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Review Article

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The Asphaltene Fraction – Demystified

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Abstract

The asphaltene constituents of crude oil are the highest molecular weight heaviest and most polar constituents in the oil and the fraction is isolated a dark brown to black friable solids that have no definite melting point and usually foam and swell on heating to leave a carbonaceous residue. The fraction is obtained from crude oil by the addition of a hydrocarbon liquid (such as n-pentane or n-heptane).

Any molecular models derived for asphaltene constituents must be in keeping with behavioral characteristics. Efforts have been (and continue to be) made without justification to describe the asphaltene fraction in terms of a single, representative asphaltene molecule or molecules incorporating, in the correct proportions, all of the chemical constituents known to be present in a given asphaltenic matrix. Obviously, the chemistry and structural features of the constituents of crude oil asphaltene fractions will be dictated by the distribution of functional and structural type that occur in the fraction. This makes the representation of the structure and functionality of the constituents by so-called average structures very difficult (if not, impossible) to conceive.

Keywords: Asphaltene fraction, Separation, Constituents, Molecular weight, Polarity, Fractionation, Composition, Structure

Introduction

The asphaltene constituents of crude oil are the highest molecular weight heaviest and most polar constituents in the oil and the fraction is isolated a dark brown to black friable solids that have no definite melting point and usually foam and swell on heating to leave a carbonaceous residue. The fraction is obtained from crude oil by the addition of a hydrocarbon liquid (such as n-pentane or n-heptane) [1-4].

The use of n-pentane or n-heptane is exemplified by differences in the elemental analysis. For example, the H/C ratio of the heptane-asphaltene fraction is lower than the H/C ratio of the pentane asphaltene fraction, indicating a higher degree of aromaticity in the heptane asphaltene fraction. The N/C, O/C, and S/C atomic ratios are usually higher in the heptane asphaltene fraction, indicating higher proportions of the hetero elements in this material. Nevertheless, each type of asphaltene fraction obtained from a variety of crude oils can be sub-divided (sub-fractionated) into structural and functional types illustrated elsewhere in this review.

The issues arising from the presence of problems with asphaltene constituents have increased due to the increased use of need to extract even the heaviest crude oils as well as the trend to extract large amounts of light fractions out of crude oil by amongst other methods cracking and visbreaking. Examples of the problems that arise due to asphaltene flocculation and/or sedimentation are: (i) well bore plugging and pipeline deposition during recovery and transportation operations, (ii) water contamination during wellhead storage and in pipelines can lead to the formation of emulsions because the asphaltene constituents highly polar and surface active, (iii) sedimentation and plugging during crude oil storage (and during product storage) can occur due to oxidation of the asphaltene constituents and the increased polarity of the oxidized products, and (iv) thermally degraded asphaltene constituents are more aromatic (loss of aliphatic chains) and less soluble and appear as sediment (the onset of coke formation) during the visbreaking process and during cracking processes.

Separation and Composition

The asphaltene fraction is, by definition, a solubility class and is the fraction is precipitated from feedstocks by the addition of 40 volumes of the low-boiling liquid hydrocarbon (typically, n-pentane or n-heptane) to one volume of crude oil (Table 1) used commercially in processing crude oil residua for asphalt production. On the other hand, the asphaltene constituents are soluble in liquids with a surface tension above 25 dyne cm-1, such as pyridine, carbon disulfide, carbon tetrachloride, and benzene [1,2,5-12].

Table 1: Standard Methods for Asphaltene Separation

Method	Precipitant	Volume precipitant per g of sample
ASTM D893	n-pentane	10 ml
ASTM D2006	n-pentane	50 ml
ASTM D2007	n-pentane	10 ml
ASTM D3279	n-heptane	100 ml
ASTM D4124	n-heptane	100 ml

Asphaltene fractions isolated from different sources are remarkably constant in terms of the elemental composition, although there can be variations in terms of heteroatom (nitrogen, oxygen, sulfur, and metals) content because of local and regional variations in the types of precursors that formed the asphaltene constituents as well as mineralogical composition of the nearby geological formations. Thus, differences between the asphaltene constituents reflect differences in the relative amounts of the functional molecular types present and the way in which the structural types are combined in the various asphaltene constituents. This is reflected, in part, by changes in the functional group composition of asphaltene fractions from different crude oils (see, for example, Koots and Speight, Huc et al.,) [4,13,14].

One aspect of asphaltene characterization that has provided strong evidence for the complexity of the fraction arises from composition studies using fractionation techniques. Indeed, the asphaltene fraction can be sub-divided by a variety of techniques [15-20].

Also, the fractionation of the asphaltene component of crude oil showed that it is possible to obtain asphaltene fractions characterized by different degrees of aromaticity or heteroatom content by using benzene/pentane (toluene/pentane) or benzene/methanol (toluene/methanol) mixtures in variable ratios. In addition, the fractionation of asphaltene constituents into a variety of functional (and polar) types (Figure 1) has confirmed the complexity of the asphaltene fraction [19, 21-23].

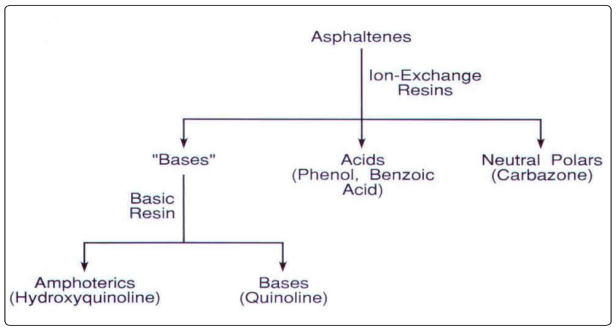

Figure 1: Separation of Asphaltene Constituents Based on Functional Polarity, Using Model Compounds as Examples of the Polar Functions

These findings are of particular interest since they correspond to the ring systems that have been identified by application of the HPLC technique to the asphaltene constituents (Figure 2). Similar fractionation schemes have been applied to various asphaltene fractions from different crude oils with similar results but with variations in the yield of the polar different fractions. In addition, the application of the carbon residue test to the different sub-fractions of the asphaltene fraction confirms the different behavior of the sub-fraction under the standard conditions of the carbon residue test (ASTM D189) [1,2,24] .

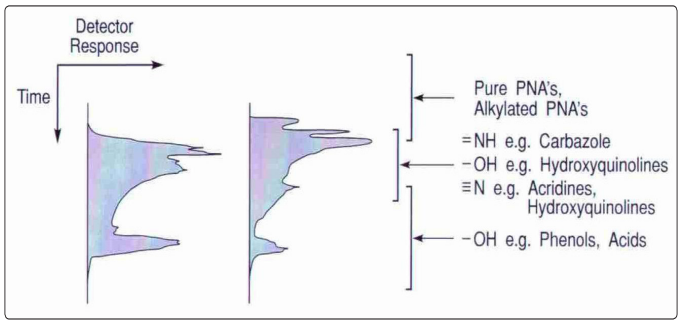

Figure 2: The Complexity of the Asphaltene Fraction as Shown by HPLC – the Figure also Refutes the Concept of Using an Average Structure to Determine the Behavior and Properties of the Asphaltene Fraction.

Obviously, the chemistry and structural features of the constituents of crude oil asphaltene fractions will be dictated by the distribution of functional and structural type that occur in the fraction. This makes the representation of the structure and functionality of the constituents by so-called average structures very difficult (if not, impossible) to conceive [1] (Figure 3).

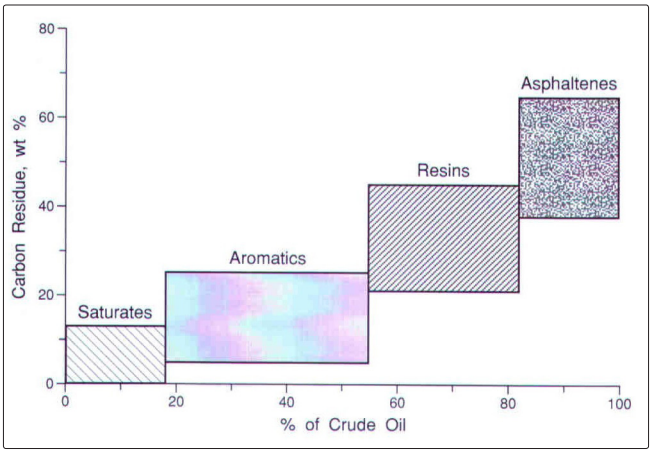

Figure 3: Sub-Fractionation of the Various Fractions of Crude Oil Yield Sub-Fractions with Different Carbon Residues – Particularly Worthy of Note in this Instance is the Variation of the Carbon Residue Yield for the Sub-Fractions of the Asphaltene Fraction

Molecular Weight

The molecular weights of asphaltene fractions span a wide range from a few hundred to several million leading to the concept of self-association of the asphaltene constituents [1,13,25-27].

The tendency of the asphaltene constituents to form aggregates in hydrocarbon solution is one of their most characteristic features and complicates the determination of asphaltene molecular weight [26, 28-31]. For any one method, the observed molecular weights suggest that asphaltene constituents form molecular aggregates, even in dilute solution, and this association is influenced by solvent polarity, asphaltene concentration, and the temperature at which the determination is made. The precise mechanism of the association has not been conclusively established, but hydrogen bonding and the formation of charge-transfer complexes have been cited as

responsible for intermolecular association. In fact, intermolecular hydrogen bonding could be involved in asphaltene association and may have a significant effect on observed molecular weights [1,2,26,33,34].

A note of caution is that the determination of asphaltene molecular weight is subject to the presence of occluded resin constituents and removal of the resin constituents gives rise to higher observed molecular weights of the purified asphaltene constituents. In addition, and as noted previously for the whole asphaltene constituents, the molecular weights of the purified asphaltene constituents also varied with the solvent used for the determination; that is, solvents of high dielectric constant decrease the observed molecular weights. Furthermore, extraction of freshly precipitated asphaltene fractions using a Soxhlet extractor and different solvents followed by molecular weight determinations of the insoluble material show a decrease in the asphaltene molecular weight with the dielectric constant of the solvent [28,34].

Structural Aspects

The structural nature of the asphaltene constituents has been open to question for some time. Of all the methods applied to determining the types of polynuclear aromatic systems in crude oil asphaltene constituents, one with considerable potential, but given the least attention, is ultraviolet spectroscopy. Typically, the ultraviolet spectrum of a crude oil asphaltene shows two major regions with very little fine structure, and interpretation of such a spectrum can only be made in general terms. What is often not realized is that the technique can add valuable information about the degree of condensation of polynuclear aromatic ring systems through the auspices of high-performance liquid chromatography [24,35-38].

For more detailed information on ring size distribution, fractionation of the asphaltene is advocated. A high-performance liquid chromatographic investigation of a mixture of standard polynuclear aromatic systems with the UV detector at fixed wavelengths from 240 to 360 nm confirmed the applicability of the technique to determine the presence of ring size distribution using the different selectivity of the poly nuclear aromatic systems [24]. The one-ring and two-ring polynuclear aromatic systems were more prominent in the chromatogram at 240 mm but were not at all evident in the chromatogram at wavelengths above 300 nm. The converse was true for the three-ring to six-ring systems. This was confirmed examination of a standard solution of polynuclear aromatic (one-ring to seven-ring) systems, which confirmed that one-ring to three-ring systems gave prominent ultraviolet detector signals at <300 nm but gave no signals at >300 nm. On the other hand, compounds with four-ring to seven-ring systems still gave signals at >300 nm but gave no signals at 365 nm. Similar data were obtained from a suite of asphaltene fractions from different crude oils.

These data provided evidence of the ring size distribution of the polynuclear aromatic systems in crude oil asphaltene constituents. For example, amphoteric species and basic nitrogen species contain polynuclear aromatic systems having two to six rings per system. On the other hand, the acid sub-fractions (phenolic or carboxylic functions) and the neutral polar sub-fractions (amides and imino functions) contain few if any polynuclear aromatic systems with more than three rings per system. In no case was there any strong or conclusive evidence for polynuclear aromatic ring systems containing more than six condensed rings. In all cases, the evidence favored the preponderance of the smaller one-ring to four-ring systems [1,24].

It must not be forgotten that the method is subject to the limitation of the sensitivity of polynuclear aromatic systems and the fact that some of the asphaltene material (<2% wt/wt) was irreversibly adsorbed on the adsorbent. In this latter case, the missing material is polar material and any deviation from the ring size distribution just outlined is not believed to be significant enough to influence the general conclusions about the nature of the polynuclear aromatic systems in crude oil asphaltene constituents.

These observations led to a readjustment to the previous postulates of the asphaltene structure. Previously conceived hypotheses relating to the hypothesis of an average structure of asphaltene fraction the in which the central system is a condensed polynuclear aromatic system is not in keeping with the evidence. In addition, the products of the thermolysis of the whole fraction and the individual constituent fractions are not in keeping with an average structure that consists of a condensed ring system. Indeed, the failure to detect (during the chromatographic examination) any strong evidence for the existence of large multi-ring polynuclear aromatic systems in the asphaltene fractions is evidence against structures invoking this concept.

The concept of asphaltene constituents as a sterane-sulfur polymer or even a regular hydrocarbon polymer has arisen because of the nature of the products obtained by reaction of an asphaltene fraction with potassium naphthalide [39]. It was erroneously assumed that this particular organometallic reagent, one of several known to participate in rapid, complex reactions with organic substrates, cleaved only carbon-sulfur-carbon bonds but not carbon-carbon bonds. In fact, the reaction of potassium naphthalide with tetrahydrofuran under conditions identical to those reported in which asphaltene constituents were also present, produces a light brown amorphous powder [30]. This product could erroneously be identified as a major degradation product of the asphaltene constituents had any asphaltene been present. Errors of this type have only added confusion to the already complex area of asphaltene structure!

A major constraint in the acceptance of proposed average structures for asphaltene constituents is the validity of the proposed structures in terms of the complex maturation process [40]. Highly condensed polynuclear aromatic structures, which have been used to explain the high yields of thermal coke from asphaltene constituents, are not consistent with the natural product origins of crude oil asphaltene constituents [1,2].

It is sufficient to state that any molecular models derived for asphaltene constituents must be in keeping with behavioral characteristics. Efforts have been (and continue to be) made without justification to describe the asphaltene fraction in terms of a single, representative asphaltene molecule or molecules incorporating, in the correct proportions, all of the chemical and elemental constituents known to be present in a given asphaltenic matrix [1,2].

Although this approach gives an idea of the structural complexity of the compounds making up the asphaltene component, it obscures the highly differentiated chemical nature of the molecules in this crude oil fraction [1, 41-43].

A serious shortcoming, common to all molecular models, is that they have fixed bond angles and that rotation about single bonds is excessively facile, especially in the first two types of models. In contrast, in the real situation there are relatively easily definable bond angles and substantial barriers to rotation about single bonds. Moreover, if it is desired to measure intramolecular and/or intermolecular bond distances, the model must first be fixed in its actual conformation. For molecules having a number of single bonds, this may be quite inconvenient (even though mechanical devices to stop bond rotation are available) and it may be difficult to set the actual torsion angles with any kind of precision. As a result of all these difficulties, modeling of the macromolecules in the asphaltene fraction has proved to be speculative [1,2].

It is not possible to compose a model that represents all the properties of all of the constituents of the asphaltene fraction. The molecular size, as deduced from molecular weight measurements, prohibits this. It will be necessary to compose models that are representative of the various constituent fractions of an asphaltene. Then, perhaps, we will truly have representative models [44-54].

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