

PETROLEUM ASPHALTENE MOLECULAR SIZE AND STRUCTURE

Henning Groenzin and Oliver C. Mullins

Schlumberger-Doll Research

Ridgefield, CT 06877

Key words: Asphaltene molecular size, Asphaltene molecular structure, Fluorescence depolarization

Abstract

The rotational correlation times of individual petroleum asphaltene molecules have been determined using fluorescence depolarization techniques, addressing an active, long standing controversy. Using simple theoretical models and using model independent comparisons with known chromophores, a range of asphaltene molecular diameters is obtained of 12 Å to 24 Å and indicates a molecular mass for asphaltene molecules of 500 to 1000 amu. An alkyl-substituted aromatic hydrocarbon with 7 fused rings is shown to correspond to the average molecular size of asphaltenes. Furthermore, the very strong correlation between molecular size and individual chromophore size establishes that the bulk of asphaltene molecules possess 1 or 2 aromatic chromophores per molecule.

I. INTRODUCTION

Petroleum asphaltenes are the heaviest, most aromatic component of crude oil. Asphaltenes are a complex molecular mixture which are colloiddally dispersed in crude oil with a mass fraction of 0 to 10% or more.¹⁻⁶ Asphaltenes generally impede producing, transporting and refining of crude oil resources for a variety of reasons; mitigation of deleterious effects requires a thorough knowledge of the chemical and physical properties of asphaltenes. In addition, the heavy ends of crude oils have many familiar applications related to protective coatings and road paving which can be enhanced by judicious application of asphaltene science. Many bulk properties of asphaltenes have been extensively studied by traditional methods such as NMR, IR, EPR, XANES and optical spectroscopy revealing a great deal about their molecular structure and aggregation propensities.¹⁻⁶

In spite of the wealth of information about asphaltenes, several fundamental properties are not known. The molecular weight of asphaltene molecules has been a matter of controversy for more than a decade. Colligative methods such as vapor pressure osmometry (VPO) generally yield high values¹⁻⁶ quite possibly due to aggregation. Mass spectral techniques yield much lower values (in spite of significant effort to rule out fragmentation).⁷⁻⁹ In addition, there has been considerable uncertainty about the (dominant) number of fused aromatic rings in the asphaltene moieties; estimates have ranged from 4 to >20.¹⁻⁶ Scanning tunneling microscopy (STM) has been used to image directly the aromatic (conductive) components of asphaltene molecules.¹⁰ Size estimates of the fused aromatic ring moieties from these images are approximately 10 Å. NMR¹¹ and optical techniques¹² indicate 7 fused rings on average. Furthermore, there has been uncertainty in the number of fused ring systems per asphaltene molecule with estimates varying widely.

Here, we analyze the fluorescence depolarization rates of very dilute solutions of asphaltenes. These rates give the molecular size with a robust, widely used model. In addition, we analyze known chromophores to provide a model independent analysis of these results. Furthermore, the known dependence of chromophore size to spectral properties has allowed us to correlate the rotation rate of chromophores imbedded in asphaltene molecules with the rotation rate of the molecule as a whole. The excellent correlation of chromophore size to total molecular size over a very broad range strongly implies that asphaltene molecules have one or two fused ring systems per molecule.

II. EXPERIMENTAL SECTION

For all solutions used for fluorescence work, we checked optical densities using a CARY 5 UV-visible-NIR spectrometer. For collection of fluorescence spectra, we employed the PTI C-72 + A-720 fluorescence spectrometer using a 75 watt Xe compact arc lamp source.

The PTI C-72 system was used for collection of fluorescence time-dependent depolarization spectra. This system employs a PTI GL-3300 nitrogen laser source along with a PTI GL-302 high-resolution dye laser with a fiber optic coupling to the measurement cell to excite the

fluorescence. The excitation and emission light from the cell are oriented 90° from each other with vertical polarization defined to be perpendicular to this plane. The wavelength of the PTI model 101 M emission monochromator is fixed while two Glan-Thompson polarizers are used to select the polarizations. One polarizer is placed at the output of the fiber optic, immediately before the measurement cell, and the other polarizer is placed at the entrance to the emission monochromator. Fluorescence time decay curves are collected for four polarizations; vertical on the source side, vertical on the emission side (v-v), vertical-horizontal (v-h), horizontal-vertical (h-v), and horizontal-horizontal (h-h).

The following procedure is used to acquire the time decay spectra; the laser firing triggers a box car delay gate which then triggers a high voltage pulse at known delay to the PMT. The short duration of the high voltage pulse "turns on" the PMT for a short time interval. The integrated current over this time interval from the PMT is detected. The delay time is sequentially scanned over the desired time range providing the fluorescence decay curve. The time resolution of the system is about 80 picoseconds.

A complete data set for one excitation and emission wavelength pair corresponds to acquisition of the four polarization combinations mentioned above. Typically, the total acquisition time for the four curves is 2 hours. Reproducibility of signal levels were checked periodically during the acquisition time to validate the data. Duplicate (or more) runs were performed for all wavelength pairs to assure precision. Typically, chi-square values of 1.2 or less were obtained for a good run. Changes in laser power during the run was associated with large values of chi-square.

The v-h curve has a higher intensity than the v-v curve. This is due to the fact that horizontal and vertical polarized light have different transmission efficiencies through the emission channel of the instrument. This effect can be compensated by introducing a calibration factor, which is usually denoted with a capital *G* and is defined as $G = I_{hv} / I_{vh}$. Where I_{ij} refers to excitation with *i* polarization and emission with *j* polarization. All experimental data sets are corrected by multiplication of *G* with I_{vh} . I_{vh} then refers to I_h , and $I_{hv} \cdot G$ to I_v .

The crude oil sample we used was obtained from Kuwait (UG8). We prepared the n-heptane insoluble asphaltene from this oil. Optical densities of all solutions were kept below 0.2 OD to avoid complications from self absorption. We maintained asphaltene concentrations at or below 0.025 g/liter for analysis. All rotational correlation times were determined at room temperature 19°C, and in toluene with a viscosity of 0.59 cP. Two dyes, obtained from Aldrich Chemicals, were also used in this study, octaethyl porphyrin (OEP) and a solar dye, N,N'-Ditridecyl-3,4,9,10-perylene-tetracarboxylic diimide.

In order to determine the rotational correlation time of the anisotropy decay, a difference curve $D(t)$ and a sum curve $S(t)$ according to Eq. 1 and 2 were created and fitted by a least squares method. The sum curve corresponds to the fluorescence decay alone. For the fluorescence intensity decay (sum curve) a double exponential decay was assumed. Since the anisotropy decay is much faster than the fluorescence decay for our cases, then the difference curve is governed by the anisotropy decay. Consequently, the difference curve was fitted in accordance to the theory to a single exponential decay. A mean lifetime of the fluorescence intensity decay was calculated and the rotational correlation time was obtained by combining the mean fluorescence intensity lifetime of the sum curve with the fluorescence intensity lifetime of the difference curve according to Eq. 3.

III. THEORY

We use the anisotropy decay treatment¹³ which approximates molecules as spheres. This model is widely used to analyze experimental data in part because inclusion of moderate molecular asymmetries does not affect calculated parameters too much.

The following definitions are used:

$$D(t) = I_v(t) - I_h(t) \quad (1)$$

$$S(t) = I_v(t) + 2I_h(t) \quad (2)$$

and

$$r(t) = \frac{D(t)}{S(t)} \quad (3)$$

where $I_{\parallel}(t)$ and $I_{\perp}(t)$ denote a detection of light linear polarized parallel and perpendicular to the linear polarized excitation and $r(t)$ represents the anisotropy of the fluorescence emission. The anisotropy is given by¹³

$$r(t) = \frac{2}{5} e^{-6Dt} \quad (4)$$

where D is given by

$$6D = \frac{kT}{V\eta} \quad (5)$$

where η is the viscosity of the solvent, which makes it easy to relate the fluorescence anisotropy to the volume of the sphere. The decay time of the anisotropy $\tau_{r,spk}$, the parameter of our experiment, can now be written as

$$\tau_{r,spk}^{-1} = \frac{kT}{V\eta} \quad (6)$$

IV. RESULTS AND DISCUSSION

Figure 1b shows the fluorescence emission spectrum of a dilute solution of UG8 asphaltene obtained with 365 nm excitation. This spectrum represents the overlapping spectra of the many chromophores contained within the asphaltene and indicates the range of aromatic moieties in asphaltenes. The asphaltene fluorescence emission is significant in the range of from 400 nm to 650 nm indicating the number of fused rings in the asphaltene chromophores is on the order to 4 to 10.¹² By selection of excitation and emission wavelength, one can select a subset of chromophores. Long wavelength excitation precludes excitation of small chromophores. Correspondingly, with short wavelength excitation, detection of fluorescence from large chromophores can be precluded by detecting short wavelength emission; large chromophores emit long wavelength fluorescence. The full range of chromophores is probed by tuning the excitation wavelength over the relevant spectral range, while keeping a fixed wavelength difference between excitation and emission.

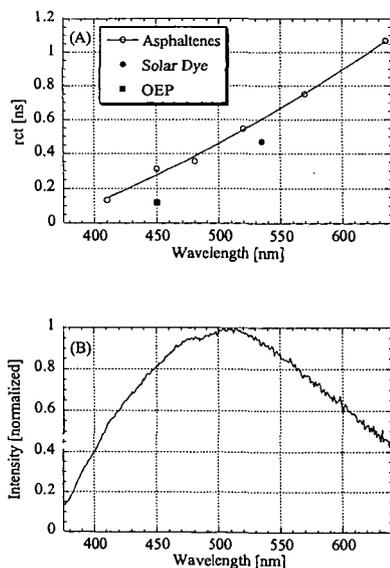


Figure caption 1. a) The rotational correlations of asphaltenes (and two dyes) vs emission wavelength. For each wavelength, the excitation wavelength is about 40 nm to shorter wavelength. b) the emission spectrum of the asphaltenes, showing the relevant spectral range.

Figure 1a shows the rotational correlation time of asphaltenes as a function of the emission wavelength. These emission wavelengths correspond to the largest populations of asphaltene chromophores as seen in Fig. 1b. For each point in Fig. 1a, the excitation wavelengths are ~40 nm to shorter wavelength. In addition, two known chromophores are also plotted in figure 1a to provide a model independent estimate of molecular size and molecular weight. Figure 1a is rich in results. The variation of a factor of 10 for the rotational correlation times for the most prominent asphaltene molecules. Using Eq. 6, one finds that the radius varies by about a factor of two. In table 1, we list molecular rotational correlation times along with the calculated diameters.

Table 1. Fluorescence absorption and emission wavelengths, rotational correlation times and the molecular diameter for asphaltenes and two dyes.

Sample	λ_{ex} (nm)	λ_{em} (nm)	τ_{rc} (ns)	Diameter(Å)
Asphaltenes	365	410	0.1340	12.0
	406	450	0.3115	15.9
	440	480	0.3561	16.6
	480	520	0.5464	19.2
	530	570	0.7518	21.3
	595	635	1.0688	24.0
Solar Dye	480	535	0.4704	18.2
OEP	406	450	0.1194	11.6

Table 1 shows the diameters for the asphaltenes to be in the range of 12 Å to 24 Å. The STM results quoted a mean value of the aromatic component of asphaltenes to be 10 Å in diameter. The fluorescence depolarization technique is sensitive to the size of the entire molecule, while the STM method is sensitive to the size of the aromatic portion only which is roughly 40% of the molecule. Both techniques yield comparable and small sizes for the asphaltene molecules.

Table 1 also lists the diameters for two dyes. Previously, the size of a metallo-OEP was determined by measuring the rotational correlation time using the very different technique, perturbed angular correlation of gamma rays (PAC).¹⁴ (The central metal in the porphyrin has no impact on the diameter of the porphyrin.) In that work, a spherical model was used and a diameter of 11.6 Å was found in excellent agreement with results reported here.

The two disk shaped dyes provide a good estimation of the molecular weight for asphaltenes. The rotational correlation time of the porphyrin OEP is at the lower limit for the asphaltenes. The molecular weight of the porphyrin is 535 amu giving the lower value estimation for the asphaltene molecular weights of 500 amu. The rotational correlation time of the solar dye is located roughly at the mean correlation time of the asphaltenes. The molecular weight of the solar dye is 755 amu giving an estimate of 750 amu for the mean asphaltene molecular weight. Extrapolating the size, molecular weight relation, we estimate the maximum molecular weight of the asphaltenes to be about 1000 amu.

Fig. 1 also shows that there is a monotonic, order-of-magnitude increase in the rotational correlation time across the asphaltene spectral range. That is, there is a strong correlation between the size of the asphaltene chromophore given by the emission wavelength and the size of the molecule, given by the rotational correlation time. This correlation requires that asphaltene molecules have only one or two chromophores per molecule. If an asphaltene molecule possessed say 10 chromophores per molecule, then there would be no correlation between chromophore size and molecular size. A small chromophore attached to a large molecule would exhibit the slow rotational correlation time of the entire, large molecule. The fact that we measure fast rotation for small chromophores and a factor of 10 slower rotation for large chromophores means that these chromophores are an appreciable fraction of the asphaltene molecule. Thus, asphaltene molecules possess one or two chromophores per molecule on average.

V. CONCLUSIONS

The asphaltene rotational correlation times have been measured and corresponding asphaltene molecular diameters are in the range of 12 Å to 24 Å. Using known chromophores, asphaltene molecular weights are estimated to be in the range of 500 to 1000 amu. Furthermore, a strong correlation between chromophore size and asphaltene molecular size indicates that asphaltenes possess 1 or 2 chromophores per molecules, confirming the small molecular weights. Our results

are consistent with previously reported STM results and mass spectroscopy results for petroleum asphaltenes. The confluence of evidence from three very different techniques should end the controversy over the values of asphaltene molecular weights.

VI. REFERENCES

- 1) G. V. Chilingarian, T. F. Yen, Eds., "Bitumens, Asphalts, and Tar Sands," Elsevier Scientific Publishing Co., New York, (1978)
- 2) J.G. Speight, "The Chemistry and Technology of Petroleum," Marcel Dekker, New York, (1980)
- 3) B.P. Tissot, D.H. Welte, "Petroleum Formation and Occurrence," Springer-Verlag, Berlin, (1984)
- 4) J.W. Bunger, N.C. Li, Eds., "Chemistry of Asphaltenes," American Chemical Society, Washington D.C., (1984)
- 5) E.Y. Sheu, O.C. Mullins, Eds., "Asphaltenes, Fundamentals and Applications," Plenum Press, New York, (1995)
- 6) O.C. Mullins, E.Y. Sheu, Eds. "Structures and Dynamics of Asphaltenes," Plenum Press, New York, (1998)
- 7) M.M. Boduszynski, in ref. 4.
- 8) M.M. Boduszynski, *Energy & Fuels*, 2, 597, (1988)
- 9) J.T. Miller, R.B. Fisher, P. Thiyagarajan, R.E. Winans, J.E. Hunt, *Energy & Fuels*, 12, 1290, (1998)
- 10) G.W. Zajac, N.K. Sethi, J.T. Joseph, *Scan. Micros.* 8, 463 (1994)
- 11) R. Scotti, L. Montanari, Ch 3 in ref. 6.
- 12) O.C. Mullins, Ch 2 in ref. 6.
- 13) T. Tao, *Biopolymers*, 8, 607, (1962)
- 14) O.C. Mullins, M. Kaplan, *J. Chem. Phys.* 79, 4475, (1983)