

# About the Colloidal Nature of Asphaltenes and the MW of Covalent Monomeric Units

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Problems surrounding molecular aggregation, covalent molecular weight, and their experimental investigation in asphaltene chemistry are reviewed. Chromatographic, fluorescence spectroscopic, and mass spectroscopic (MS) methods for the investigation of these problems are surveyed and their merits and limitations discussed. Dissociation of asphaltene in dilute solution can be followed in time by monitoring the gel permeation retention time variation with the age of the solution. This way, Athabasca asphaltene was reported to dissociate from several thousand to less than about 1000 g mol<sup>-1</sup> molecular weight (MW) species in CH<sub>2</sub>Cl<sub>2</sub> solution to an extent of at least 80% in 14 days' time. The dissociation products represent the monomeric covalent molecules of asphaltene, and the remaining undissociated 20% could be slowly dissociating aggregates or high-MW covalent asphaltenes. The vapor pressure osmometry (VPO) determined number average MW of the same asphaltene was of the order of 4000 g mol<sup>-1</sup>, manifesting the aggregated state of the asphaltene at the higher concentrations used for VPO measurements. Of the MS methods, the most thoroughly investigated and proposed to be the best suited to asphaltene studies are the laser desorption ionization/matrix-assisted laser desorption ionization (LDI, MALDI) time-of-flight (TOF) MS. However, results obtained from various laboratories do not compare well; in some cases the bulk of the *m/z* lies below 1000, and in others it lies well above *m/z* 1000. <sup>252</sup>Cf plasma desorption MS data are more self-consistent in the sense that the bulk of *m/z* values always lie below *m/z* 1000. The upper *m/z* limit in most cases is around a few thousand *m/z* but may extend up to tens of thousands *m/z*. The problems affecting these methods for the determination of covalent, monomeric asphaltene MW distributions are fragmentation of covalent bonds, multiple ionization, and the production of cluster ions. Fluorescence-based methods are not suitable for MW measurements in asphaltene; the reasons for this are discussed in detail.

## Introduction

Molecular weight and its distribution, along with the dynamic association of individual covalent molecules, represent attributes that determine the colloidal behavior of asphaltene solutions. Many researchers have investigated each of these attributes over the past decades and each has been found to be a difficult problem to explore, especially in quantitative terms.

Until 1979, petroleum asphaltenes in solution were thought of as aggregates of several high-MW covalent asphaltene molecules that were peptized in crude oil by lower-MW resins molecules. It was in that year that Selucky, Kim, Skinner, and Strausz (SKSS)<sup>1</sup> showed that gel permeation chromatography GPC of very dilute solutions of Athabasca *n*-pentane (*n*-C<sub>5</sub>) asphaltene features a trimodal distribution, indicating three different MW distribution domains. Moreover, it was also found<sup>1</sup> that the distribution depends on the age of the

asphaltene solution and with increasing time, redistribution occurs primarily toward later elution (lower MW and size). This process is extremely slow in terms of typical molecular times (10<sup>-12</sup> s) and can be observed over several weeks (10<sup>6</sup> s). Its presence provides unambiguous evidence for a dynamic equilibrium in asphaltene solutions between low-MW single molecules and their aggregates. At that time, it was felt that given sufficient time (or shifting the equilibrium by other means) the dissociation would go to completion. However, subsequent studies on asphaltenes prepared by conventional solvent precipitation using *n*-C<sub>5</sub> revealed

(1) (a) Selucky, M.; Kim, S. S.; Skinner, F.; Strausz, O. P. Structure-Related Properties of Athabasca Asphaltene and Resins. Presented in the Division of Petroleum Chemistry at the Fall Meeting of the American Chemical Society in Washington, DC, 1979; (b) Selucky, M.; Kim, S. S.; Skinner, F.; Strausz, O. P. In *Chemistry of Asphaltenes*; Bunger, J. W., Li, N. C., Eds.; Advances in Chemistry Series 195; American Chemical Society: Washington, DC, 1981; pp 83–118.

the presence of substantial concentrations of non-asphaltenic substances (low-MW hydrocarbon and resins) in the precipitated asphaltene. This, along with the observation that the fluorescence yield from dilute solutions of asphaltene depends on the MW of the GPC-separated fractions of the asphaltene and the direct experimental observation of equipartitioning of the non-asphaltenic substances between the *n*-C<sub>5</sub> precipitant and the precipitating asphaltene, necessitated the revision of this assumption. At the present time, there is no experimental evidence against the presence of high-MW molecules in petroleum asphaltenes. Consequently, the question to formulate today is not whether there are any low-MW asphaltene molecules present—that was answered affirmatively years ago—but whether any high-MW molecules are present alongside the lighter constituents.

Recently, the question of the size of the covalent molecules has awakened renewed interest and has become the focus of investigations employing different methods. Since these current investigators apparently were unaware of SKSS's earlier work on the subject, in the following, we will reexamine the puzzle of covalent molecular size, the process of molecular aggregation of asphaltenes, and related problems in some detail, along with the shortcomings of several methods employed for its investigation at the present time.

### Discussion

The composition of asphaltene varies with the methods used for its isolation—usually, precipitation with *n*-C<sub>5</sub> or *n*-C<sub>7</sub>. Precipitation with *n*-C<sub>7</sub> affords smaller amounts (by 15–98%) of asphaltene than with *n*-C<sub>5</sub>. This difference represents resins and low-MW asphaltene components which can be separated from the asphaltene by several methods, including: (i) acetone extraction<sup>2–5</sup> (Soxhlet, one week); (ii) successive precipitations (7–8 times);<sup>6</sup> and (iii) GPC.<sup>7</sup> In the case of Athabasca asphaltene and *n*-C<sub>5</sub> as precipitant, the three methods give about the same yield for the material removed from the asphaltene, (~21–22%). The color of the material isolated by acetone extraction is deep reddish-brown and that of the residual asphaltene is black (as opposed to the dark brown color of the whole asphaltene). The MW of the reddish-brown material is about one-third to one-half of that of the whole asphaltene and the MW of the residual asphaltene is correspondingly higher.<sup>2</sup>

The acetone extract of Athabasca asphaltene was examined for its chemical composition. Series of hydrocarbon-type biological markers<sup>3</sup> along with oxygen,<sup>4</sup> nitrogen,<sup>5</sup> and sulfur compounds,<sup>4</sup> (see Table 1), were identified. Similarly, several series of N compounds,

**Table 1. Compounds Identified in Athabasca *n*-C<sub>5</sub> Acetone Extract**

Oxygen compounds	Name	Structure	Number of Species
ketones	fluorenones		16
	benzofluorenones		28
	dibenzofluorenones		19
carboxylic acids	tricyclic terpenoid		6
	pentacyclic terpenoid		6
	– of dibenzothio- phene		20
	– of <i>n</i> -alkanes		17
	– of anthracene/ phenanthrene		12
	– of fluorene		7
	– of fluorene-9-ol		10
– of fluorene-9-one		9	
alcohols	<i>n</i> -alcohols, C <sub>8</sub> –C <sub>18</sub>		11
sulfoxides	terpenoid:		
	bicyclic		12
	tricyclic		6
	tetracyclic		12
	hexacyclic		4
	(tetrahydrobenzo) dibenzothiophene		5
Hydrocarbons		Structure	
	dicyclic terpanes		
	tricyclic terpanes		
	hopanes		
	rearranged steroids		
		etc.	

(2) Strausz, O. P.; Mojelsky, T. W.; Faraji, F.; Lown, E. M.; Peng, P. *Energy Fuels* **1999**, *13*, 207–227.

(3) Peng, P.; Morales-Izquierdo, A.; Hogg, A.; Strausz, O. P. *Energy Fuels* **1997**, *11*, 1171–1187; Ignasiak, T. M.; Kemp-Jones, A. V.; Strausz, O. P. *J. Org. Chem.* **1977**, *42*, 312–320.

(4) Frakman, Z.; Ignasiak, T. M.; Lown, E. M.; Strausz, O. P. *Energy Fuels* **1990**, *4*, 263–270.

(5) Frakman, Z.; Ignasiak, T. M.; Montgomery, D. S.; Strausz, O. P. *AOSTRA J. Res.* **1988**, *4*, 171–179. Frakman, Z.; Ignasiak, T. M.; Montgomery, D. S.; Strausz, O. P. *AOSTRA J. Res.* **1987**, *3*, 131–138.

(6) Torres, M.; Laun, E. M.; Strausz, O. P. To be published.

(7) Ignasiak, T. M.; Kotlyar, L.; Samman, N.; Montgomery, D. S.; Strausz, O. P. *Fuel* **1983**, *62*, 363–370.

Table 2. GPC Separation of Athabasca Asphaltene

fraction	wt %	MW g mol <sup>-1</sup>	wt %			H <sub>a</sub> /C <sub>a</sub>	C <sub>arom</sub> % C <sub>tot</sub>
			N	O	S		
1	22.5	16900	1.2	3.0	7.9	1.21	35
2	30.5	13700	1.2	2.8	8.0	1.23	34
3	13.6	7100	1.1	2.6	7.9	1.25	39
4	11.1	3400	1.1	2.9	7.4	1.29	41
5	20.8	1200	1.1	3.9	7.0	1.23	48
whole asph.		3800 (calcd)					
		3600 (expt)					

including alkylated benzocarbazoles along with smaller amounts of carbazoles, dibenzocarbazoles, and tetrahydrobenzocarbazoles with series formulas C<sub>n</sub>H<sub>2n-21</sub>N, C<sub>n</sub>H<sub>2n-15</sub>N, C<sub>n</sub>H<sub>2n-27</sub>N, and C<sub>n</sub>H<sub>2n-23</sub>N, respectively, as well as series of vanadyl porphyrins in the carbon range 22–52 and small amounts of vanadyl porphyrin tetra-carboxylic acids, C<sub>n</sub>H<sub>2n-24</sub>N<sub>4</sub>O<sub>8</sub>, were detected.<sup>5</sup>

Needless to say, the several hundred compounds identified cannot be considered to belong to the asphaltene fraction. They are present as coprecipitated resins incorporated into the high-MW, polydispersed asphaltene aggregates. The same resin molecules are also present in the *n*-pentane-soluble maltene fraction of the bitumen. In other words, the resin fraction of the maltene is equipartitioned between the *n*-C<sub>5</sub> solution and the solid asphaltene. This is not unusual since the simple initial steps in compound class separation of the bitumen or crude oil never afford ideal separation. To obtain relatively clean fractions the initial separation step always has to be followed up with further refining.

Asphaltene is defined as the toluene-soluble but *n*-C<sub>5</sub>- or *n*-C<sub>7</sub>-insoluble portion of crude oil. However, as discussed above, on precipitation some *n*-C<sub>5</sub>-soluble maltene material coprecipitates with the asphaltene. Upon dissolution of the precipitate, the coprecipitated *n*-C<sub>5</sub>- or *n*-C<sub>7</sub>-soluble maltene material redistributes itself between the bulk solution phase and the asphaltene aggregates in solution. After six or seven precipitations nearly all the *n*-C<sub>5</sub>- or *n*-C<sub>7</sub>-soluble material is removed from the asphaltene. The maltene fraction cannot be removed from the asphaltene part by simply washing the precipitate with the precipitant, suggesting that this material is strongly bound to the asphaltene aggregates. However, the maltene fraction can be removed by exhaustive Soxhletting the acetone extract with *n*-pentane.<sup>3</sup>

When an asphaltene solution is further diluted, the equilibrium between solution and adsorbed phase shifts, and this material desorbs from the asphaltene molecular aggregates. The desorbed components then go into the solution phase, causing an apparent decrease in the vapor pressure osmometry VPO MW of the dissolved asphaltenes. Further dilution may lead to more complicated changes in the asphaltene aggregates, as will be described below.

Chromatographic studies<sup>1</sup> have led to new insights into the colloidal structure and properties of Athabasca asphaltene solutions and will be discussed first.

**GPC Fractionation.** Athabasca asphaltene has been separated by GPC (solvent CH<sub>2</sub>Cl<sub>2</sub>, column  $\mu$ -Styragel 1000) into five fractions<sup>7</sup> (Table 2) ranging in MW from 1200 to 16900 g mol<sup>-1</sup>. It is seen there that Athabasca asphaltene in 3–5% benzene solution shows a (VPO) MW distribution extending from at least 1200 to over

Table 3. Separation of Athabasca Asphaltene on Silica Gel

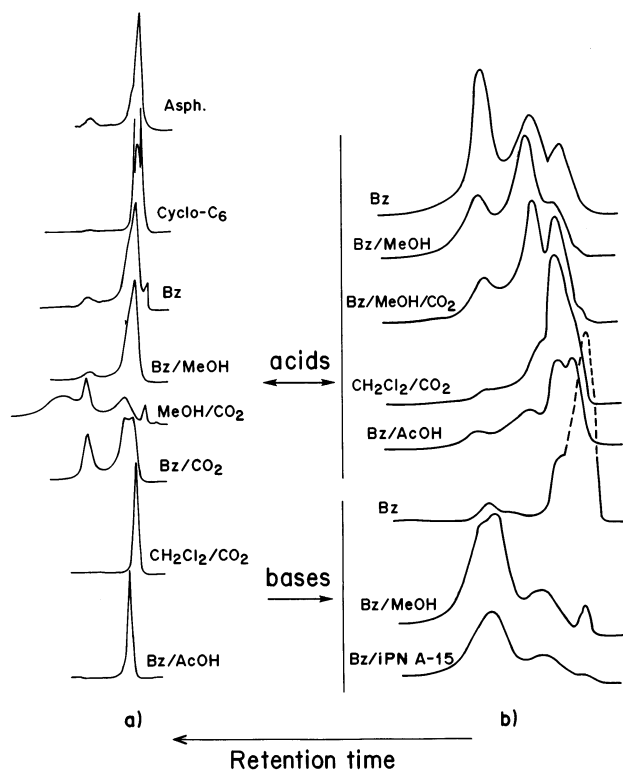
fraction	wt %	cumulative wt %	MW g mol <sup>-1</sup>
<i>n</i> -pentane	0.3		
<i>n</i> -C <sub>5</sub> /15% Bz <sup>a</sup>			
<i>n</i> -C <sub>5</sub> /30% Bz-I	5.4		8200
<i>n</i> -C <sub>5</sub> /30% Bz-II	1.9	7.3	6400
<i>n</i> -C <sub>5</sub> /45% Bz	3.5	10.8	4900
<i>n</i> -C <sub>5</sub> /60% Bz-I	3.8	14.6	4400
<i>n</i> -C <sub>5</sub> /60% Bz-II	2.8	17.4	5400
<i>n</i> -C <sub>5</sub> /80% Bz	3.4	20.8	3500
Bz	2.5	23.3	3500
Bz/15% CH <sub>2</sub> Cl <sub>2</sub>	2.5	25.8	2600
Bz/50% CH <sub>2</sub> Cl <sub>2</sub>	1.1		4200
CH <sub>2</sub> Cl <sub>2</sub>	1.7		2900
CH <sub>2</sub> Cl <sub>2</sub> /15% MEK <sup>b</sup>	17.3		<sup>e</sup>
CH <sub>2</sub> Cl <sub>2</sub> /50% MEK	1.1		
MEK	1.5		
MEK followed by Bz	0.9		
MEK followed by THF <sup>c</sup>	22.9	72.3	
THF/15% MeOH-I	4.5	76.8	
THF/15% MeOH-II	12.0	88.8	
THF/50% MeOH	2.5		
followed by Bz	0.5		
followed by CH <sub>2</sub> Cl <sub>2</sub>			
followed by THF	0.6		
THF/15% H <sub>2</sub> O	6.6		
THF/10% <i>i</i> PrN <sup>d</sup>	0.5		
THF/25% <i>i</i> PrN	0.9	100.4	

<sup>a</sup> Bz = benzene. <sup>b</sup> MEK = methyl ethyl ketone. <sup>c</sup> THF = tetrahydrofuran. <sup>d</sup> *i*PrN = isopropylamine. <sup>e</sup> MWs were not determined, either for lack of sample or because of some problems with THF and MEK.

16900 g mol<sup>-1</sup>. Interestingly, Table 1 shows the presence of molecules with MW as low as 200 g mol<sup>-1</sup>. The composition and properties of the fractions isolated vary and, for example, the percentage aromaticity appears to slightly decline with increasing MW except in going from fraction 5 to 4 where it is more substantial.<sup>8</sup>

**Adsorption on Silica Gel.** The first fraction eluted (*n*-C<sub>5</sub>/30% Bz) in 5.4% yield had the highest VPO MW (8200 g mol<sup>-1</sup>) of all the fractions (Table 3). It exhibited IR absorptions most closely resembling those of a high-MW hydrocarbon fraction, with hardly any contributions from functional groups. The next several fractions, eluted with increasing solvent-power hydrocarbon mixtures up to an aggregate amount of eluates of 24%, featured a progressive decline in MW down to 3500 g mol<sup>-1</sup>. With increasing polarity of the solvent, that of the eluted fraction increased, as indicated primarily by the carboxylic carbonyl and OH absorptions (1700 and 3400 cm<sup>-1</sup>). In the methyl ethyl ketone eluate, these absorptions, along with those in the 1030–1250 cm<sup>-1</sup> region, were quite prominent. The last-eluting material (23%) with the solvents tetrahydrofuran + (CH<sub>3</sub>OH or H<sub>2</sub>O or isopropylamine) would probably correspond to fraction 5 in the GPC separation whereas the first seven fractions eluted with hydrocarbons, amounting to 23.3% (Table 3) would approximately correspond to the highest-MW fraction 1. Thus, from these experiments, we can conclude that the highest-MW (23%) represents the least polar, least aromatic portion of Athabasca asphaltene even though its elemental composition does not show any substantial difference from the other fractions. Therefore, the differences in polarity must be due to

(8) Cyr, N.; McIntyre, D. D.; Toth, G.; Strausz, O. P. *Fuel* **1987**, *66*, 1709–1714.



**Figure 1.** (a) GPC of acidic subfractions of Athabasca asphaltene: 50  $\mu$ L, 0.05% solution; column, Styragel 1000; solvent,  $\text{CH}_2\text{Cl}_2$ . (b) GPC profiles of acidic and basic subfractions from Athabasca asphaltene (0.05% solution). UV detector at 254 nm.<sup>1</sup>

**Table 4. Ion Exchanger Chromatographic Fractionation of Athabasca Asphaltene**

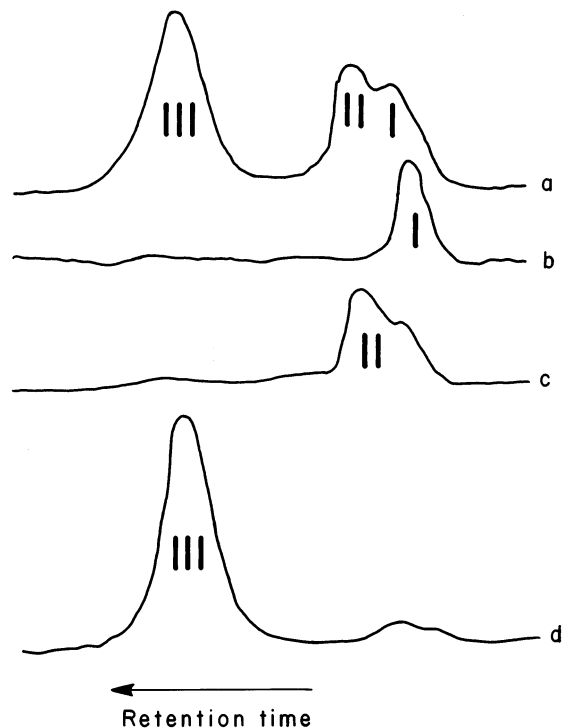
fraction	yield, wt %
acids	39.8
bases	23.3
neutrals	20.2
amphoterics	16.9

differences in the nature and molecular distribution of the polar groups present in the fraction.

**Ion Exchanger Adsorption.** The functionalities in the asphaltene molecules were examined by ion exchanger chromatography (Table 4). Of the four fractions listed, the least polar (20.2%), should be the neutrals, in reasonably good agreement with the silica gel adsorption and GPC fractionation results (*v.s.*).

In the following, we will consider the available data on the dynamics of MW fractionation.

**GPC Studies on Dilute Asphaltene Solutions.** In very dilute solutions ( $\leq 0.05$ – $0.01\%$ ), asphaltene gave GP fingerprints that were different from those of more concentrated ones.<sup>1</sup> Also, when the various anion and cation exchanger subfractions were subjected to GPC (Figure 1) they produced characteristically different fingerprints. Another observation reported was that the GP fingerprints varied with the time that had elapsed since the dissolution of the sample in  $\text{CH}_2\text{Cl}_2$ . This can be seen by comparing the GP chromatograms of the cation subfractions (Figures 1a and 1b). The only difference between the experimental conditions for the two acidic subfraction sets was that in the former one (Figure 1a) the samples were dissolved and run on the same day. In the latter set (Figure 1b), the samples were

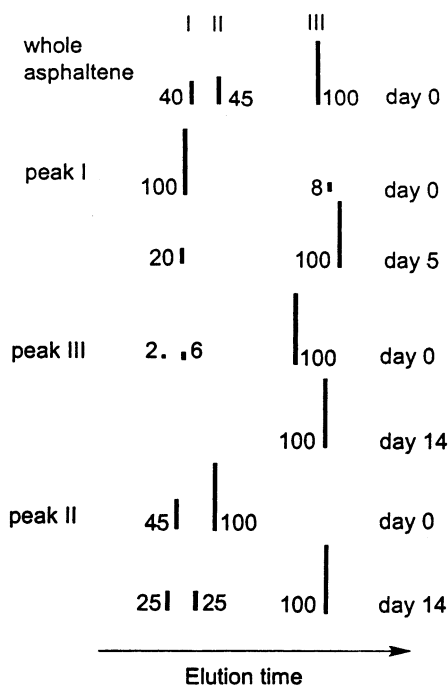


**Figure 2.** GPC chromatograms of whole asphaltene, a, and rechromatographed fractions I, II, and III (b–d). UV detector at 254 nm.<sup>1</sup>

dissolved on one day and the separation was done on the following day. Only the last two fractions ( $\text{CH}_2\text{Cl}_2/\text{CO}_2$  and  $\text{Bz}/\text{AcOH}$ ) in Figure 1a appear to show unimodal distribution while all the others and the whole asphaltene (Figure 1) show polydispersity. In some cases the polydispersity was such that a number of distinctly separate peaks can be recognized in the chromatograms. Among all the acidic and basic subfractions, there is only one, namely, the benzene eluant from the cation exchanger column that displays fingerprints similar to those of the whole asphaltene.

The differences between the various anion exchanger subfractions shown in Figures 1a and 1b are caused by the difference in the “age” of the solution, manifesting the occurrence of extensive redistribution in the size of the aggregates of asphaltene. To explore this phenomenon in more detail, samples of the whole asphaltene and its various fractions from the ion exchangers were freshly dissolved in  $\text{CH}_2\text{Cl}_2$  to give 0.05% solutions and the first GP chromatograms (using  $\text{CH}_2\text{Cl}_2$  as eluent) were immediately recorded. The individual peaks were separately collected and the separation was repeated to produce sufficient amounts of sample. The separated fractions were then rechromatographed under identical conditions as before. After each injection the sample was flushed with nitrogen, sealed airtight, and stored in the dark at room temperature.

The GP chromatograms obtained for the whole asphaltene and its fractions are shown in Figure 2 and the results of repetitive analyses on each fraction in Figure 3. As seen there, the distribution for the whole asphaltene is trimodal and one of the peaks, (lowest-MW), is completely detached from the others. The relative peak areas are plotted in Figure 3 in the form of bar diagrams. The measured area of peak 3 was corrected for the presence of the 22% acetone solubles,



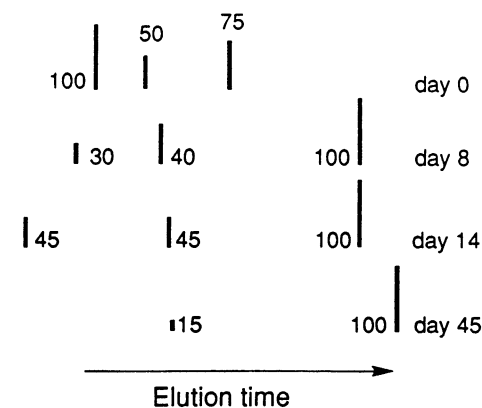
**Figure 3.** Time study of changes in the GPC profiles of fractions I–III in Figure 2.<sup>1</sup>

assuming that all these materials (cf. Table 1, etc.) would elute with peak 3 and the total residue was then normalized to 100%. The percentage values thus obtained for peaks 1, 2, and 3, which represent only a ballpark distribution of materials, were 27.7, 31.2, and 41.1%. Peak 1 represents the highest-MW fraction, which, in 5 days, underwent extensive redistribution to longer retention time (lower-MW). The residue left behind after 5 days is ~18%. Careful microscopic examination of the stored solution prior to chromatographic analysis showed no signs of any precipitate formation. Therefore, the occurrence of redistribution is a proof that 82% of this fraction consists of molecular aggregates which, upon standing in  $\text{CH}_2\text{Cl}_2$  solution, slowly dissociate into their low-MW components.

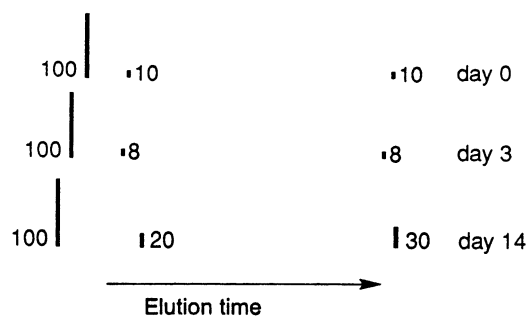
Peak 3, (lowest-MW), is contaminated by small amounts of material from peaks 1 and 2. After 14 days, the small amounts of contaminants disappeared and the major peak drifted to somewhat longer time (lower MW).

Peak 2 (Figure 2) is incompletely separated from peak 1 and the starting material in Figure 3 seems to contain about 31% material from the latter peak. Moreover, after 14 days' redistribution, the two peaks in the residual material are even less resolved and attempts for their separation would thus be even less reliable. Therefore, the best route to follow is to treat the whole doublet peak as if it was a single one and, on this basis, the residue amounts to 33% of the starting material.

From these diagrams, it can also be observed that in each case the residual redistributed peak drifted to shorter retention times relative to their original position in the zero-day distribution. We attribute this phenomenon to the faster dissociation rate of the lower-MW species within each envelope and/or to the various types of reassociations once some part of the aggregate had dissociated to small-MW species. The dependence of the dissociation rate on aggregate size is then due to the variation in the number of individual molecules and of



**Figure 4.** Time study of changes in the GPC profiles of the acidic Bz/MeOH fraction of Athabasca asphaltene.<sup>1</sup>



**Figure 5.** Time study of changes in the GPC profiles of the acidic Bz fraction of Athabasca asphaltene.<sup>1</sup>

the changes in the intermolecular contact area with the size of the aggregates. Apparently, a smaller number of individual molecules are present in the lower-MW aggregates and each one is bound to them by weaker intermolecular bonds as compared to the higher-MW aggregates. Weaker bonds mean shallower potential wells and thus shorter lifetimes for the molecular bound states.

Next examined were the redistribution processes of two of the anionic ion exchanger acidic subfractions, namely, the lowest MW (5.3%, VPO 1450  $\text{g mol}^{-1}$ ; benzene/MeOH fraction, IRA-904 column) and the highest MW (10.9%, VPO 5300  $\text{g mol}^{-1}$ ; benzene fraction, A-27 column) Figures 4 and 5. In Figure 4 (concentration ~ 0.0026%) three peaks are initially visible, constituting ~ 44.4, 22.2, and 33.3% of the total. The longest-retention-time peak disappears rapidly and after 8 days is converted to a much longer-retention-time peak. After 14 days, there is still 47.4% residue left and at 45 days, 13%. In Figure 5 (concentration ~ 0.0055%) one major (83.3%) and two minor (8.3% each) peaks are visible. The major peak and one of the minor ones have a very short retention time and do not convert appreciably to low-MW products upon standing. After 14 days, 12.7% conversion of the two high-MW peaks took place.

From the results on the time dependence of the size distribution and aggregation processes observed, we can conclude that:

- at sufficiently low concentrations,  $\leq 0.05\%$ , the GPC chromatograms of a solution of asphaltenes from Athabasca bitumen, as well as its ion exchanger chromatographic subfractions, display considerable polydispersity

which, in some cases, may manifest itself in the appearance of a number of discrete peaks in the chromatogram;

- GP chromatograms of the various subfractions of asphaltenes from the Athabasca bitumen exhibit characteristic differences;

- in dilute solutions,  $\leq 0.05\%$ , upon standing in the dark at room temperature in an inert atmosphere a slow but extensive redistribution of the asphaltene molecular units takes place, manifesting itself in a drift of the GPC peaks to longer retention times (smaller aggregate sizes);

- the occurrence of redistribution provides an unambiguous proof for the presence of molecular aggregates comprising a sizable portion of the asphaltene;

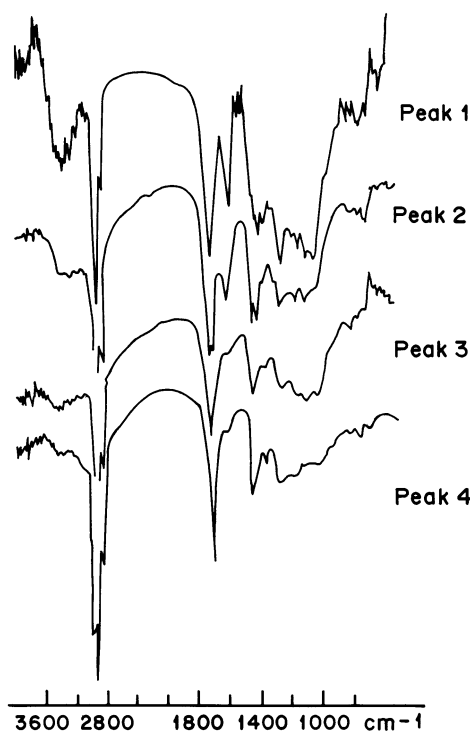
- the conversion of the various high-MW fractions in 14 days to low-MW products as described above ranged from 13% to  $\geq 83\%$ , with the exception of the lowest-MW fraction, peak 3, of the whole asphaltene (Figure 2), of which 100% converted to still lower-MW products (Figure 3). Even after standing for 45 days, some fraction left a significant amount of *unconverted* high-MW residue behind. In the whole asphaltene from Athabasca bitumen, the unconverted residue is estimated to be  $\sim 16\%$ . This observation suggests that the core of the asphaltene aggregates in concentrated solutions,  $\geq 1\%$ , may comprise high-MW covalent molecules, which are surrounded by varying numbers of smaller ones held together by various intermolecular bonds. This result may be interpreted as providing additional support for the model proposed by Nellesteyn, and Pfeifer and Saal for the colloidal particles of asphaltenes in solution many years ago. Current studies in the initial stages of the aggregation process are intended to shed light on the question of the existence of a high-MW covalent core in the aggregates of asphaltenes.

- the GPC method is ideally suited to the investigation of the aggregation–dissociation processes and dispenses with the necessity of employing any expensive equipment requiring theories with complex interpretations;

- the GPC method gives an insight into the details of molecular and aggregate size distribution without distorting or affecting it; moreover, it makes possible the separation of the distinct molecular aggregates under any given chromatographic peak and study them separately.

It should be noted that in a recent size exclusion chromatographic (SEC) study on coal tar pitches,<sup>9</sup> similar patterns of elution profiles have been observed, insofar as each of the reported chromatograms featured two discrete peaks separated by several minutes in elution time.

The splitting of the GPC peaks into discrete bands is an interesting molecular phenomenon. Minor effects due to variations in solubility, molecular size, or sorption processes could not explain such large splitting. One potential source of the splitting in the molecular size distributions could be some form of selectivity in the aggregation. To gain information about the nature and role of the chemistry involved here, one of the acidic subfractions (the MeOH/CO<sub>2</sub> one in Figure 1a) was further separated into its four components yielding ca.



**Figure 6.** FTIR spectra of fractions collected from the individual peaks of the MeOH/CO<sub>2</sub> fraction (cf. Figure 1a).<sup>1</sup>

0.01% solutions. The IR spectra of each of these components are shown in Figure 6. As seen, the hydroxylic H bonding region (3600–2500 cm<sup>-1</sup>) features a large, sharp peak in the first spectrum and gradually decreases and becomes broader in subsequent ones. Another progressive change that can be observed is in the proportion of the carboxylic carbonyl absorption (ca. 1700–1725 cm<sup>-1</sup>) to that of the aromatic C–C one (ca. 1600 cm<sup>-1</sup>) where the ratio tends to increase with increasing retention times of the peaks. At the same time, the combined absorption over the 1250–1000 cm<sup>-1</sup> range (carboxylic acids, alcohols, etc.) becomes less articulated and smaller, hand in hand with the decreasing H bond absorption. These IR spectra reveal different chemical compositions in the four different MW peaks in the GP chromatogram. This points to the continuous nature of the changes in the chemical compositions of these four different size aggregate peaks. Evidently, the highest-MW aggregates are formed from those molecules, which have the highest aromatic, carboxylic acid, and, perhaps, alcohol content. These findings are in line with asphaltene being a typical representative of a random self-assembling supra-molecular system. In these aggregates, the intermolecular interactions, according to molecular mechanics calculations in model asphaltenes that have a large aromatic part,<sup>10</sup> are dominated at the equilibrium distances by van der Waals forces whereas Coulombic ones contribute around 10%. Consequently, for this type of asphaltene the primary interaction is between the electron-rich aromatic systems followed by H bonding. H bonding, involving carboxylic acids and, less efficiently, alcohols, has also been computed to have sizable adsorption enthalpies and thus contribute to the aggregation. If the

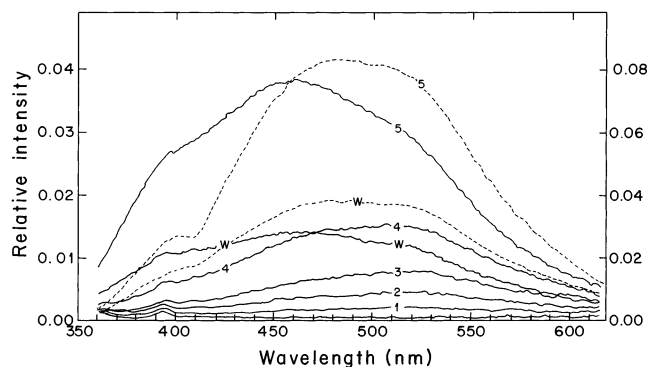
(9) Lazaro, M.-J.; Islas, C. A.; Herod, A. A.; Kandiyoti, R. *Energy Fuels* **1999**, *13*, 1212–1222.

(10) Murgich, J.; Abanero, J. A.; Strausz, O. P. *Energy Fuels* **1999**, *13*, 278–286.

aromatic regions of asphaltenes are small or not readily available for interaction, H bonding may become the strongest intermolecular bond. Therefore, it follows that molecules rich in such type of adsorption sites will tend to form larger and more stable aggregates than the other ones. Molecular recognition processes will favor the interaction between molecules: (a) of complementary shapes that have the least steric interference, and (b) that have the strongest H bonding sites. Asphaltene molecules that fulfill these requirements will form the most stable aggregates. In systems of great chemical complexity such as solutions of asphaltenes, this means that only the molecules that have the right shapes and/or sites will form the more stable aggregates and others with less efficient ones form aggregates of much shorter lifetimes. The existence of well-defined GPC peaks around certain MW values suggests that the aggregates are formed by a small set of different molecules, indicating the existence of significant selectivity in the intermolecular interactions. If only nonselective interactions were operating there, one should find a continuous distribution around the most likely MW values for the aggregates. The extraordinary long lifetime of some of the aggregates ( $10^6$  s) shows that the detachment of asphaltene molecules from them is a very rare event. This may be due to several reasons. One of them may be the fact that many favorable intermolecular contacts have to be broken simultaneously during the separation. It is also likely that some degree of molecular tangling may be present in these aggregates due to the existence of polymethylene-bridged structures with long chain lengths in these asphaltenes. Molecules containing such structures can become intertwined and until they reach a set of specific conformations that allows the detangling, the asphaltene aggregates will not separate. In complex intertwined molecules such as these asphaltenes, it may take a long time to reach the mutual conformation where detangling can occur because (a) many different sequential conformations may be required for it, or (b) some of the steps are quite unlikely to occur thus requiring a very long time before the appropriate conformation could be reached by the molecules.

Additionally, a negative contribution from entropic effects related to the adsorption of additional solvent molecules at both molecular areas of contact of asphaltenes when separated is also present. The adsorption of solvent molecules in these areas (solvation) generates losses in the solvent degrees of freedom and produces a contribution that tends to prevent the separation of the asphaltenes.

Last, the available data on elemental composition revealed no dramatic variations across the different ion exchanger subfractions.<sup>1</sup> In general, the acids contained more O, and the bases somewhat more N and S. Thus, the highest O level occurred in the strongest acid sub fraction and the highest N level in the strongest basic one. From silica gel chromatography, the least polar fraction featured the highest MW and that fraction also happened to contain the highest ash level, 3.5%. The ash levels of the other subfractions were low except for the strongest acid one, which had a level of 2.1%. (The ash content of this whole asphaltene was 2.1%.)

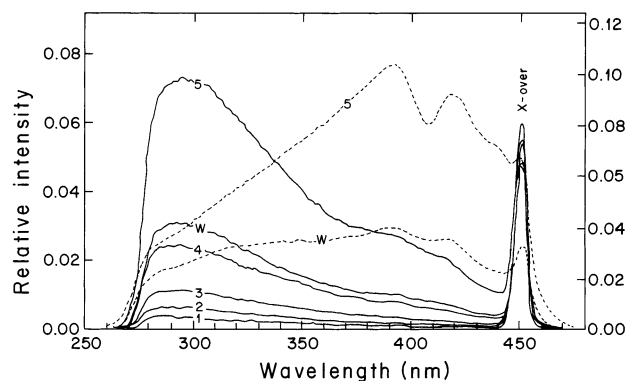


**Figure 7.** Corrected emission spectra of whole asphaltene (W) and its fractions 1–5 in benzene. Concentration:  $3.0 \text{ mg L}^{-1}$ . The dotted lines refer to a concentration of  $60 \text{ mg L}^{-1}$  and correspond to the right-hand scale intensity.  $\lambda_{\text{ex}} = 350 \text{ nm}$ . Reprinted from Yokota, T.; Scriven, F.; Montgomery, D. S.; Strausz, O. P. Absorption and Emission Spectra of Athabasca Asphaltene in the Visible and Near Ultraviolet Regions. *Fuel* **1986**, *65*, 1142–1149, with permission from Elsevier Science.

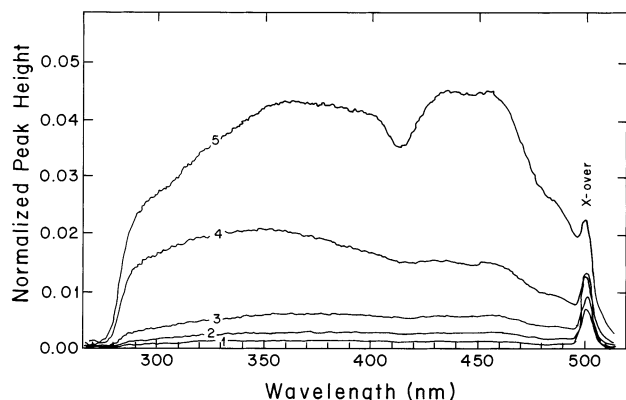
The work of SKSS was the first report of the time-dependent dissociation of bulk asphaltenes into small molecules. It demonstrated that, even after making allowance for the presence of coprecipitated resinous material, a large portion of the asphaltene fraction consists of aggregates built of relatively low-MW covalent molecules. At the same time, it also suggested the presence of smaller quantities of high-MW, mainly neutral, low-polarity materials in that fraction. Originally, it was proposed that at lower concentrations and higher temperatures and given enough time for equilibration, the high-MW species present would also completely disappear via dissociation to low-MW covalent molecules. They then represent the fundamental molecular units of asphaltene fraction. Subsequent studies on GPC and solvent separation and the spectroscopy of GPC-separated fractions, however, raised the possibility that this might not be so, and that some of the high-MW fractions may contain indeed high-MW covalent molecules. Both the rate of dissociation of the aggregates and the dissociation equilibrium should be affected by temperature, and by carrying out the experiments described above for longer times, at higher temperatures and at lower concentrations, in a more powerful solvent it should be possible to estimate the relative proportions of high- and low-MW constituents on a more quantitative basis. Further studies along these lines are in progress.

**Fluorescence Spectroscopic Studies.** It was shown<sup>11</sup> that the fluorescence yield from solutions of *n*-C<sub>5</sub>-asphaltenes of Athabasca bitumen is a function of MW and that the lowest-MW fraction (21%, Table 2, fluoresces the strongest (Figure 7). Thereafter, the fluorescence yield progressively falls off with increasing MW of the fraction, and the highest-MW fraction (22%) barely emits. This applies to concentrations of 3–60  $\text{mg L}^{-1}$  (and beyond) and for excitation wavelengths from 290 to at least 520 nm with emission wavelengths up to at least 600 nm (see Figures 8–10). Here, the fluorescence yield as well as the spectral profiles are affected by MW and concentration. Also, as can be seen,

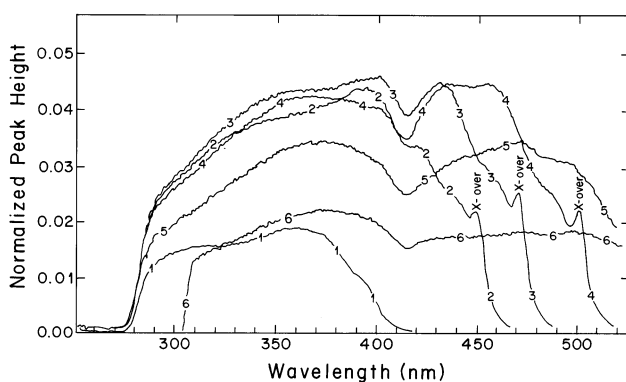
(11) Yokota, T.; Scriven, F.; Montgomery, D. S.; Strausz, O. P. *Fuel* **1986**, *65*, 1142–1149.



**Figure 8.** Corrected excitation spectra of whole asphaltene (W) and its fractions 1–5 in benzene. Concentration: 3.0 mg L<sup>-1</sup>. The dotted lines refer to a concentration of 60 mg L<sup>-1</sup> and correspond to the right-hand scale intensity.  $\lambda_{em} = 450$  nm. Reprinted from Yokota, T.; Scriven, F.; Montgomery, D. S.; Strausz, O. P. Absorption and Emission Spectra of Athabasca Asphaltene in the Visible and Near Ultraviolet Regions. *Fuel* **1986**, 65, 1142–1149, with permission from Elsevier Science.



**Figure 9.** Excitation spectra of fractions 1–5 at emission wavelength 500 nm and concentration 60 mg L<sup>-1</sup> in benzene.



**Figure 10.** Excitation spectra of fraction 5 taken at emission wavelengths:  $\lambda = 400$  (1), 450 (2), 470 (3), 500 (4), 550 (5), and 600 (6) nm; concentration 60 mg L<sup>-1</sup> in benzene.

the fluorescence yield from the lowest-MW fraction at  $\lambda_f = 600$  nm and  $\lambda_{exc} = 520$  nm, is quite significant and undoubtedly would be detectable to longer wavelengths. Evidently, the fluorescence from the whole asphaltene fraction is not *uniformly* representative of the fractions or of all the constituent molecules. It is, for example, quite possible that the highest-MW molecules do not emit at all and that the feeble fluorescence emerging from fractions 1 and 2 is due to the presence of low-MW contaminants. Militating against this possibility is the shift of the fluorescence maximum to longer wave-

lengths with increasing MW of the fractions, which may be taken as being indicative of the increasing size of the polynuclear aromatic chromophores. However, an alternative or supplementary to size increase effects will be offered below in terms of the intervention of intramolecular exciplex/excimers.

In any event, the variation of fluorescence intensity with MW suggests a gradual trend in the covalent molecular structure of asphaltenes. For the low concentrations of the solutions employed (3 mg L<sup>-1</sup> asphaltene), Figure 3, it may be assumed that dissociation of the aggregates is complete and intermolecular quenching processes are unimportant. Therefore (especially in view of the increasing value of the per gram absorption coefficient with the MW of the fractions, indicating increasing size of the polynuclear aromatic chromophores) the quenching of fluorescence is intramolecular and its efficiency appears to be intimately related to the properties of the individual covalent asphaltene molecules.

Among the papers published recently on the problems of MW and molecular aggregation phenomena in petroleum asphaltenes, one was based on a method new in petroleum chemistry involving optical fluorescence spectroscopy, while the others were based on more conventional methods involving a variety of mass spectrometry (MS), small-angle X-ray scattering (SAXS), and small-angle neutron scattering (SANS) methods.

**Molecular Rotational Correlation Time-Fluorescence Depolarization.** (RCT-FDP)<sup>12,13</sup> measurements have been used mainly to determine the size of rigid molecules of a pure compound in solution. The method has now been applied to the molecular size determination of asphaltene molecules in dilute solutions. However, adaptation of a fluorescence-based method for a complex, polydispersed solute composed of many thousands of different, unknown kinds, shapes, and sizes of molecules places serious limitations on sampling and registering the entire bulk of the test material. To be more specific, the problems with this method may be summarized as follows:

(i) not all molecular species in asphaltene would necessarily absorb in the spectral range of the study (ca. 300–700 nm):

- the principal absorbers are the aromatics;
- the existence of alkylnaphthenics *cannot* be *a priori* dismissed since the average carbon distribution in (petroleum) asphaltene is  $C_{arom}:C_{naphth}:C_{alk} \sim 40:35:25$  and aliphatics such as the aliphatic carboxylic acids, cyclic terpenoid hydrocarbons, and sulfoxides (Table 1) would not absorb, nor would their larger aliphatic-attached analogues represented by the compound classes in peaks 3 and 4 of the MeOH/CO<sub>2</sub> subfractions, (Figures 1 and 6).

(ii) not all absorbing molecular species would necessarily fluoresce.<sup>14</sup> Fluorescence can be quenched in a host of competing intramolecular processes:

(12) Groenzin, H.; Mullins, O. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1999**, 42, 728–732; idem, *J. Phys. Chem. A* **1999**, 103, 11237–11245; idem, *Energy Fuels* **2000**, 14, 677–684.

(13) Ralston, C. Y.; Mitra-Kirtley, S.; Mullins, O. C. *Energy Fuels* **1996**, 10, 623–630.

(14) Acridine, for example, has been reported not to fluoresce in hexane and benzene (*Luminescence in Chemistry*; Bowen, E. J., Ed.; Van Nostrand Co. Ltd.: Princeton, NJ, 1968; p 96).



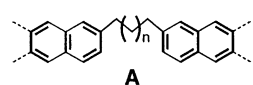
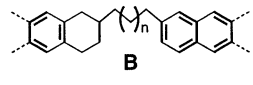
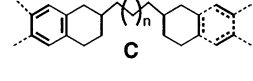
•quenchers may include moieties such as  $-\text{CO}_2\text{H}$ ,<sup>15</sup> heavy atoms<sup>16</sup>(S), metal salts and complexes, clay organics, intramolecular H-bonded complexes,<sup>17</sup> etc.;

- intramolecular excimer/exciple formation;
- intramolecular chemical reactions, e.g., intramolecular cyclomerization;
- intersystem crossing followed by phosphorescence or collisional deactivation of the triplet.

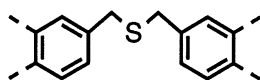
(iii) in effect, as discussed above, studies on GPC-separated Athabasca asphaltene<sup>11</sup> have clearly shown that the fluorescence yield depends on the MW of the fraction and gradually decreases with increasing weight to the point that the highest-MW fraction (22%) barely emits.

(iv) diminishing quantum yields for fluorescence and shifts to longer wavelengths with increasing MW of the fractions have also been reported recently<sup>18</sup> for coal pitch fractions.

(v) in addition to the above, the effect of molecular shape on the intensity, spectral profile, and polarization of fluorescence, as well as the absorption spectra of the asphaltene molecules, should also be taken into consideration. It is known from Ru-ion catalyzed oxidation (RICO) that polymethylene-bridged structures with chain lengths up to  $\text{C}_{24}$  (see below) are important structural elements in many asphaltenes:<sup>19,20</sup>

	Ath. asphaltene <sup>18</sup>	Boscan	Duri
	29	27	49
<b>A</b>			
	23.2	+	+
<b>B</b>			
	1.2		
<b>C</b>			
	~53%		

The percentages of aromatic C in the various bridged structures listed above were calculated from the number of bridges (RICO) and  $\text{C}_{\text{arom}}$  (NMR) data with the assumption that the average size of the aromatic moieties in the asphaltene molecule is dinuclear. As seen, more than half of the aromatic carbon in Athabasca asphaltene is present in polymethylene bridged structures. Four of five asphaltenes from mature crude oils studied yielded similar values for structure **A**, indicating that the values for **A** + **B** + **C** would also be similar, that is, = 50%. This is a conservative estimate since the average size of the aromatic moieties in asphaltene should be larger than diaromatic and also because of the well-established presence of sulfide linkages,<sup>3</sup> e.g.,



(15) Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum Press: New York, 1976; p 255.

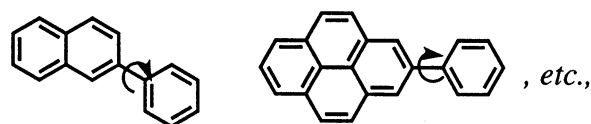
(16) Becker, R. S. *Theory and Interpretation of Fluorescence and Phosphorescence*; Wiley-Interscience: New York, 1969.

(17) Brauman, J. I. *Science* **2000**, *290*, 286–287.

(18) Herod, A. A.; Lazaro, M.-J.; Domin, M.; Islas, C. A.; Kandiyoti, R. *Fuel* **2000**, *79*, 323–337.

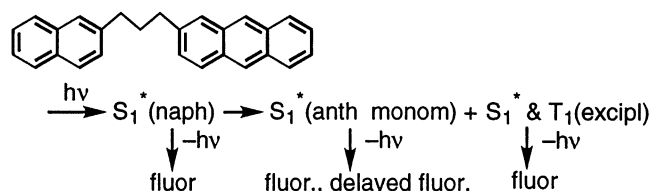
where a methylene group is substituted with a sulfur atom in the chain.

(vi) in all the above bridged structures and their endless number of derivatives and analogues, the aromatic units execute relatively free rotation about the C–C and/or C–S bonds of the chain, mimicking a “free” aromatic unit, whereas the whole molecule undergoes quite a complex motion which could hardly be approximated by a sphere or any simple, rigid geometric object. Thus, what is seen in rotation is not necessarily the rotation of the whole asphaltene molecule, but rather the rotation of its individual aromatic structural moieties. In structures **B** and **C**, the naphthenic sides may have attached aromatic moieties for which the same considerations apply. Also, from RICO studies the presence of biaryl structures, e.g.,



in which motion about the biaryl linkages is independent of other internal or molecular rotations is well established. Taking into effect all the above structural elements, essentially all the aromatic entities—at least in the Athabasca asphaltene—would be in bridged structures. Boscan, Duri, and Arabian asphaltenes, and petroleum asphaltenes in general would have these structural features as common elements in their molecular architecture.

(vii) with regard to the fluorescent properties of asphaltene, it is well established in organic photochemistry that aromatic units connected with flexible polymethylene bridges and even bridges with restricted mobility (e.g., a sterane C skeleton) readily undergo intramolecular energy transfer processes (from the higher to the lower energy units)<sup>21,22</sup> e.g.,



where the  $\text{S}_1^*$ (exciplex) fluorescence may be considerably shifted to the red, compared to the fluorescence of the monomers; the efficiency of exciplex fluorescence for simple mono- through trinuclear aromatic substituents depends on the chain length and maximizes at  $\text{C}_3$ , where the maximum concentration of structure **A** in the asphaltenes investigated happens to be. Similar phenomena have been observed in paracyclophanes—polymers consisting of stacked benzene rings.

(19) Strausz, O. P.; Mojelsky, T. W.; Lown, E. M.; Kowalewski, I.; Behar, F. *Energy Fuels* **1999**, *13*, 228–247; Strausz, O. P.; Mojelsky, T. W.; Lown, E. M. *Fuel* **1992**, *71*, 1355–1363; Mojelsky, T. W.; Ignasiak, T.; Frakman, Z.; McIntyre, D. D.; Lown, E. M.; Montgomery, D. S.; Strausz, O. P. *Energy Fuels* **1992**, *6*, 83–96.

(20) Wang, Z.; Liang, W.; Que, G.; Qian, J. *Pet. Sci. Technol.* **1997**, *15*, 559–577.

(21) De Schryver, F. C.; Boens, N. Excited State Behavior of Some Bichromophoric Systems. In *Adv. Photochem.* **1977**, *10*, 359–465.

(22) Torro, N. J. *Modern Molecular Photochemistry*; Benjamin Cummings Publishing Co.: Menlo Park, CA, 1978; p 145.

(viii) as illustrated by the above example of the fluorescence from 1-anthracyl-3-naphthylpropane, the fluorescence spectrum of this compound upon irradiation in the short-wavelength side of the naphthalene absorption spectrum where anthracene would not absorb will be shifted to the red compared to the fluorescence spectrum of naphthalene since  $\lambda_{F(\text{exc})} > \lambda_{F(\text{anth})} > \lambda_{F(\text{naph})}$ . Oversight of such complexities in the photo-physics of asphaltenes would lead to erroneous conclusions regarding their concentration distribution of polynuclear aromatic moieties and a decided underestimation of the lower condensed and overestimation of the higher condensed species.

(ix) the formation of triplets, regardless of their ultimate fate, represents quenching of the fluorescence; thus, quenching with or without triplet involvement by increasing concentrations of **A** – **C**, paracyclophanes, and inorganic constituents in the heavier fractions of the asphaltene may be responsible for the observed fluorescence yield vs VPO-MW relationship in Athabasca asphaltene fractions (and likely in coal pitch fractions as well).

(x) in more complex systems involving polar moieties where exciplexes would have some stability in their ground electronic state, the bridge chain length dependence of fluorescence may be modified or disappear altogether,<sup>22</sup> and exciplex absorption may compete with the absorption by individual aromatic moieties;

(xi) from the above facts one may conclude that:

- the fluorescence spectra of asphaltenes are composites of the fluorescence of individual structural moieties within the asphaltene molecules and the fluorescence of intramolecular exciplexes; the absorbing and emitting chromophores would not necessarily be the same;

- as a consequence the spectra are considerably shifted to the red, compared to those of the individual chromophore moieties in the molecules;

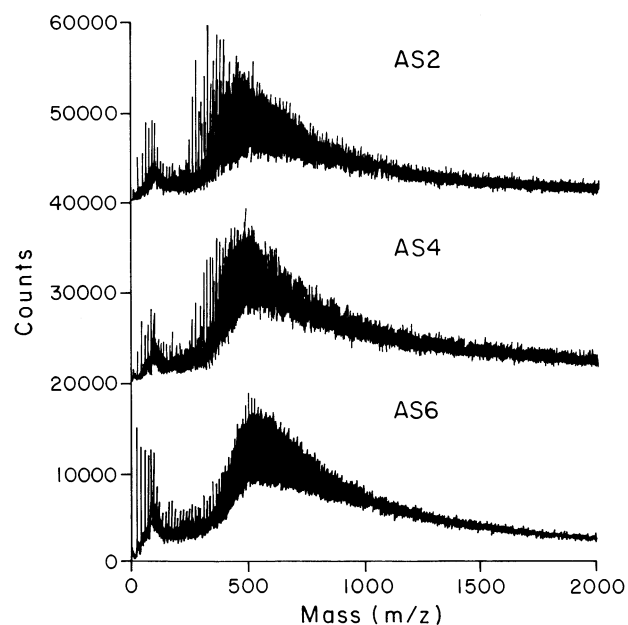
- the rotational motion of the two (or more) aromatic chromophores connected by varying lengths of polymethylene and/or sulfide and/or C–C bridges cannot be approximated by rigid geometrical objects;

- the depolarization process may reflect the combination of hindered rotational motion of individual aromatic moieties in the asphaltene and the rotation of their intramolecular exciplexes;

- the fluorescence yield of asphaltene fractions depends on their VPO-MW, and progressively declines with increasing VPO-MW of the fractions; therefore the depolarization of the fluorescence does not represent with equal weight the depolarization of every molecule and the molecules which do not fluoresce are not represented at all;

- in light of the above observations, molecular rotational correlation time measurements from fluorescence depolarization cannot be considered to be a reliable method for the estimation of molecular size of asphaltenes or similarly complex materials.

**Mass Spectroscopy.** Along with NMR, MS is the most widely used method in organic chemical analysis. For pure compounds and moderately complex mixtures, in addition to precise MW, MS can provide valuable structural information even on samples of low volatility. However, in the case of highly complex mixtures such as the heavy fractions of fossil fuels—pitches, asphal-



**Figure 11.** LDI MS spectra of three asphaltene subfractions. From ref 23.

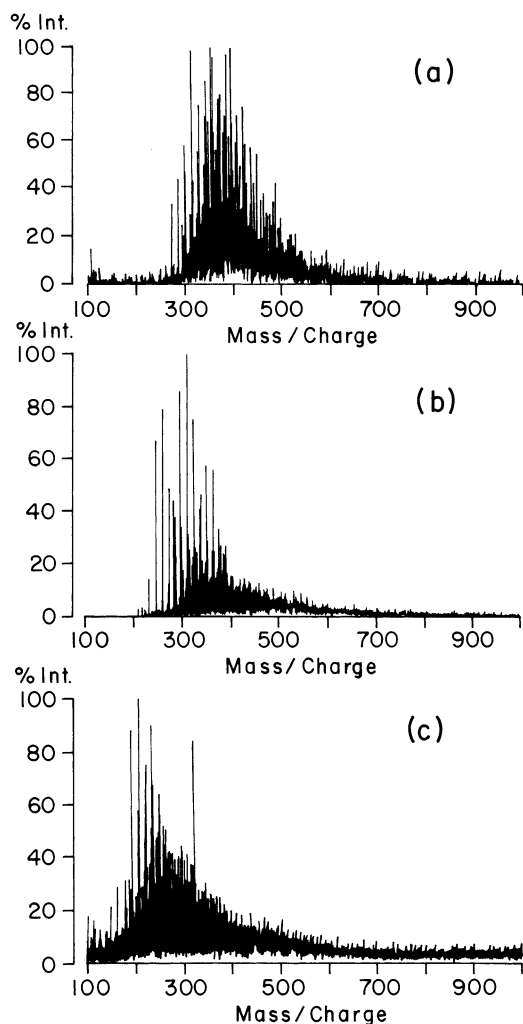
tenes, and like materials containing many thousands of different compounds with broad spectra of MW, volatility, stability, and tendency for agglomeration—even the most advanced methods of MS available today furnish results the interpretations of which are difficult, requiring scrutiny, and are not without contention.

Some of the main impediments afflicting MS methods for the determination of the MW of the covalent monomeric asphaltene molecules lie in: (a) the difficulty in selecting the appropriate experimental conditions and instrumental parameters necessary to liberate the individual covalent molecules from their aggregates without causing the cleavage of any covalent bonds, and (b) in ensuring that the singly ionized vapor composition entering the detection chamber be representative of the bulk sample composition.

Numerous studies have been reported on the MS of petroleum asphaltene fractions. The variety of methods ranged from conventional electron impact MS, low-voltage electron impact, high-resolution electron impact, field ionization desorption, laser desorption (LDI), and matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) to <sup>252</sup>Cf-plasma desorption (PD-TOF) MS.

The difficulties in the interpretation of asphaltene mass spectra can be discerned from some of the samples reproduced here. Figure 11 shows the mass spectra obtained in LDI-MS on three solvent-precipitation-separated fractions of a residue asphaltene.<sup>23</sup> All three spectra feature intense fragment ion peaks at  $m/z \leq 100$  which, if they are not instrumental artifacts, arise from the fragmentation of covalent molecules. The lowest, (AS6) spectrum was obtained on the least soluble (highest-MW) fraction and the uppermost spectrum (AS2) on the most soluble one containing asphaltene-incorporated resins. The AS4 spectrum is due to an intermediate fraction. The overall shapes of all three spectra are similar; following the 0–100  $m/z$  range a U-shaped valley is apparent, going into maximum

(23) Yang, M.-G.; Eser, S. *Prepr. Pap.—Am. Chem. Soc., Div. Pet. Chem.* **1999**, *42*, 768–771.



**Figure 12.** Laser desorption mass spectra (LDMS): (a) Mayan maltene, (b) noncolloidal asphaltene, (c) colloidal asphaltene. From ref 25a.

intensities at  $m/z$  300, 350, and 500 for samples AS2, AS4, and AS6. The AS6 spectrum extends well beyond  $m/z = 2000$ , where its intensity is ca. 15% of the maximum value. No uppermost value for  $m/z$  can be established for any of the spectra but in each case it is beyond  $m/z = 2000$ .

The conclusions that can be drawn from these spectra are as follows. LDI causes significant fragmentations or multiple ionizations of the covalent molecules of asphaltenes under the experimental conditions employed in this study. This casts serious doubts about the validity of the assumption that the spectra represent the distribution of the *parent* covalent asphaltene molecules and even with this in mind it is seen that the spectra extend beyond  $m/z = 2000$ . A similar spectrum was reported<sup>24</sup> for unfractionated  $n$ -C<sub>5</sub> Athabasca asphaltene. In this case the 0–100  $m/z$  range was not reported and the spectrum was inundated by well-resolved individual peaks due to the presence of large amounts of resin molecules in the sample.

The three LDI mass spectra (Figure 12) were obtained on Mayan asphaltene<sup>25</sup> ( $n$ -C<sub>7</sub>), part A, an  $n$ -C<sub>7</sub> reflux extract from  $n$ -C<sub>7</sub> asphaltene, part B, and the  $n$ -C<sub>7</sub>

extracted asphaltene, part C. The salient features of these spectra are the abundance of well-resolved individual peaks and again a peculiar distribution of  $m/z$  densities, occurring around  $m/z = 380$  for spectra A and B, and 280 for spectrum C. The extracted asphaltene would be expected to have the highest MW and therefore spectrum C would be expected to extend to the highest  $m/z$  values and to give the highest average MW. The low value for the latter could then perhaps again be an indication that significant multiple ionization in the LDI of asphaltenes takes place, especially under the experimental conditions employed in these studies.

A MALDI-TOF mass spectrum obtained on an Arabian residue asphaltene<sup>26</sup> indicated “ionization” above  $m/z = 200$  with a sharp individual peak-structured maximum around  $m/z = 480$  and a gradual, smooth, small-amplitude decline to beyond  $m/z = 3500$ . The matrix employed was not specified. The spectrum is significantly different from the above-cited LDI spectra in the sense that “ionization”, i.e., the appearance of ions, is reportedly not evident below  $m/z = 200$  and the highest  $m/z$  value discernible from the spectrum is higher. The difference may be attributable to the matrix employed.

Many of the apparent contradictions in the MS studies of asphaltene are due to the limited understanding of the underlying physical chemistry and the influences of experimental circumstances that were available at the time the experiments were carried out. Considerable progress has since been made in this respect and reviewed recently in connection with MS studies of coal liquids.<sup>18</sup> Even though the compositions of coal liquids are distinctly different from those of petroleum asphaltenes, the problems responsible for the source of the difficulties in the MS determinations of MW are of similar nature (unknown, random molecular structures, polydispersity, tendency for agglomeration, etc.).

Some of the more important observations made regarding the widely used MALDI-TOF MS method discussed in ref 18 are as follows:

- removal of the MALDI-TOF instruments’ reflector from the flight path improves sensitivity to high-MW material;
- high power levels of laser fluency lead to the formation of C clusters (probably arising from extensive cleavage of covalent bonds and multiple ionization);
- increasing the ion-extraction voltage assists in detecting higher-MW species by providing a more complete inventory of already-ionized species;
- the compositions of the matrix and sample, as well as the method of mixing the matrix and the sample, could influence the MW distribution;
- high-MW materials may be greatly underestimated when the determinations take place in the presence of a greater abundance of low-MW material;
- the signal-to-noise ratio of spectra increases with the numbers of co added scans;
- methods for the estimation of high-mass limits in spectra were developed and compared: according to the

(25) (a) Miller, J. T.; Fisher, R. B.; Thiyagarajan, P.; Winans, R. E.; Hunt, J. E. *Energy Fuels* **1998**, *12*, 1290–1298; (b) Winans, R. E.; Hunt, J. E. *Prepr. Pap.—Am. Chem. Soc., Div. Pet. Chem.* **1999**, *42*, 725–727

(26) Artok, L.; Su, Y.; Hirose, Y.; Hosokawa, M.; Murata, S.; Nomura, M. *Energy Fuels* **1999**, *13*, 287–296.

(24) Mathews, J. P.; Eser, S.; Rahimi, P. *Prepr. Pap.—Am. Chem. Soc., Div. Pet. Chem.* **1999**, *42*, 783–785.

**Table 5. Molecular Weights of Athabasca 525+ °C Residue GPC Fraction<sup>28</sup>**

fraction	$\bar{M}_n$ (VPO) g mol <sup>-1</sup>	$\bar{M}_n$ (PDMS) g mol <sup>-1</sup>	$\bar{M}_w$ (PDMS) g mol <sup>-1</sup>	$M$ (GPC) g mol <sup>-1</sup>	MALDI <sub>mpi</sub> <sup>a</sup> m/z
1	3228	790	1360	3200	2800
2	1319	590	990	1005	1400
3	1047	540	840	480	<1000
4	911	540	830	390	<1000
5	988	530	800	370	<1000
feed	1682	630	1020	430	<1000

<sup>a</sup> mpi = maximum peak intensity.

preferred method the calculated “true” high-mass limit is where signal becomes > 5 standard deviations.

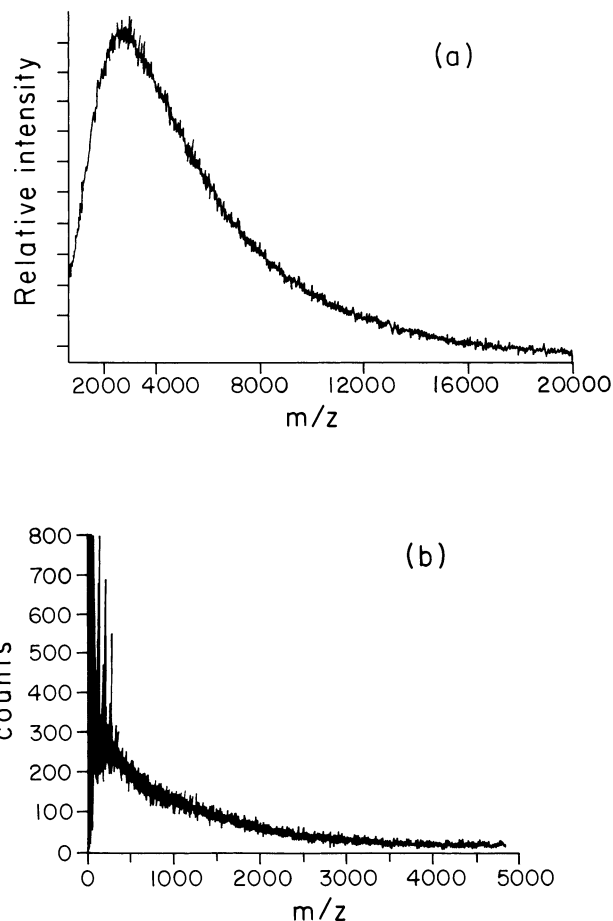
In a comparative study<sup>27</sup> of PD-TOF MS and MALDI-TOF MS methods on coal liquids, it was noted that the two methods gave qualitatively similar results, which were characterized by a far larger range of MW than those reported before by any other MS-based method. And after developing methods for the estimation of high-mass limits in spectra, even larger “true” high mass limits—as large as 42000 and 95000–96000 u were derived for a coal tar pitch and its pyridine-insoluble fraction. The corresponding  $\bar{M}_w$  and  $\bar{M}_n$  values obtained were 11700; 1500, and 28400; 7100 u, respectively.

A more recent comparative study<sup>28</sup> extended the range of methods investigated to include VPO, GPC, PDMS, LDMS, and MALDI. In this case the work material was Athabasca 525+ °C residue and five fractions prepared from it by GPC separation. In Table 5 is seen that the various methods yield numerically significantly differing values but similar trends throughout the fractions. The numerical values among VPO, GPC, and MALDI<sub>mpi</sub> are closer to one another than to PDMS, Figure 13, which consistently reports lower values. Fraction 1, with VPO  $\bar{M}_n = 3228$  g mol<sup>-1</sup> by and large should correspond to the asphaltene content of the residue. The VPO, GPC, LDMS, and MALDI<sub>mpi</sub> values correlate quite well for this fraction with an average value of 3076 g mol<sup>-1</sup>, (as compared to the  $\bar{M}_n$ (PDMS) value of 790 g mol<sup>-1</sup>) which was taken as lending support to the belief—but does not prove—that these methods measure the MW of dissociated, individual covalent molecules. It has also been stated in this paper that the MW of this residue is continuous up to and perhaps beyond a MW of 15000 u and, as it would appear from Figure 13, the molecular range of Fraction 1 extends to at least 20000 u.

However, it should be pointed out that the VPO measurement of MW requires a much higher concentration of asphaltene solution, and consequently the asphaltene would be expected to be in an aggregated state in the VPO measurement. This is in line with the measured VPO MW of 3228 g mol<sup>-1</sup> as compared to the GPC retention time estimated value of <1000 g mol<sup>-1</sup> at a 0.05 wt % concentration, which is below where the aggregates begin to dissociate. Thus, it appears that the PDMS values, Figure 13, are better representations of the MW of monomeric covalent asphaltene than the other listed in Table 5.

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**Figure 13.** Molecular weight distributions of fraction 1 from Athabasca 525+ °C residue by (a) MALDI and (b) PDMS. From ref 28.

**SAX and SAN Scattering.** Small-angle scattering methods are powerful tools to probe into the colloidal properties of asphaltene solutions. However, they do not lend themselves readily to the measurement of the covalent MW of asphaltene.

SAXS<sup>29</sup> and SANS<sup>30</sup> have been used to investigate the colloidal properties of crude oil and asphaltenes since 1960 and 1967, respectively. It became known early on that in many crude oils asphaltene occurs in the form of 20–40 Å radius of gyration colloids, which would grow in size upon diluting the oil with an asphaltene precipitant (e.g., *n*-hexane, etc.) to several thousand angstroms.

Molecular weight determinations based on scattering phenomena yield weight average MW<sub>w</sub>, whereas colligative property-based ones yield number average MW<sub>n</sub>. For polydispersed particles, the numerical values of the weight and number average MWs are different and the

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ratio  $(MW_w)/(MW_n)$  is greater than unity and increases with the degree of polydispersity of the system. Hence, part of the well-known incongruity between MW measured by scattering and by colligative methods such as VPO originates from this difference. Additional reasons for this discrepancy may be as follows. Asphaltene features a variety of functional groups, e.g., polycyclic aromatics, carboxylic acids, alkanolic esters, sulfoxides, N bases, alcohols, ketones, ethers, sulfides, naphthenics, alkyls, etc., which participate in intermolecular associations by forces ranging from the quite strong to the very weak. Consequently, the strengths of the intermolecular interactions in the asphaltene aggregates cover a broad spectrum, extending from subthermal to well above thermal energies. When two particles are bound by very weak forces, the status of the particles—whether they register as a single particle or two separate ones—may depend on the phenomena involved in the measurement. In scattering phenomena in which the time interval for the interaction of the scattering particle with the electron cloud or atomic nuclei of the molecules is very short compared to atomic motions ( $<10^{-12}$  s), two very weakly bound particles may register as a single entity. On the other hand, in colligative properties-based measurements, which rely on relatively slow equilibrium processes affording sufficient time for the cleavage of the weaker intermolecular bonds, the particles may register as two separate entities. At room temperature, scattering measurements give values for the MW one or two orders of magnitude greater than VPO measurements.<sup>25b</sup> With rising temperature, the aggregates dissociate, first with the cleavage of the feeblest bonds followed by that of gradually stronger intermolecular bonds, resulting in corresponding decreases in the measured MW. The problem here lies in the difficulty, at low temperature, of defining intermolecular bond strength in the complex species that would separate aggregates from nonaggregates and, at high temperatures, in separating aggregate dissociation from fragmentation of covalent bonds. Moreover, it has to be borne in mind that the method is quite insensitive and in order to obtain reliable measurements, very high concentrations of asphaltenes in the solution must be used. This then precludes the application of scattering phenomena for the measurement of the covalent molecular size of asphaltene.

### Summary and Conclusions

Determination of the molecular weight and molecular weight distribution of the covalent molecules forming the fundamental units in petroleum asphaltene is a formidable task. Many of the difficulties arise from the following circumstances: structural and size diversity of the random asphaltene molecules with unknown precise structure; the particular structural feature of dense atomic centers interconnected with varying lengths of polymethylene (up to at least  $C_{24}$ ) and C–S–C bridges, as well as C–C linkages; and the propensity of the asphaltene molecules for aggregation by a variety of intermolecular forces.

Four approaches, based on different analytical methods (namely, GPC and related chromatography, UV–vis fluorescence, MS and SAX, SAN scattering) were examined here.

The GPC method described was used in a novel manner. Instead of attempting to measure MW, the retention time variation was followed as a function of time elapsed from the preparation of a very dilute sample solution of Athabasca asphaltene used in the measurement. With increasing age of the solution, the retention time of the asphaltene on the GPC column increased from the MW range of thousands to below 1000, signaling the slow dissociation of the asphaltene molecular aggregates. This was the first observation of the asphaltene aggregates' dissociation, which became evident once the concentration of asphaltene in the solution was lowered to 0.05 wt % or below. Up to about 80–84% dissociation was observed in semiquantitative studies after a period of 14 days. The rest of the asphaltene might have comprised still undissociated aggregates or dissociated high-MW covalent molecules. According to silica and ion exchange chromatographic results this highest-MW fraction is the least polar and, in fluorescence spectroscopy, the least fluorescent fraction. The GPC method outlined is simple and requires no complicated instrumentation, involved theory for interpretation or standardizations.

Subsequent UV–vis fluorescence studies revealed significant differences in the fluorescence properties of the various MW fractions of Athabasca asphaltene in highly dilute solutions ( $3 \text{ mg L}^{-1}$ ) where complete dissociation can be expected. Namely, it was found that the fluorescence intensity varied with the MW of the fraction and that the lowest-MW fraction was the most fluorescent, whereas the highest-MW fraction barely fluoresced. Thus, this fluorescence property is an intrinsic one of the covalent molecule (and not the aggregate) and the covalent molecules present in the various MW aggregates have different properties. Consequently, the possibility exists that the gradual reduction of fluorescence is due to the increasing size (or perhaps changing composition) of the covalent molecules in the heavier fractions, in turn leading to increasing intramolecular quenching. This question, along with that of the extent of maximum possible dissociation, should be settled in the future by carrying out the GPC studies at elevated temperatures and still lower concentrations, in more powerful solvents and at longer times, to drive the dissociation/association equilibrium to completion as close as possible.

RCT-FDP measurements on dilute solutions have been suggested recently as a method for the determination of the size of covalent asphaltene molecules. However, fluorescence properties of systems with the great chemical complexity of the asphaltene fractions are not readily correlatable to individual or average, intensive or extensive, molecular properties. Some constituent molecules may fluoresce, others may not, some may not even absorb light in the spectral range studied. Moreover, the method gives results, which are more dependent on molecular size and shape than on MW and the numerical values are obtained from calculations based on theories with several assumptions and approximations. Also, a dominant characteristic feature of petroleum asphaltene fraction, as deduced from quantitative RICO reaction measurements, is its bi- or oligochromophoric character, in which individual chromophoric moieties are interconnected by varying

lengths of polymethylene bridges and biaryl linkages. S-containing asphaltene would also possess S in bridge positions, as has been shown in K/naphthalene and Ni boride reduction studies, and the possibility that alkanolic ester and ether bridges are also present in asphaltene must also be taken into consideration as well. Nearly all the chromophores—the polynuclear aromatic moieties in the asphaltene molecule—are present in such structural configurations. This, then, dictates the examination of the role of intramolecular exciplexes/excimers in the fluorescence since such species are common intermediates in the photophysics of bichromophoric molecules. There are a number of troublesome consequences of the presence of excimers/exciplexes, such as: (a) the dominance of internal rotational motion of the individual chromophores over the rotational motion of the entire molecule in governing the depolarization process; (b) the contribution of excimer/exciplex fluorescence to the fluorescence spectrum; (c) enhancement of the fluorescence from the lowest excitation energy chromophore in the molecule via intramolecular excitation transfer which, along with the excimer/exciplex fluorescence, causes the fluorescence spectrum to be shifted to the red, compared to the fluorescence from the lowest excited state of the absorbing chromophore; (d) the quenching of the fluorescence and its increasing probability with increasing MW, leading to the complete extinction of fluorescence from the highest-MW fraction of asphaltene, etc. The red shift of the excimer/exciplex fluorescence would also result in the overestimation of the average size of the polynuclear aromatic centers. As outlined above, these are the main reasons why the molecular RCT-FDP method is not suitable for size measurements for asphaltene molecules.

The MS method has been used in nearly all of its presently available variations for the determination of asphaltene MW. The main strength of this method is its ability to yield absolute MW directly, without the need to resort to theories or complicated mathematical exercises and the measurement can be carried out readily in more or less routine operations. Nevertheless, the method is not without pitfalls, as illustrated by the divergent results reported from various laboratories. Some of the principal problems lie in the difficulty in differentiating molecular ions from fragment ions, single molecules from molecular clusters, and singly ionized species from multiply ionized species. There are also abundant sources of experimental error. In connection with asphaltene studies, insufficient attention has been paid to the systematic investigation of error sources. These shortcomings in experimental work have recently been remedied in work mainly on coal liquids.

In extensive research on coal liquids, it was found that of the several varieties of MS in current use, the best suited to the investigation of the heavy fractions of fossil fuel products is the MALDI-TOF MS. In this method a number of error sources have been identified, relating

to laser fluence, ion-extraction voltage, chemical composition of the matrix, the method of sample preparation, and the degree of sample polydispersity.

Employing LDI and MALDI MS and experimental procedures to minimize errors from the sources mentioned above, it was shown that the spectrum of (Athabasca) asphaltene (from the GPC separation of the 525+ °C residue) features a smooth mass distribution with a maximum around  $m/z = 2800$  and extends to very high  $m/z$  values, at least ca. 16000 and possibly even far beyond. This mass range far exceeds the ones reported before from MS measurements for petroleum asphaltene. Comparison of the  $\bar{M}_n$ VPO,  $\bar{M}_n$ PDMS, MW GPC, and MALDI maximum peak intensities for the five GPC-separated fractions of the above residue revealed a fairly good numerical correlation between  $\bar{M}_n$ VPO, MW GPC, and MALDI<sub>mpi</sub> and a reasonable correlation in trend but not in numerical value among all the methods.

One question of fundamental importance, then, is whether the high-MW values determined by the above methods apply to single, covalent molecules or to molecular clusters or a mixture thereof. We know that Athabasca asphaltene in dilute (0.05 wt %) CH<sub>2</sub>Cl<sub>2</sub> solution is partially aggregated up to at least 80%. In the more concentrated solutions required in VPO measurements the monomer–aggregate equilibrium would be shifted toward the aggregate side and therefore it follows that in the measurements of the above-mentioned study (THF, 45 °C) the asphaltene would be aggregated. This would then suggest the same degree of aggregate participation in the LDI and MALDI spectra as well and render the  $\bar{M}_n$ (PDMS) values, Table 5, closer to expectation than the MALDI<sub>mpi</sub> values.

The question of the extent of molecular aggregation in asphaltene (and in coal liquids) could be resolved through the study of aggregate dissociation under various conditions with the GPC retention time measurement method over a concentration range where dissociation is still detectable. Until the conclusion of such a study it may be assumed that in petroleum asphaltene low-MW and smaller amounts of high-MW covalent molecules coexist.

#### Note Added in Proof

Aggregation of Athabasca asphaltene in aromatic solvents involving up to six molecules has been recently observed by VPO measurements.<sup>31</sup>

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