

Petroleum Asphaltenes

Part 1

Asphaltenes, Resins and the Structure of Petroleum

J.G. Speight¹

¹ CD&W Inc., 2476 Overland Road, Laramie, Wyoming 82070-4808, United States
e-mail: jamesSp8@aolo.com

Résumé — Les asphaltènes, composés pétroliers. Partie 1 : Asphaltènes, résines et structure du pétrole — La définition précise des composés non volatils d'un pétrole (asphaltènes, résines, autres constituants plus spécifiques aux résidus et aux charges lourdes) constitue une donnée nécessaire aux opérateurs. Il est difficile de distinguer des espèces suivant de simples caractéristiques chimiques ou structurelles. Ceci est particulièrement valable pour les asphaltènes et les résines dont la procédure de séparation détermine non seulement le rendement mais aussi la qualité de la fraction. Par exemple, l'emploi de différents solvants influence considérablement le rendement. La technique appliquée entraîne ou non la présence de résines coprécipitées avec les asphaltènes. Ceci provient de la définition générale des asphaltènes et des résines, respectivement comme composés insolubles et solubles dans le *n*-pentane (ou le *n*-heptane). Les résultats de récentes études de structure contredisent les anciennes descriptions d'asphaltènes en tant que composés contenant de larges plages de noyaux aromatiques polycondensés et montrent qu'une grande diversité de fonctions chimiques jouent aussi un rôle dans le comportement des asphaltènes. Ainsi, la stabilité d'un pétrole peut-elle être représentée par un système de trois phases : les asphaltènes, la fraction aromatique (incluant les résines) et la fraction saturée, le tout se trouvant en équilibre suivant une délicate harmonie. Plusieurs facteurs, tels que l'oxydation, peuvent altérer ce système, conduisant à une instabilité ou une incompatibilité des espèces due à la modification de leur polarité et de leurs liaisons.

Abstract — Petroleum Asphaltenes - Part 1: Asphaltenes, Resins and the Structure of Petroleum — The definition of the nonvolatile constituents of petroleum (i.e., the asphaltene constituents, the resin constituents, and, to some extent, part of the oils fraction insofar as nonvolatile oils occur in residua and other heavy feedstocks) is an operational aid. It is difficult to base such separations on chemical or structural features. This is particularly true for the asphaltene constituents and the resin constituents, for which the separation procedure not only dictates the yield but can also dictate the quality of the fraction. For example, the use of different hydrocarbon liquids influences the yield by a considerable factor. The technique employed also dictates whether or not the asphaltene contains coprecipitated resins. This is based on the general definition that asphaltene constituents are insoluble in *n*-pentane (or in *n*-heptane) but resins are soluble in *n*-pentane (or in *n*-heptane). The results of structural studies of asphaltene constituents are moving away from the older ideas that asphaltene constituents contained large polynuclear aromatic systems and there are a variety of functional types that also play a role in asphaltene behavior. The stability of petroleum is dependent upon the molecular relationships of the asphaltene and resin

constituents and the balance with the other constituents of petroleum. Thus, the stability of petroleum can be represented by a three-phase system in which the asphaltene constituents, the aromatic fraction (including the resin constituents), and the saturate fraction are in a delicately balanced harmony. Various factors, such as oxidation, can have an adverse effect on the system, leading to instability or incompatibility as a result of changing the polarity, and bonding arrangements, of the species in crude oil.

1 ASPHALTENE CONSTITUENTS

Asphaltene constituents are the highest molecular weight heaviest and most polar constituents in crude oil. The amount and the characteristics of the asphaltene constituents in crude oil depend to a greater or lesser extent on the source of the crude oil. During petroleum refining, the asphaltene constituents are nondistillable and remain in the residua fuels as the distillable fractions are removed. This, asphaltene content is of prime importance.

Asphaltene constituents are dark brown to black friable solids that have no definite melting point and usually foam and swell on heating to leave a carbonaceous residue. They are obtained from petroleum by the addition of a nonpolar solvent (such as a hydrocarbon) with a surface tension lower than that of 25 dyne cm^{-1} at 25C (77°F). Liquids used for this purpose are low-boiling petroleum naphtha, petroleum ether, *n*-pentane, *iso*-pentane, *n*-heptane, and the like (Speight, 1999, 2001, and references cited therein). Asphaltene constituents are soluble in liquids with a surface tension above 25 dyne cm^{-1} , such as pyridine, carbon disulfide, carbon tetrachloride, and benzene. Asphaltene constituents are insoluble in liquefied petroleum gases, such as methane, ethane, and propane; in fact, propane is used commercially in processing petroleum residues for asphaltene constituents and resin constituents.

On the other hand, the resin fraction is a collection of those constituents that are soluble in *n*-pentane or *n*-heptane (*i.e.*, whichever hydrocarbon is used for the separation of asphaltene constituents) but insoluble in liquid propane

(Koots and Speight, 1975; Andersen and Speight, 2001). In addition, *resin constituents* are also those materials soluble in *n*-pentane or *n*-heptane but that cannot be extracted from an earth by *n*-pentane or *n*-heptane. The oils fraction is, therefore, that fraction of crude oil soluble in *n*-pentane or in *n*-heptane that are extractable from an earth by *n*-pentane or by *n*-heptane. The oils fraction is composed of saturates and aromatics fractions (*Fig. 1*).

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:

- well bore plugging and pipeline deposition during recovery and transportation operations.
- water contamination during wellhead storage and in pipelines can lead to the formation of emulsions because the asphaltene constituents highly polar and surface active.
- 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.
- thermally degraded asphaltene constituents are more aromatic (loss of aliphatic chains) and less soluble and appear as sediment (the onset of coke formation) during visbreaking and cracking processes. Preheating fuel oil prior to combustion causes the precipitation of reacted asphaltene constituents for a similar reason.

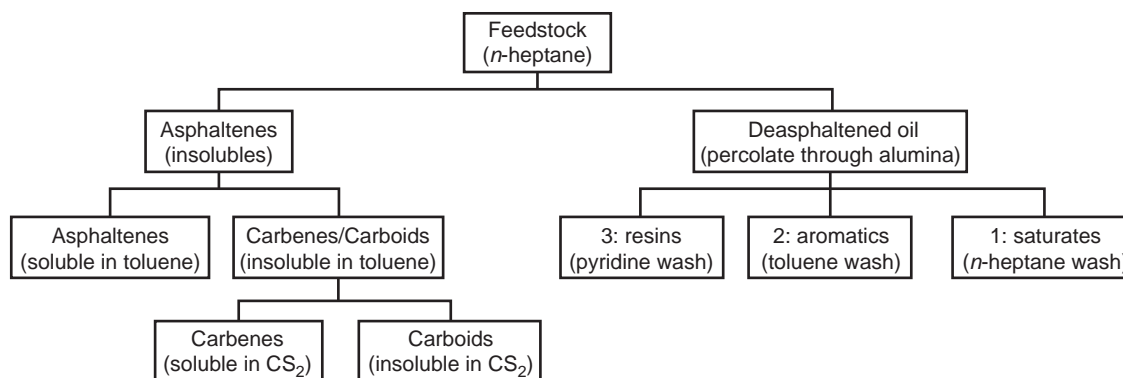


Figure 1

Simplified petroleum fractionation method.

- the change of medium during fuel oil blending as well as fuel oil-heavy crude oil blending can cause destabilization of asphaltene constituents.
- a high content of asphaltene constituents ($\geq 6\%$) in fuel oil often causes ignition delay and poor combustion leading to boiler fouling, diminished heat transfer, stack (particulate) emissions, and corrosion.

1.1 Separation

The definition of the nonvolatile constituents of petroleum (*i.e.*, the asphaltene constituents, the resin constituents, and, to some extent, part of the oils fraction insofar as nonvolatile oils occur in residua and other heavy feedstocks) is an operational aid. It is difficult to base such separations on chemical or structural features (Girdler, 1965; Speight *et al.*, 1984; Yen, 2000; Speight, 1994, 1999, 2001). This is particularly true for the asphaltene fraction, for which the separation procedure not only dictates the yield but can also dictate the *quality* of the fraction. For example, the use of different hydrocarbon liquids influences the yield by a considerable factor. The technique employed also dictates whether or not the asphaltene contains coprecipitated resins. This is based on the general definition that asphaltene constituents are insoluble in *n*-pentane (or in *n*-heptane) but resins are soluble *n* pentane (or in *n*-heptane).

There is no one parameter that is operational in the separation of asphaltene constituents; the relevant parameters for asphaltene separation are physical and chemical in nature and include:

- polarity (the presence of functional groups derived from the presence of heteroatoms in the asphaltene constituents) (Long, 1979, 1981; Speight, 1994);
- aromaticity (the presence of polynuclear aromatic systems in the asphaltene constituents) (Girdler, 1965; Mitchell and Speight, 1973);
- molecular weight (molecular size) (Long, 1979, 1981);
- three-dimensional structure (the micelle) of the asphaltene constituents as they exist in relationship with the other constituents of crude oil (Speight, 1994);
- solvent power of the precipitating/extracting liquid used for the separation (Girdler, 1965; Mitchell and Speight, 1973);
- time required to allow the precipitating/extracting liquid to penetrate the micelle which is dependent upon the ability of the hydrocarbon liquid to penetrate the micelle, indicating that the process is diffusion-controlled (Speight *et al.*, 1984);
- ratio of the precipitating/extracting liquid to crude oil that dictates the yield and character of the asphaltene product (Girdler, 1965; Mitchell and Speight, 1973; Speight *et al.*, 1984);

- temperature, which may reduce the induction period that is a requirement of diffusion-controlled processes (Mitchell and Speight, 1973);
- pressure, as employed in several refinery processes as a means of maintaining the low-boiling liquid hydrocarbon in the liquid phase.

It is recognized that the different yield of the asphaltene fraction can be related to the variation in the solubility parameter of the hydrocarbon solvent (Mitchell and Speight, 1973). The tendency of the asphaltene constituents to vary with the solubility parameter of the hydrocarbon medium is related to the aromaticity and the polarity of the asphaltene constituents rather than to the molecular size or dimensions of the asphaltene constituents (Long, 1979, 1981; Long and Speight, 1989; Cimino *et al.*, 1995).

Other parameters may be defined as subsets of those enumerated above. It is also worthy of note that, in order to remove entrained resin material, precipitation of the asphaltene constituents from benzene or toluene is often necessary (Speight *et al.*, 1984; Ali *et al.*, 1985). But, none of these parameters applied to the separation of petroleum can be related to the separation of distinct chemical types.

Thus asphaltene constituents are by definition a *solubility class* that is separated from feedstocks by the addition of 40 volumes of the liquid hydrocarbon (Table 1) (Girdler, 1965; Mitchell and Speight, 1973; Speight *et al.*, 1984; Andersen and Birdi, 1990; Speight, 1994; Cimino *et al.*, 1995).

TABLE 1
Standard methods for asphaltene precipitation

Method	Precipitant	Volume precipitant per g of sample (ml)
ASTM D-893	<i>n</i> -pentane	10
ASTM D-2006	<i>n</i> -pentane	50
ASTM D-2007	<i>n</i> -pentane	10
ASTM D-3279	<i>n</i> -heptane	100
ASTM D-4124	<i>n</i> -heptane	100
IP 143	<i>n</i> -heptane	30
Syncrude method	<i>n</i> -pentane	20

ASTM Annual Book of Standards, 2002.

Cooley *et al.*, 1988.

Syncrude Research, 1979.

Despite this, there are still reports of *asphaltene constituents* being isolated from crude oil using insufficient amounts of the liquid hydrocarbon that leads to errors not only in the determination of the amount of asphaltene constituents in the crude oil but also in the determination of the compound type. When insufficient amounts of the liquid hydrocarbon are used, resin constituents appear within the asphaltene fraction by adsorption onto the asphaltene constituents from the supernatant liquid. Thus, questionable isolation techniques throw serious doubt on any conclusions drawn from subsequent work on the isolated material.

In fact, to ensure *stable* asphaltene yields it is necessary to employ the following parameters:

- >30 ml hydrocarbon per gm feedstock;
- *n*-pentane or *n*-heptane are the hydrocarbons of choice although volatility constraints and consistency of asphaltene composition tend to favor the use of *n*-heptane; and
- 8- 10 h contact time is the preferable period;
- a precipitation sequence to remove any adsorbed resin from the asphaltene fraction.

The precipitation sequence involves dissolution of the asphaltene constituents in benzene or toluene (10 ml per gm asphaltene) followed by the addition of the hydrocarbon (50 ml precipitant per ml toluene or benzene) to the solution. This sequence should be repeated three times to remove adsorbed lower molecular weight resin material and to provide consistency of the asphaltene fraction.

1.2 Composition

Asphaltene constituents isolated from different sources are remarkably constant in terms of ultimate composition, although careful inspection of the data shows extreme ranges for the composition. Asphaltene constituents from different sources have never before been compared with any degree of consistency.

The elemental composition of asphaltene constituents isolated by use of excess (greater than 40) volumes of *n*-pentane as the precipitating medium show that the amounts of carbon and hydrogen usually vary over only a narrow range. These values correspond to a hydrogen-to-carbon atomic ratio of 1.15–0.5%, although values outside this range are sometimes found. The near constancy of the H/C ratio is surprising when the numbers of possible molecular permutations involving the hetero elements are considered. In fact, this property, more than any other, is the cause for the general belief that unaltered asphaltene constituents from crude oil have a definite composition. Furthermore, it is still believed that asphaltene constituents are precipitated from petroleum by hydrocarbon solvents because of this composition, not only because of solubility properties.

In contrast to the carbon and hydrogen contents of asphaltene constituents, notable variations occur in the proportions of the hetero elements, in particular in the proportions of oxygen and sulfur. Oxygen contents vary from 0.3 to 4.9% and sulfur contents vary from 0.3 to 10.3%. On the other hand, the nitrogen content of the asphaltene constituents has a somewhat lesser degree of variation (0.6–3.3% at the extremes). However, exposing asphaltene constituents to atmosphere oxygen can substantially alter the oxygen content and exposing a crude oil to elemental sulfur or even to sulfur-containing minerals can result in excessive sulfur uptake. Perhaps oxygen and sulfur contents vary more markedly than do nitrogen contents because of these conditions.

The use of *n*-heptane as the precipitating medium yields a product that is substantially different from the *n*-pentane-insoluble material. For example, the hydrogen-to-carbon atomic ratio of the *n*-heptane precipitate is lower than that of the *n*-pentane precipitate. This indicates a higher degree of aromaticity in the *n*-heptane precipitate. Nitrogen-to-carbon, oxygen-to-carbon, and sulfur-to-carbon ratios are usually higher in the *n*-heptane precipitate, indicating higher proportions of the hetero elements in this material (Speight, 1999).

One aspect of asphaltene characterization that has provided strong evidence for the complexity of petroleum asphaltene constituents arises from composition studies using fractionation techniques (Bestougeff and Darmois, 1947; Bestougeff and Mouton, 1977; Francisco and Speight, 1984; Cimino *et al.*, 1995). Of specific interest is the observation that when asphaltene constituents are fractionated on the basis of aromaticity and polarity, it appears that the more aromatic species contain higher amounts of nitrogen, suggesting that the nitrogen species are located predominantly in aromatic systems.

The solvent-based fractionation of the asphaltene component of petroleum 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 (Girdler, 1965; Mitchell and Speight, 1973; Speight, 1979; Andersen, 1997). The use of mixtures of a polar and a nonpolar solvent in order to fractionate an asphaltene sample will tend to direct the fractionation by introducing polar forces and hydrogen bonding, as well as dispersion forces, as factors determining which components of the asphaltene sample are soluble in the mixture. Molecular weight, aromaticity, and polarity combine to determine asphaltene solubility in hydrocarbon media and that the solubility properties of the asphaltene fractions of different crude oils can vary markedly (Acevedo *et al.*, 1995).

The fractionation of asphaltene constituents into a variety of functional (and polar) types (Francisco and Speight, 1984) has confirmed the complexity of the asphaltene fraction. High performance liquid chromatography (HPLC) has also been used to illustrate the diversity of the structural and functional types in asphaltene constituents to the extent that different high performance liquid chromatographic profiles can be expected for different asphaltene constituents (Speight, 1994).

It is unfortunate that such studies have not received more recognition as they provide valuable information about the nature of petroleum asphaltene constituents. As a result of one simple fractionation scheme, asphaltene constituents can be regarded as mixtures of aromatic types and nitrogen types, there being the suggestion that the more aromatic species (i.e., lower H/C types) contain the predominance of the nitrogen. Asphaltene composition has also been studied using

silica gel chromatography (Selucky *et al.*, 1981), as well as ion-exchange chromatography (Francisco and Speight, 1984). Such data reinforce the concept that asphaltene constituents are distributions of molecular and functional types (Long, 1979).

Studies on the disposition of *nitrogen* in petroleum asphaltene constituents indicated the existence of nitrogen as various heterocyclic types (Clerc and O'Neal, 1961; Nicksic and Jeffries-Harris, 1968; Moschopedis and Speight, 1976b, 1978; Jacobson and Gray, 1987; Mullins, 1995). The application of X-ray absorption near-edge structure (XANES) spectroscopy to the study of asphaltene constituents has led to the conclusion that a large portion of the nitrogen present is aromatic, in pyrrolic rather than pyridinic form (Mitra-Kirtley *et al.*, 1993). Other studies (Schmitter *et al.*, 1984) have brought to light the occurrence of four-ring aromatic nitrogen species in petroleum.

Oxygen has been identified in carboxylic, phenolic, and ketonic (Nicksic and Jeffries-Harris, 1968; Petersen *et al.*, 1974; Moschopedis and Speight, 1976a, 1976b; Ritchie *et al.*, 1979; Rose and Francisco, 1987) locations but is not usually regarded as located primarily in heteroaromatic ring systems.

Sulfur occurs as benzothiophenes, dibenzothiophenes, and naphthene benzothiophenes (Clerc and O'Neal, 1961; Nicksic and Jeffries-Harris, 1968; Drushel, 1970; Yen, 1974; Speight and Pancirov, 1984; Rose and Francisco, 1988; Keleman *et al.*, 1990; Mullins, 1995); more highly condensed thiophene types may also exist but are precluded from identification by low volatility. Other forms of sulfur that occur in asphaltene constituents include the alkyl-alkyl sulfides, alkyl-aryl sulfides, and aryl-aryl sulfides (Yen, 1974).

Metals (i.e., nickel and vanadium) are much more difficult to integrate into the asphaltene system. Nickel and vanadium occur as porphyrins (Baker, 1969; Yen, 1975), but whether these are an integral part of the asphaltene structure is not known. Some of the porphyrins can be isolated as a separate stream from petroleum (Branthaver, 1990; Reynolds, 1998, 2000).

Thus, the functionality of the asphaltene constituents is defined in terms of several commonly occurring natural product types that are more in keeping with the *recognized* maturation pathways than any of the structures heretofore conceived.

1.3 Molecular Weight

The molecular weights of asphaltene constituents span a wide range from a few hundred to several million leading to speculation about self-association (Sakhanov and Vassiliev, 1927; Mack, 1932; Katz, 1934; Lerer, 1934; Hillman and Barnett, 1937; Pfeiffer and Saal, 1940; Grader, 1942; Kirby, 1943; Labout, 1950; Ray *et al.*, 1957; Griffin *et al.*, 1959;

Winniford, 1963; Wales and van der Waarden, 1964; Altgelt, 1968; Markhasin *et al.*, 1969; Reerink, 1973; Koots and Speight, 1975; Speight *et al.*, 1985).

The existence of asphaltene constituents aggregates in hydrocarbon solvents has been demonstrated by means of small-angle neutron scattering (SANS) studies. The physical dimensions and shape of the aggregates are functions of the solvent used and the temperature of the investigation (Ravey *et al.*, 1988; Overfield *et al.* 1989; Thiyagarajan *et al.*, 1995). In addition, surface tension measurements have been used to study the self-association of asphaltene constituents in pyridine and nitrobenzene (Sheu *et al.*, 1992). A discontinuous transition in the surface tension as a function of asphaltene concentration was interpreted as the critical asphaltene concentration above which self-association occurs.

The tendency of asphaltene constituents to undergo association and/or dissociation depending upon the nature of the solvent also appears true for the series of higher molecular weight fractions. However, it should be noted here that although the results with asphaltene constituents available from several crude oils (Moschopedis *et al.*, 1976) suggest that molecular weight varies with the dielectric constant of the solvent, there may be other factors which may in part also be responsible for this phenomenon. The final phenomenon that influences the molecular weight of the asphaltene is the relative polarity of the solvent used in the precipitation technique.

In summary, asphaltene molecular weights are variable (Yen, 1974; Speight *et al.*, 1985) because of the tendency of the asphaltene constituents to associate even in dilute solution in nonpolar solvents. However, data obtained using highly polar solvents indicate that the molecular weights, in solvents that prevent association, usually fall in the range 2000 ± 500 .

1.4 Solubility Parameters

Any change in the physical and chemical properties of crude oil can be a key factor in the stability of the system. For example, as the degree of conversion in a *thermal process* increases, the solubility power of the medium towards the heavy and polar molecules decreases due to the formation of saturated products (Speight, 1994). This is reflected in a relative change in the solubility parameters of the dispersed and solvent phases leading to a phase separation (Wiehe, 1993, 1994; Speight, 1994).

The most prevalent thermodynamic approach to describing asphaltene solubility has been the application of the solubility parameter or the concept of cohesive energy density. The application of solubility parameter data to correlate asphaltene precipitation, and, hence, crude oil-solvent interaction, has been used on prior occasions (Labout, 1950; Mitchell and Speight, 1973; Lin and Yen, 1994; Wiehe, 1995).

Solubility parameters of asphaltene constituents can be estimated from the properties of the solvent used for separation (Yen, 1984; Long and Speight, 1989) or be measured by the titration method (Andersen and Speight, 1992) but relative to the experimental parameters such as time, solvent and solute (asphaltene or oil) concentration. The recovery of a toluene insoluble fraction from a toluene soluble fraction shows the complexity of the asphaltene aggregation during precipitation. Evidence of rearrangements of molecular interactions is suggested.

The solubility parameter difference that results in a phase separation of two materials, such as asphaltene constituents in a solvent, can be estimated using the Scatchard-Hildebrand Equation:

$$\ln a_a = \ln x_a + M_a/RT\Delta_a[N_s^2(*_s - *_a)^2]$$

where a_a is the activity of the solute a , x_a is the mole fraction solubility of a , M_a is the molecular weight of a , D_a is the density of a , N_s is the volume fraction of solvent, and $(*_s - *_a)$ is the difference between the solubility parameters of the solute a and the solvent s . Assuming that the activity of the asphaltene constituents a_a is 1 (solid asphaltene constituents in equilibrium with dissolved asphaltene constituents) and the volume fraction of an excess of solvent is essentially 1, the equation can be rearranged into a form that can be used to gain insight into the solubility of asphaltene constituents:

$$\ln x_a = -M_a/RT\Delta_a[(*_s - *_a)^2]$$

Assuming a density for asphaltene constituents of 1.28 g/cc and a molecular weight of 1000 g/mol, the solubility of asphaltene constituents as a function of the differences between solubility parameters of the asphaltene constituents and precipitating solvent can be calculated. Thus, the solubility of asphaltene constituents can be shown to decrease as the difference between solubility parameters increases, with the limit of solubility attained at a difference of about 2. Thus, if the asphaltene constituents are part of a polarity and molecular weight continuum in a crude oil, their precipitation is not as straightforward as it would be for a single species with a particular solubility parameter.

Both polarity and molecular weight of asphaltene constituents in a solvent define the solubility boundaries and explains conceptually how asphaltene constituents are precipitated from the mixture in crude oils that can be considered a type of continuum of molecular weights and polarities. Furthermore, as the molecular weight of a particular solute decreases, there is an increased tolerance of polarity difference between solute and solvent under miscible conditions.

The majority of the incompatibility phenomena can be explained by the use of the solubility parameter for asphaltene constituents and other petroleum fractions (Speight, 1994). As an extension of this concept, there is sufficient data to draw an approximate correlation between hydrogen-to-carbon atomic ratio and the solubility parameter, δ , for

hydrocarbon solvents and petroleum constituents (Speight, 1994, 1999, 2001, and references cited therein). In general, hydrocarbon liquids can dissolve polynuclear aromatic hydrocarbons where there is, usually, less than a three-point difference between the lower solubility parameter of the solvent and the solubility parameter of the hydrocarbon.

1.5 Structural Aspects

There is adequate evidence (Speight, 1994, 1999, 2001, and references cited therein) to show that the asphaltene constituents contain a higher proportion of small aromatic ring system that previously thought. Previously conceived hypotheses in which the polynuclear aromatic system is large (> 10 rings) are unlikely despite their frequent and recent occurrence in the literature.

The manner in which these moieties appear within the asphaltene molecule must for the present remain largely speculative, but above all it must be remembered that asphaltene constituents are a solubility class and, as such, may be an accumulation of (literally) thousands of structural entities. Hence caution is advised against combining a range of identified products into one (albeit hypothetical) structure.

Thermal studies using model compounds confirm that volatility of the fragments is a major influence in carbon residue formation and a pendant-core model for the high molecular weight constituents of petroleum has been proposed (Wiehe, 1994). In such a model, the scission of alkyl side chains occurs thereby leaving a polar core of reduced volatility that commences to produce a carbon residue (Speight, 1994; Wiehe, 1994). In addition, the pendant-core model also suggests that even one-ring aromatic cores can produce a carbon residue if multiple bonds need to be broken before a core can volatilize (Wiehe, 1994).

A number of molecular models have been proposed for asphaltene constituents and are described in detail elsewhere (Speight, 1994, 1999), and repetition is not warranted here. 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 petroleum fraction (Long, 1979, 1981). The idealized molecular structures defined by this method, however, are of some utility for inferring the chemistry and physical-chemical properties of the asphaltene constituents (Speight, 1994).

Briefly, there are essentially three types of models:

- those that help to visualize the three-dimensional architecture and stereochemistry but are not to scale.
- framework-type models that indicate correct bond distances and bond angles and can be used to measure distances between nonbonded atoms in molecules but do not show the atoms as such.

- space-filling models that provide a fairly realistic three-dimensional representation of what the molecule actually looks like.

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, although some success has been achieved in attempting to understand the nature of the constituents and their behavior in thermal processes (Speight, 1994). Success notwithstanding, the chemical dynamics are still speculative because of the speculative nature of the model!

The properties of macromolecules depend on both the chemical structure and physical structure. The term *primary structure* describes the chemical sequence of atoms in a macromolecule. The ordering of the atoms in space relative to each other is referred to as the *secondary structure*, and the three-dimensional structure of a molecule is called the *tertiary structure*.

By analogy, the *primary structure* of asphaltene constituents is the two-dimensional structure derived by a variety of analytical techniques and is often presented on paper as an *average structure*. The *secondary and tertiary structure*, and perhaps an often ignored but extremely important aspect of asphaltene chemistry and physics, is the micelle structure, which represents the means by which asphaltene constituents exist in crude oil.

2 RESIN CONSTITUENTS

The resin constituents play an important role in the stability of petroleum and prevent separation of the asphaltene constituents as a separate phase (Swanson, 1942; Koots and Speight, 1975; Buckley, 1997; Wiehe and Liang, 1996; 1997; Li *et al.*, 1997, 1999; Premuzic and Lin, 1999).

Like the asphaltene fraction, the resin fraction cannot be defined in terms of the chemical constituents of the fraction. Both fractions are defined operationally by the method of separation.

Many different methods of fractionation have been applied to petroleum (Speight, 1999 and references cited therein). Many methods are similar with only subtle differences between the actual experimental procedures whilst

some methods differ considerably in the manner of fractionation and in the way in which the resins are separated. Thus, compositional differences in the resin fraction must be anticipated. The method of choice must be followed rigidly according to the prescribed procedures if *reproducibility* and *accuracy* are to be achieved. And it is on the basis of the method employed that resins are defined.

Any deviation from the prescribed parameters as well as use of different methods will yield *different* resin fractions. The products will show marked differences in the quantity and chemical composition as well as the important asphaltene/resin ratio. There have been attempts to use this ratio to define the potential stability and potential instability of petroleum. However, whether or not the ratio is meaningful remains to be answered since it is dependent on the method employed as well as the reproducibility and accuracy of the method.

2.1 Separation

Resin constituents are soluble in the liquids that precipitate asphaltene constituents and are usually soluble in most organic liquids, except in the lower alcohols and acetone, but they are precipitated by liquid propane and liquid butane(s). Thus, resin constituents often coprecipitate with the asphaltene constituents in controlled propane deasphalting procedures, and the product, called *propane asphalt*, contains appreciable amounts of adsorbed resins and has a low melting point, and is generally used for asphalt manufacture. The composition of the resins fraction can vary considerably and is dependent on the kind of precipitating liquid and on the temperature of the liquid system. The fraction becomes quite fluid on heating but often show pronounced brittleness when cold.

Standard laboratory methods have been defined for the fractionation of petroleum. The older ASTM D-2006 method and ASTM D-2007 method are no longer in official use but may still find use in private laboratories. Indeed, these methods found such wide use that many modifications have been proposed that are still in use (Speight, 1999, 2001, and references cited therein). The overall product of these fractionation methods, which with the ensuing sub-fractionation, provides the representation of petroleum a composite of the four fractions (saturates, aromatics, resins, and asphaltenes) (Fig. 1). The data also provide a representation of the distribution of the heteroatoms (nitrogen, oxygen, and sulfur) in the fractions in addition to other properties.

2.2 Composition

Elemental constitutions of a suite of petroleum resins isolated by the same procedure, and therefore comparable (Speight, 1999), show that the proportions of carbon and hydrogen,

like those of the asphaltenes, vary over a narrow range: $85 \pm 3\%$ carbon and $10.5 \pm 1\%$ hydrogen (Speight, 1999). The proportions of nitrogen ($0.5 \pm 0.15\%$) and oxygen ($1.0 \pm 0.2\%$) also appear to vary over a narrow range, but the amount of sulfur (0.4 to 5.1%) varies over a much wider range.

There are notable increases in the H/C ratios of the resins relative to those of the asphaltenes. Indeed, whereas the asphaltenes may have in excess of 50% of the total carbon as aromatic carbon, in the resins the proportion of the total carbon occurring as aromatic carbon is significantly lower (Koots and Speight, 1975; Kam'yanov *et al.*, 1996; McLean and Kilpatrick, 1997).

2.3 Molecular Weight

The molecular weights of resin fractions in benzene are substantially lower than the molecular weights of the corresponding asphaltenes in benzene. Compared to the molecular weights of the asphaltenes, the molecular weights of the resins do not usually vary, except for the limits of experimental error, with the nature of the solvent or the temperature of the determination indicating that there is no association in nonpolar solvents such as benzene. In addition, and in keeping with the observed trend, the molecular weights of resin fractions (1200-1700) from a North Sea crude oil determined using tetrahydrofuran as the solvent are also substantially lower than that of the corresponding pentane-asphaltene (4200). Therefore, the molecular weights of resin fractions, as determined by various methods, are true molecular weights and that forces that result in intermolecular association contribute very little, if anything, to their magnitude.

One area of investigation that has shed some light on the behavior of resins during refining is the construction of molecular weight and polarity *maps* based on gel permeation chromatographic data (Long and Speight, 1998). These data clearly show the placement of the resin fraction on a crude oil map followed by the behavior of the resin constituents during various refining scenarios.

2.4 Structure

Investigations have shown that a variety of hydrocarbon types and functional types occur in resin fractions (Koots and Speight, 1975; Speight and Moschopedis, 1981; Li *et al.*, 1992; Petrova *et al.*, 1995; Li *et al.*, 1997; McLean and Kilpatrick, 1997; Speight, 1999 and references cited therein).

In addition, the resin constituents contain a variety of functional groups (Moschopedis and Speight, 1976b; Moschopedis and Speight, 1978) including thiophene, benzothiophene, and dibenzothiophene systems, hydrogen-bonded hydroxyl groups, pyrrole (and indole) N-H functions, ester functions, acid functions, carbonyl (ketone or quinone) functions, and sulfur-oxygen functions.

3 RESIN-ASPHALTENE INTERACTIONS

There is evidence that the structural aspects of the constituents of the resin fraction may differ very little from those of the corresponding asphaltene fraction, the main difference being the proportion of aromatic carbon within each fraction (Koots and Speight, 1975; Selucky *et al.*, 1981; Speight, 1999 and references cited therein). It has also been postulated that resin constituents and asphaltene constituents are small fragments of kerogen (Tissot, 1984) or at least have the same origins as the kerogen and, therefore, a relationship might be anticipated. The analogy is to a lock and key mechanism in which the asphaltene constituents and resin constituents with similar structural features form a bonding union.

In addition, when resins and asphaltenes are present together, resin-asphaltene interactions appear to be preferred over asphaltene-asphaltene interactions, resin-resin interactions appear to be inconsequential in petroleum. It has also been reported that hydrogenation and concurrent desulfurization cause a decrease in asphaltene molecular weights, and the reduction in molecular weight is presumed to be caused by a decrease in hydrogen-bonding interactions as a direct result of loss of the heteroelement. If the same intermolecular forces are present in crude oils it would not be surprising perhaps that asphaltenes exist not as the more cumbersome agglomerations but as single entities that are peptized and effectively dispersed by the resins.

Furthermore, if the composition and properties of the separated asphaltene constituents and resin constituents reflect those of the asphaltene-resin micelles, homogeneous micelles cannot be predicted.

An important corollary of petroleum composition is that the mole fraction of resins is always larger than that of asphaltenes and hence the micelles are expected to be richer in resins (Schabron and Speight, 1998). The micelle center would be formed from polar asphaltene molecules that would be surrounded by one or more of the resin molecules that are placed between the center and the periphery thereby masking the polar functions. If other asphaltene species are included in the micelle, they are not seen as a graphite-type stack as has been proposed previously. It is more likely an association of convenience that facilitates the association of the central asphaltene with resin species. In many cases, more than one asphaltene molecule per micelle is considered unlikely. However, the functionality of the asphaltene constituents as well as the number of aromatic centers in the constituents could conceivably dictate the number of resins that are required to peptize any particular asphaltene molecule. On this basis, the micelle would be expected to vary in size and also be heterogeneous.

An alternative explanation for the stabilizing influence of the resins, and for the stability of asphaltenes in hydrocarbon media in general, is that individual asphaltene species and micelles are in thermodynamic equilibrium (Cimino *et al.*,

1995). Thus, the degree of association is determined by the relative energies of solvation of the monomers and the micelles and the entropy and enthalpy changes associated with the self-association of the asphaltene monomers.

On this basis, the stability of petroleum can be represented by a three-phase system in which the asphaltene constituents and the resin constituents (because of the high coke-forming tendencies of the constituents of both fractions), the aromatic constituents, and the saturate constituents are in a delicately balanced harmony that can be disrupted by non-solvent and/or by thermal means (Speight, 2001). Various factors, such as oxidation, can have an adverse effect on the system, leading to instability or incompatibility as a result of changing the polarity, and bonding arrangements, of the species in crude oil.

CONCLUSIONS

The definition of the nonvolatile constituents of petroleum (*i.e.*, the asphaltene constituents, the resin constituents, and, to some extent, part of the oils fraction insofar as nonvolatile oils occur in residua and other heavy feedstocks) is an operational aid. It is difficult to base such separations on chemical or structural features. This is particularly true for the asphaltene constituents and the resin constituents, for which the separation procedure not only dictates the yield but can also dictate the *quality* of the fraction. For example, the use of different hydrocarbon liquids influences the yield by a considerable factor. The technique employed also dictates whether or not the asphaltene contains co-precipitated resins. This is based on the general definition that asphaltene constituents are insoluble in *n*-pentane (or in *n*-heptane) but resins are soluble *n* pentane (or in *n*-heptane).

The stability of petroleum is dependent upon the molecular relationships of the asphaltene constituents and resin constituents and the balance with the other constituents of petroleum. Thus, the stability of petroleum can be represented by a three-phase system in which the asphaltene constituents, the aromatics (including the resins), and the saturates are in a delicately balanced harmony. Various factors, such as oxidation, can have an adverse effect on the system, leading to instability or incompatibility as a result of changing the polarity, and bonding arrangements, of the species in crude oil.

Thus, the results of structural studies of asphaltene constituents are moving away from the older ideas that asphaltene constituents contained large polynuclear aromatic systems and there are a variety of functional types that also play a role in asphaltene behavior.

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