min.

Spectroscopic Measurements. Fluorescence spectra were recorded over the range 370–650 nm, at room temperature, using a PTI (Photon Technologies Inc.) spectrofluorometer outfitted with a xenon arc lamp. The spectral bandwidth was set to 2 nm with a dwell time of 0.1 s/point. A constant step size of 0.25 nm was used in all fluorescence and excitation spectra. All spectra were recorded using front-face cuvettes (SUPRASIL quartz from Hellma Canada Ltd.), following the procedure of Cramb et al.\textsuperscript{38}

Results and Data Reduction

Fluorescence Spectra of Solutions. In the present work, we examined the fluorescence spectral shifting of PRODAN over various concentrations of asphaltenes in toluene and in o-dichlorobenzene (DCB), as a novel and sensitive method to determine changes in asphaltene behavior. Because asphaltene solutions are dark and became opaque with increasing concentration, the standard geometry used for fluorescence measurements (the right-angle geometry) was not suitable for asphaltene mixtures. Instead, all the spectra were recorded employing the type of illumination used for the study of optically dense solutions: the front-face geometry. At each asphaltene concentration, a set of three fluorescence spectra was recorded, both in toluene and in DCB: one of the pure asphaltene solution, one of the pure PRODAN solution, and one of the asphaltene–PRODAN mixture. These sets allowed the deconvolution of the PRODAN component, as will be further described.

Figure 1 shows the fluorescence spectra of a series of asphaltene solutions in toluene, obtained using 360 nm light.
solutions in toluene (where, for example, $8 \times 10^5$), $A_{ex} = 360$ nm. The arrow is meant to guide the eye to a red-shift in the PRODAN component of the spectrum.

Excitation. These asphaltenes were extracted from the Imperial Oil bitumen, using n-pentane. Asphaltene concentration in the mixtures ranged from 0.199 to 13.567 g/L. For clarity, the diagram does not show the entire series of recorded spectra.

Asphaltene fluorescence spectra appear to change with concentration. With increasing asphaltene concentration, a red peak gains intensity in the emission spectra. This could represent excimer (excited-state dimer or multimer) emission resulting from aggregation. All the mixtures examined showed similar behavior. Their long-wavelength features are characteristic of systems with extended aromaticity and are expected since asphaltenes are polycyclic aromatic compounds. Fluorescence intensities are proportional to concentration over only a limited range of optical densities. When the concentration of the fluorescent species is large enough to absorb significant amounts of the exciting light, the dependence of fluorescent intensity on the concentration no longer appears to follow the Beer–Lambert law. This is known as the inner filter effect and is responsible for the apparent decrease in the fluorescence intensity for the solutions with high asphaltene concentration.

Figure 2 shows the fluorescence spectra for a series of asphaltene–PRODAN solutions in toluene. The asphaltene stock was extracted from Imperial Oil bitumen using n-pentane. For spectral deconvolution, considerable effort was made to keep the concentration of asphaltene in the asphaltene–PRODAN solutions the same as the concentration of pure asphaltene in the two solvents. Upon close inspection of the asphaltene–PRODAN spectra, a wavelength shift in the fluorescence of the PRODAN component with the increase in asphaltene concentration was observed. The red shift (shift to longer wavelength or to lower wavenumbers) in the fluorescence maxima indicates that PRODAN senses a change in solvent electronic properties in these asphaltene-containing solutions compared to when it is alone in the aromatic solvent. It is assumed that with the increase of asphaltene concentration, PRODAN senses a more polarizable microenvironment, which might indicate the existence of probe molecules with different solvent stabilization. The red shift

![Figure 2](image)

**Figure 2.** Fluorescence spectra of asphaltene–PRODAN solutions in toluene (where, for example, $8 \times 10^5$), $A_{ex} = 360$ nm. The arrow is meant to guide the eye to a red-shift in the PRODAN component of the spectrum.

was present in all the stocks examined for both solvents. The spectra for the other asphaltene stocks are presented in Figures S1–S4 (Supporting Information).

**Deconvolution of PRODAN Spectra.** To determine the solvatochromic shift of PRODAN, it was necessary to deconvolute its contribution to the total fluorescence spectrum. The measured spectrum of asphaltene–PRODAN solutions can be deconvoluted into contributions of pure asphaltene and contributions of pure PRODAN, using a fitting algorithm. Mathematically this is indicated as

$$I(\lambda)_{fl} = aI(\lambda)_{fl}^{\text{PRODAN}} + bI(\lambda)_{fl}^{\text{asph}}$$  \hspace{1cm} (1)

Coefficient $a$ represents the fractional contribution of PRODAN to the overall spectrum, whereas coefficient $b$ represents the fractional contribution of asphaltene. $I(\lambda)_{fl}^{\text{PRODAN}}$ and $I(\lambda)_{fl}^{\text{asph}}$ are the fluorescence spectra of PRODAN and asphaltene, respectively, alone in the solvent. $I(\lambda)_{fl}$ represents the fluorescence spectrum of the mixture when both PRODAN and asphaltene are present. For each series of solutions, all experimental fluorescence spectra of asphaltene–PRODAN solutions were fitted by eq 1 using a nonlinear least-squares fitting computer program. Constants $a$ and $b$ were allowed to vary until the best fit to the fluorescence experimental spectrum was obtained. Their values are unique within experimental error and were not used further in the mathematical modeling. Figure 3 compares the experimental fluorescence spectrum for one of the asphaltene–PRODAN solutions in toluene (0.597 g/L) with its calculated fit.

The contribution of PRODAN in each mixture was determined using eq 1, by subtracting from the experimental fluorescence spectra of asphaltene–PRODAN mixtures, the spectra of asphaltene alone in the solvent multiplied by the parameter $b$ from the fit.

**Peak Fitting: The Gaussian Line Shape.** To determine the exact extent of the shift, the center wavenumbers of experimental PRODAN fluorescence spectrum was determined using a Gaussian line shape defined by

$$I(\nu) = \text{baseline} + I_0e^{-[0.693(\nu-\nu_0)^2/\sigma^2]}$$  \hspace{1cm} (2)

In this equation, $I_0$ represents the amplitude of the spectrum, $\nu$ is the variable wavenumber, $\nu_0$ is the band
center of the PRODAN fluorescence spectrum, and \( \gamma \) is the full spectral width at half-maximum. Because the PRODAN fluorescence spectrum is asymmetrical, only the blue side was used in the fitting procedure. Figure 4 is an example of Gaussian fit, for the asphaltene concentration of 0.597 g/L.

The goodness of the fit was determined by the closeness of the experimental data to the calculated fit. For the blue side of the spectra, the difference between the Gaussian models and the experimental spectra (i.e. the residuals) were plotted as a function of asphaltene concentration in Figure 5. The residuals showed a random distribution around zero, which indicates no systematic deviation from the model. Furthermore, the values of the residuals were very close to the instrument noise level, which also confirms the goodness of the fit. Therefore, we conclude that the fit represents well the blue side of PRODAN contribution.

For comparison, fluorescence data were collected for asphaltene–PRODAN mixtures in DCB, and the Gaussian fits of the experimental data in DCB are similarly good. The constants derived from the Gaussian fits for each asphaltene source are presented in Tables 1–3. The shift of PRODAN \( \Delta(\nu_H) \) is defined as the difference between the fluorescence maximum of PRODAN with and without asphaltene in solution:

\[
\Delta(\nu_H) = \nu_H(\text{with asphaltene}) - \nu_H(\text{pure solvent})
\]

\[(3)\]
Fluorescence Spectral Shifting of PRODAN. The fits to the Gaussian line shape minimized the uncertainty in determining the fluorescence intensity maximum and provided the value of the band center of each peak. By knowing this value for every solution, it was possible to determine the extent of the shift by simply taking the difference between the band center of the PRODAN contribution in each PRODAN-asphaltene solution and the band center of PRODAN alone in the solvent. The Gaussian fits proved the shifting of PRODAN and indicated quantitatively how much each experimental fluorescence spectrum of asphaltene-PRODAN solution was red shifted with the increase in asphaltene concentration. The shift in fluorescence maxima as a function of asphaltene concentration helped in determining the changes in asphaltene solution characteristics. Any shifting of the fluorescence maximum arises from PRODAN experiencing a different environment. Figure 6 shows the standard error in the spectral shifting of PRODAN vs asphaltene concentration, \([A]_g/L\). Asphaltenes were extracted from Imperial Oil bitumen.

Fluorescence Spectral Shifting of PRODAN. The fits to the Gaussian line shape minimized the uncertainty in determining the fluorescence intensity maximum and provided the value of the band center of each peak. By knowing this value for every solution, it was possible to determine the extent of the shift by simply taking the difference between the band center of the PRODAN contribution in each PRODAN-asphaltene solution and the band center of PRODAN alone in the solvent. The Gaussian fits proved the shifting of PRODAN and indicated quantitatively how much each experimental fluorescence spectrum of asphaltene-PRODAN solution was red shifted with the increase in asphaltene concentration. The shift in fluorescence maxima as a function of asphaltene concentration helped in determining the changes in asphaltene solution characteristics. Any shifting of the fluorescence maximum arises from PRODAN experiencing a different environment. Figure 6 shows the standard error in the spectral shifting of PRODAN vs asphaltene concentration in toluene for one series of C5-asphaltene solutions.

For dilute asphaltene solutions, the shifting of PRODAN maximum fluorescence seems to be linearly dependent on asphaltene concentration. At higher asphaltene concentrations, a leveling off of the shift was observed after a certain concentration. All the asphaltene solutions studied exhibited the same type of behavior, although the magnitudes of the shifting were not the same. In Figure 7 the fluorescence spectral shifting of PRODAN in asphaltene–toluene solutions is presented for asphaltene representing different sources. The shifting of PRODAN in asphaltene solutions prepared in DCB showed the same tendency of reaching a plateau at higher concentrations and is presented in Figure 8. Experimental data for C7-asphaltene is not available. The turnover points observed suggest that some characteristic of the solution is changing above a certain asphaltene concentration.

There is an interesting characteristic that was noticed in all the shifting graphs; namely, none of the linear plots go through zero. This might be an indication that, at very low concentrations, asphaltene molecules experience a different aggregation behavior. Literature reports suggest that the association of asphaltene in bitumen is not micellization. At low concentrations, the solution may contain structures that are different from asphaltene monomers. According to other studies, this may correspond to asphaltene molecular aggregation and small-
in the fluorescence maximum as a function of the solvent polarizability. In the asphaltene solutions, the various microenvironments sensed by PRODAN suggest that the probe molecules experience different polarizabilities. We will use this modified form of the Lippert equation to account for the effect of asphaltene behavior on PRODAN fluorescence properties. The plots shown in Figures 7 and 8 are the difference between the fluorescence maximum of PRODAN with asphaltene in solution and without asphaltene, \( \Delta \lambda_{\text{fl}} \).

**Discussion**

(a) Asphaltene Fluorescence Spectra. In the first order, the fluorescence spectra of aromatic structures are related to the size of the emitting molecule,\(^{41}\) that is, to the dimensions of the \( \pi \)-electron hyperconjugation within the fluorophore. Therefore, the spectral location of fluorescence maximum can be used to imply the average distribution of aromatic rings in a molecule. Asphaltenes do not have a definite or unique chemical formula. Within an asphaltene sample, there are thousands of different molecular structures. Their fluorescence spectra represent overlapping contributions of all the chromophores within the asphaltene molecule. The inspection of the experimental fluorescence spectra for the various asphaltene sources studied in this work supports the general belief that asphaltenes contain multiring aromatics.\(^{11,12,41-49}\)

Significant fluorescence emission for these asphaltene solutions occurs between 400 and 550 nm, an interval characteristic of heteroaromatic systems with 4–10 rings.\(^{27}\) For that reason, we assume that the asphaltene solutions examined may contain mostly molecules possessing the same range of aromatic rings as estimated by earlier reports.\(^{27,41,50}\) Moreover, recently published emission spectra for Athabasca asphaltene\(^{51}\) seem to show a similar spectral profile and fluorescence emission range. The broad, red peaks observed in the 10 g/L fluorescence spectrum suggests a change has taken place in this solution. This could represent dimer/multimer emission maxima due to aggregation. Further analysis of this effect is beyond the scope of this paper.

(b) PRODAN Solvatochromism. As mentioned previously, PRODAN showed a wavelength shift of the maximum fluorescence as a function of asphaltene concentration. This is indicative of changes in solution characteristics, since PRODAN provides clues as to its local electronic environment. Previous thermooptical studies have already suggested that asphaltenes modify the solvent microenvironment in their immediate vicinity.\(^{52}\) It is hypothesized that, with the increase of asphaltene concentration, the solvent electronic properties

\[ \Delta \nu_{\text{Stokes}} = \frac{2}{hc \epsilon} \left( \frac{n^2 - 1}{2n^2 + 1} \right) \left( \frac{\mu^* - \mu}{a^3} \right) + \text{constant} \]

where \( \mu^* \) and \( \mu \) are the dipole moments in the excited and ground states, respectively, \( a \) is the radius of the cavity, \( \epsilon \) is Planck’s constant, \( c \) is the speed of light, \( n \) is the dielectric constant, \( n \) is the refractive index, and \( \Delta \nu_{\text{Stokes}} \) is the shift between excitation and emission.

In our system, it is assumed that the biggest change is in the refractive index of the solution, i.e., in solvent polarizability. Were this not the case, then the DCB solutions should result in a blue shift of the fluorescence as adding asphaltene actually decreases the dielectric constant. If the fluorescence shifting of PRODAN is a function only of the refractive index, the Lippert equation for the fluorescence shift from its value in a vacuum becomes:\(^{40}\)

\[ \Delta \nu_{\text{fl}} = \frac{2}{hc \epsilon} \left( \frac{n^2 - 1}{2n^2 + 1} \right) \left( \frac{\mu^* - \mu}{a^3} \right) \]

Therefore, the experimental fluorescence spectra are a measure of the change in energy, reflected by the shifting

\[ \Delta \lambda_{\text{fl}} \]

Figure 8. Spectral shift of maximum PRODAN fluorescence, \( \Delta \lambda_{\text{fl}} \), in various asphaltene solutions in DCB vs asphaltene concentration, [A].

- Streifer, J. Ph.; Saal, R. N. J.; Phys. Chem. 1940, 44, 139.
- Strausz, O. P.; Peng, P.; Murphy, J. Energy Fuels 2002, 16, 809.

change and PRODAN finds itself in a more refractive (i.e., polarizable) microenvironment compared to the bulk solvent. This suggests the presence of more than one microenvironment and/or the existence of probe molecules with different solvent stabilization. According to the fluorescence spectral shifting of PRODAN, at low asphaltene concentrations there is a linear dependence between shifting and asphaltene fraction (see Figure 6).

We conclude that the molecular weight of asphaltene is not changing significantly in this concentration range. The linear regime of spectral shifting is consistent with the change in refractive indices observed from direct measurements of asphaltene solutions.16 This is not surprising, considering that the interactions between the solvent and the fluorophore can be defined in terms of solvent refractive index, which is an indicator of oil polarizability.

The slopes of the linear dependence of spectral shifting at different asphaltene concentrations from around 0.6 to 1.7 g/L, depending on the asphaltene source and solvent.

The slopes of the linear dependence of shifting on asphaltene concentration or weight fraction could be related to changes in the refractive index of the solution and may contain information about the free small asphaltene particles. A larger slope means a faster increase in polarizability. Since the shifting is a measure of the refractive index of the solution, larger slope also means a higher value of the asphaltene component refractive index. Therefore, the slopes indicate how much the refractive index changes per gram of added asphaltene. A more refractive medium means higher aromaticity, i.e., more asphaltene and less resins. From Table 4, by comparing the slopes in toluene, fraction C7 suggests that it is the most resin-free asphaltene fraction. This also means that the C7 soxhlet-washed asphaltene should be the first to aggregate in solution, because they do not have protective resins. Indeed, these asphaltene have the lowest CAC (reflected by the turnover point) and the highest slope. Their refractive index changes the fastest under the given conditions, and this possibly means that these asphaltene entities have the largest size and highest density among the three stocks.

Table 4 shows the values of the slopes and turnover points for the asphaltene mixtures in the two solvents. Since the shifting is plotted as a function of asphaltene weight fraction, the slope of the linear regime will be expressed in cm⁻¹.

It is well-known that the solvent surrounding the asphaltene entity and the origin of the sample affect the behavior of asphaltene in solution.54 Our data suggest that the larger asphaltene aggregates begin to form at asphaltene concentrations from around 0.6–1.7 g/L, depending on the asphaltene source and solvent.

The leveling off of the shift at higher asphaltene concentration could be modeled as a departure from a binary mixture. The turnover points suggest that the solution characteristics are changing after a certain asphaltene concentration. These points are defined as critical aggregation concentration points, where we predict that the smaller self-associated asphaltene molecules begin to form large aggregates. As more asphaltene are added, the solution becomes saturated with the small “free” asphaltene particles, and a third component occurs in the solution—the big asphaltene aggregates. However, the concentration of the new component in solution is low, and the weight fraction of large aggregates is very small compared to the fractions of smaller asphaltene entities and of solvent. Therefore, no noticeable changes in the shifting are observed. At concentrations higher than the turnover point, the weight fraction of the smaller asphaltene entities, remains practically constant. PRODAN does not sense any increase in the polarizability of its microenvironment and stops shifting its maximum fluorescence intensity.

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were purified by soxhlet extraction, and this method of washing renders the purest, heaviest, and densest fraction. The results indicate that the polarity/polarizability of the medium has a clear effect on the aggregation propensity. One might think that the steeper slopes in toluene solutions can in part be accounted for considering eq 7. By plotting the right-hand side of eq 7 versus the weight fraction of asphaltene and using the known values of refractive index and density for toluene and DCB, one can take the ratios of the slopes. If the differing slopes in Table 4 result from the different densities of the solvents, then these ratios should agree. In fact, the predicted ratio is in the opposite sense to the data. That is, we predict that the ratio of slopes toluene/DCB = 0.7 and the smallest observed ratio, for the same asphaltene source, is 1.8 (source 1). Our results suggest that the asphaltene/toluene mixtures are more refractive, more polarizable than the mixtures in DCB. In DCB, the values of the turnover points are somewhat higher than in toluene, which is not surprising because DCB is a more polar solvent and aggregation should occur at higher asphaltene concentration. The slopes have lower values in DCB than in toluene, as the change in the refractive index of the solution is slower. A smaller refractive index indicates that in DCB the asphaltene entities are smaller than in toluene, which is consistent with their higher CAC. Additionally, if the asphaltene particles are smaller in DCB, their molar mass should be smaller. This is in agreement with work which found that the average molar mass of asphaltene is reduced with increasing polarity of the solvent. Other studies have also shown that fractions with greater solubility should exhibit lower tendency for aggregation. Our results support these findings, as asphaltene entities are smaller in the better solvent (DCB).

The leveling off of the solvatochromic shifts above the turnover point indicates that, after CAC, PRODAN no longer senses an increase in the refractive index. From the point of view of its local electronic microenvironment, the solution is not changing anymore. This could mean that as the solution near PRODAN becomes saturated with asphaltene and the weight fraction of free asphaltene particles (asphaltene molecules self-associated into small particles at very low concentrations, but not aggregated into large features) becomes constant, there are two explanations. First, PRODAN becomes surrounded by asphaltene and cannot sense any more changes. Second, PRODAN is still sensitive to changes in polarizability, but as more asphaltene are added to the solution, the formation of large aggregates does not affect the sensitivity of PRODAN. The first possibility suggests extremely high concentrations of asphaltene, which is not possible for the range of concentrations used here. More likely is the second explanation, because the weight fraction of the large aggregates is very small compared to that of the free particles, and possibly no large aggregates are located in the vicinity of PRODAN.

The asphaltene critical aggregation concentrations determined by us using the shifting method, i.e., the concentrations at which the smaller self-associated asphaltene particles begin to form larger aggregates, are within the range of other previously published values. Literature data suggest that, at room temperature, asphaltene molecules in toluene associate in small particles at a very low concentration (near 0.05 g/L). From fluorescence depolarization results, it was assumed that the onset of molecular self-association (most likely dimer formation) in toluene was observed at asphaltene concentrations as low as 0.06 g/L. If these values are true, the minimum asphaltene concentration that we used is well above the onset of dimer formation. This suggests that in our asphaltene solutions, the asphaltene molecules are already associated into small asphaltene particles, and the turnover points that we observed correspond to the formation of even bigger aggregates than dimers. Thermoptical studies suggest that aggregation continues up to around 2 g/L. These data are based as well on changes in the refractive index and appear to support our results, showing a similar linear trend for the low asphaltene concentration regime and a leveling off with further increase in concentration. The mechanism of asphaltene self-association into small particles proposed in this study is in agreement with others previously published. Recently, the molecular aggregation of asphaltenes was modeled as a simple linear polymerization. In this model, asphaltene were treated as free molecules in solution, with multiple active sites that can participate in the polymerization process and form aggregates between asphaltenes and PRODAN. Therefore, it was concluded that PRODAN is not specifically associating with the asphaltene molecule; i.e., PRODAN molecules are not distributed on the asphaltene particles. As more asphaltene particles are added to the solution, they simply alter the nature of the solvent that PRODAN senses. Thus, regardless of the number of PRODAN molecules, the average environment sensed by each of these molecules is the same. If we imagine that around each PRODAN molecule there is a meshlike distribution of asphaltene particles, then with the increase in asphaltene concentration the mesh points get closer together. In turn, with dilution we are just stretching the mesh below the CAC point.
gregates. From VPO (vapor pressure osmometry) molar mass experiments at elevated temperatures (50–130 °C), Cold Lake asphaltene aggregation appears to begin at concentrations below 0.5 g/L.\textsuperscript{9} The molar mass was found to increase with asphaltene concentration until a limiting value was obtained between 10 and 20 g/L.\textsuperscript{57} In these measurements, the leveling off of the molar mass suggested that asphaltenes reach a limiting size distribution.

From extrapolated values for the asphaltene molecule molar mass, it was estimated that the asphaltene polymer consists of two to six associated molecules. If we were to compare our results with those of the VPO method extrapolated at room temperature, then the limiting size region of the asphaltene polymer would correspond to our linear regime of shifting. This suggests that, at our starting concentration, the polymerization had already reached the size distribution limit. Otherwise, we should have observed a continuing increase in linear shift as the solutions became more concentrated, and not the leveling off of fluorescence. Unfortunately, the results from fluorescence and VPO cannot be directly compared since the temperatures at which the experiments were done are significantly different (22 °C vs 50 °C, respectively).

Recent viscometry investigations\textsuperscript{5} on asphaltene solutions at high temperatures identified and reported a second self-association point for asphaltenes. Defined as asphaltene “micelle coacervation point” (MCP), it signifies the formation of larger asphaltene entities. Following the same logic, these points might represent the CAC observed by us. Comparison of our data with the data obtained by viscometry is again not possible because of the temperatures employed (22 °C vs 90 °C, respectively).

In an attempt to confirm the aggregation model suggested by the shifting method, we have initiated studies of the asphaltene aggregate using atomic force microscopy (AFM). Our preliminary studies look promising and the results will be presented in a future paper.

Conclusions

This work presents a novel method to examine asphaltene association in aromatic solvents, by using the fluorescent probe PRODAN. Based on experimental information, a model was developed to explain the effect of asphaltene behavior on PRODAN fluorescence properties, and a definition for the critical aggregation concentration for asphaltene at room temperature was proposed. For low asphaltene concentrations (approximately 0.2–1.5 g/L, depending on the asphaltene source and solvent used), the shifting of PRODAN increased linearly with asphaltene fraction. The solvatochromism model for preaggregation developed in this work is valid for the linear regime, where we believe that the mixture can be regarded as a binary system. Following this logic, we obtained an equation that explains the linear dependence between the fluorescence shifting and asphaltene weight fraction. At higher concentration, PRODAN reports an asphaltene–solvent system which maintains constant polarizability. This implies a saturation effect, whereby the asphaltene entity that most affects the refractive index proximal to PRODAN is no longer increasing in concentration. Finally, the solvatochromic slopes and the critical aggregation concentrations appear to be correlated with the amount of resins present. However, more data are needed to confirm this.

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Supporting Information Available: Fluorescence spectra for PRODAN asphaltene solution from sources 2 and 3 in toluene and 1 and 3 in o-dichlorobenzene. This material is available free of charge via the Internet at http://pubs.acs.org.

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