



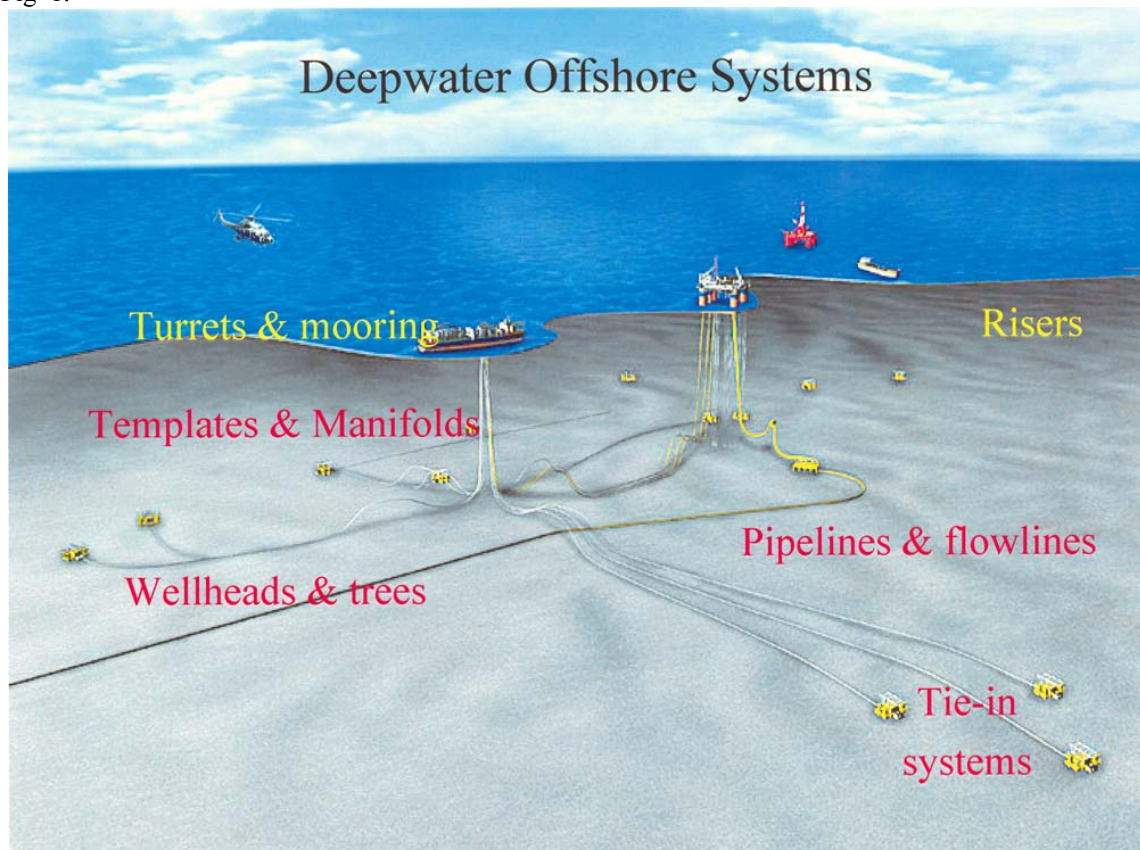
The Measurement Asphaltene Molecular Weight Using Time-Resolved Fluorescence Depolarization Spectroscopy

Introduction

Asphaltenes¹ are the most aromatic portion of crude oil varying in mass fraction from 0 %–20 %. High concentrations of asphaltenes adversely affect the value of crude oil; the high viscosities of asphaltic crude oils impede production and transportation, the low gasoline yield, coking proclivity and metal content of asphaltenes adversely impact refining. An increasing problem associated with asphaltenes is their tendency to phase separate as a tarry deposit of production pipe in Deepwater installations (see Fig. 1). Intervention is extremely costly in this arena, it is essential to understand asphaltene phase behavior.

Asphaltenes are defined by a solubility classification, for example, soluble in toluene insoluble in *n*-heptane. This definition captures the most aromatic component of crude oil, but does not specify asphaltene molecular structure. Clearly a broad range of compounds will be captured within this asphaltene definition. Many bulk measurements have been made on these materials to elucidate properties; ¹³C NMR yields the saturate fraction, X-ray Absorption Near Edge Structure (XANES) yields the sulfur and nitrogen functionalities, IR the oxygen functionalities. Various techniques including optical absorption and emission data coupled with ab-initio calculations, Scanning Tunneling Microscopy (STM), and ¹³C NMR all indicate that asphaltenes have between 4 to 10 fused rings in individual aromatic ring systems. One glaring problem has existed for 20 years, asphaltene molecular weight.

Fig 1.

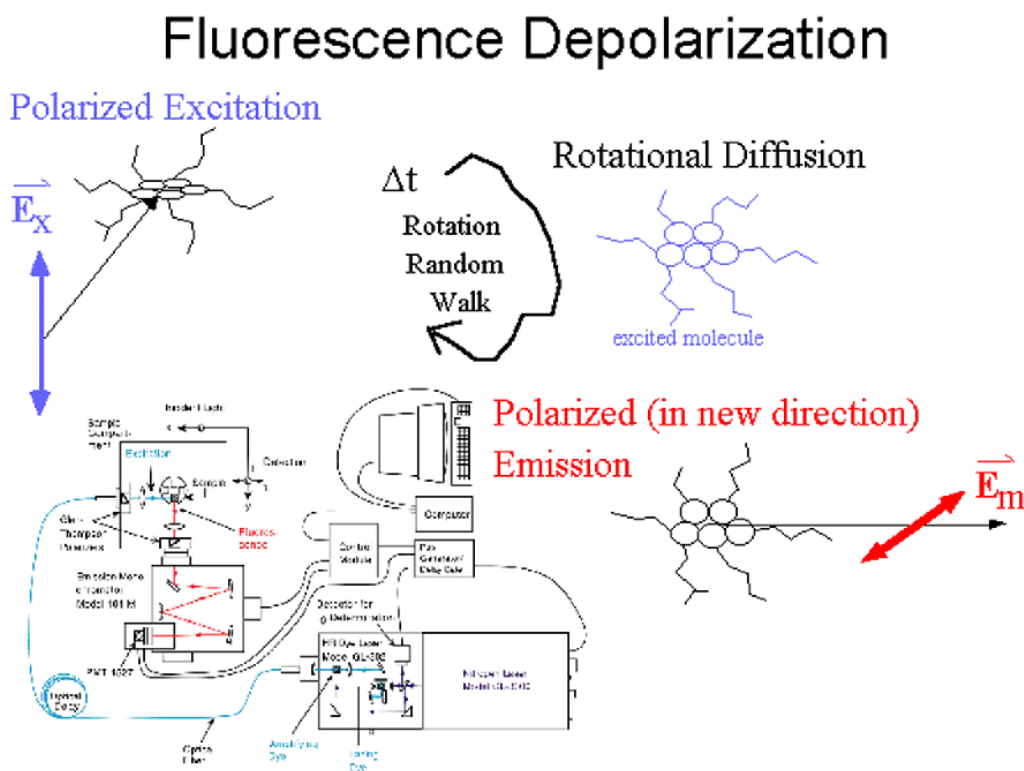


Asphaltenes are known to exhibit strong aggregation in solution, which impedes molecular weight determination. Colligative methods such as Vapor Pressure Osmometry with their requisite high concentrations yield high mass numbers (5000 amu is typical) presumably due to aggregation. Mass spectroscopy results generally yield low (~700 amu) but may suffer from volatilization problems and perhaps fragmentation. In addition, some techniques such as Laser Desorption Mass Spectrometry give widely varying results depending how baseline subtraction is performed. An order of magnitude controversy of molecular weight had persisted for two decades. The controversy essentially has been rooted in the question: is there a single fused ring system per molecule, or are the ring systems crosslinked by alkane linkages incorporating ~10 fused ring systems? A new technique that works with very dilute solutions and that is very sensitive to mass was needed.

Technique

Time-resolved Fluorescence Depolarization spectroscopy (FD) is optimally employed with very dilute solutions. The resulting rotational correlation times depend on the r^3 , the cube of the molecular radius achieving great sensitivity to molecular size, thus mass. Finally, the ability to select excitation and emission wavelengths allows interrogation of certain chromophores within the polydisperse asphaltenes. This technique is ideally suited to resolve the controversy over asphaltene molecular weight. Figure 2 shows a schematic of how the FD technique works.

Fig. 2



The exciting photon is polarized creating a preferred direction within the randomly oriented chromophores in solution. The excited molecules undergo rotational random walk, and at some measured Δt later, emission takes place. The loss of emission polarization with time provides a value for the rotational

correlation time τ_c . The Stokes-Einstein equation leads to the following expression for τ_c the rotational correlation time in terms of the molecular volume V , solvent viscosity η , and temperature T .

$$\tau_c = \frac{V\eta}{kT} \quad \text{Eq. 1}$$

Alternatively, known model compounds can be run to compare with the unknown asphaltenes. Both analysis methods have been employed for asphaltenes. FD gives molecular size that then has to be related to molecular weight. However, the order-of-magnitude uncertainty of asphaltene molecular weight can be resolved with FD in spite of the error incurred in converting size to weight.

Fluorescence depolarization studies were performed on the PTI LaserStrobe™ system which uses nitrogen pumped dye laser as the exciting source. Fluorescence emission is collected at right angles to the exciting light and sent through oriented crystal polarizers to measure the amount of depolarization. By using PRI's patented stroboscopic detection method, the amount of polarized light at any time after the laser pulse can be measured, producing a time-dependent fluorescence depolarization curve. The curve can be mathematically solved to produce a τ_c .

Results and Discussion

Figure 3 shows the results for a typical petroleum asphaltene.² The small correction times indicate the asphaltene molecules are not so big. The average τ_c is equivalent to that of an alkyl aromatic with a molecular weight around 750 amu. Eq. 1 provides a consistent analysis with corrections for molecular asymmetry being relatively small.² In concert with the well known case of a 'quantum particle in a box,' the smaller chromophores fluoresce to the blue while the larger chromophores fluoresce to the red. Here we see that small asphaltene chromophores have a τ_c that is 10 times smaller than that of the big, red-emitting asphaltene chromophores. This means that the chromophores are not crosslinked, otherwise they would show nearly equivalent τ_c 's.

Fig. 3

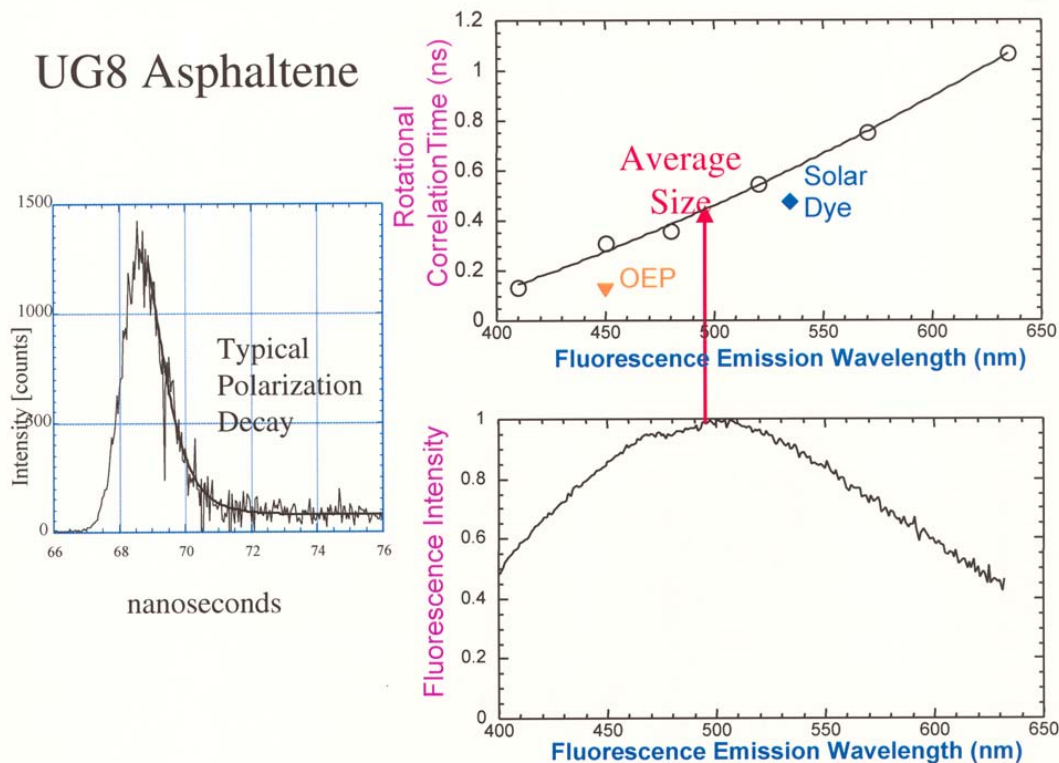
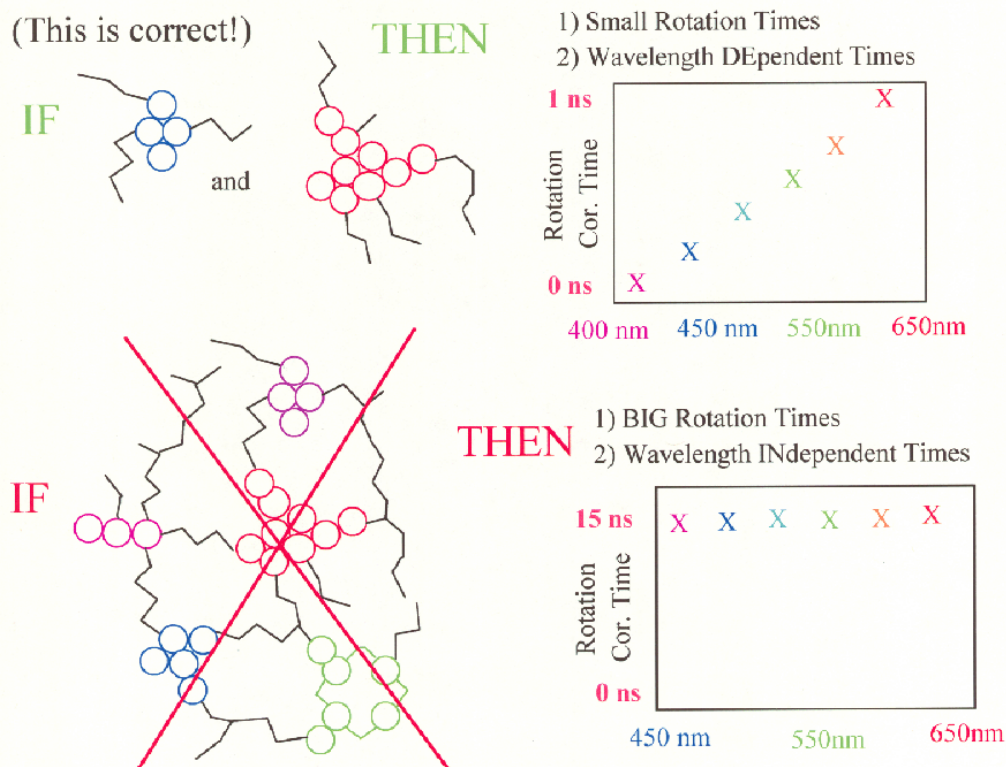


Figure 4 shows FD results expected for the two different scenarios. Thus, both the magnitude and the dispersion of τ_c with wavelength establishes independently that the asphaltene molecules are in the range of 500 amu to 1000 amu, not 10 times bigger. A previous fluorescence lifetime study shows that there is little energy transfer between chromophores in dilute asphaltene solutions obviating concern over this potential problem.³

Fig. 4



A comparison of many asphaltenes from different source materials (petroleum, distillation residue, coal) has established the range of variation of these materials, and strengthening the ‘low molecular weight’ result.⁴ By knowing the molecular weight, Francis Crick’s exhortation “To understand function, study structure”, can finally be followed. A recent study employing FD along with several other techniques has established that asphaltene solubility (and thus identity) is determined by the balance between van der Waals interaction in π -bond stacks vs. steric repulsion from alkane chains.⁵ Recent results from High-Resolution Transmission Electron Microscopy (HRTEM) strongly support these findings. This conversion of asphaltenes from enigmatic to first principles understanding is an enormous shift in vantage. Continuing studies of petroleum asphaltene particularly from problematic crude oils from Deepwater fields illustrate the power of FD studies to clarify the important asphaltene properties thereby enabling optimal solutions in crude oil production and refining.

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